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Spectrum of doubly-ionised nitrogen (N III). L. J. FREEMAN (Proc. Roy. Soc., 1928, **A**, 121, 318—343).—The spectrum was examined from λ 8000 to λ 850. The N III lines observed are tabulated and their positions compared with those found by calculation. J. L. BUCHAN.

Structure of the band spectrum of helium. V. W. E. CURTIS and A. HARVEY (Proc. Roy. Soc., 1928, **A**, 121, 381—401; cf. *A.*, 1928, 449).—Details are given of four new bands and of one of the "ordinary" orthohelium family. The new bands are: $3D(1) \rightarrow 2P(1)$ of *o*-He₂ near λ 5750; $3X \rightarrow 2P$ of *p*-He₂ near λ 6250; $3Z \rightarrow 2P$ of *o*-He₂, and $4Z \rightarrow 2P$ of *o*-He₂. These last two bands are very similar to $3Z \rightarrow 2P$ of *p*-He₂ near λ 6300, which is also described. J. L. BUCHAN.

Hyperfine structure in the arc spectrum of caesium and nuclear rotation. D. A. JACKSON (Proc. Roy. Soc., 1928, **A**, 121, 432—447).—The caesium vapour was mixed with helium at about 2 mm. pressure in a discharge tube and excited by external electrodes. It was necessary to warm the tube in order to obtain the caesium spectrum, chiefly the *1s*—*3p* lines, and at the same time that due to helium was extinguished. On raising the temperature the yellow, red, and infra-red lines of caesium develop and those of the principal series become broader and blurred, their hyperfine structure being extinguished. In the principal series the lines were close doublets of equal intensity. Tables of measurements are given and those lines found to be simple are also tabulated. The results are discussed and a theory is put forward to account for the doublets. J. L. BUCHAN.

Absorption bands in the spectrum of cadmium vapour. A. JABLONSKI (Bull. Acad. Polonaise, 1928, *A*, 163—170).—The absorption spectrum of cadmium vapour has been investigated with a view of finding the positions of bands corresponding with the fluorescence bands, and to show that both series have the same convergence point. The apparatus used is described. The frequency of the bands is plotted against the difference of frequency between one band and the next, and it is found on extrapolating the curve that the point of convergence of the bands is at a wave-length of 2561 Å. Assuming that this is connected with the dissociation of the cadmium molecule, Cd₂, and activation to the state 2^3P_1 of one of the atoms resulting from the dissociation, the energy of dissociation of the cadmium atom is calculated to be 1.035 ± 0.031 volts, a value in good

agreement with that calculated by consideration of the system Cd II (1.023 ± 0.006 volts). The absorption spectrum of cadmium shows a great predominance of continuous absorption over band absorption, an observation which shows the existence of metastable states of long duration. It seems probable that the only essential difference between the molecules of cadmium (and mercury) and other diatomic molecules (*e.g.*, iodine, selenium, tellurium, etc.) consists in the existence of metastable states of these molecules. A. J. MEE.

Origin of the band λ 2476.3—2482.7 in the spectrum of mercury. S. PIENKOWSKI (Bull. Acad. Polonaise, 1928, *A*, 171—179).—The band of wave-lengths 2482.72—2476.35 Å. has been resolved into rays which can be arranged in a series of seven doublets. In each of the branches of these doublets there is an irregular ray; the displacement occurs for the same quantum number in both branches and in opposite directions. The moment of inertia of the molecule emitting the light is calculated and it is concluded that the band is due to a mercury hydride, the hydrogen having been supplied probably by a trace of water vapour. All photographs of spectra of hydrogen and mercury vapour show the presence of the band. A. J. MEE.

Wave-lengths and Zeeman effects in yttrium spectra. W. F. MEGGERS (U.S. Bureau Stand. Res. Paper No. 12, 1928, 319—341).—The wave-lengths corresponding with approximately 1000 lines photographed in the arc and spark spectra of yttrium were measured relative to secondary standards in the iron spectrum, the values extending from 2127.99 Å. in the ultra-violet to 9494.81 Å. in the infra-red. Four classes of lines were distinguished; about 500 are ascribed to neutral atoms and constitute the Y I spectrum; 240 originate with singly-ionised atoms, the Y II spectrum; 10 belong to doubly-ionised atoms, the Y III spectrum, and most of the remainder describe the band spectrum characteristic of molecular compounds, presumably yttrium oxide. Tables are given of the wave-lengths, line intensity estimates, wave numbers, and classification. Measurements of Zeeman effects for 220 lines from 3173 to 6896 Å. are included. N. M. BLIGH.

Spectra of mercury at atmospheric pressure. W. H. CREW and L. H. DAWSON (J. Opt. Soc. Amer., 1928, **17**, 261—270).—The light emitted from a mercury arc in quartz was photographed through a quartz spectrograph. As the current through the arc was increased the lines of the line spectrum

broadened, and under the influence of a condensed discharge thirteen lines were found to be self-reversed. Two of these were spark lines and eight were lines of the diffuse series. Hence lines of the diffuse series are the most readily reversed. The reversal of the line of wave-length 1942 Å. supports the view of Carrol, Turner, and Compton that it is a member of the first doublet of the principal series of Hg^- . The continuous spectrum appeared in four discrete bands when a high current was passed through the arc. Three of these bands have intensity maxima near the three spectral series limits, i.e., 4580, 3320, and 2240 Å. A modification of Bohr's theory which accounts for bands of continuous radiation by the recombination of electrons with atomic or molecular ions agrees with the observations. Theoretically, a velocity distribution of the free electrons in the arc corresponding with a temperature of 2500° Abs. gives an intensity distribution of the continuous spectrum in agreement with that observed. Some observations made by Rayleigh agree with the theory.

A. J. MEE.

"Ultimate rays" of mercury and aluminium.

A. T. WILLIAMS (Compt. rend., 1928, 187, 761—763).—Contrary to Croze's rule (A., 1924, ii, 1), the ultimate rays of mercury have been found to be 2537 and 1942 Å., the latter being the least refrangible of the $2S^2P$ series of the ionised mercury atom. The persistence of the resonance rays $1S^3P$ of cadmium, zinc, and mercury is in direct relationship with the value of the difference $2^3P_1 - 2^1P_1$. The ultimate rays of aluminium are probably 1862.90, 1854.67 ($2S^2P$), 1980.80 ($1P^1D$), and 1670.98 ($1S^1P$). The ultimate rays corresponding with those of the neutral atom of the elements of the first column of the periodic table ($2S^2P$ doublets) are the doublets of the ionised and doubly-ionised atoms of the elements in the second and third columns, respectively. In the fourth column silica has as an ultimate ray a doublet of a singly-ionised atom.

J. GRANT.

Interpretation of the continuous spectrum of hydrogen. Y. TAKAHASHI (Sci. Rep. Tohoku Imp. Univ., 1928, 17, 963—966).—Theoretical. It is suggested that the continuous spectrum of hydrogen is caused by the collision with molecules of free electrons having a kinetic energy intermediate between those corresponding with the resonance and dissociation potentials (cf. A., 1927, 1004).

A. R. POWELL.

Light-emission from atoms. J. KLEIBER (Ann. Physik, 1928, [iv], 87, 461—468).—Starting from the idea of electronic shells, it is shown that the mechanical analogy of a spiral spring moving like a pendulum is of assistance in picturing the atomic disturbances which lead to emission of light. Each shell is regarded as possessing a characteristic frequency, equal to the Rydberg constant divided by i^2 , where i is the number of the shell.

R. A. MORTON.

Rate of decay in the Balmer series. J. PORT (Ann. Physik, 1928, [iv], 87, 581—589).—Hydrogen canal rays projected into a high vacuum through a narrow slit give out light decreasing in intensity along the path of the particles. The decrease corresponds accurately with an exponential law. No deviation

from this law is recorded in the neighbourhood of the slit, so that observations made by Wien and Stark cannot be ascribed to atomic properties. In opposition to the requirements of the classical theory, the rate of decay in the Balmer series is independent of wave-length.

R. A. MORTON.

Oscillating discharges in hydrogen. Z. BAY and W. STEINER (Z. Elektrochem., 1928, 34, 657—662).—The continuous hydrogen spectrum is obtained on passing oscillating discharges of high frequency through intensively dried gas. The character of the spectrum is independent of the frequency (Lawson, A., 1913, ii, 911). Suitable electrodeless discharge tubes of quartz are described: they afford useful sources for light between 3300 and 1900 Å. (cf. A., 1927, 1117).

S. K. TWEEDY.

Lyman bands of hydrogen. E. C. KEMBLE and V. GUILLEMIN, jun. (Proc. Nat. Acad. Sci., 1928, 14, 782—787).—The $B-A$ bands of hydrogen have been re-examined to see whether an interpretation based on the two-branch hypothesis might not be more desirable than the one favoured by Hori (A., 1927, 1005), namely, that the Lyman bands consist of P , Q , and R branches. Frequency data are given and also the intensities of the emission lines, and an analysis of the data appears to favour this alternative hypothesis.

M. S. BURR.

Stark effect of helium. Y. ISHIDA and G. KAMIJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 117—140).—Photographs obtained using transformer electrical supply are compared with those obtained using battery supply and found to be in satisfactory agreement. Photographs were obtained for the first time of the lines parahelium 6631.89 ($2P-3P$); 4054.8 ($2S-4S$); 5043.6 ($2S-3D$), orthohelium 6068.77 ($2p-3p$); 4277.1 ($2s-3s$), and their polarisation and deflexion found. 5380.3 ($2S-3S$) of parahelium at a high electric field was observed with a direct-vision spectroscope. Results are in general agreement with the theoretical work of Foster (A., 1928, 101) based on the new quantum mechanics, and are considered to justify the use of a high electric field with an electrical supply not totally rectified.

N. M. BLIGH.

Stark effect of lithium. Y. ISHIDA and M. FUKUSHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 141—150).—Using a special cathode the effect was investigated and photographed, and was observed for the first time for the following lines: 6708.2 ($1s-2p$ and $2p-1s$), 6103.77 ($2p-3d$), 4971.98 ($2p-3s$), and 4273.3 ($2p-4s$). Further analogies of line combinations with those of orthohelium are noted. The inverse Stark effect for the p -component of the line 4132.4 ($2p-5f$) was observed.

N. M. BLIGH.

Structure of the $1'S_0-2'P_1$ and other lines in the cadmium spectrum. (FRL.) A. SCHRAMMEN (Ann. Physik, 1928, [iv], 87, 638—652).—The work of Wood (A., 1926, 986) on the cadmium line at 2288 Å. ($1'S_0-2'P_1$) indicated resolution into two lines 0.021 Å. apart. The data are, however, consistent with self-reversal, and as a result of a close investigation of the absorption and emission of this

line, an attempt is made to demonstrate the existence of a satellite (not separated) at a distance $d\lambda = -0.35 \times 10^{-3} \text{ \AA.}$ from the main line. The structure of a few other cadmium lines is given: Wood's resolution of the 2537 \AA. mercury line into five components is confirmed. R. A. MORTON.

Intensities of "forbidden" lines in a magnetic field. W. C. VAN GEEL (Z. Physik, 1928, 51, 51—61).—The intensities of the "forbidden" lines in the pd -multiplet of the neutral zinc atom have been investigated with respect to their dependence on a magnetic field and the ratios of their intensities to those of the non-forbidden lines. The results are in general accord with the theory, but the observed intensities are a little higher than those calculated. Some anomalies exist, however. J. W. SMITH.

Intensity calculations for the partial Paschen-Back effect. A. ZWAAN (Z. Physik, 1928, 51, 62—70; cf. van Geel, A., 1927, 83).—Mathematical. The matrix theory of Jordan and Heisenburg is used to calculate the intensities of the Zeeman components in the $(2p-3d)$ -multiplet ($\lambda \approx 3300 \text{ \AA.}$) of the zinc iodide spectrum in terms of the strength of the magnetic field applied. The intensities of the forbidden lines $2p_0-3d_3$, $2p_1-3d_3$, and $2p_0-3d_2$ are also calculated. The results are compared with those of Darwin (A., 1927, 707). J. W. SMITH.

Spark spectrum of argon. II. T. L. DE BRUIN (Z. Physik, 51, 108—113; cf. A., 1928, 450).—By generating an argon spark spectrum in a Geissler tube at a pressure of about 2 cm. a number of new lines have been found and measured. These have been fitted into the classification scheme previously developed. From the term values, the ionisation potential of the A II spectrum is evaluated as 27.75 ± 0.05 volts. Adding to this the ionisation potential of the A I atom—15.69 volts—a value of 43.44 volts is obtained for the second ionisation potential of argon, in fairly good agreement with the experimentally determined value. A table is given of 180 classified lines in the A II spectrum in the wavelength range 5300—3100 \AA. J. W. SMITH.

Zeeman effect in the argon spark spectrum (A II). C. J. BAKKER, T. L. DE BRUIN, and P. ZEEMAN (Z. Physik, 1928, 51, 114—135).—The Zeeman effect has been investigated with respect to 110 A II lines, the results confirming de Bruin's analysis of this spectrum (cf. preceding abstract). It follows from the Zeeman effect that in the spectrum of ionised argon, normal and abnormal combinations appear: in the higher energy levels the combinations are abnormal. For one term group the law of summation of the g -terms has been established. J. W. SMITH.

Origin of the green auroral line. L. A. SOMMER (Naturwiss., 1928, 16, 219; Chem. Zentr., 1928, i, 2484).—Experiments on the Zeeman effect of the green auroral line 5577.35 \AA. ascribe it to neutral oxygen ($^3P_1-^1S_0$); the excitation potential is 2.23 volts. A. A. ELDRIDGE.

Multiplets in the spectra of V III. R. C. GIBBS and H. E. WHITE (Physical Rev., 1927, [ii], 29, 606—607).—The triad of multiplets of V III designated as

$^4F_{2,3,4,5}$, $(^4G_{7,4,5,6})$, $^4F_{2,3,4,5}$, and $_{2,3,4}$ and the $^4F_{2,3,4,5}-^4F_{7,4,5,6}$ multiplet of Cr IV have been identified. A. A. ELDRIDGE.

Multiplets in the spectra of Cr III and Mn III. R. C. GIBBS and H. E. WHITE (Physical Rev., 1927, [ii], 29, 917).—The multiplet $^5F-^5G$ has been extended for four electron systems from Ti I and V II to Cr III, and the multiplet $^6D-^6F$ for five electron systems from V I and Cr II to Mn III. A. A. ELDRIDGE.

Absorption spectra of iron, cobalt, and nickel. W. F. MEGGERS and F. M. WALTERS, jun. (Physical Rev., 1927, [ii], 29, 358—359).—Results of absorption spectra observations confirm the known spectral structures for neutral and for ionised iron, cobalt, and nickel; many new levels have been established. A. A. ELDRIDGE.

Chemical valency and multiplicity of spectra. A. T. WILLIAMS (Contrib. Estud. Ciencias físic. mat. La Plata, 1928, 4, 243—252; Chem. Zentr., 1928, ii, 126).—Except for rare earths, iron, cobalt, and iridium, the chemical valency $V=r+1$, where r is the multiplicity of the spectrum. The derivation of the sign is discussed, and various values for an element are ascribed to particular electron configurations. A. A. ELDRIDGE.

Effect of temperature on the auto-electronic discharge. N. A. DE BRUYNE (Proc. Camb. Phil. Soc., 1928, 24, 518—520).—When both thermionic and auto-electronic emissions are present in a discharge it is possible to find the value of the auto-emission by subtracting from the total emission current the value of the thermionic emission as calculated by Schottky's relationship. This separation of the two emissions has been carried out, and it has been found that, within the limits of experimental error, the auto-emission is independent of temperature up to the highest cathode temperature used (1944°). This agrees with the theory of auto-electronic emission put forward by Fowler and Nordheim. A. J. MEE.

Determination of ionisation potentials. S. DATTA and S. SEN (Z. Physik, 1928, 50, 849—860).—measurements have been made of the current flowing through a Bunsen flame in which metallic salt vapours may be introduced as a function of the $P.D.$ between two platinum electrodes under the following conditions: (A) the cathode covered with a thorium preparation, (B) thorium-coated cathode and metallic salt vapour in flame, and (C) uncoated cathode and metallic salt vapour in flame. The difference between the current (B) and the sum of the currents (A) and (C) when plotted against the electrode $P.D.$ attains maxima corresponding with $V_r - V_i$, and with V_i , respectively, where V_r denotes the resonance potential and V_i the ionisation potential. Data are given for sodium, potassium, lithium, magnesium, calcium, strontium, barium, and mercury. R. W. LENT.

Systematic variations of the constant A in thermionic emission. L. A. DEBRIDGE (Proc. Nat. Acad. Sci., 1928, 14, 788—793).—The data for thermionic emission from various metallic surfaces, viz., platinum, tungsten, thoriated tungsten, potassium, and liquid silver, gold, and copper, have been examined

with the view of testing the relationship, first observed by Richardson (Proc. Roy. Soc., 1915, **A**, **91**, 524) for platinum and tungsten, that, when the work function b of a given surface, in the equation $I = AT^2e^{-b/T}$, is changed by any method, *e.g.*, heating, out-gassing, coating, etc., the constant A also changes in such a way that $\log A$ is a linear function of b . This was confirmed in all cases. All the curves may be represented by a simple empirical equation, $\log_e A = \log_e A_0 + \beta(b - b_0)$, where $A_0 = 60$, β , the slope, is a constant depending on the nature of the surface, and b_0 has the same value for all the more refractory metals. It can be shown that the observed variations of A might be ascribed to a small temperature variation of the surface work function b , which is in agreement with the conclusion reached by Bridgman (*A.*, 1928, 682) that, in Dushman's simple theory, a term has been neglected which is related to the temperature derivative of the work function. The coefficient of the temperature change can be obtained from measurements on the shift of the photoelectric threshold with temperature. The values thus obtained are found to be of the right sign and order of magnitude.

M. S. BURR.

Photoelectric long-wave limit of potassium vapour. R. C. WILLIAMSON (Proc. Nat. Acad. Sci., 1928, **14**, 793—796).—The ionisation currents, obtained by illuminating a jet of potassium vapour with ultra-violet light, have been studied by a method previously described (Physical Rev., 1923, [ii], **21**, 107) using a monochromator instead of filters, and making also some slight modifications in dimensions of apparatus etc. The results give an approximate indication of the relative ionising efficiencies of the different wave-lengths of light. Ionisation sets in sharply near 3027 Å. In general the ionisation current rises to a maximum at about 2800 Å., falls to a minimum at about 2600 Å., rises sharply to a maximum at about 2150 Å., and drops again down to 2050 Å. Since the spectroscopic limit for the potassium atom is 2856 Å., ionisation is occurring in this case at least 170 Å. above the expected limit, and may perhaps be accounted for on the basis of molecular ionisation. On this assumption the ionising potential of the molecule would be between 4.08 and 3.94 volts, corresponding with a limit between 3027 and 3131 Å. for ionisation without dissociation. The 2610 Å. limit gives 4.74 volts, corresponding with ionisation with dissociation. Thus the energy of dissociation of the ionised molecule is between 0.66 and 0.80 volt. From the limit for atomic ionisation, 2856 Å., corresponding with 4.32 volts, the dissociation potential of the neutral molecule is 0.42 volt, which is rather low compared with the value of 0.61 volt estimated by Carrelli and Pringsheim (*A.*, 1927, 1018). The dissociation potential of the ionised molecule appears to be larger than that of the neutral molecule, and atomic ionisation is probably obscured by molecular ionisation.

M. S. BURR.

Emergent energy of photoelectrons in potassium vapour. R. C. WILLIAMSON (Proc. Nat. Acad. Sci., 1928, **14**, 796—801).—Preliminary experiments are described for determining the negative photo-electronic currents obtained when potassium vapour

is illuminated by ultra-violet light. Both total and monochromatic radiation have been used.

M. S. BURR.

Generation of the helium spectrum by electrical excitation. L. S. ORNSTEIN, H. C. BURGER, and W. KAPUSCINSKI (Z. Physik, 1928, **51**, 34—50).—The intensities of the helium lines produced by electrical excitation have been measured by a thermoelectric method, and their variation with current strength and with pressure has been followed. The cross-section of the capillary of the discharge tube was found to exert a considerable influence on the intensities of the lines at constant pressure and current density. The changes with pressure of the ratios of the intensities of the triplets and single lines at different current densities have also been measured. It is concluded that the emission is not produced by the reunion of ions and electrons, but that atomic collision plays a major rôle. In direct excitation by electronic collision, a priority rule holds which is analogous to the selection rule for radiation.

J. W. SMITH.

Effect of electric fields on the emission of electrons from conductors. A. T. WATERMAN (Proc. Roy. Soc., 1928, **A**, **121**, 28—40).—Houston's explanation (*A.*, 1928, 467) of the extraction of electrons from metals by intense electric fields, based on Sommerfeld's modification of the Lorentz electron theory of metals (*A.*, 1928, 467), is shown to be inadequate. Houston's work is to be regarded as a treatment of the Schottky effect for very intense fields, but, according to Sommerfeld's theory, the Schottky equation should be modified, and this modification becomes significant at high fields. The degree of penetration of a surface electrical charge into the body of a conductor is worked out on the basis of the Sommerfeld electron theory.

L. L. BIRCHMUNSHAW.

Time function of the light emission of active nitrogen. A. KOENIG and G. H. KLINKMANN (Z. physikal. Chem., 1928, **137**, 335—351).—The total illumination from active nitrogen is indicative of a bimolecular reaction, but little can be said of the individual bands in the spectrum. The bands in the β -group of the afterglow spectrum at 4310—4300 Å. and 4040—4025 Å. are not represented in the arc discharge spectrum, whilst the weak afterglow band at 5050 Å. could not be observed. The rate of fading of the band diminishes as the wave-length decreases, being about twice as great for the red bands as for the violet. Bands of the α -group disappear with very much greater velocity than do those of the β -groups. The reactivity and the intensity of the afterglow of active nitrogen do not follow parallel courses.

H. F. GILLBE.

New resonance series of selenium. B. SCHMIDT (Bull. Acad. Polonaise, 1928, **A**, 61—68).—A new series in the resonance spectrum of selenium, produced by excitation with the magnesium 4481 line, has been observed and measured. This band first becomes visible at 300°, attains a maximum intensity at 400°, and disappears at about 500°. Even under the most favourable conditions the intensity is very low. The wave-lengths of the lines may be expressed

by the general formula $1/\lambda = 22312 - 362m + 1.3m^2$. It is deduced that absorption of the exciting ray 4481 corresponds with the passage from the normal state $n=14$ to the excited state $n'=1$. On this supposition the results are in good agreement with former observations.

J. W. SMITH.

Retarded luminescence observed in air. W. BERNHARDT (Bull. Acad. Polonaise, 1928, A, 69—83).—It has been shown that the retarded luminescence of air occurs mainly in the space occupied by the positive columns and penetrates very little into the Faraday dark space. Since the intensity of the field has been shown to be very low in the positive column, it is concluded that it is the consequent longer free path of the molecules which permits the formation of molecules capable of giving rise to this luminescence. New types of retarded luminescence have been observed in air under pressures varying from hundredths of a mm. to 170 mm. Below 1 mm. pressure the luminescence is pale green, at 1 mm. darker green. This luminescence may be propagated to distances of 80 cm. and more. Above 1 mm. pressure the colour is emerald-green and it is propagated only about 10 cm. Using relatively high pressures (30—40 mm.) and a high-tension discharge, a yellow retarded luminescence may be obtained. The time of retardation of the green luminescence diminishes with pressure, varying from 20 to 0.01 sec. In all cases the spectra of the luminescence are of a continuous nature. The temperature limits between which the effect can be obtained are -130° and $+200^\circ$.

J. W. SMITH.

Absolute magnitude effects in stellar spectra. E. A. MILNE (Nature, 1928, 122, 840—841).

Polarisation of Compton scattering according to Dirac's new relativistic dynamics. Y. NISHINA (Nature, 1928, 122, 843).

Atomic moments. P. WEISS and G. FOEX (Compt. rend., 1928, 187, 744—746).—The published values of the atomic moments of iron, nickel, cobalt, oxygen, copper, chromium, platinum, palladium, and vanadium in various states of combination but corrected for the diamagnetism of the atoms concerned are assembled, and their probable accuracies discussed. With the exception of that of the cobaltous ion in the hexagonal sulphate (25.67) and of ferrous iron in the ammonium sulphate (26.5) they are all approximately whole numbers and multiples of Bohr's theoretical magneton (equal to 5 experimental magnetons).

J. GRANT.

Liberation of secondary electrons by electrons of 1—30 kilovolts. E. BUCHMANN (Ann. Physik, 1928, [iv], 87, 509—535).—The number s of secondary electrons liberated in a 1 cm. path at 1 mm. of mercury by electrons of $1-30 \times 10^3$ volts has been determined to within 3% for air, argon, carbon dioxide, and hydrogen. Earlier results are confirmed. At the K -limit for argon (2.9 kilovolts), s exhibits no sudden change. For a few velocities, the total number of electrons S has been measured directly and found to vary as the energy of the primary electron. The mean energy e necessary for the formation of an ion-

pair is 31 ± 3 volts. The range of the electrons has been calculated from S , s , and e . R. A. MORTON.

Polarisation of canal-ray light in weak electric fields. II. The accompanying emission of in various arrangements of the field. E. RUPP (Ann. Physik, 1928, [iv], 87, 285—297; cf. A., 1928, 454).—In homogeneous fields parallel or at right angles to the canal rays, no influence is noticeable on the polarisation. If the weak electric field is directed at an angle of 45° to the canal rays, periodic variations of the polarisation ratio occur which are in accordance with the theory of anharmonic oscillators.

W. E. DOWNEY.

Influence of positive ions on the electronic space charge within a two-plate system. H. COHN (Ann. Physik, 1928, [iv], 87, 543—568).—In a symmetrical two-plate tube, the gas is ionised by electrons traversing the tube. The ions formed in this way tend to neutralise the space charge. The magnitude of this effect varies as the number of gas molecules, *i.e.*, as the pressure, also as the mass of the atoms, and inversely as the absorption of electrons by the molecules of the gas. At very low pressures, the voltage needed for neutralisation exceeds the ionisation potential, and depends on the number of electrons traversing the tube before neutralisation. The neutralisation occurs independently of the magnitude of the cathode saturation current. For different gases with the same ionising potential, the pressure necessary for the neutralisation effect at the same neutralisation voltage varies inversely as the mass of the gas atom. Positive potassium ions, according to their velocity, effect a more or less marked decrease in the space charge. Comparison of the results with potassium and argon ions shows that an ion-current of about 2 milliamp. is necessary for neutralisation of the space charge to follow.

R. A. MORTON.

Mobility of ions in air. IV. Investigations by two new methods. A. M. TYNDALL, L. H. STARR, and C. F. POWELL (Proc. Roy. Soc., 1928, A, 121, 172—184).—Details are given of two new methods of mobility measurement. The advantages of the first (known as the "four-gauze" method) are that the apparatus can be made air-tight, that there is no commutator, that the method has a higher resolving power than the older method (cf. Tyndall and Grindley, A., 1926, 219), that the time of measurement is shorter, and that, within certain limits, the ions may be given any required age before their mobility is measured. The second method (the "two-slit" method) also has a high resolving power and gives ions of controlled age, but it involves the use of an alternating field of the "square-wave" type, produced by a revolving commutator, so that the time of measurement is necessarily long. Neither of the methods gives absolute values. The rate of transformation of the positive ion in air is found to be considerably higher by these methods than in earlier work (*loc. cit.*), and there is evidence that the transformation is a more complicated phenomenon than was supposed. In many cases the ionisation-current-frequency curve suggests the presence, not only of initial and final ions, but also of ions of intermediate mobility. Moreover, the results for short-

age (0.016 sec.) positive ions in air containing water vapour, unlike those for negative, are found to be variable. At long ages (0.25 sec.) the results are more definite. The positive ions in air are found to have mobilities distributed over a small range with a mean value of about 1.25 cm./sec. per volt/cm., independent of the humidity of the air. No evidence is obtained of the presence of initial positive ions in very dry air or in pure nitrogen. If any are formed, they must nearly all transform in less than 1/100 sec. The mobility of both positive and negative ions in air containing propyl alcohol vapour is independent of the age of the ions from 1/65 to 2/3 sec.

L. L. BIRCUMSHAW.

Mobility of ions in air. V. Transformation of positive ions at short ages. A. M. TYNDALL, G. C. GRINDLEY, and P. A. SHEPPARD (Proc. Roy. Soc., 1928, A, 121, 185—194).—To investigate the possibility that the variable results obtained for the rate of transformation of short-age positive ions in air (cf. preceding abstract) might be partly due to products of chemical action arising from the α -rays or to impurities given off from the walls which would accumulate in a closed vessel, the effect of adding certain gases and vapours to the air in which positive ions are formed has been studied by an air-blast method. The method is identical in principle with that used by Erikson (A., 1925, ii, 79), but the brass plates are much closer together, thereby reducing the portion of the life of the ion spent in the measurement of the mobility to about 1/1200 sec. The effects of using dry air, ozonised air, ozonised oxygen, oxides of nitrogen, nitrogen, and methyl and propyl alcohol vapours were investigated. A small quantity of ozone, generated either by an ozoniser or by a point discharge, produces a marked increase in the rate of transformation, and there is evidence that sufficient ozone may be generated by α -rays from polonium in a closed vessel to produce an appreciable effect. If the rate of decomposition of ozone is accelerated by the presence of manganese dioxide in the ionisation chamber, or if a rapid air stream is blown over the polonium so that the ozone generated by the α -rays is continuously removed, an increase in the relative number of initial ions is observed, due to a decrease in the rate of transformation. It is argued that the ozone effect may explain certain discrepancies between the results of mobility measurement made by various observers using different methods. The rate of transformation is greatly retarded if, before entering the air blast, the ions are formed in the presence of methyl or propyl alcohol vapours. The significance of the results obtained is discussed. It is suggested that the initial ion depends for its formation on the presence of water vapour, and is transformed into a final stable ion on collision with an ozone molecule. The relatively slow rate of transformation may perhaps be due to the dependence of the change on some type of three-body collision.

L. L. BIRCUMSHAW.

Application of Ebert's ion counter to the determination of the number and mobilities of small ions in the atmosphere. W. J. BARANOW and E. S. SRSCHEPOTJEWA (Physikal. Z., 1928, 29, 741—750).—For accurate determinations of the mobilities of ions

in the atmosphere, it is necessary to consider three groups of ions, larger, medium, and smaller, and to determine the mean mobility in each group by means of a special technique.

R. A. MORTON.

Magnetic moments of hydrogen-like atoms. F. B. PIDDUCK (Nature, 1928, 122, 925).

Rate of emission of α -particles from radium. H. J. J. BRADDICK and H. M. CAVE (Proc. Roy. Soc., 1928, A, 121, 367—380).—A direct determination of Z , the number of α -particles from disintegrations taking place in 1 g. of radium in 1 sec., has been made by the "total charge" method. The apparatus and method are described and the average value of Z from a number of determinations is given as $3.68 \times 10^{10} \pm 1\%$. Radium-C was used as the source. This result is discussed with regard to the heat evolved by radium and its products, and it is concluded that there is no need to assume any other form of heat production than those already recognised.

J. L. BUCHAN.

Internal conversion of γ -rays. II. (Miss) B. SWIRLES (Proc. Roy. Soc., 1928, A, 121, 447—456; cf. A., 1927, 1004).—Mathematical. J. L. BUCHAN.

Quantum theory of nuclear disintegration. G. GAMOW (Nature, 1928, 122, 805—806).—A brief account of investigations which have afforded a quantitative explanation of certain features of natural α -ray disintegration and throw light on the phenomenon of artificial disintegration. The results support Rutherford's observations, in which artificial disintegration was not observed with elements heavier than phosphorus, but not those of Petterson and Kirsch.

A. A. ELDRIDGE.

Loss in velocity of α -particles in passing through metal foils. S. ROSENBLUM (Physikal. Z., 1928, 29, 737—739).—The author's data on the retardation suffered by α -particles after passing through thin sheets of various metals are summarised (cf. A., 1926, 879; 1927, 1120). Each metal is shown to be characterised by a constant K . The work of Kohlrausch (A., 1928, 455) allows K to be calculated theoretically, and comparison shows fairly close agreement with experiment for the elements of low atomic number, and agreement as regards order for elements of high atomic weight.

R. A. MORTON.

Duration of excited sodium atoms as deduced from the brightness of sodium flames and the degree of dissociation of sodium salts in flame. R. LADENBURG and R. MINKOWSKI (Ann. Physik 1928, [iv], 87, 297—306).—Polemical against Ornstein and van der Held (A., 1928, 679). W. E. DOWNEY.

Nature of active nitrogen. H. O. KNESER (Ann. Physik, 1928, [iv], 87, 717—736, and Physikal. Z., 1928, 29, 895—896).—Three mechanisms have been advanced to account for the afterglow in active nitrogen: (a) metastable excited molecules (+11 volts) revert to the normal state on impact with neutral molecules and emit light (A., 1924, ii, 803); (b) triple collisions between two nitrogen atoms and one nitrogen molecule result in the formation of one activated molecule which then reverts to the normal state as in (a) (A., 1926, 8); (c) the Cario-Kaplan explanation (A., 1928, 683) combining (a) and (b). The rate of decay of the afterglow has

been calculated on the basis of the alternative mechanisms, and deactivation by the walls of the containing vessel has also been considered. The rate of decay has been studied experimentally by means of visual photometry using a Lummer cube, and varying the nature of the wall, rare gas additions, and pressure. Observations have been made on the increase in brightness in the afterglow which results from the addition of inactive particles for triple collisions. The results are definitely inconsistent with (a), consistent with (b), and with certain assumptions perhaps consistent with (c) (cf. also A., 1928, 961).

R. A. MORTON.

Attempt to polarise electron waves by reflexion. C. J. DAVISSON and L. H. GERMER (Nature, 1928, 122, 809).

Possible role of diffusion by electrons in the propagation of short waves. PONTE and Y. ROCARD (Compt. rend., 1928, 187, 942—943).—If it is assumed that the Heaviside (*H*) layer is not analogous to a perfect gas, but is made up of small groups of electrons forming "molecules," the distance apart (*d*) of which is of the order of a short wavelength, then the analogy of the diffusion of X-rays by a crystalline powder may be applied to the diffusion of wireless waves by the *H*-layer (cf. Eckersley, Nature, 1928, 121, 245). The great variations in the zones of silence may then be explained by relatively small variations in *d*, or by large variations in the height of the layer, a mean value for which of 360 km. is obtained.

J. GRANT.

Wave theory of the electron. J. M. WHITTAKER (Proc. Camb. Phil. Soc., 1928, 24, 501—505).—In Darwin's method of accounting for the "duplexity" of the atom without using the spinning electron hypothesis, the work can be given invariance of form only by replacing the four wave functions by sixteen. This complication is avoided by specifying the electron wave as a six-vector analogous to the electromagnetic force vector, the first three components being the components of a space vector analogous to the electric force, and the last three the components of a space vector analogous to the magnetic force. The differential equations satisfied by these functions are obtained by assuming that in a null magnetic field they admit a solution representing a plane wave advancing with uniform velocity. The theory leads to the correct energy levels for the fine structure of the hydrogen atom, and gives correct results for the free motion of the electron.

A. J. MEE.

Quantum theory of atomic nuclei. G. GAMOW (Z. Physik, 1928, 51, 204—212).—The mechanism of the emission of α -particles is analysed by wave mechanics and a theoretical basis is found for the relationship between the decay constant and the energy of the α -particle.

R. W. LUNT.

Reason why an elementary quantum of electricity cannot split up into still smaller charges. W. ANDERSON (Ann. Physik, 1928, [iv], 87, 536—542).—If a particle of mass m_0 and charge e "explodes" into n_1 equal parts, these must have mass m_0/n_1 and charge e/n_1 . In a vessel of finite volume, the null-point energy of the gas must be smaller than

$m_0 c^2$, where c is the velocity of light. This is conditional on the original charge being greater than a definite universal minimal charge.

Calculation shows that e_{\min} is certainly greater than 1.14×10^{-11} e.s.u., probably greater than 1.14×10^{-10} e.s.u., and perhaps even greater than 1.14×10^{-9} . The last-named limit gives a simple reason for the stability of electrons and protons with a charge of 4.774×10^{-10} e.s.u.

R. A. MORTON.

Origin of magnetism based on the structure of atoms. K. HONDA (Sci. Rep. Tohoku, 1928, 17, 997—1009).—See A., 1928, 568.

Is it possible to test by a direct experiment the hypothesis of a spinning electron? L. BRILLOUIN (Proc. Nat. Acad. Sci., 1928, 14, 755—763).—The possibility of determining by direct experiment whether or not the multiplet structure of line spectra is due to rotation of the electron and the influence of the magnetic field on its angular momentum and magnetic moment is discussed mathematically, and a former assumption (cf. Compt. rend., 1927, 184, 82) corrected. A form of electromagnet suitable for such a purpose is described.

M. S. BURR.

Structure of the atom. F. J. VON VISNIEWSKI (Physikal. Z., 1928, 29, 716—720).—An attempt is made to develop an atomic structure on the supposition that each atom contains one electron in the *K* energy level, one in the *L*-level, and one in one of the 5*M*-levels etc.

J. W. SMITH.

Dynamics of an electron. D. MEKSYN (Phil. Mag., 1928, [vii], 6, 977—991).—The general theory of relativity is applied to the dynamics of an electron.

W. E. DOWNEY.

Homopolar combination in excited hydrogen molecules. E. A. HYLLEAAS (Z. Physik, 1928, 51, 150—158).—Mathematical. With the help of wave mechanics, calculations are made of the reciprocal action between hydrogen atoms, of which one is in the fundamental state and the other in an excited state. Of the four solutions to the wave equation, two apply to elastic reflexion and two to molecule formation. Of the latter, both show symmetry in both nuclei, but the electrons are symmetrical in the one case and asymmetrical in the other, corresponding with a para- and an ortho-term of the hydrogen molecule. In such a state the energy of dissociation is less and the moment of inertia is greater than in the fundamental state.

J. W. SMITH.

Limitation of the system of elements. W. KOSSEL (Naturwiss., 1928, 16, 298—299; Chem. Zentr., 1928, i, 2689).—A possible explanation of the absence of atomic numbers greater than 92 is based on a consideration of the relative importance of electrostatic and magnetic attraction within the atom.

A. A. ELDRIDGE.

Heat of dissociation of nitrogen. R. T. BIRGE (Nature, 1928, 122, 842).—The author gives reasons for considering that the heat of dissociation of nitrogen cannot well be greater than 9.5 volts (cf. Gaviola, A., 1928, 1075, 9.8 volts; Birge and Spomer, A., 1926, 993, 11.4 volts). Other probable values of heat of dissociation are: oxygen 7.0, carbon monoxide 11, nitric oxide 7 volts.

A. A. ELDRIDGE.

[Heat of dissociation of nitrogen.] R. S. MULLIKEN (Nature, 1928, 122, 842—843).—A consideration of the products of dissociation supports the value 9.5 volts for the heat of dissociation of nitrogen (see Birge, preceding abstract).

A. A. ELDRIDGE.

Fluorescence and photo-sensitisation in aqueous solution. I. W. WEST, R. H. MULLER, and E. JETTE (Proc. Roy. Soc., 1928, A, 121, 294—298).—A discussion of the problem.

J. L. BUCHAN.

Fluorescence and photo-sensitisation in aqueous solution. II. E. JETTE and W. WEST (Proc. Roy. Soc., 1928, A, 121, 299—312).—The apparatus used is described. Two photo-electric cells were connected differentially with a standard solution in front of one and the solution under investigation in front of the other. By this means fluctuations in the intensity of the source (a mercury lamp) were automatically corrected. The effect of various salts in extinguishing the fluorescence of different substances has been studied, and the results are expressed as percentage extinction of the fluorescence due to the pure fluorescent substance. Tables are given showing the extinction of the fluorescence of quinine hydrogen sulphate by various salts and it is concluded that the effect is due chiefly to the negative ions. Silver ions, however, exert some influence. Non-electrolytes, such as sucrose and carbamide, were practically without effect, whilst the influence of electrolytes seemed to be decreased by a high viscosity of the solution. When solutions of disodium fluorescein were used instead of quinine hydrogen sulphate much the same extinction effect was observed, but higher concentrations of the added salt were necessary to produce the same percentage extinction. The amount of added salt necessary to reduce the fluorescence of uranyl sulphate to zero has also been found. From an examination of these substances the inhibiting power of various ions has been shown to be $I' > CNS' > Br' > Cl' > C_2O_4'' > Ac' > SO_4'' > NO_3' > F'$. The cause of this effect is discussed and it is pointed out that the order of the ions in the above series is the same as in that of their deformabilities. The deformability of the silver ion is greater than that of other cations. It is concluded that the energy of the activated fluorescent molecule is used to deform the inhibiting ion with which it collides, instead of being given out as light.

J. L. BUCHAN.

Fluorescence and photo-sensitisation in aqueous solution. III. R. M. MULLER (Proc. Roy. Soc., 1928, A, 121, 313—317; cf. preceding abstract).—The fluorescence of 0.1*M*-uranyl sulphate solution in the presence of varying amounts of oxalic acid has been measured. It has been shown that the greater the concentration of oxalic acid the less is the amount of light emitted and the greater is the amount of oxalic acid decomposed photo-chemically, until the ratio $H_2C_2O_4/UO_2$ becomes unity, after which it remains constant. The order in which anions diminish the photolysis of oxalic acid is the same as that in which they extinguish the fluorescence of uranyl salts.

J. L. BUCHAN.

Depolarisation of the secondary radiation in the complex light resulting from the molecular diffusion of monochromatic light. J. CABANNES (Compt. rend., 1928, 187, 654—656).—The depolarisation of secondary radiations observed by Raman (A., 1927, 1127; 1928, 1075) has been studied for benzene and ethyl ether, and the following conclusions are reached: (1) If the liquid is illuminated with different radiations N, N'_1, \dots , all the secondary rays $N-n_1, N'-n_1, \dots$ with the same diminution in frequency have the same depolarisation. (2) This depolarisation varies within wide limits according to the particular diminution in frequency. The results indicate that the molecules fall into groups, each group producing its own diminution in frequency and depolarisation. The groups probably represent molecules in different orientations relative to the incident ray.

W. HUME-ROTHERY.

New bands of mercury hydride in the ultra-violet. H. JEZEWSKI (Bull. Acad. Polonaise, 1928, A, 143—162).—The existence of a new series of bands in the ultra-violet emitted when a discharge is passed through a mixture of hydrogen and mercury vapour has been demonstrated. The apparatus used is described, and the conditions for appearance of the bands are enumerated. The spectrum is analysed, and equations are given showing the frequency of the rays as a function of the quantum number. From the equations the moment of inertia of the molecules and the distance apart of the nuclei are calculated. It is shown that the use of fractional quantum numbers is justified. The purity of the hydrogen and mercury used leaves no doubt that the bands are emitted by some combination of the two. The moment of inertia of the molecules, however, is smaller than that of the molecules emitting Hulthén's bands; also the bands degrade towards the red, instead of towards higher frequencies as in Hulthén's case. These observations, together with the fact that the bands are always accompanied by a spark spectrum, indicate that the molecules are ionised. This is confirmed by an application of Ludloff's rule. The emission is probably due to the considerably deformed molecule of mercury hydride.

A. J. MEE.

X-Ray phosphorescent and thermophosphorescent radiations of kunzite. O. STUHLMAN and A. F. DANIEL (J. Opt. Soc. Amer., 1928, 17, 289—293). The spectral distribution of phosphorescence excited in kunzite crystals by X-rays was determined. There are two emission bands, one weak and of wavelength about 0.50 μ , the other stronger and having a maximum at 0.65 μ . The thermophosphorescence was also determined. A rose-coloured light began to be emitted at about 168°, the radiation being composed of a broad orange band with a maximum near 0.64 μ and a weaker band with a maximum near 0.50 μ . As the temperature was raised the bands gradually widened up to a temperature of 400°, when the phosphorescence suddenly ceased. The colour changes of kunzite on heating or on exposure to ultra-violet light, X-rays, or radium radiation may be explained on an oxidation and reduction hypothesis connected with the manganese contained in the mineral.

A. J. MEE.

Scattering of light by crystals. G. LANDSBERG and L. MANDELSTAM (*Z. Physik*, 1928, 50, 769—780).—The light scattered by quartz and calcite when mercury arc light is incident on these crystals has been examined spectroscopically. It has been found that each line in the incident radiation appears in the light scattered by the crystal together with a number of satellites of greater and of less frequency. The frequency difference between the satellite lines and the incident line for quartz correspond with the wave-lengths 9.0, 13.5, 21.5, 48, and 81 μ and for calcite with 9.1 and 34 μ . The relation of these wave-lengths to known infra-red wave-lengths is discussed.

W. LUNT.

Delayed green fluorescence of mercury vapour. S. PIENKOWSKI (*Bull. Acad. Polonaise*, 1928, 4, 241—256, and *Z. Physik*, 1928, 50, 787—792).—The average duration of the delay of the fluorescence of mercury vapour excited by ultra-violet rays was measured and found to be of the order 10^{-6} sec. and decreased with increasing vapour density. The intensity of the fluorescence was examined with the aid of photo-micrometric curves, and was shown to increase from the moment of excitation and to reach a maximum. The rate of intensity rise and of extinction increased with the vapour density. Evidence pointed to the existence of an intermediate state of the mercury, from which the fluorescence arises as a molecular and not as an atomic phenomenon.

N. M. BLIGH.

Ultra-violet fluorescence of iodine bromide. A. FILIPPOV (*Z. Physik*, 1928, 50, 861—873).—When iodine bromide vapour is irradiated with radiation of shorter wave-length than 2000 Å. the fluorescent light consists of a number of bands between 2750 and 4900 Å. Arguments are advanced to show that the fluorescence must arise from excited IBr molecules. The spectrum is modified by the addition of nitrogen or helium, the structure of some of the bands being more clearly defined; the spectrum from an iodine chloride-nitrogen mixture is similar.

R. W. LUNT.

Absorption of ultra-violet light by the inversion products of sucrose. L. KWIECINSKI and L. MARCHLEWSKI (*Bull. Acad. Polonaise*, 1928, 4, 257—261).—If the inversion products of sucrose contained only dextrose and *d*-levulose, only a faint absorption band due to the latter would be expected (cf. A., 1928, 346). Absorption measurements made at various stages of the inversion process show that other products of unknown nature are formed.

N. M. BLIGH.

Absorption of ultra-violet light by the glucosans. L. KWIECINSKI and L. MARCHLEWSKI (*Bull. Acad. Polonaise*, 1928, 4, 263—269).— β -Glucosan was purified by repeated recrystallisation. The absorption of ultra-violet light by the successively purer crystallisation products, and by the products recovered from the mother-liquors, showed a band weakening and finally disappearing in the former case, and stronger in the latter, due to the accumulation of unknown impurities. An unpurified sample of α -glucosan showed a band the position of which indicated that impurities, if present, were not identical with those

in β -glucosan. Results were supported by molar extinction coefficients, given in all cases.

N. M. BLIGH.

Absorption of ultra-violet light by arabinose, maltose, sucrose, raffinose, and by mannitol and dulcitol. L. KWIECINSKI and L. MARCHLEWSKI (*Bull. Acad. Polonaise*, 1928, 4, 271—282; cf. preceding abstract).—Highly purified specimens of each of the above carbohydrates showed no selective absorption. Sucrose required especially careful purification, the extent of which was determined with certainty by measurement of extinction coefficients.

N. M. BLIGH.

Formation of phosphorescence centres in calcium sulphide. F. BANDOW (*Ann. Physik*, 1928, [iv], 87, 469—508).—Preparatory to a more accurate determination of the absolute energy output from a phosphor, i.e., the maximum number of electrons separable from one heavy metal atom, it has been necessary to investigate more closely the rôle of the flux. For the three emissions CaS-Cu α , CaS-Mn α , and CaS-Bi α , the maximum light-sum with ordinary preparations considered with reference to a definite heavy metal content can be obtained only when fluorides are added to form a flux. Fluoride additions do not affect the distribution of phosphorescence centres corresponding with emissions differing in duration, which is obtained with sodium sulphate or borax additions. The fluoride addition necessary for maximal effect varies directly as the metal content. Secondary factors such as volatilisation of metal etc. are not influenced.

“Nursulfidphosphores,” i.e., phosphors in which the base consists solely of calcium sulphide, exhibit without addition of fluoride the maximum effect, which is obtained only by adding fluoride to the ordinary phosphors. The increase in initial photo-electric effect which appears in mechanically disturbed phosphors without irradiation has been studied in relation to the effect of various added substances on the formation of centres, but considerable difficulties are encountered. Phosphors containing additions of sodium chloride are in many respects abnormal. In phosphors to which calcium oxide has been added, the light-sum decreases regularly with increasing lime content, but a rearrangement of the types of centres occurs.

Addition of fluoride does not cause the appearance of new centres, but rather acts directly on the atoms of heavy metal, apparently by changing the number of electrons separable from a single atom. It seems possible that the phosphorescence centre must contain every constituent of the phosphor.

R. A. MORTON.

Ultra-violet luminescence of calcium oxide and calcium sulphide excited by X-rays. E. RUMPF (*Ann. Physik*, 1928, [iv], 87, 590—594).—Under the action of X-rays (Cu-K α), calcium oxide and calcium sulphide exhibit ultra-violet luminescence, due apparently to traces of impurity which cannot be eliminated. In the case of the oxide, the emission shows a strong band with a maximum near 345 375 μ , and a weaker band extending from 280 to 330 μ , with a maximum near 320—330 μ . Addition of traces of copper or manganese excites another

band near 450 The emission from calcium sulphide is similar, but the wave-lengths are about 10 μ greater, and the luminescence is very much weaker. The work provides a test for the presence of appreciable quantities of oxide in sulphide preparations. R. A. MORTON.

Light absorption and the nature of molecular combination in gases and vapours. (Miss) H. SPONER (Z. Elektrochem., 1928, 34, 483—489).—Atomic molecules (e.g., non-polar molecules like hydrogen, halogens, and polar molecules like silver halides) are dissociated by absorption of light into a normal and an excited atom. In ionic molecules this dissociation may also be accompanied by dissociation into two normal atoms. S. K. TWEEDY.

Fluorescence and solid solution. (Miss) M. K. SLATTERY (Proc. Nat. Acad. Sci., 1928, 14, 777—782; cf. A., 1926, 659).—When activated by traces of uranium, which must be in solid solution in the salts, alkali fluorides fluoresce under excitation by ultra-violet light at the temperature of liquid air. A spectrum of fine lines is obtained, the position of these being independent of the amount of activator present. The lines can be arranged in four sets of constant frequency separation with a slightly different interval for each set, the intervals being 17.9, 17.6, 17.2, and 16.7 units, respectively. The lines for fluorescent lithium fluoride can be arranged in four sets with the same separation as those of sodium fluoride. Three of the sets are slightly displaced from the sodium fluoride positions, but the one with the 17.2 interval is identical with that of sodium fluoride. The average of these frequency intervals is 17.6, the interval for uranium. The meaning of constant frequency emission for a solid is not very clear, but the different intervals are probably dependent on vibrating systems of slightly different moments of inertia. An attempt was made by the X-ray powder method to determine whether the introduction of uranium into the crystal, although in such small quantity—one part in 200 parts at the most—might not produce a measurable change in the crystal structure of the solid solvent surrounding it. No such change was observed. This contradicts the view put forward by Ewles (A., 1926, 455). The fluorescence of mixtures of sodium and lithium fluorides when mixed with uranium in the proportion of one part of the latter to 2000 parts of the former has been studied. There is a gradual change of colour of fluorescence towards the green as the amount of lithium increases, and both lithium and sodium lines are shifted, sodium about 3 Å. towards shorter wave-lengths and lithium to a smaller extent in the opposite direction. The amount of shift was the same for all mixtures, contrary to what was observed by Travnicek (A., 1923, 106) for calcium-strontium sulphide mixtures with samarium. Corresponding changes in the crystal structure were also observed by X-ray methods, and these, too, were constant for all mixtures. Hence an increase in crystal dimensions causes an increase in wave-length of fluorescence. In order of size of lattice lithium fluoride is 2.007 Å., sodium fluoride 2.310 Å., and potassium fluoride 2.664 Å. The fluorescence colours are green yellow, and orange, respectively. M. S. BURR

Valency. XI. Molecular conductivities and extinction coefficients of derivatives of cyclo-telluropentane. F. L. GILBERT and T. M. LOWRY (J.C.S., 1928, 2658—2667; cf. A., 1928, 349, 1098).—The extinction coefficients in dry alcohol and conductivities in water of the dihalides of the three series (i) $C_5H_{10}TeX_2$, (ii) $C_5H_{10}TeX \cdot CH_2 \cdot [CH_2]_3 \cdot CH_2X$, (iii) $C_5H_{10}TeX \cdot CH_2 \cdot [CH_2]_3 \cdot CH_2 \cdot TeX \cdot C_5H_{10}$ (Morgan and Burgess, A., 1928, 435) have been measured. The following compounds have also been prepared and examined: monocyclic base, $C_5H_{10}Te(OH)_2$, and the following derivatives, hydroxy-halides, $C_5H_{10}Te(OH)X$, tetraiodide $C_5H_{10}TeI_4$, dicyclic base, $(C_5H_{10})_3Te_2(OH)_2$ and derivatives, bistribromide and bistri-iodide, $(C_5H_{10})_3Te_2I_6$. The dihalides of series (ii) and (iii) behave as binary and ternary electrolytes, respectively, but those of series (i) give anomalous values due to hydrolysis to hydroxy-halides. The monocyclic di-iodide is found to resemble α -dimethyl-telluronium di-iodide rather than the isomeric β -di-iodide in its absorption spectrum and its behaviour towards iodides and alkalis. This resemblance is further borne out in the conductivity of the monocyclic base and the form of the curve obtained from potentiometric titration which has also been determined. The curve obtained by the latter method for the dicyclic base is anomalous. R. N. KERR.

Ultra-violet bands of alkaline-earth sulphide phosphors. O. SCHELLENBERG (Ann. Physik, 1928, [iv], 87, 677—715).—In the preparation of phosphors showing the maximum emission of ultra-violet light the important factor is the heavy metal content. Accepting as "normal" the proportion of heavy metal recommended by Lenard and Klatt for the preparation of phosphors emitting visible light, decreasing the heavy metal content causes a marked increase in the intensity of the ultra-violet bands, e.g., for CaS-Bi very good results are obtained at 1/1600N. Conditions for preparing alkaline-earth sulphide-iron phosphors emitting ultra-violet light are described for the first time, and CaS-Zn, together with sulphide phosphors of bismuth, lead, silver, and antimony, are also described and studied with special reference to ultra-violet phosphorescence. In conformity with the known shift of the visible bands in the direction of longer wave-lengths for the calcium-barium-strontium sulphide phosphors, a similar shift is recorded for the ultra-violet bands. The relation between temperature and emission has been studied; as regards the upper momentary state the phosphors can be divided into two classes, those in which it begins at 70° and at 100°; as regards duration, the phosphors are noteworthy for the short range of temperature over which the time-emission extends.

The 368 μ band of CaS-Pb is shown to be connected with the known blue β -band. At the temperature of liquid nitrogen it has been possible to obtain resolution into fine bands, using calcium sulphide phosphors (CaS-Pb β).

The long wave-limit of the excitation-distribution for the ultra-violet bands has been fixed at 280 for the first band and 237 μ for the remaining bands. A number of new visible bands are recorded and fully characterised. R. A. MORTON.

Vibration and rotation spectra of a molecule of the type CH_4 . W. ELERT (Z. Physik, 1928, 51, 6—33).—On the assumption that the equilibrium arrangement of a molecule which is composed of four similar nuclei and one other is a regular tetrahedron with the odd nucleus at the centre, the nature of the vibrational and rotational spectra of such a molecule has been deduced. The specific heat of methane has also been calculated from this supposition.

J. W. SMITH.

Raman effect in the X-ray region. M. PONTE and Y. ROCARD (Compt. rend., 1928, 187, 828—829).—The work of Davis and Mitchell (A., 1928, 1168) shows that after diffusion by a body the structure of an X-ray is more complex than that of the incident ray, and therefore when rays of high frequency are used for the production of the Raman effect the phenomena fall in the domain of X-rays, and should be explained by a theory of light quanta in place of the classical theory.

J. GRANT.

Ultra-violet absorption curves of isoeugenol and eugenol. J. SAVARD (Bull. Soc. chim., 1928, [iv], 43, 1072—1075).—The curves of both substances are similar, showing two bands and the start of a third in the extreme ultra-violet; the maxima are eugenol 2807, 2288 Å., isoeugenol 2925, 2565 Å. The first band is attributed to the phenol-phenolic ether grouping and the second to the ethylenic linking. Both curves are similar to that obtained for veratrol; the resemblance is very close for eugenol, but there is a displacement towards the red, especially marked in the second band, for isoeugenol. This is attributed to the ethylenic linking in the latter compound being in the $\alpha\beta$ -position in the side-chain and therefore conjugated with the benzene nucleus.

R. N. KERR.

Band spectra and flame phenomena. K. F. BONHOEFFER and F. HABER (Z. physikal. Chem., 1928, 137, 263—288).—The reactions and energy relationships existing in a burning gas are discussed in the light of the flame spectra, especially with reference to hydrogen, carbon monoxide, and hydrocarbons.

H. F. GILLBE.

Band spectra and electron terms of the molecules Na_2 , NaK , and K_2 . R. RITSCHL and D. VILLARS (Naturwiss., 1928, 16, 219—220; Chem. Zentr., 1928, i, 2484).—The calculated isotope effect for $(\text{K}^{39})_2$ and $(\text{K}^{39}\text{K}^{41})$ was observed. With Na_2 and K_2 , two systems correspond with equal atomic excitation if the excited molecules dissociate.

A. A. ELDRIDGE.

Rotation of molecules induced by light. C. V. RAMAN and K. S. KRISHNAN (Nature, 1928, 122, 882).—In agreement with the view that the probability of a spin being induced in a molecule when it collides with a light quantum should depend (among other factors) on the degree of optical anisotropy of the molecule, benzene, toluene, and piperidine exhibit wings accompanying mercury arc lines after scattering, whilst carbon tetrachloride, ether, and alcohol do not. The effect is marked with carbon disulphide.

A. A. ELDRIDGE.

Secondary radiations observed in the molecular diffusion of light by fluids (Raman effect). P. DAURE (Compt. rend., 1928, 187, 826

828; cf. A., 1928, 813).—If N is the frequency of the exciting ray and n the characteristic frequency of the substance studied, then the frequencies of the so-called positive and negative rays situated symmetrically on the short and long wave-length sides of the exciting ray, respectively, are given by the expressions $(N+n)$ and $(N-n)$, respectively. The intensities of rays of opposite characteristic frequencies excited by the mercury line 4358 Å. have been compared photometrically, and also those (I_1 and I_2) of the two secondary rays of the same characteristic frequency excited by two different radiations (4358 and 5460 Å.). If D_1 and D_2 are the intensities of those radiations normally diffused by the fluid, and S_1 and S_2 are those of the corresponding Raman rays, then D_2/D_1 : $D_1/I_1=2.5$, and S_2/S_1 : $I_2/I_1-S_2/I_2$: 1.5. J. GRANT.

Secondary radiations observed in the molecular diffusion of light (Raman effect). P. DAURE (Compt. rend., 1928, 187, 940—941).—The Raman spectra of phosphorus tribromide, carbon, silicon, titanium, and tin tetrachlorides, and the trichlorides of phosphorus, arsenic, antimony (at 100°), and bismuth (in hydrochloric acid) consist of four principal rays (a, b, c, d), the characteristic frequencies of which decrease regularly with the atomic weights of the constituent elements. Of the negative rays the a and c rays were always of equal intensity, and equal to that of the b rays for the carbon series but four times as strong as those of the phosphorus series. The intensities of the d rays were variable and usually the weakest. Positive rays were also observed.

J. GRANT.

Molecular spectra in sunspots. G. PICCARDI (Nature, 1928, 122, 880).—Comparison of Gale, Monk, and Lee's measurements of the secondary (molecular) spectrum of hydrogen (A., 1928, 1166) with observations on sunspot spectra discloses numerous coincidences (± 0.03 Å.) between 6400 and 4450 Å. All the lines presumed to be those of the secondary spectrum of hydrogen show no trace of the Zeeman effect.

A. A. ELDRIDGE.

Influence of substitution of halogens, alkyl and amino-groups on the colour and absorption spectra of indigotin, thioindigotin, and indirubin. J. FORMANEK (Chem. obzor, 1928, 3, 133—141).—Introduction of chlorine, and particularly of bromine, atoms into the benzene nucleus of indigotin displaces the absorption bands towards the red, to an extent which increases with the number of halogen atoms. Introduction of alkyl groups into the benzene nucleus of indigotin displaces the absorption slightly, but into the imino-group considerably. Analogous observations with monothioindigotin, thioindigotin, and indirubin are described.

CHEMICAL ABSTRACTS.

Ionisation accompanying oxidation of nitric oxide. A. PINKUS and L. HENRY (Bull. Soc. chim. Belg., 1928, 37, 285—303; cf. A., 1918, ii, 286; 1924, ii, 463).—Measurements of the ionisation accompanying the reversible reaction $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ have been made in an apparatus in which it is possible to detect currents of the order of 10^{-15} amp. At temperatures of about 100° the replacement of oxygen

in the ionisation chamber by a mixture of oxygen with nitric oxide or nitrogen peroxide produces only momentary electric effects, which are attributed to the difference in dielectric constant of oxygen and nitrogen peroxide. In the region of 300°, however, ionisation currents of from 10^{-14} to 5×10^{-13} amp. are obtained, whatever the sign of the field applied. The current intensity increases with the potential applied and with the proportion of oxides of nitrogen, provided sufficient oxygen is present to bring about the complete oxidation of the nitric oxide. The ions are not of thermionic origin, since neither gas separately produces any electrical effect. The fact that no ionisation can be detected below 100° may be explained either by supposing that it is due solely to the dissociation of the peroxide into nitric oxide and oxygen, or by assuming the presence on the electrodes of an insulating adsorbed layer of molecules of nitrogen peroxide in the form of oriented dipoles, preventing the discharge of ions by the metal at low temperatures (cf. Brewer and Daniels, A., 1923, ii, 721; 1924, ii, 745).
M. S. BURR.

Ionisation accompanying the thermal decomposition of ozone. A. PINKUS and R. RUYSEN (Bull. Soc. chim. Belg., 1928, 37, 304—325; cf. A., 1921, ii, 368).—By passing ozonised oxygen through an ionisation chamber at 220—240°, and combining measurements of the ionisation current with analyses of the gases entering and leaving the chamber, it is shown that the decomposition of 10^{-6} to 10^{-7} g.-mol. of ozone per sec., in a field of 845 volts per cm., produces currents of 10^{-11} to 10^{-12} amp. The ionisation current increases in direct proportion to the number of molecules of ozone dissociated per sec. The current intensity is independent of the sign of the electric field, indicating the formation of equivalent numbers of positive and negative ions of similar mobility. In a field of 845 volts per cm. only about one elementary charge reaches the electrodes for 10^{10} mols. of ozone decomposed. The ionisation current increases rapidly with the intensity of the electric field, but saturation is not reached, even with a potential gradient of 3000 volts per cm. The results obtained are substantially in agreement with those of Brewer and Daniels (A. 1923, ii, 721; 1924, ii, 745). A theory of the mechanism of the thermal dissociation of ozone is suggested. There are probably two stages in the process, viz., ionisation by collisions between molecules of ozone, resulting in the formation of positive and negative ions which are charged atoms of oxygen, followed by recombination of the ions with the formation of neutral molecules of oxygen.

M. S. BURR.

Lattice constants of calcium oxide and calcium hydroxide. E. RUMPF (Ann. Physik, 1928, [iv], 87, 595—596).—For calcium oxide (sodium chloride lattice type) the constant is 4.799 ± 0.002 Å., and for calcium hydroxide (hexagonal lattice of the calcium iodide type), $a = 3.582 \pm 0.001$ and $c = 4.904 \pm 0.008$ Å.

R. A. MORTON.

Ionisation potential of the molecule of water. R. GRINFELD (Contrib. Estud. Ciencias fisic. mat. La Plata, 1928, 4, 283—293; Chem. Zentr., 1928, ii, 125).—A critical potential, corresponding with the

change $(\text{H}_2\text{O})^+ + e$, was observed by Lenard's method at 18.0 volts.
A. A. ELDRIDGE.

Electric moments of molecules and the intermolecular forces. P. DEBYE (Z. Elektrochem., 1928, 34, 450—452).—The molecular refraction method of measuring dipole moments eliminates that part of the moment due to orientation and measures only the deformation polarisation. Intermolecular forces are likewise made up of two parts. The relation between the dissymmetry of compounds, as characterised by the dipole moments, and the constitution is discussed with the aid of examples. The dielectric method enables conclusions to be reached regarding the formulation of compounds.
S. K. TWEEDY.

Dielectric constants of solutions of electrolytes. H. HELLMANN and H. ZAHN (Ann. Physik, 1928, [iv], 87, 716).—An addendum (cf. A., 1928, 1089).

R. A. MORTON.

Application of the resonance method to the measurement of the dielectric constants of conducting liquids. H. KNEPKAMP (Z. Physik, 1928, 51, 95—107).—The theory is worked out for the influence of a non-inductive capacity shunt on the standardisation of the current and voltage resonance in a vibration circuit. It is shown that current resonance is dependent on the capacity shunt, but not the voltage resonance. Hence the latter measurements are much preferable to the former in the determination of dielectric constants of conducting liquids. Measurements made on solutions of sucrose and carbamide confirmed these predictions, the values obtained by voltage measurements being in agreement with those of previous workers.
J. W. SMITH.

Dielectric constants of aqueous solutions of methyl-orange, helianthin, and other ampholytes. A. THIEL and E. HORN (Z. anorg. Chem., 1928, 176, 403—415).—The variation of dielectric constant with concentration in solutions of methyl-orange, helianthin, *o*- and *p*-aminobenzoic acids, δ -amino-*n*- and α -amino-*iso*-valeric acids, and glycylglycine has been determined. Contrary to the observations of Blüh (A., 1923, ii, 823; 1924, ii, 658), the dielectric constant falls with increasing concentration of methyl-orange or aminobenzoic acids. The dielectric constant of helianthin solutions does not deviate to an appreciable extent from that of the solvent alone, whether water or solutions of acetic or hydrochloric acid in water. This may be due to the small solubility. The dielectric constant for aliphatic amino-acids falls to a minimum with increasing concentration, and then rises to much higher values than for water alone. This may be explained by the fact that, whilst ordinary ions cause a lowering of the dielectric constant of the solvent, the doublet ion, being really a polar molecule, causes an increase. At higher concentrations, the proportion of doublet ion increases until its influence predominates. This dielectric behaviour is in agreement with both optical and electrochemical observations on the presence of the doublet ion.
M. S. BURR.

Influence of an electrostatic field on the dielectric constant of liquid crystals. M. JEZEWSKI (Z. Physik, 1928, 51, 159—164).—Measurements

have been made of the dielectric constant of *p*-azoxyphenetole and *p*-azoxyanisole in the form of liquid crystals in an electrostatic field of 0–1000 volts per cm. A diminution in the dielectric constant was found which decreased with the intensity of the field and came asymptotically to a limiting value.

J. W. SMITH.

Measurement of dielectric constants in liquids at high electrical field strengths. J. MALSON (Physikal. Z., 1928, 29, 770–777).—A method is described for measuring dielectric constants of conducting liquids in very high fields with an accuracy of 0.06%. The principal source of error is the change in conductivity with field strength described by Wien. The data on water, nitrobenzene, and alcohol show that $\epsilon = \epsilon_0(1 - \alpha E^2)$, E being the field strength. This expression agrees with the Debye theory, and from the point of view of the dipole theory the variations arise partly from association phenomena. The absolute values $\Delta\epsilon/\epsilon$ at 250,000 volts/cm. are 0.7, 1.0, and 1.5%, respectively, for water, nitrobenzene, and alcohol, so that the effect varies inversely as the dielectric constant. The simple Debye theory, using the Clausius-Mosotti relation for calculating the inner field and neglecting association phenomena, leads to values considerably greater than those observed.

R. A. MORTON.

Refractometric researches. VII. Deformation of ions and molecules and refractometric data. K. FAJANS (Z. Elektrochem., 1928, 34, 502–518).—Most substances exhibit a type of chemical combination which falls between the limits of the ideal ionic and the non-polar combinations, which may be explained by the displacement of the electron orbits of the anion towards the cation to an extent controlled by the polarising (or deforming) action of the latter. In a molecule or lattice, then, the combination will be further removed from the ideal ionic type to the non-polar type the smaller the cation and the higher its charge, and the more the anion is capable of deformation. Further, under similar conditions, cations which have not the inert gas character (e.g., Ag^+ , Cu^{2+}) will produce greater deformation than those which have the inert gas structure.

From these points of view the influence of the four fundamental ionic properties, viz., charge, size, and structure of the electron orbits, and polarisability, on the type of combination in compounds is investigated with the aid of previously published data (Wulff, following abstract). In almost all cases of combination of ions with ions or with neutral molecules, or even combination of neutral molecules with each other, deviation from the additive rule of molecular refractivity (Lorentz-Lorenz) results, in agreement with the above conclusions.

S. K. TWEEDY.

Refractometric researches. VI. Interferometric method of determining the refractive index of crystals. P. WULFF (Z. Elektrochem., 1928, 34, 611–616).—The crystal (0.5–10 mm.) is immersed in a liquid, the composition of which is varied until its refractive index equals that of the crystal. The latter stage is determined accurately by an interferometric method. Some values for

inorganic salts are recorded (cf. Fajans, Kohner, and Geffcken, A., 1928, 477).

S. K. TWEEDY.

Degree of association in liquid dielectrics. M. WOLFFKE (Physikal. Z., 1928, 29, 713–716).—A statistical theory of association in liquid dielectrics has been developed and the degree of association deduced as a function of the concentration and temperature of the mixture. The values so calculated are found to be in good agreement with practical data.

J. W. SMITH.

Optical properties of arsenic. II. E. GRYSZKIEWICZ-TROCHIMOWSKI and S. F. SIKORSKI (Rocz. Chem., 1928, 8, 405–422).—The refractive index of a number of derivatives of tervalent arsenic has been measured. The atomic refraction of arsenic is affected to the same extent by combination with chlorine, hydrogen, or aliphatic radicals. It is diminished by the substitution of fluorine, cyanogen, methoxy-, or ethoxy-groups, and is augmented by the introduction of aryl groups, bromine, or iodine.

R. TRUSZKOWSKI.

Expression of refractive power. R. DE MALLEMANN (Compt. rend., 1928, 187, 888–890; cf. A., 1928, 1310).—From a consideration of the molecular discontinuities of a substance in the gaseous and liquid states the expression $M(n^2-1)/d[1+(n^2-1)/\alpha]$ is derived as a first approximation for the refractive power of the gas, where d is the density of the liquid and α a pure number (4.4 according to Henriot) depending on the nature and diameter of the molecules. The rotatory power is obtained when (n^2-1) is replaced by the rotation, and in the case of isotropic substances two independent expressions are then obtained.

J. GRANT.

Co-ordinative combination and the electronic theory of valency. N. V. SIDGWICK (Z. Elektrochem., 1928, 34, 445–450).—A general account from the point of view of “effective atomic numbers” dealing with the co-valency rule, valency groups, and the distinction between electro- and co-valent combination. Recent work of Debye (this vol., 12) renders it likely that the capacity of an acceptor to enter into co-ordinative combination depends on the existence of a dipole in which it is positive. Association in the liquid state also is probably a co-ordination phenomenon.

S. K. TWEEDY.

Stereoisomeric carbonisation theory. D. WIELUCH (Z. Oberschles. Berg- u. Hüttenmannisch. Ver. Katowice, 1928, No. 3, 6 pp.; Chem. Zentr., 1928, i, 2567).—The theory postulates that the molecules of carbonised substances contain “inorganic as well as “organic” carbon linkings. Graphite belongs to the hydroaromatic series. Carbonisation is not associated with aromatic structure.

A. A. ELDRIDGE.

Theory of valency of boron, and the constitution of the simplest boron hydride. E. MÜLLER (Z. anorg. Chem., 1928, 176, 205–208).—Polemical against Wiberg (cf. A., 1928, 936).

H. F. GILLBE.

Production and absorption of soft X-rays and secondary electrons. E. RUDBERG (Proc. Roy. Soc., 1928, A, 121, 421–432; cf. A., 1928, 1173).—The work of several investigators is considered, and it has

been calculated that the number of photoelectrons produced in a solid conductor by soft X-rays is of the same order of magnitude as the number produced in gases by the same radiation. Also the number of primary electrons inside the conductor is about ten times the number escaping from the surface. In the case of the production of secondary by primary electrons, it is suggested that the apparent loss in efficiency may be accounted for (1) by the absorption of slow electrons by the body in which they are produced, (2) by collisions which reduce the energy of the escaping electron, and (3) by the fact that there may be slow electrons the energy of which is not sufficient to overcome the surface field. It is therefore concluded that all the energy of the bombarding electrons can be converted into that of secondary electrons within the target. The source of the secondary electrons has been considered and it is concluded that on the whole the evidence points to their origin as being the free electrons initially present in the conductor.

J. L. BUCHAN.

Reflexion of soft X-rays. J. E. HENDERSON and E. R. LAIRD (Proc. Nat. Acad. Sci., 1928, 14, 773—777).—A method is described for investigating reflexion in the region of long wave-length X-radiation using a mirror of polished iron and also one of optically flat glass. It was found that there is no sharply-defined total reflexion such as occurs in the hard X-ray region, with the possible exception of the 4000-volt radiation reflected from glass. The results may be explained in the case of glass by taking into account the adsorption. In practice, the reflecting power of iron appears to fall more rapidly with increase of glancing angle than for glass. This is contrary to theory, and the results suggest the presence of iron oxide.

M. S. BURR.

Continuous X-radiation from thin aluminium foil. H. KULENKAMPEFF (Ann. Physik, 1928, [iv], 87, 597—637).—With a massive anticathode, the properties of the continuous X-ray emission are masked by velocity losses and diffusion of cathode particles. When, however, the anticathode consists of a very thin strip of metal, e.g., aluminium foil 0.6 μ thick, these disturbing factors are reduced to a minimum. An arrangement is described whereby the X-rays can be studied over the angle range 22—150° with the direction of the stream of cathode particles: intensity measurements are made by means of ionisation, and data involving wave-length are obtained by the use of filters, as the intensity of the radiation is so low that spectrometric measurements are precluded. Control determinations with a massive anticathode and a thin foil anticathode, using definite thicknesses of aluminium for the purpose of intensity calibration, indicate that at 90° and 31 kilowatts the spectral intensity distribution from foil follows the relation $i_\nu = \text{const.}$ No marked differences occur when the direction of emission is varied between 90° and 55°, but at 30° and 140° the radiation is softer. whilst the maximum hardness occurs at about 67°. A fair degree of homogeneity can be attained by the use of silver, tin, and zirconium as selective filters, so that the voltage-intensity curve can be followed in relation to wave-length. Over a limited range of

voltages the intensity decreases approximately as $1/V$. The voltage/intensity curves for different angular settings of the ionisation chamber show that over the range 27—40 kilovolts the intensity decreases slowly with increasing voltages over the range 140—40°, the rate of decrease being least marked at either extreme, whilst at 22° the intensity is independent of voltage.

The azimuthal intensity distribution has been investigated over the range 22—150°, both in relation to wave-length and voltage. The greatest differences occur with the limiting wave-lengths, and it is probable that the intensities increase from zero at 0° to a maximum near 60—70° and slowly decrease to zero at 180°. The maximum hardness occurs at 73—64° depending only on the electron velocity over the range 16.4—37.8 kilovolts.

R. A. MORTON.

Dependence of the intensity of X-ray spectral lines on the tube voltage, with special reference to the K series of aluminium. E. LORENZ (Z. Physik, 1928, 51, 71—94).—The changes of the intensities of X-ray spectral lines with voltage were investigated up to very high potentials, 30—40 times the excitation potential. The shortest wave-length 'Stielstrahlung,' which have been measured from a tungsten anticathode, are explained as due to the emission of secondary electrons from the point of impact on the anticathode. From the *P.D.* between the shortest wave-lengths of the "Brennfleckstrahlung" and of the "Stielstrahlung" the energy level of the tungsten atom from which the secondary electrons arise may be deduced. These measurements also lead to the conclusion that the emission of secondary electrons ceases when the tube voltage reaches about 40 times the excitation potential of the energy level. This was proved by measurement of the intensity-voltage curve of the K series of aluminium, up to 33 times the excitation potential. A maximum was reached at about 11 times the excitation potential and then a decrease was observed.

J. W. SMITH.

Intensity distribution of the general and characteristic X-radiation from molybdenum. L. R. G. TRELAAR (Phil. Mag., 1928, [vii], 6, 1008—1019).—Using a Bragg spectrometer and a Shearer tube fitted with a molybdenum target, measurements were made to determine the intensity distribution of the general radiation at various voltages, the corresponding intensities of the $K\alpha$ and $K\beta$ lines, and the ratio of the homogeneous to the general radiation.

W. E. DOWNEY.

Quantitative study of the reflexion of X-rays by sylvine. R. W. JAMES and G. W. BRINDLEY (Proc. Roy. Soc., 1928, A, 121, 155—171; cf. A., 1928, 112, 225, 462).—An extension to sylvine of previous work on the intensity of reflexion of X-rays from rock salt (*loc. cit.*). It is found that, from the temperature of liquid air up to about 400° Abs., the dependence of the intensity of reflexion from sylvine on temperature is in quantitative agreement with the Debye-Waller formula. The decrease of intensity for higher temperatures is much greater than that indicated by the law. The value of the temperature factor found from observations at the ordinary temperature and at the temperature of liquid air is in

good agreement with that calculated from the elastic constants of the crystal and also with that calculated from the Debye-Waller law. The observed results are compared with calculations from atomic models.

L. L. BIRCUMSHAW.

Soft X-ray levels of iron, cobalt, nickel, and copper. O. W. RICHARDSON and F. C. CHALKLIN (Proc. Roy. Soc., 1928, A, 121, 218—236; cf. A., 1928, 692).—In a previous investigation of the excitation of soft X-rays from iron, cobalt, nickel, and copper by the photo-electric method (*loc. cit.*), a considerable number of discontinuities which had been detected were attributed to transitions from provisional X_1 and X_2 levels and a series of Rydberg terms. An attempt has now been made to arrange the remaining discontinuities which have been observed into the same scheme. Experimentally observed breaks are attributed to transitions from levels denoted by X_3 and X_0 to the b/n^2 terms, so that there are now four initial states from which jumps can be made to the " b " series of terms. The values in volts of all the L and X levels for the four metals are tabulated, and the values of the square roots are plotted as a Moseley diagram against atomic number. The L levels are found to fall accurately on a straight line, in agreement with the view that this level is unaffected by the external atom-building. The X_1 , X_2 , and X_3 levels are practically the same for each element, the slight variations shown being common to all these levels. The X_0 level shows a variation very similar to the shape of the Moseley diagrams of the L and M levels when they are being completed. This may explain the constancy of the X_1 , X_2 , and X_3 levels. If the number of electrons in the X_0 level increases by unity from element to element with increasing atomic number, the approximate constancy of the factor b for all the virtual orbit levels b/n^2 would be accounted for. Some of the soft X-ray level differences show a marked agreement with corresponding X-ray emission transitions. The value of the constant b corresponds in each case with an effective nuclear charge of $13.2e$ — $13.3e$. The case for the inclusion of copper in the suggested scheme is not so definite as that for the other metals. The $L_{II\ III} \rightarrow X_2$ transition and the $X \rightarrow X$ transitions are absent, and their important differences are found. It was at first considered that the X levels were identical with the M levels, but evidence has since been obtained that the systems of levels here described are only parts of much larger systems, so that any association between the X and M levels now appears to be highly improbable.

L. L. BIRCUMSHAW.

Measurement of the size of crystal particles by X-rays. A. L. PATTERSON (Z. Krist., 1928, 66, 637—650; Chem. Zentr., 1928, i, 2692).

Crystallographic optics of X-rays. W. EHRENBURG, P. P. EWALD, and H. MARK (Z. Krist., 1928, 66, 547—584; Chem. Zentr., 1928, i, 2692).

Method of increasing the accuracy of Debye-Scherrer photographs. A. E. VAN ARKEL (Z. Krist., 1928, 67, 235—238; Chem. Zentr., 1928, i, 2773).—The higher order lines are received in the middle of the film.

A. A. ELDRIDGE.

Structure of topaz $[\text{Al}(\text{F}, \text{OH})_2\text{SiO}_4]$. N. A. ALSTON and J. WEST (Proc. Roy. Soc., 1928, A, 121, 358—367).—The structure of a topaz has been examined and is believed to be essentially the same as that of other specimens. It is holohedral in character. The aluminium and silicon atoms are distributed through a core of oxygen and fluorine atoms. These latter form a close-packed arrangement of a new type, which is a combination of the hexagonal and cubic forms. The unit cell, containing four molecules, has sides $a = 4.64(1)$, $b = 8.78(3)$, $c = 8.37(8)$ Å.

J. L. BUCHAN.

Röntgenographic and chemical investigations of oxides of iron and cobalt. S. B. HENDRICKS and W. H. ALBRECHT (Ber., 1928, 61, [B], 2153—2161).—The interferences of tricobaltic tetroxide are distributed similarly to those of magnetite, but the differences in the lattice dimensions indicate closer proximity of the atoms in the cobalt compound. The crystalline structure is identical in each case. The diagram of the ferromagnetic oxide, $\text{CoO}, \text{Fe}_2\text{O}_3$, prepared by the gradual addition of M -solutions of cobalt chloride and ferric ammonium sulphate to boiling 10% sodium hydroxide (cf. Hilpert, A., 1909, ii, 672) is identical with that of tricobaltic tetroxide and magnetite. The oxide, $\text{Co}_2\text{O}_3, \text{Fe}_2\text{O}_3$, can be obtained in the homogeneous state only if potassium persulphate is present at the moment of precipitation of the lower oxide (contrast Hilpert, *loc. cit.*); it is paramagnetic. The compound cannot be completely dehydrated at 100° , the residual water being merely adsorbed. Examination of the magnetic susceptibility of preparations oxidised in varying degree indicates an increase of this property with diminishing content of $\text{Co}_2\text{O}_3, 2\text{Fe}_2\text{O}_3$, the value for the homogeneous material being $\chi = 45.6 \times 10^{-6}$. The oxidised product exhibits the same interferences as the oxide, $\text{CoO}, \text{Fe}_2\text{O}_3$, but the lines are less defined. When the substance is heated, the lines become more distinct and completely identical with those of the lower oxide if the temperature has been raised above 250° .

H. WREN.

Constitution of hydroxides and hydrates. II. Complexes containing water of co-ordination. G. NATTA (Gazzetta, 1928, 58, 619—626; cf. A., 1928, 822).—In order to determine the nature of the water present in crystalline lattices, an X-ray examination has been made by the Laue and powder methods of the two complex cobalt salts $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ and $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$. Both compounds crystallise in the cubic system. The unit cell contains four molecules and has a length 10.88 and 10.84 Å., respectively; d_{calc} 2.83 and 2.81. Each cobalt atom is at the centre of an octahedron the vertices of which are occupied by the ammonia and water groups, which behave as isomorphous groups. The substitution of a molecule of ammonia by one of water produces a slight contraction in the lattice, which otherwise remains unaltered.

O. J. WALKER.

Orientation of single crystals of zinc. K. TANAKA (Mem. Coll. Sci. Kyoto, 1928, 11, A, 361—365).—Commercial zinc plates 1.5 mm. thick were rolled to 20—70% reduction in thickness, and large crystals grown by annealing at 400° for 1 day. X-Ray examination showed that in most of these crystals

the base of the hexagonal crystal was parallel to the plane of the plate. A similar arrangement was found when the plates were extended instead of being rolled before annealing. On drawing commercial zinc wires 1.5 mm. diameter through a 0.5-mm. die and then annealing, most of the resulting crystals had their [1120] axes parallel to the axis of the wire. A rather random distribution was obtained after annealing a wire extended for a small percentage only. When a circular zinc plate is melted, and then cooled gradually from the circumference, large crystals grow towards the centre, and most of them grow parallel to the plane of the base of the hexagonal crystal.

W. HUME-ROTHERY.

Arrangement of micro-crystals in compressed magnesium and aluminium plates. S. TSUBOI (Mem. Coll. Sci. Kyōto, 1928, 11, A, 375—382).—A circular plate of magnesium 2.4 mm. thick was compressed to a thickness of 0.4 mm., and the arrangement of the micro-crystals investigated by X-ray analysis. Most of the crystals were arranged fibrously with the principal axis of the hexagonal crystal in the direction of compression, but the arrangement was not exact. Aluminium sheets of 1.8 mm. thickness were similarly reduced to 0.13 mm. by compression, both circular and approximately elliptical specimens being used. The micro-crystals tended to take up a fibrous structure with the (110) planes parallel to the surface of the plate, and their [112] axes parallel to the direction of flow of the metal. Consequently, with the elliptical specimens the arrangement was different at the extremities of the major and minor axes owing to the different directions of flow.

W. HUME-ROTHERY.

Arrangement of micro-crystals in bismuth and antimony deposited by electrolysis. H. HIRATA (Mem. Coll. Sci. Kyoto, 1928, 11, A, 429—450).—The arrangement of crystals of antimony and bismuth deposited electrolytically has been studied by X-ray analysis. The bismuth was deposited on a cathode of sheet copper, the anode being bismuth, and the electrolyte various solutions of bismuth hydroxynitrate and hydrochloric acid in water. The apparently non-metallic deposits obtained under some conditions are in reality small, irregularly oriented micro-crystals of metallic bismuth, and are not a bismuth compound. When the current density and concentration of the electrolyte are high, the crystals are not deposited in a fibrous form, but at lower current densities and concentrations a perfect fibrous form is obtained in which the crystals have their [211] axes parallel to the fibrous axis. At very low current densities and concentrations, comparatively large acicular crystals are formed with the [211] axis in the direction of the needle, and with most of the crystals in the same orientation. With antimony deposited from a solution of the sulphide in aqueous sodium carbonate, the apparently amorphous deposits are also really irregularly oriented micro-crystals.

W. HUME-ROTHERY.

Crystal structure of potassium sulphate. F. P. GOEDER (Proc. Nat. Acad. Sci., 1928, 24, 766—771).—Crystallographic data for potassium sulphate have been obtained by the X-ray powder method. The following lattice constants are given: $a_0=5.771$,

$b_0=10.064$, and $c_0=7.518$ Å. These are similar to the results of other investigators obtained by reflexion measurements on a rotating crystal. A quantitative three-dimensional structure for the potassium sulphate molecule is deduced from the geometrical theory of space-groups and is confirmed by experimental results. In agreement with the observations of other investigators, the SO_4 ion appears to be an entity of the molecule and to maintain its tetragonal structure irrespective of the compound of which it forms a constituent.

M. S. BURR.

Structure of crystals of heulandite. P. GAUBERT (Compt. rend., 1928, 187, 829—831).—The sectors and bands in the cleavage planes of crystals of heulandite are due to the presence of foreign matter which may produce various orientations of the plane of the optical axes. In almost every case the angle of the optical axes is smaller in the sector corresponding with the face $a'(101)$ than with the face $p(001)$. Pure heulandite contains hydrated silicoaluminates of sodium, potassium, strontium, and barium in solid solution, or forming mixed crystals with the pure heulandite.

J. GRANT.

Crystal structure of some rhombic formates. I. NITTA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 151—163).—Using the Laue photographic and ionisation spectrometric methods, the crystal structure of some orthorhombic formates was investigated. The dimensions of the unit cells are as follows: strontium formate, $a=6.86$, $b=8.72$, $c=7.24$; strontium formate dihydrate, $a=7.30$, $b=11.99$, $c=7.13$; barium formate, $a=6.78$, $b=8.89$, $c=7.68$; lead formate, $a=6.52$, $b=8.75$, $c=7.41$. In the last four salts the number of molecules in the unit cell was 4, and space-group V^4 . Lithium formate monohydrate (4 molecules in the unit cell, space-group C_{2v}^2 or V_8^4), $a=6.49$, $b=10.01$, $c=4.85$; calcium formate (8 molecules in the unit cell, space-group V_8^4), $a=10.16$, $b=13.38$, $c=6.26$. The accepted isomorphism of the formates of strontium, barium, and lead was confirmed. The space-group V^{22} for calcium formate is different from V_8^4 assigned by Yardley (A., 1925, ii, 430). The former V_8^4 contains V^4 as a subgroup. The molecules of the formates of these bivalent metals are all structurally asymmetric.

N. M. BLIGH.

Crystal structure of silver subfluoride. H. TERREY and H. DIAMOND (J.C.S., 1928, 2820—2824).

Photographs taken by the powder method indicate a hexagonal unit cell, $a=2.989$, $c=5.710$ Å.; one molecule of Ag_2F per unit cell requires d 8.78 (found 8.64). A "cadmium iodide" structure is suggested in which fluorine occupies the position (0, 0, 0) and silver the positions ($\frac{1}{3}$, $\frac{2}{3}$, μ) and ($\frac{2}{3}$, $\frac{1}{3}$, μ); the value of μ is deduced from intensity considerations to be 0.3. Such a structure gives values for the atomic diameter of silver with respect to silver and with respect to fluorine equal to the atomic diameter of silver in the metallic state and in normal combination, respectively; some support is obtained therefore for the existence of sub-ions.

R. N. KERR.

Crystal structure of mercury, copper, and copper amalgam. H. TERREY and C. M. WRIGHT (Phil. Mag., 1928, [vii], 6, 1055—1069).—The structures

were determined by means of a Shearer tube with a copper target and a camera similar to that used by McLennan and Wilhelm for their work on solid carbon dioxide and oxygen. At -150° , mercury was found to have a rhombohedral structure. The value for the plane spacing of copper was found to be 3.603 ± 0.002 Å. Copper amalgams appear to be merely mechanical mixtures of the two metals so long as the amalgam is soft. When the amalgam sets a change in structure takes place and a definite compound containing 30–35% Cu is formed. This compound appears to possess a simple tetragonal lattice with axial ratio 0.64 and a composition Cu_2Hg_3 .

W. E. DOWNEY.

X-Ray spectrography of copper and some brasses. J. LOISEAU (Rev. Mét., 1928, 25, 572–584).—Laue spectrograms for hard-rolled copper, 67 : 33 and 60 : 40 brass, and 60 : 40 brass with lead after varying periods of anneal at temperatures up to the m. p. are reproduced and discussed. In copper, the orientation of the (100) planes to the direction of rolling determines the recrystallisation and grain growth. The appearance of separate spots on the spectrogram indicates that overheating occurs at 1000° , but even at 1050° traces of the original rolling structure can be detected, and these disappear only on melting. Recrystallisation of 67 : 33 brass commences at 300° , is rapid at 400° , and continues up to 500° . At 600° , reflexion from the (110) planes and at 700° from the (111) planes commences to take place, but no change in the crystal structure is apparent until 875° . Similar effects are obtained with 60 : 40 brass and, as lead has no effect on the crystal structure, it does not influence the character of the spectrograms. The value of X-rays in determining the mechanical and heat treatment which copper and brass have undergone is discussed. A. R. POWELL.

Röntgenographic interpretation of the nature of the C–C linking. A. REIS and W. SCHNEIDER (Z. physikal. Chem., 1928, 137, 126–130).—The crystal structures of a number of symmetrical compounds having the C–C linking have been correlated from the stereochemical point of view. The only space-groupings so far found for the C_2 and $\bar{4}$ crystal classes are C_2^2 and $\bar{4}^2$, wherein unsymmetrical molecules are oriented along spiral axes. In the D_2 and D_4 classes, however, the only space-groupings known are formed from the C_2 unit. For all the cases studied Weissenberg's theory of crystal structure is substantiated.

H. F. GILLBE.

Banded structures in metal crystals. C. ELAM (Proc. Roy. Soc., 1928, A, 121, 237–244).—Crystals of aluminium are rarely formed with a banded structure after treatment which would normally produce it, although the metal has the same crystal structure (face-centred cubic) as copper, silver, and gold, which form twins of the spinel type. It is found, however, that when a large aluminium crystal is strained about 10% and heated until it recrystallises, the new crystals have very straight boundaries, and some of these take on the typical banded structure of twinned copper. The plane of composition can be the twin plane, but is not always so. In one case, in which the orientation of each part relative to the

surface was determined by means of X-rays, the two components were united in one plane by a ragged boundary, indistinguishable from an ordinary crystal boundary. It is suggested that twins may be more common than hitherto supposed, but that they are overlooked because they are not united along the twin plane. There are also similar banded structures which are not of the spinel type of twin. In one example investigated, obtained when a crystal of aluminium in the form of a round bar was pulled in tension, the plane of composition had the indices {113}, so that the specimen as a whole can be considered as a reflexion twin about this plane. This may be described as “mechanical twinning.”

In an appendix, G. I. TAYLOR discusses the connexion between the formation of “mechanical twins” and the known manner in which aluminium crystals are distorted under tensile stress. If the laws previously discovered regarding the distortion of aluminium crystals are applied to the case of a tensile specimen of which the longitudinal axis lies in a cubic crystal plane and close to the normal to an octahedral plane, “mechanical twins” of the type described above might have been predicted as possible, and the orientation of the two sets of crystal axes would bear the same relationship to the plane of union and the longitudinal axis of the specimen as that actually found.

L. L. BIRCHUMSHAW.

Change in lattice spacing at a crystal boundary. J. E. LENNARD-JONES and (Miss) B. M. DENT (Proc. Roy. Soc., 1928, A, 121, 247–259).—The recent work of Davisson and Germer (A., 1927, 492; 1928, 683) on the reflexion of electrons by a crystal of nickel has directed attention to the conditions at a crystal boundary. With the view of explaining their results, the change in spacing at a (100) boundary of a crystal of the sodium chloride type is considered theoretically. Two effects are anticipated: (a) a change of spacing between planes at the boundary; (b) a change of spacing between atoms in the surface layer itself. These effects are considered separately, assuming that their mutual action is a correction of the second order. It is found that the contraction of the lattice at the boundary is due almost entirely to the polarisation of the surface layer and is of the order of 5%. An upper limit is found for the decrease in the interatomic spacing in the surface layer, also of the order of 5%. The surface tensions of a number of crystals of the sodium chloride type are calculated. The general results obtained provide independent evidence against the contraction theory of Davisson and Germer, for they show that the contraction is too small and localised to produce an observable effect on the reflexion pattern of an electron stream.

L. L. BIRCHUMSHAW.

Structure of the benzene ring. K. LONSDALE (Nature, 1928, 122, 810).—Hexamethylbenzene, triclinic, contains 1 mol. in the unit cell. Variations in reflexion intensities prove the existence of pseudo-hexagonal or hexagonal symmetry in the benzene ring, and show that the ring in hexamethylbenzene is almost, if not quite, flat, with distance between the centres of neighbouring carbon atoms $1.42\text{--}1.48$ Å.

A. A. ELDRIDGE.

Crystal form of magnesium tungstate. F. MACHATSCHKI (Z. Krist., 1928, 67, 163—165; Chem. Zentr., 1928, i, 2591).—Magnesium tungstate, MgWO_4 , is monoclinic, prismatic, $a:b:c=0.8263:1:0.8703$; β $89^\circ 40'$. A. A. ELDRIDGE.

Structure of zirconium silicide. H. SEYFARTH (Z. Krist., 1928, 67, 295—328; Chem. Zentr., 1928, i, 2775).—Zirconium silicide, ZrSi_2 , forms small, rhombic crystals, d 4.88; it is rhombic-bipyramidal, a 3.72, b 14.61, c 3.67 Å., with 4 mols. in the unit cell. A. A. ELDRIDGE.

Crystal structure of the soluble modification of germanium dioxide. W. ZACHARIASEN (Z. Krist., 1928, 67, 226—234; Chem. Zentr., 1928, i, 2775—2776).—Water-soluble germanium dioxide has a 4.972 ± 0.005 , c 5.648 ± 0.005 Å. (for α -quartz, 4.903 and 5.393, respectively), space-group D_4^1 or D_2^1 . A. A. ELDRIDGE.

Production of corrosion faces with precious stones. M. SEEBACH (Deut. Goldschmiede-Ztg., 1925, 28, 159—163; Chem. Zentr., 1928, i, 2795).—The use of chemical reagents is described. A. A. ELDRIDGE.

Titanium cyanonitride. V. M. GOLDSCHMIDT (Nachr. Ges. Wiss. Göttingen, 1927, 390—393; Chem. Zentr., 1928, i, 2692).—The crystal structure of "titanium cyanonitride" is of the sodium chloride type, with edge of unit cube 4.243 ± 0.002 Å. The intensity data support the view that the substance consists of mixed crystals of titanium carbide and nitride. A. A. ELDRIDGE.

Crystal structure of skutterudite and smaltite-chloanthite. I. OFTEDAL (Z. Krist., 1928, 66, 517—546; Chem. Zentr., 1928, i, 2693).—The edge of the unit cube of skutterudite is 8.189 ± 0.002 Å., and of smaltite 8.240 ± 0.005 Å. The formula is RAs_3 . The space-group is T_h^3 . A. A. ELDRIDGE.

Crystal structure of monoethylammonium bromide and iodide. S. B. HENDRICKS (Z. Krist., 1928, 67, 119—130; Chem. Zentr., 1928, i, 2777).—Monoethylammonium bromide and iodide have d_{100} 8.30 and 8.67 Å., respectively. There are 2 mols. in the unit cell; the space-group is C_2^2 . A. A. ELDRIDGE.

Crystal structure of monomethylammonium halides. S. B. HENDRICKS (Z. Krist., 1928, 67, 106—118; Chem. Zentr., 1928, i, 2777).—Monomethylammonium chloride has a 4.28, c 5.13 Å., with 1 mol. in the unit cell; the bromide has a 5.09, c 8.76 Å. and the iodide a 5.11, c 8.97 Å., each with 2 mols. in the unit cell. The forms of ammonium bromide and iodide stable at high temperatures have the sodium chloride structure, whilst those stable at low temperatures are of the caesium chloride type. Monomethylammonium chloride possesses a modified ammonium chloride structure of the form stable at the ordinary temperature, whilst monomethylammonium bromide and iodide crystallise according to the type of ammonium bromide stable at high temperatures. The distances between the atoms have been determined. A. A. ELDRIDGE.

Crystal structure of tetramethylammonium halides. R. W. G. WYCKOFF (Z. Krist., 1928, 67,

91—105; Chem. Zentr., 1928, i, 2777).—Tetramethylammonium iodide has a 7.96, c 5.75 Å.; bromide, a 7.76, c 5.53 Å.; chloride, a 7.78, c 5.53 Å.; space-group D_2^1 , with 2 mols. in the unit cell. The positions of the atoms are discussed. A. A. ELDRIDGE.

Theory of crystal growth. W. KOSSEL (Nachr. Ges. Wiss. Göttingen, 1927, 135—143; Chem. Zentr., 1928, i, 2689).

Crystal structure of chromite from Tiszafa. L. TOKODY (Z. Krist., 1928, 67, 338—339; Chem. Zentr., 1928, i, 2795—2796).—The structure is cubic, a 8.05 Å.; space-group O_h , with 8 mols. in the unit cell. A. A. ELDRIDGE.

Test of crystals for piezoelectricity. S. B. ELINGS and P. TERPSTRA (Z. Krist., 1928, 67, 279—284; Chem. Zentr., 1928, i, 3040).—Positive results were obtained with: zinc blende, boracite, sodium bromate, hexamethylenetetramine, potassium lithium sulphate, nepheline, potassium bromate, cinnabar, mercuric cyanide, potassium dihydrogen phosphate and arsenate, ammonium dihydrogen arsenate, strychnine sulphate, melinophane, willemite, strychnine, sodium santonate, benzophenone, cinchonidine, glutamic acid, hippuric acid, nickel sulphate heptahydrate, strontium, barium, and lead formates, iodic acid, tartar, tartar emetic, lactose, α -rhamnose, glucosamine hydrochloride, haematoxylin trihydrate, skolezite, and strontium hydrogen tartrate. Negative results were obtained with: diamond, zinc oxide, benitoite, carborundum, lead molybdate, sulphur, and potassium dichromate. A. A. ELDRIDGE.

Comparative X-ray examination of lime-soda silicates. B. GOSSNER and F. MUSSAUG (Zentr. Min. Geol., 1928, A, 129—138; Chem. Zentr., 1928, i, 2796).—Gehlenite has a 11.11, c 5.06 Å., with 4 mols. in the unit cell; it is regarded as $\text{CaSiO}_4 \cdot \text{Al}_2\text{O}_3$, with isomorphous replacement of the alumina by magnesium silicate. Melilite has a 11.12, c 5.09 Å., with 4 mols. of $\text{CaO}(0.527\text{CaSiO}_3 \cdot \text{MgSiO}_3 + 0.069\text{CaSiO}_3 \cdot \text{FeSiO}_3 + 0.164\text{CaSiO}_3 \cdot \text{Al}_2\text{O}_3 + 0.238\text{NaAlSi}_3\text{O}_8)$ in the unit cell. Sarkolite has a 17.6, c 15.6 Å., with 6 mols. of $3\text{CaO} + (0.825\text{NaAlSi}_3\text{O}_8 + 1.080\text{CaAl}_2\text{Si}_2\text{O}_8 + 0.057\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8)$ in the unit cell. A. A. ELDRIDGE.

X-Ray examination of *o*- and *m*-nitroaniline. K. HERRMANN and M. BURAK (Z. Krist., 1928, 67, 189—225; Chem. Zentr., 1928, i, 2778—2779).—*o*-Nitroaniline has a 10.09, b 29.44, c 8.52 Å., axial ratios 0.3427:1:0.2894. The unit cell contains 16 mols.; the space-group is considered to be V_4^1 . *m*-Nitroaniline has a 19.23, b 6.48, c 5.06 Å.; axial ratios 2.96:6:1:0.7808. The unit cell contains 4 mols.; space-group probably C_2^2 . A. A. ELDRIDGE.

Isomorphism in cubic crystals of hexammino- and pentammino-aquo-complex salts. O. HASSEL (Norsk geol. Tidsskr., 1928, 10, 92—96; Chem. Zentr., 1928, i, 3030—3031).—The salt $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$, which has a structure similar to that of the corresponding iodide, contains 4 mols. in the unit cell. The six ammonia groups are equivalent. In $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ the water and ammonia groups appear to be crystallographically equivalent. The salt $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$ is not very stable; it forms

optically isotropic octahedra, a 10.81 Å., and exhibits differences in the positions of the ammonia and water groups. The iodosulphate has the fluorite structure, calcium being substituted by the complex cation and fluorine by the two anions. The action of substituents on the lattice constant is shown by the following values: $[\text{Co}(\text{NH}_3)_6]\text{SO}_4\text{I}$ 10.71, $[\text{Co}(\text{NH}_3)_6]\text{SO}_4\text{Br}$ 10.51, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{SO}_4\text{I}$ 10.62, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{SO}_4\text{Br}$ 10.45, $[\text{Co}(\text{NH}_3)_6]\text{SeO}_4\text{I}$ 10.79 Å.

A. A. ELDRIDGE.

Comparative X-ray studies of lime-soda silicates. IV. Melilite, gehlenite, sarkolite, and skapolite. B. GOSSNER and F. MUSSGÜNGER (Zentr. Min. Geol., 1928, A, 167—181; Chem. Zentr., 1928, ii, 7).—Skapolite and sarkolite, which are distinct both chemically and structurally from the melilite-gehlenite group, are structurally related. The unit cell is a face-centred prism with edges 17.25, 7.65 Å. and 17.6, 15.59 Å., respectively. Skapolite contains 4 mols. in the unit cell, and has space-group C_{2h}^2 or C_{2h}^3 ; sarkolite contains 12 mols., and the space-group is probably C_{2h}^3 or C_{2h}^4 . Melilite and gehlenite, space-group D_{2h}^{11} , have a tetragonal prismatic unit cell with a 11.1, c 5.09 Å. and a 11.12, c 5.06 Å., respectively, containing 4 mols.

A. A. ELDRIDGE.

Structure of rutile. L. TOKODY (Math. Therm. Ertesitő, 1927, 44, 247—254; Chem. Zentr. 1928, ii, 28).—Rutile has a 4.4923, c 2.8930 Å., with 2 mols. in the unit cell; 4.511. The shortest distance between titanium and oxygen atoms is 2.11 Å.

A. A. ELDRIDGE.

Occurrence of titanium in titaniferous slags. C. W. CARSTENS (Z. Krist., 1928, 67, 260—278; Chem. Zentr., 1928, i, 3045).—Titanium in slags may be present as titanium-augite. In basic reduced slags the titanium may be present as an independent mineral which may be black in colour, and contains less oxygen than the dioxide. The extent of the reduction depends on the temperature. In ultra-basic slags and "alcement" clinker, titanium monoxide occurs as branched crystals of *fulvite*. The monoxide obtained from the dioxide and titanium by heating at 1450—1500° in a reducing atmosphere belonged (BRÄKKEN) to the cubic system; it was of the sodium chloride type, having a 4.230 Å., a_{calc} . 5.53, H 6.

A. A. ELDRIDGE.

Piezoelectric method for determining crystal classification. W. SCHNEIDER (Z. Physik, 1928, 51, 263—267).—An extension of the technique of Giebe and Scheibe (*ibid.*, 1925, 33, 760) is described suitable for the detection of piezoelectric properties in crystals. A large number of crystals have been examined in this way. All substances having a centre of symmetry show no piezo-effect; the following substances show the effect: sucrose, isohydrobenzoin, lithium sulphate, lead formate, asparagine, ammonium oxalate, sodium chlorate, rubidium tartrate, potassium bromate, pentaerythritol, succinic anhydride, and acetamide.

R. W.

Magnetostriction of a single crystal of nickel. Y. MASIYAMA (Sci. Rep. Tohoku Imp. Univ., 1928, 17, 945—961).—The longitudinal and transverse effects of magnetic elongation of a single crystal nickel ellipsoid have been determined for different

orientations and for varying strengths of magnetic fields. Contraction always takes place in a longitudinal direction and elongation in a transverse direction. The contraction is greatest in the (100) direction and least in the (111) direction, the converse being true for the transverse elongation. With a constant field, the variation of these effects with respect to the orientation of the ellipsoid is periodic, the period being 90°, 180°, and 60° for the planes (100), (110), and (111), respectively.

A. R. POWELL.

Magnetic susceptibility of single crystals of zinc and cadmium. J. C. McLENNAN, R. RUEDY, and (Miss) E. COHEN (Proc. Roy. Soc., 1928, A, 121, 9—21).—Single crystals of zinc and cadmium, of about 0.5 cm. in diameter and 6 cm. long, were prepared by the method of very slowly lowering the molten metal, contained in a pyrex mould, out of an electric furnace. The glass moulds were of a special constricted shape, designed to increase the probability of obtaining a single crystal through the whole length of the tube. The magnetic susceptibility χ_{\parallel} (parallel) and χ_{\perp} (normal) to the hexagonal axis of each metal was determined by the Gouy method, the crystal being weighed in the presence and absence of a strong magnetic field. The values, in c.g.s.u. $\times 10^{-6}$, are found to be: cadmium, $\chi_{\parallel} = -190$, $\chi_{\perp} = -145$; zinc, $\chi_{\parallel} = -261$, $\chi_{\perp} = -160$. From these values, the magnetic susceptibilities of isotropic aggregates of zinc and cadmium crystals arranged at random would be -0.160×10^{-6} and -0.194×10^{-6} , respectively. An attempt was made to grow single crystals of mercury by the same method, the metal being lowered from the ordinary temperature into a tube surrounded by liquid air. On rotating the solid mercury thus prepared about its vertical axis, the pull caused by the magnetic field remained constant, indicating either that the metal was not in the form of a single crystal, or, more probably, that the mercury was crystallised and in a rhombohedral form. L. L. BIRCHMANS.

Determination of the piezoelectric moduli of sodium ammonium tartrate. W. MANDELL (Proc. Roy. Soc., 1928, A, 121, 130—140).—The general theory of piezoelectricity as applied to crystals of the rhombic system is discussed, and it is shown that in the case of sodium ammonium tartrate all the moduli vanish excepting d_{14} , d_{25} , and d_{36} , so that excitation takes place only through pressures Y_x , Z_x , and X_y . To measure the moduli, rectangular slabs of the required orientations were cut from the crystals and placed vertically on hard rubber blocks, similar blocks being placed on the upper ends. Two copper electrodes were fixed on the side faces of the crystal slab, one electrode being connected to a pair of quadrants of an electrometer, the other electrode and the second pair of quadrants being earthed. It was found necessary to use specimens as large as possible, and to carry out the measurements under the driest conditions obtainable. The following values, in c.g.s.u. $\times 10^{-8}$, were found: $d_{14} = +56.0$, $d_{25} = -149.5$, and $d_{36} = +28.3$. For the piezoelectric constants: $e_{14} = +6.37 \times 10^4$, $e_{25} = -4.11 \times 10^4$, and $e_{36} = +2.39 \times 10^4$. The values of the moduli for the potassium salt are: $d_{14} = +1000 \times 10^{-8}$, $d_{25} = -165 \times$

10^{-8} , and $d_{36} = +35.4 \times 10^{-8}$. Thus for pressures in the direction bisecting the *bc* axes, the polarisation along the *a* axis decreases by about 95% on substituting the ammonium group. An investigation of the effect of temperature on the piezoelectric response showed that, between -17° and $+30^\circ$, there was no appreciable change for the ammonium salt, but on raising the temperature above 30° , the crystal gradually became conducting, the charges leaking away in a few minutes.

L. L. BIRCUMSHAW.

Magneto-resistance effect in single crystals of nickel. S. KAYA (Sci. Rep. Tohoku Imp. Univ., 1928, 17, 1027—1037).—The electrical resistance of single crystal nickel rods with a rectangular cross-section has been measured in magnetic fields parallel to and perpendicular to the direction of the current. In the case of the longitudinal effect, the resistance increases with the orientation of the axis of the rod in the order (100), (110), and (111). In the case of the transverse effect, the resistance varies with the direction of the magnetic field, the curves having an undulating form, the shape of which varies with the orientation of their longitudinal axis.

A. R. POWELL.

Magnetism of hydrated zirconia. F. BOURION and (MLLE.) O. HUN (Compt. rend., 1928, 187, 886—888).—Since the specific susceptibility of hydrated zirconia prepared by precipitation from ammonia and pure zirconium tetrachloride is a linear function of its water content for more than 5% of water, this substance is considered to be a weakly paramagnetic mixture of water and the hypothetical oxide ZrO_2 , the susceptibility of which, calculated by extrapolation, is of the order 0.4×10^{-7} . Anhydrous zirconia, obtained by prolonged calcination at 500° , is diamagnetic, but the results are vitiated by the high temperatures required for the removal of less than 5% of water.

J. GRANT.

Loosening, electrical conductivity, and reactivity of the crystal lattice. J. A. HEDVALL (Svensk Kem. Tidskr., 1928, 40, 65—98; Chem. Zentr., 1928, i, 2902—2903).—A survey of the results of investigations on reactions between solid substances.

A. A. ELDRIDGE.

Enantiotropy and monotropy. II. N. NAGASAKO (Bull. Chem. Soc. Japan, 1928, 3, 209—217).—The dimorphism of carbon and phosphorus is studied. By the application of the Nernst heat theorem, the affinity of transition can be obtained if the specific heats over a range of temperature and the heat of transition are known. The method is of value especially in the case of diamond and graphite, where it is almost impossible to measure the affinity directly. It is found that from 0° to 1100° Abs. graphite is more stable than diamond, and that the dimorphism of the system is truly monotropic, and not pseudo-monotropic as has previously been supposed. The heat of transition changes sign at 850° Abs. Above this temperature diamond changes into graphite with absorption of heat. For the dimorphism of phosphorus it is found that red phosphorus is more stable than white from 0° Abs. to the m. p. of white phosphorus, the system being truly monotropic. Where this method is difficult to apply, e.g., when a modifica-

tion exists over a narrow range of temperature over which the specific heats are not known or are difficult to find, an approximate formula can be used if the m. p. and latent heats are known. Using this method it is shown that the dimorphisms of ethyl ether, iodine monochloride, benzophenone, bromonitrobenzene, phthalide, acetamide, monochloroacetic acid, nitro-*p*-toluidide, and erythritol are monotropic. The effect of pressure on the affinity of transition is investigated, and it is found that the diamond-graphite transformation will probably be enantiotropic at high pressures, whilst the phosphorus transition will remain monotropic. (Cf. A., 1928, 709.) A. J. MEE.

Electrical conductivity and optical absorption of metals. E. H. HALL (Proc. Nat. Acad. Sci., 1928, 14, 802—811; cf. A., 1928, 825).—Theoretical. The various hypotheses as to the relation of electrons in metals to the electrical conductivity are discussed. It is considered that the evidence is, on the whole, in favour of the view that the electric current is maintained in part by free electrons sharing the energy of heat agitation, but mainly by an interchange of electrons in encounters between atoms and positive ions, the latter being, naturally, just as numerous as the free electrons.

M. S. BURR.

Electrical conductivity of metals as a function of pressure according to the Sommerfeld electron theory. A. T. WATERMAN (Phil. Mag., 1928 [vii], 6, 965—970).—A formula is developed for the effect of hydrostatic pressure on the electrical conductivity of metals.

W. E. DOWNEY.

Variations in the resistivity of thin layers of platinum as functions of thickness and temperature. A. FERY (Compt. rend., 1928, 187, 819—821; cf. A., 1928, 353).—For thicknesses above 287 m μ the resistance of films of platinum-black produced by cathodic sputtering is 4.19×10^{-4} . Such films are considered to be composed of massive metal, but differ from ordinary metallic platinum, which may, however, be produced by a discharge at 340° . From studies of the catalytic properties and changes in resistance with temperature of these films, it is concluded that there are a large number of forms of platinum intermediate in properties between bright and black platinum.

J. GRANT.

Electrical conductivity of metals. R. RUEDY (Nature, 1928, 122, 882).

Theoretical meaning of the relations between electrical conductivity and voltage and frequency. G. JOOS (Physikal. Z., 1928, 29, 755—760).—The theoretical interpretation of the work of Wien (cf. this vol., 32) is considered in the light of the new theory of electrolytes developed by Debye, Huckel, Onsager, and Falkenhagen. Calculation of approximate solutions of the Debye-Onsager differential equations leads to relations between conductivity and voltage which agree well with Wien's data. The ionic forces require a finite time before coming into play, and both for rapidly alternating fields and high voltages the interionic forces decrease or disappear entirely. True values for the degree of dissociation should therefore be obtainable in this way,

since the values obtained by the older methods are unduly low owing to the actions between ions.

R. A. MORTON.

Conduction of electricity and discharge in dielectric liquids. A. NIKURADSE (Physikal. Z., 1928, 29, 778—781).—An attempt has been made to elucidate the discharge phenomenon by means of current/voltage relationships at low voltages, especially just before the discharge occurs. The relations between conductivity, viscosity, temperature, pressure, and breakdown voltage have been studied, and ionic constants at spontaneous ionisation have been determined for highly purified transformer oil. The relation between conductivity and ionic constants has been investigated for various temperatures and pressures.

R. A. MORTON.

Thermal conductivities of carbon monoxide and nitrous oxide. H. GREGORY and C. T. ARCHER (Proc. Roy. Soc., 1928, A, 121, 285—293; cf. A., 1926, 231).—The thermal conductivities of nitrous oxide and carbon monoxide have been measured at various pressures and the results tabulated. The conductivities have also been measured at different temperatures and the temperature coefficient is given. The same apparatus has also been used to determine the thermal conductivity of air. J. L. BUCHAN.

Heat capacity at low temperatures of zinc oxide and of cadmium oxide. R. W. MILLAR (J. Amer. Chem. Soc., 1928, 50, 2653—2656). The specific heats of the oxides are recorded between 71 and 300° Abs. (cf. A., 1928, 936); the results may be represented by the sum of Debye and Einstein functions over limited temperature ranges. The calculated molar entropy and heat of formation at 25 are 10.28 g.-cal./1° and -83,130 g.-cal. for zinc oxide; for cadmium oxide, the molar entropy is 15.11 g.-cal./1° and the free energy of formation -54,200 g.-cal./mol.

S. K. TWEEDY.

Absolute velocity of a water molecule emitted on the dehydration of a crystalline hydrate. I. A. PREDVODITELEV (Z. Physik, 1928, 51, 136—149). A method has been developed for calculating the velocity of molecules emitted on the breakdown of a solid material, and the velocity of the water molecules emitted on the dehydration of the crystal hydrates $(\text{CO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ has been determined. The heats of hydration calculated from these velocities are in good agreement with the values obtained by thermochemical measurements.

J. W. SMITH.

Thermal expansion of air-sensitive crystalline salts. W. KLEMM (Z. Elektrochem., 1928, 523—528).—The mean coefficients of cubical expansion, α , between 20° and 150°, of some metal halides, hydroxides of lithium, sodium, and potassium, and some organic substances were measured by a dilatometric method. The results are discussed in the light of theoretical considerations. Halides with ionic lattices have values of α which are smaller than the higher the charges on the cation, and agree fairly well with those calculated. A sudden change in α occurs on passing from compounds of ionic to those of molecular lattices. The relationships between α and the m. p. and α and the co-ordination number are discussed.

The ratio between α for the crystalline and molten states lies within 0.3 and 0.5, except for aluminium chloride and potassium hydroxide (cf. Biltz and Voigt, A., 1923, ii, 324). The expansion has practically no influence on the ratio of the molecular volumes in the solid and liquid states (Klemm, A., 1926, 669, 670).

S. K. TWEEDY.

Hydroxyl radical in flames. K. TAWADA and W. E. GARNER (Nature, 1928, 122, 879—880).—The maximum emission of radiation is not associated with the mixture $2\text{H}_2 + \text{O}_2$, which gives the highest flame temperature, but with the mixture $\text{H}_2 + \text{O}_2$, indicating that the hydroxyl radical may be responsible for the emission of part of the radiation from the hydrogen flame. An explanation of the mechanism of the reaction, which accounts for the observed radiation-composition curve, is offered.

A. A. ELDRIDGE.

Relations between physical constants of liquids. V. PERSCHKE (J. Russ. Phys. Chem. Soc., 1928, 60, 1019—1035).—The general relation $\log X - a + b \times \log(t_k - t)$ is derived, where X is any physical constant of a liquid, a and b are constants for the given liquid and property, and t_k and t are respectively the critical and the given temperature. This equation is verified for a number of liquids for density, surface tension, latent heat of vaporisation, viscosity, specific heat, refractive index, and conductivity of sound. Any number of physical constants can be connected by combining the same number of equations of the above type: thus for any pair of constants X and Y , $\log X = p + q \times \log Y$, where $p = a_x b_y - a_y b_x / v_x / v_y$, and $q = b_x / b_y$.

R. TRUSZKOWSKI.

Physical constants of rhenium. (FRAU) I. NODDACK (Z. Elektrochem., 1928, 34, 629—631). The wave-lengths of the L -series of the X-ray spectrum are tabulated. The optical spectrum contains more than 100 lines; the "later" lines, especially the triplet at 3640 Å., serve for detecting minute quantities of the element. The black metal powder obtained by heating the sulphide in hydrogen has d 10.4. Metal which has been fused on the anticathode of an X-ray tube forms small, bright granules having d about 20. The m. p. and b. p. are probably higher than those of tungsten, and the mean specific heat between 0° and 20 is 0.0346. By heating the disulphide, ReS_2 , in hydrogen the monosulphide, ReS , is formed, and then, at about 1000°, metallic rhenium. Using this conversion, the at. wt. is found to be 188.71 ± 0.25 .

S. K. TWEEDY.

Main types of first-order chemical compounds, illustrated by the carbides. A. VON ANTROPOFF (Z. Elektrochem., 1928, 34, 533—536).—Carbides are divided into two main groups: (a) carbides in which the two elements have their normal valencies ("valency compounds"), and (b) those in which the elements are combined in a manner independent of their valencies ("atom compounds or packed compounds," because they have atomic lattices as distinct from molecular or ionic lattices, and because there is a packing effect in the molecule). Group (a) is further divided: (i) polar compounds (infusible salt-like carbides having ionic lattices and conducting electricity well, e.g., sodium carbide); (ii) non-polar

compounds (non-conducting, non-metallic carbides, mostly fluid, with molecular and pseudo-atomic lattices, *e.g.*, carbon tetrachloride). Group (b) embraces non-polar, mostly metallic, carbides, which exhibit electrolytic conduction and have true atomic lattices, *e.g.*, tungsten carbide. Diamond belongs to group (a), (ii). This classification is extended to other first-order compounds; *e.g.*, water belongs to group (a), (ii), and sodium chloride to group (a), (i).

S. K. TWEEDY.

Metastability of the elements as a result of enantiotropy or monotropy. XI. Physico-chemical constants of silver iodide. I. E. COHEN and W. J. D. VAN DOBBENBURGH (*Z. physikal. Chem.*, 1928, 137, 289—334).—The discrepancies among the values given in the literature for the density of silver iodide are too great to be ascribed to the presence of chemical impurities, and cannot be due to the influence of light, which produces a negligible change of density even after long exposure; further, the temperature coefficient is relatively small. The ordinary chemically pure precipitated material consists of a number of physical modifications. A physically pure α -silver iodide of d_{20}^{25} 5.68 is produced by heating at 90—140° with a concentrated solution of calcium chloride or by melting and cooling to the ordinary temperature. The transition temperature of the $\alpha \rightleftharpoons \beta$ change at 1 atm. pressure is 145.80°; $d_{145.8}^{145.8}$ for the α modification is 5.68₅, and for the β , 6.00₉, whilst the volume change of the transition $\alpha \rightleftharpoons \beta = -0.0094_5$ cm.³/g. H. F. GILLBE.

Vapour pressures and chemical constants of silver, gold, copper, lead, gallium, and tin. P. HARTECK (*Z. physikal. Chem.*, 1928, 134, 1—20).—The vapour pressures of these metals have been measured at temperatures near 1000° and above over a pressure range of 10⁻⁴ to 10⁻² mm. Except in the case of lead, where a boiling method was used, the method of Knudsen has been employed. The results of other workers are discussed. The chemical constants can be represented by the equation $j_p = -1.59 + \log M^{1/5} + k$, where k has the value $+0.39 \pm 0.36$ for lead, 0.65 ± 0.40 for silver, -0.10 ± 0.40 for copper, $+0.56 \pm 0.40$ for gold, and $+0.50$ or -0.20 for carbon. The deviations from the theoretical values are all positive and approximate to 0.3 unit. A Trouton constant of 22.5 is obtained for the metals of high b. p. Langmuir's method for the measurement of small vapour pressures is discussed, and certain of the data (A., 1927, 927) are considered to be erroneous. L. S. THEOBALD.

Vapour pressure and chemical constant of chlorine. P. HARTECK (*Z. physikal. Chem.*, 1928, 134, 21—25).—An apparatus for the determination of the saturation pressure of chlorine between pressures of 2.6 and 634 mm. (162.7—245.2° Abs.) is described. Extrapolation gives for the b. p. at 760 mm. the value -33.95 ± 0.10 , and the intersection of the sublimation and vapour-pressure curves gives for the triple point the value -100.5 ± 0.30 at a pressure of 9.8 mm. The data agree well with those of previous workers. The chemical constant of diatomic chlorine is $1.67_5 \pm 0.7$ or -0.12 .

L. S. THEOBALD.

Density of molten metals and alloys. Y. MATSUYAMA (*Bull. Inst. Phys. Chem. Res.*, Japan, 1928, 7, 1054—1077).—The densities of tin, cadmium, bismuth, lead, zinc, the binary alloys Sn—Cd, Sn—Bi, Bi—Pb, Zn—Sn, Bi—Cd, Cd—Pb, Cd—Zn, and the ternary alloys Sn—Bi—Cd, Bi—Cd—Pb, Sn—Bi—Pb, Sn—Cd—Pb, Sn—Cd—Zn, Cd—Pb—Zn were determined at different temperatures. It was shown that the expansion coefficient of a molten metal decreased slightly with temperature, and the density of a metal at its m. p. obtained from this coefficient was in satisfactory agreement with the value obtained by extrapolating the density-temperature curve.

In the case of alloys it was found that the atomic volume of a mixture was greater than the mean of the atomic volumes of the components by not more than 1%. The maximum deviation did not occur in mixtures containing equal molar amounts of each component, but in mixtures containing less of the component of smaller density. The equation of van Laar and Lorenz for the heat of mixing may hold for the alloys Sn—Cd, Pb—Cd, Sn—Zn, Cd—Zn.

F. S. HAWKINS.

Density of boric oxide glass and atomic weight of boron. A. COUSEN and W. E. S. TURNER (*J.C.S.*, 1928, 2654—2657).—The density of boric oxide glass prepared by fusing boric acid at 1400° and annealing the product thoroughly has been determined both by the specific gravity bottle and the flotation method; over the temperature range 18° to 25° $d = 1.844$. Inadequate annealing or fusion of the boric acid at too low a temperature is shown to give a glass with a lower density; this explains the low value obtained by Briscoe, Robinson, and Stephenson (A., 1926, 219). As the variations obtained by these authors in the density results of boric oxide glass from six different terrestrial sources can readily be ascribed to varying degrees of strain, it is not justifiable to use them as evidence of variation in the atomic weight of boron.

R. N. KERR.

Crystallisation of mesomorphic substances in the magnetic field. Obtaining a solid with oriented molecules. G. FOËX (*Compt. rend.*, 1928, 187, 822—823).—The molecular orientation of the solid prepared by almost completely melting *p*-azoxyanisolephenetole in a magnetic field and allowing it to cool has been shown by the author's method (A., 1925, ii, 755) to be the same as that of the oriented nematic phase produced as a result of fusion. Crystallisation of the smectic phase of ethyl *p*-azoxybenzoate in a magnetic field also gives an anisotropic solid, but the diamagnetism is stronger in the direction of the orienting field than perpendicular to it.

J. GRANT.

Molecular state of liquids. W. KISTIakovSKI (*Z. physikal. Chem.*, 1928, 137, 383—392).—Liquids are classified in seven groups: (1) Non-associated, (2) slightly associated, (3) moderately associated, (4) strongly associated but yielding normal vapours, (5) strongly associated and yielding associated vapours, (6) electrolytes, (7) those exhibiting metallic conductivity. Modern conceptions of molecular structure have been applied to the problem of the physical state of liquids, assuming the com-

pletion of an eight-electron shell to be a hindrance to association as it is to chemical reactivity. The ease of association of the elements is periodic, conforming to the long periods of the Mendeleev system. Molecular association in liquids is frequently caused by the hydrogen atom, but only to a considerable extent if the hydrogen is combined with oxygen or nitrogen. The whole problem of the association of liquids is closely related to the deformation of the electron shells.

H. F. GILLBE.

Quantum theory of the specific heat of hydrogen chloride. E. HUTCHISSON (Physical Rev., 1927, [ii], 29, 360—361).—The specific heat of hydrochloric acid at various temperatures has been recomputed using new quantum theory *a priori* probabilities. The curve rises to a maximum above the classical value at about 12° Abs. A. A. ELDRIDGE.

Dilatometric measurements of the expansion with heat of crystalline salts. W. KLEMM, W. TILK, and S. VON MULLENHEIM (Z. anorg. Chem., 1928, 176, 1—22).—Dilatometric determinations have been made of the coefficients of expansion of a large number of inorganic salts and of some organic compounds, and in certain cases density measurements have been made.

H. F. GILLBE.

Oxides of ruthenium and osmium. F. KRAUSS and G. SCHRADER (Z. anorg. Chem., 1928, 176, 385—397).—Densities of the dioxides and tetroxides of ruthenium and osmium have been determined and the atomic volume of oxygen at 0° Abs. has been calculated to be about 10.7. According to the work of other investigators, crystallised specimens of the dioxides may be obtained in which the atomic volume of oxygen is only half this value. The possibility of the existence of two modifications of OsO₂ and RuO₄ is discussed.

M. S. BURR.

Volume chemistry. IV. Mixed oxygen compounds. I. Carboxyl group. F. WRATSCHKO (Pharm. Presse, 1928, 33, 124—126, 138—139, 160; Chem. Zentr., 1928, i, 2897).

Change in elastic properties on replacing the potassium atom of sodium potassium tartrate by ammonium. W. MANDELL (Proc. Roy. Soc., 1928, A, 121, 122—130; cf. *ibid.*, 1927, A, 116, 623).—The nine elastic moduli and nine elastic constants of crystals of sodium ammonium tartrate, prepared by very slow cooling from 28° of a concentrated solution of the salt, have been determined by the method previously used for sodium potassium tartrate (*loc. cit.*). In the bending and twisting experiments, the results with the ammonium salt were much more satisfactory than those with the potassium salt, the deflexions acquiring their maximum values almost immediately except for the stretching experiment in the direction of the *a* axis. The ammonium salt, both for the twisting and stretching experiments, is less elastic than the potassium salt, and the deformation magnitudes are increased fairly uniformly with the former salt. There is a considerable amount of similarity between the elastic curves of the two salts, which, however, show some small differences, especially in the directions where tensions or pressures give a maximum piezoelectric response. The general

results agree with what is to be expected from the fact that the salts are isomorphous, but it is considered remarkable that the simple chemical change made in so complex a molecule should diminish the elastic properties in all directions of the crystal. A comparison of the elastic properties of isomorphous crystals which have already been determined indicates that, in a salt of simple constitution, individual atomic forces exert a marked influence on the elasticity in certain directions, whilst in more complex substances the individual effects are more or less marked by the large number of other forces in the molecule.

L. L. BIRCUMSHAW.

Determination of cohesion temperatures [of powders]. G. TAMMANN and A. SWORYKIN (Z. anorg. Chem., 1928, 176, 46—48).—The temperatures at which various powdered salts, oxides, and silicates commence to cohere have been determined by observing the effect of allowing air to impinge on the substance. The quantity T_s/T_f , where T_s is the cohesion temperature and T_f the m. p., is for the oxides and salts about 0.52, and for the silicates about 0.88.

H. F. GILLBE.

Fused salts. III. W. HERZ (Z. Elektrochem., 1928, 34, 682—684).—The capillary constants of the fused alkali halides at the m. p. and b. p. have been calculated from the equation $a^2 = 2\gamma/d$, using the data of Jaeger (A., 1918, ii, 33). Except in the case of caesium chloride, the values obtained obey the law of corresponding states, the ratio a_c^2/a_s^2 (where a_c^2 is the capillary constant at the m. p., and a_s^2 that at the b. p.) having the approximate value 1.63. The formulæ connecting capillary constant with mol. wt. given by Walden, $Ma_s^2/T_c - C$ (cf. A., 1909, ii, 119, 122), and Kistiakowsky, $Ma_s/T_s - C$ (A., 1906, ii, 655), are calculated for the fused salts, and the molecular state of the substances under investigation is discussed in the light of the results obtained. Walden's ratio is found to increase with increasing atomic weight of anion or cation, i.e., the lighter ion has the greater tendency towards association.

L. L. BIRCUMSHAW.

Viscosity of gases and vapours. II. Mercury, cadmium, and zinc. H. BRAUNE, R. BASCH, and W. WENTZEL (Z. physikal. Chem., 1928, 137, 447—457).—The viscosities of vaporised mercury, zinc, and cadmium relative to that of air have been measured by the rotating disc method at temperatures between 214° and 677°, and at pressures between 16 and 244 mm. The values of Sutherland's constant derived from these measurements are, respectively, 942 for mercury between 217° and 607°, 1053 for cadmium between 517° and 627°, and 876 for zinc between 607° and 677°. Using these values in Sutherland's equations the experimental viscosities agree with the calculated to within 1%. Over the respective temperature ranges, the thermal conductivities, calculated from the viscosities, are, for mercury from 1.678×10^{-5} to 2.305×10^{-5} , for cadmium 3.96×10^{-5} to 5.197×10^{-5} , and for zinc 7.158×10^{-5} to 9.275×10^{-5} . The calculated diameters of the atoms for mercury, cadmium, and zinc are, respectively, 2.53×10^{-8} cm., 2.46×10^{-8} cm., and 2.33×10^{-8} cm. These values, like that for argon,

are 0.8 times those derived from X-ray measurements. These results are discussed from the point of view of Debye's theory of molecular forces.

F. G. TRYHORN.

Influence of molecular attraction forces on the viscosity and heat conductivity of gas mixtures. H. SCHMIDT (Physikal. Z., 1928, 29, 633—640).—Earlier work (cf. A., 1928, 1180) is described together with additional experiments on viscosity. Heteropolar compounds cause deviations from the simple mixture law for both viscosity and thermal conductivity.

R. A. MORTON.

Jaeger's method as applied to the determination of the surface tension of mercury. R. C. BROWN (Phil. Mag., 1928, [vii], 6, 1044—1055).—Using Jaeger's bubble method with nitrogen as the gas, the surface tension of mercury was found to be 472 and 477 dynes/cm. for glass and platinum jets, respectively, at 18° (cf. Bircumshaw, A., 1928, 1084).

W. E. DOWNEY.

Internal friction of some gases and vapours. I. Air and bromine. H. BRAUNE, R. BASCH, and W. WENTZEL (Z. physikal. Chem., 1928, 137, 176—192).—A quartz apparatus is described containing a disc of 36 mm. diameter suspended by a quartz fibre between two fixed discs of 46 mm. diameter. Measurement of the logarithmic decrement of the rotational vibration of the movable plates when the apparatus is filled with gas at a given temperature and pressure has been employed to determine the internal friction of the gas. Results have been obtained for air and for bromine vapour over a wide range of temperature and pressure, and are compared with those obtained by other observers.

H. F. GILLBE.

Aluminium-calcium alloys. G. BOZZA and C. SONNINO (Giorn. Chim. Ind. Appl., 1928, 10, 443—449).—Alloys containing up to about 5% of calcium have been examined. Donski's equilibrium diagram (A., 1908, ii, 278) requires slight modification in the liquidus curve between the m. p. of aluminium and the first eutectic point. The differences between Donski's and Arndt's results (cf. B., 1905, 676) for the alloys corresponding with the region of partial miscibility in the liquid state are explained. The electrical conductivity and the density of the alloys diminish linearly with increasing calcium content. The hardness varies little, and the brittleness becomes very marked as soon as a small proportion of calcium is present. The tensile strength is somewhat lower than that of pure aluminium. The conditions of casting influence the properties of the alloys appreciably, but their industrial application scarcely seems feasible.

T. H. POPE.

Electrical resistance of some silver alloys. W. SCHMIDT (Z. Metallk., 1928, 20, 400—402).—The slope of the curves which are obtained by plotting the increase of resistance against the atomic composition of solid silver alloys increases with the nature of the alloying element in the order: cadmium, magnesium, zinc, manganese, aluminium, tin, antimony.

A. R. POWELL.

Mixed crystals and alloys. L. VEGARD and H. DALE (Z. Krist., 1928, 67, 148—162; Chem.

Zentr., 1928, i, 2573).—The systems lead nitrate-barium nitrate and copper-nickel, but not copper-cobalt, exhibit complete miscibility. The lattice dimensions show that the additivity law holds. The copper lattice can accommodate up to 13% Co and the cobalt lattice up to 8% of copper. The cubic form of the cobalt lattice is stabilised by traces of copper. Rapidly cooled copper-gold alloys were in accord with the additivity law. No mixed crystals were observed in the system sodium bromide-ammonium bromide.

A. A. ELDRIDGE.

Application of the Fourier functions to diffusion. E. L. LEDERER (Kolloid-Z., 1928, 46, 169—173).—Application of the Fourier functions has led to diffusion coefficients for sodium chloride and sucrose. The values are in good agreement (although somewhat higher throughout) with those in the Stefan-Kawalki tables.

E. S. HEDGES.

Optical striation. F. EMICH (Monatsh., 1928, 50, 269—283).—An improved apparatus is described for microscopical observation of the optical striation which occurs when a stream of one liquid flows through a jet into a second of different refractive index. The striation phenomena are classified as positive or negative according as the entering liquid is more or less refractive, and as rising or falling according as it is lighter or heavier than the second liquid. The method is sensitive to a difference of about 0.0001 in refractive index, and quantitative measurements of the intensity of striation may be made. The method is applicable to testing the purity of liquids.

R. K. CALLOW.

Determination of the solubility curves of mixed crystals at low concentrations and the segregation of the foreign substance on heating. G. TAMMANN and A. HEINZEL (Z. anorg. Chem., 1928, 176, 147—151).—The solubility of a metal which is but sparingly soluble in another may be determined by microscopical examination of the residual film left after dissolving a rolled sheet of the metal in 50% ammonium nitrate solution. By this method the solubility of lead in cadmium at 270° has been shown to be greater than 0.1% and that of copper to be between 0.05 and 0.1%. The changes in the appearance of the film after the metal has been heated above the eutectic temperature are described.

H. F. GILLBE.

Invasion and solvation of gases in water. G. M. SCHWAB and E. BERNINGER (Z. physikal. Chem., 1928, 138, 55—74).—A method is described for measuring at 10° intervals between 20° and 80° the solubility and "invasion coefficients" in water of oxygen, hydrogen, nitrous oxide, carbon dioxide, ethylene, and acetylene. With rising temperature, the solubilities of carbon dioxide and acetylene pass through minimum values, that of nitrous oxide falls abruptly, and that of ethylene is little influenced. The invasion coefficients of these gases, calculated from the solubility measurements, are approximately of the same magnitude but possess different temperature coefficients which are attributed to differences in the water layers round the gas molecules. Comparison of the hydration values for 20° and 60°

shows that, relative to other gases, carbon dioxide and acetylene, which alone pass through a minimum solubility with rise of temperature, have abnormal positive temperature coefficients for the hydration number. Taking into account the influence of the viscosity of water, it is found that the temperature coefficients of the hydration number of all gases investigated are positive, and show analogy with the temperature coefficient of solubility at higher temperatures at which the effect of the dynamic allotropy of water disappears.

F. G. TRYHORN.

Solubilities of some inorganic fluorides in water at 25°. R. H. CARTER (Ind. Eng. Chem., 1928, 20, 1195).—The solubilities of various fluorides and the p_H values of these saturated solutions have been determined. The solubilities (g./100 c.c.) range from sodium fluoride 4.054 to calcium fluoride 0.004.

C. IRWIN.

Crystallisation at the surface of fused masses. A. SCHUBNIKOV and G. LAMMLEIN (Z. Krist., 1928, 67, 329—338; Chem. Zentr., 1928, i, 3027—3028).—On seeding supercooled fused phenyl salicylate the spherulites separate, and on continued rotation move radially from the point of seeding. An explanation is offered.

A. A. ELDRIDGE.

Influence of foreign substances in solution on the growth of crystals. L. KIMBLEWSKAJA (Nachr. Don. Staatsuniv. Rastow, 1925, 5, 4 pp.; Chem. Zentr., 1928, i, 2770).—A discussion of the fact that in presence of borax, alum solutions yield a precipitate of basic aluminium sulphate and aluminium hydroxide, and of the appearance of different forms of crystals.

A. A. ELDRIDGE.

Adsorption of vapour on a quartz or glass wall. A. SMITS (J.C.S., 1928, 2952—2954; cf. McHaffie and Lenher, A., 1925, 11, 854; Lenher, A., 1926, 898; 1927, 198; Frazer and others, A., 1927, 722).—By extrapolation of the vapour-pressure data of the author and Purcell it is shown that at 379° and 480 mm. pressure ammonium bromide is adsorbed by glass to an extent which corresponds with the formation of a layer 300 molecules thick. This result is similar to that obtained by Rinse (A., 1928, 829) for mercuric iodide on glass and by Smith (*ibid.*, 1087) for water on platinum surfaces.

F. J. WILKINS.

Helium. III. Behaviour of helium towards glass and palladium, and the question of helium compounds. F. PANETH and K. PETERS (Z. physikal. Chem., 1928, B, 1, 253—269; cf. A., 1928, 1341).—Glass is appreciably permeable to helium at the ordinary temperature; at 0.5 atm. pressure about 10^{-11} c.c./cm.²/hr. passes through glass of thickness 0.5 mm. At a higher temperature, the rate is considerably higher, and since the rate of diffusion of neon is under the same conditions extremely small, neon-free helium may be obtained with little difficulty. Since, on the other hand, palladium is almost completely impermeable to helium at all temperatures, hydrogen and helium may be separated with ease. Unsuccessful attempts to prepare helium compounds are described.

H. F. GILLBE.

Heat of adsorption of oxygen on charcoal.

III. D. MCKIE (J.C.S., 1928, 2870—2889; cf. A., 1927, 1134).—The heat of adsorption of small quantities of oxygen on charcoal has been measured at temperatures up to 200°. After the adsorption the pressure of the gas is so low that the apparatus serves as a vacuum calorimeter. A few measurements were also made of the adsorption of oxygen and nitrogen and their mixtures on charcoal. Pure oxygen or nitrogen adsorbed on charcoal cannot be removed by pumping out at the temperature of adsorption. When mixtures of oxygen and nitrogen are admitted either to a clean charcoal surface or to one containing adsorbed oxygen or nitrogen a portion of the gas can be desorbed by evacuation. No gas, however, can be pumped off when nitrogen is adsorbed on a surface already containing adsorbed oxygen. In agreement with the results of Saussure (Ann. Physik, 1814, 47, 113) it is found that the amount of gas adsorbed from a mixture of oxygen and nitrogen is greater than is to be expected from what is known of the separate adsorptions of these gases.

F. J. WILKINS.

Electro-capillary phenomena. IV. Role of physical factors. W. ARCISZEWSKI, E. CZARNECKI, W. KOPACZEWSKI, and W. SZNKIEWICZ (Protoplasma, 1928, 3, 345—356; Chem. Zentr., 1928, i, 2366—2367).—A study of the influence of concentration, dialysis, viscosity, surface tension, and age of solutions of various colloidal substances (dyes etc.) on the electrocapillary penetration in filter-paper.

A. A. ELDRIDGE.

Gelatin and copper sulphate solutions. M. CHANOT (Compt. rend. Soc. Biol., 1928, 98, 695—697; Chem. Zentr., 1928, i, 3078; cf. A., 1928, 1271).—With a gelatin diaphragm copper sulphate solution behaves as with an animal membrane. The electrolytic behaviour was studied. Gelatin is coloured blue by 0.001*N*-copper sulphate solution, but on addition of acid the colour is discharged, or a faint pink colour is produced.

A. A. ELDRIDGE.

Simple micro-electrodialysis apparatus. E. BAER (Kolloid-Z., 1928, 46, 176—178).—A micro-electrodialysis apparatus is described, which can be made mainly from pieces of glass tubing in the laboratory at a trifling cost. Directions are given for the preparation of a chromate-gelatin anode and a parchment cathode. The former is made by immersing crepe-georgette in a freshly-prepared potassium chromate-gelatin mixture, washing out the excess of potassium dichromate with water, and removing the last traces by electrodialysis. The electrodes consist of platinum wire in the form of a flat spiral, but the cathode may be made of silver wire or silvered brass wire.

E. S. HEDGES.

Rotatory dispersion of solutions of nicotine in the ultra-violet. (MME.) MILWARD-LIQUIER and R. DESCAMPS (Bull. Soc. chim. Belg., 1928, 37, 345—350; cf. A., 1927, 827).—The specific rotations of aqueous solutions of nicotine (0.1 g.-mol./litre) containing increasing quantities of hydrochloric acid have been measured for wave-lengths between 5780 and 2967 Å., in continuation of previous measurements made in the visible region. Aqueous solutions

of nicotine containing hydrochloric acid up to the amount necessary for the complete neutralisation of one of the basic groups behave as mixtures of two optically active constituents having different dispersions. These are the undissociated molecule of the hydrochloride and the nicotine cation.

O. J. WALKER.

Specific heats of magnesium sulphate solutions of various concentrations between 16° and 100°. F. SEROWY (Mitt. Kali-Forschungs-Anst., 1922, 2, 133—141; Chem. Zentr., 1928, i, 2701).

Thermochemistry and refractometry of strong electrolytes. E. LANGE (Physikal. Z., 1928, 29, 760—770).—Measurements carried out with a differential calorimeter accurate to 10^{-6} degree C. show that the heat of dilution in the limiting region (e.g., $<0.01M$ -potassium chloride solutions) is positive and varies as $M^{\frac{1}{2}}$, in accordance with the requirements of the Debye-Hückel theory. Above a concentration of $0.01M$, deviations from the simple theory are to be expected and do in fact occur, due possibly to residual undissociated molecules. For concentrations above $2N$, the molecular refraction of strong electrolytes varies with the concentration, and the sign and magnitude of the variations indicate the formation of ionic aggregates without intermediate molecules of water, i.e., undissociated molecules. Whilst these results do not prove the existence of undissociated molecules of strong electrolytes, a series of observations on heats of dilution, molecular refraction, and on the absorption spectra of nitrates strongly indicate incomplete dissociation. R. A. MORTON.

Application of the Fourier functions to sedimentation. E. L. LEDERER (Kolloid-Z., 1928, 46, 173—176).—Calculations have been made of the number of particles of colloid at various heights in a sol and at various times before the state of sedimentation equilibrium is reached. The results agree well with the data obtained by Perrin and do not support the arguments of Burton and Bishop (Proc. Roy. Soc., 1922, 100, 414). E. S. HEDGES.

Suspensions of kaolin. R. DUBRISAY and ASTIER (Compt. rend., 1928, 187, 978—980).—The rate of settlement of water-washed kaolin, purified by sedimentation and suspended in water or in a dilute solution of hydrochloric acid, or of sodium, lithium, or potassium hydroxide, decreases regularly with an increase in the p_H value of the solution. Phosphate buffers and very dilute solutions of the alkaline-earth bases show exceptional behaviour.

J. GRANT.

Heterogeneity of colloidal solutions and sedimentation in a centrifugal field. T. SVEDBERG (Nobel Prize Address, 14 pp.).—The construction of centrifuges is described. Measurement of the rate of sedimentation and sedimentation equilibrium lead independently to values of the mol. wt. of substances.

CHEMICAL ABSTRACTS.

Colloidal gold solution. Preparation of gold solutions and their titration with permanent hydrogen-ion concentration standards. V. CHRISTINA and C. S. GREEN (J. Lab. Clin. Med., 1928, 13, 678—681).—In Zsigmondy's method, conductivity water and a larger amount of alkali are

used. Phenol-red is employed as indicator, and the p_H determined with permanent inorganic standards.

CHEMICAL ABSTRACTS.

Preparation of a lead sulphide hydrosol and its combination with phosphate ions. J. BROOKS (J. Physical Chem., 1928, 32, 1717—1724).—A lead sulphide sol has been prepared from a solution of lead acetate and hydrogen sulphide using 0.5% of gelatin as a protective agent with the subsequent addition of sodium hydrogen carbonate to neutralise the acetic acid formed. The percentage transformation of lead salt into colloidal sulphide depends on the initial concentration of the former, and above a certain concentration the amount of colloid formed decreases abruptly. The results are similar to those obtained with lead selenide hydrosol (A., 1928, 704). The rate of combination of the lead sulphide particles with phosphate ions at 15°, 25°, and 37.5° has been measured. It is slow in comparison with the rate of diffusion of phosphate ions to the surface and is independent of the phosphate concentration. At 15°, the rate is proportional to the surface of unchanged particle, but at the higher temperatures aggregation of the particles causes a decrease in reacting surface in addition to the decrease due to combination.

L. S. THEOBALD.

Osmotic pressure of egg-albumin. J. MARRACK and L. F. HEWITT (J. Physiol., 1928, 66, Proc. Physiol. Soc., v).—The osmotic pressure of isoelectric egg-albumin has been measured by the use of sodium chloride solutions buffered with sodium acetate and acetic acid as external fluid. The calculated mol. wt. is 43,000.

B. A. EAGLES.

Ultra-microscope and colloidal solutions. R. ZSIGMONDY (Nobel Prize Address, 12 pp.).—A description of studies on gold hydrosols and of observed relations between electric charge and coagulation.

CHEMICAL ABSTRACTS.

Structure of colloidal particles and composition of sols and gels. H. FREUNDLICH (Ber., 1928, 61, [B], 2219—2233).—A lecture. H. WREN.

Constitution of micelles. IV. Colloidal oxides of iron and aluminium. R. WINTGEN and O. KÜHN (Z. physikal. Chem., 1928, 138, 135—157; cf. A., 1924, ii, 156, 534).—Previous studies of the dialysis, ageing, electrical conductance, migration velocity, and ultra-filtration of ferric hydroxide and chromium oxide sols have been extended to sols of aluminium oxide.

F. G. TRYHORN.

Alumina gels. D. G. R. BONNELL (Z. anorg. Chem., 1928, 176, 416—422).—The adsorptive power of different alumina gels for dyes is independent of differences in the other colloid-chemical properties of the gels. Acid dyes are more strongly adsorbed than basic. Fractional ultra-filtration of the hydrosols produced by peptisation with hydrochloric acid indicates that poly-disperse systems are formed. The particle size diminishes with increasing acid concentration. Curves are given showing the relation between vapour pressure and water content of the gel during hydration and dehydration. The vapour pressures of the dehydration curve are lower than those of the hydration curve.

M. S. BURN.

Constitution and stable end-state of hydrogels. A. SIMON (Kolloid-Z., 1928, 46, 161—169).—A critical discussion of the constitution of hydrogels, with particular reference to the state of the aqueous phase. The water is supposed to be bound partly osmotically and partly chemically, an equilibrium existing between the two. Attempts to separate the two forms are described. E. S. HEDGES.

Theory of charge alternation of colloidal particles. A. EUCKEN (Z. physikal. Chem., 1928, B, 1, 375—378).—Theoretical. The relation of the stability of a colloidal solution to the electrolyte concentration is discussed on the basis of Debye's theory of electrolytes. M. S. BURR.

Dielectric constant of emulsions of water and mercury in oil. A. PIEKARA (Bull. Acad. Polonaise, 1928, A, 201—222).—The formulæ proposed for the dielectric constant of a mixture express the latter as an additive function of the dielectric constants of the constituents. The various forms of this function, in particular that of Lorenz and Lorentz, have been tested by measurements on emulsions of water and mercury in oil, with concentrations of the disperse phase between 0.0002 and 0.005. The dielectric constants were measured by the resonance method, sensitivity being increased by the application of the cathodic lamp. The values obtained for the emulsions are much greater than the calculated values, and depend to a greater extent on the concentration and dielectric constant of the disperse phase than is provided for by the formula. They also increase with the degree of dispersion, and are further shown to depend on the diameter of the particles of the disperse phase, of which the formula takes no account.

N. M. BLIGH.

Relation between the dielectric constant of an emulsion of mercury in vaseline and the degree of dispersion. A. PIEKARA (Bull. Acad. Polonaise, 1928, A, 223—239; cf. preceding abstract).—It is suggested that the divergence between the experimental and calculated values of the dielectric constant of emulsions may be due to the secondary influence of the movements of droplets constituting the disperse phase and to surface charges on the droplets. This was tested experimentally by measuring the dielectric constant of emulsions of mercury in vaseline to eliminate such movements. No appreciable effect due to these secondary factors could be detected. Evidence was obtained for a negative effect diminishing the dielectric constant, which is attributable to the directing influence of the charged particles on the dipoles of the liquid phase; this appears to increase with the concentration and dispersion and thus resembles the orienting effect found in the case of colloidal solutions. N. M. BLIGH.

Hofmeister ionic series in the precipitation of the hydrophilic colloids. K. ANDO (Nagoya J. Med. Sci., 1927, 2, 110—123).—In the precipitation of the hydrophilic colloids the Hofmeister series is valid except with the buffer salts. Precipitation according to valency occurs, and increases with the distance of the p_H from the isoelectric point. At the isoelectric point the hydrophilic colloids have a minimal stability towards ethyl alcohol. On both

sides of the point the sensitiveness to salts increases abruptly.

CHEMICAL ABSTRACTS.

ζ -Potential and the lyotropic series. D. R. BRIGGS (J. Physical Chem., 1928, 32, 1616—1662).—The effect of ions on the ζ -potential at an inert interface of cellulose and water has been measured by the streaming-potential method recently described (A., 1928, 713). The ions affect the ζ -potential in the order of their mobilities, which are thus inverse measures of the attraction between an ion and its dispersion medium. The ζ -potential arises from the relative attractions of ions for the phases of a system in which the ions are distributed. The effect of a salt solution on the ζ -potential is a function of all the ions present in a system to which the interface is accessible, and the potential varies with salt concentration in a manner similar to that of the partial molal free energy, the equation representing the former variation being $c - ae^N$. In certain cases, the change in ζ -potential with ionic concentration is secondary in effect to other free surface energy changes, and is not, *per se*, the determining factor in the adsorption phenomenon. L. S. THEOBALD.

Coagulation. II. Empirical equation for gelation velocity. K. HIROTA (J. Biochem. Japan, 1928, 9, 103—115).—Measurements have been made of the viscosity of sols of Merck's powdered gelatin (2.5—5%) by the use of a viscosimeter in which the fluid travels through the capillary under a constant pressure. Results are obtained which are in harmony with the equation of Shoji (A., 1919, ii, 498). The critical concentration of gelatin is 3.8% when ∞ and the rate of change of the constant with concentration, which is linear for higher and lower concentrations, increases suddenly at this point. The viscosities of agar-agar sols change with time similarly to those of gelatin sols, but it has not been found possible to apply the above equation in this case. When heated for some time at 98° both gelatin and agar sols undergo irreversible changes. W. O. KERMACK.

Influence of lyophile colloids on the stability and electric charge of lyophobe sols. W. REINDERS and W. M. BENDIEN (Rec. trav. chim., 1928, 47, 977—988).—In acid solutions of p_H value lower than that of the isoelectric solution colloids such as gelatin, casein, and sodium lysalbuminate, which are nitrogenous, lyophile, and amphoteric in character, behave as salts with multivalent cations towards gold sols. From observation on coagulation and cataphoresis it was found that very small amounts of these colloids discharge and coagulate gold sols. The same sols are charged positively and rendered stable in the presence of larger amounts of the above colloids. A second precipitation zone occurs at higher concentrations in circumstances in which the reagent is incompletely soluble in the solution of the given acidity and, in being precipitated, carries with it the gold particles. In solutions a little less acid than the isoelectric solution and in which the gold particles retain their negative charges for all concentrations of the added colloid, the protective action of the latter becomes predominant and the sol remains stable in spite of its low electrical charge. The gold

number of these colloids is markedly dependent on and decreases with the p_H value of the solution. Non-amphoteric, nitrogen-free colloids such as dextrin, gum arabic, and tannin coagulate gold sols in both acid and alkaline solutions, but are unable to reverse the sign of the electric charge on the particles.

F. G. TRYHORN.

Ion antagonism in colloidal models. I. Regularities in ion antagonism in the coagulation of hydrophilic sulphur sols. II. Influence of anions on the antagonism of cations in the coagulation of hydrophilic sulphur sols. W. A. DORTMAN (Kolloid-Z., 1928, 46, 186—198, 198—201).—I. A study of the ion antagonism encountered in biological problems has been made in a simpler system by observing the effects of pairs of electrolytes on hydrophilic sulphur sols. The strongest antagonistic effects were observed when the hydrogen ion formed one of the pair, and the lithium ion comes next in importance in this respect. No antagonism was observed between sodium and potassium ions. In general, the more remote the two ions in the order of coagulation values the greater is the antagonistic effect. In accordance with the Schulze-Hardy rule, the degree of antagonism increases with rising valency of the ions concerned, but quadrivalent thorium is a notable exception. The curves showing the dependence of the coagulation values of magnesium chloride, calcium chloride, and sodium chloride on the amount of hydrochloric acid previously added to the sol pass through a maximum at an abscissal value corresponding with 50% of the coagulation value for hydrochloric acid. For the pair hydrochloric acid-aluminium chloride, the maximum is displaced to the right, but in this case antagonism begins later. Dilution of the sol reduces the coagulation values of uni- and multi-valent cations and raises the corresponding values of bivalent cations. The ion antagonism is less marked in the dilute sols. Reversal of charge of the sol diminishes the degree of hydration; cation antagonism disappears, and no corresponding anion antagonism is observed. The factors concerned in determining these effects are considered to be the charge on the particles and the degree of hydration.

II. The effect of substituting sulphuric acid for hydrochloric acid in the experiments described above is to increase the antagonistic effect of the cations. This increase was observed in the pairs sulphuric acid with sodium chloride, magnesium chloride, or aluminium chloride and was particularly noticeable in the pair sulphuric acid-thorium nitrate. The effect is shown only by substitution of the anion of the first member of the pairs, a slight decrease in degree of antagonism being observed when sulphate is substituted for chloride in the second member of the pairs.

E. S. HEDGES.

Spectrophotometric and cataphoretic experiments on the adsorptive power of gelatin for methylene-blue hydrochloride. A. FODOR and K. MAYER (Kolloid-Z., 1928, 46, 201—207).—The spectrophotometric and cataphoretic methods of measuring the adsorption of methylene-blue hydrochloride developed earlier by the authors (A., 1926, 1091) have been applied to gelatin as adsorbent.

Experiments on the direction of migration of mixtures of gelatin and methylene-blue hydrochloride in an electric field with addition of acid or alkali show that the dye migrates in the same direction as the gelatin. With a solution containing 1.68% of gelatin and 0.002% of methylene-blue hydrochloride, both constituents migrate together to the cathode at p_H 4.6 and in more strongly acid solutions, whereas at p_H 4.9 and above migration occurs in the direction of the anode. Gelatin alone behaves in a precisely similar way, but it was established that methylene-blue hydrochloride alone always wanders to the cathode, whatever the hydrogen-ion concentration of the solution. Experiments were also carried out on the velocity of diffusion of methylene-blue hydrochloride into gelatin gels containing added electrolytes. The presence of neutral salts scarcely alters the rate of diffusion from that in pure, dialysed gelatin, but alkalis and alkaline salts diminish the velocity and acids and acid salts increase it. The formation of rings was observed in the diffusion into gels containing neutral salts and alkalis, but not in the gels containing acids. The course of adsorption was also followed by the spectrophotometric method. The amount of adsorption depends on the thickness of the gelatin layer and it is inferred that there is no essential difference between adsorption by gelatin and by animal charcoal (cf. Fodor and Schonfeld, A., 1922, ii, 688).

E. S. HEDGES.

Influence of adsorbed silver and bromide ions on light absorption by silver bromide hydrosols. H. FROMHERZ (Z. physikal. Chem., 1928, B, 1, 324—345).—The absorption spectra of samples of silver bromide hydrosols of approximately equal particle size and containing adsorbed silver and bromine ions, respectively, have been measured in an apparatus previously described (cf. *ibid.*, 301). The sol containing adsorbed silver ion, in contrast to bromine ion, shows increased absorption in the yellow and green due to a shift of the absorption curve 150—200 Å. towards the long-wave region. This is in agreement with earlier observations according to which the general photochemical sensitivity of silver bromide, free from any binding agent, is increased by the presence of adsorbed silver ion and its spectral sensitivity is extended to longer wave-lengths. In order to equalise the particle size of the two sols relative measurements of the degree of coagulation have been made on the basis of the light scattering produced by the particles. By measuring the rate of coagulation with time and its dependence on the excess of silver or bromine ion in the solution the necessary data may be obtained.

M. S. BURR.

Influence of adsorbed ions on the light absorption and photochemical sensitivity of silver bromide-gelatin emulsions. H. FROMHERZ and G. KARAGUNIS (Z. physikal. Chem., 1928, B, 1, 346—361; cf. preceding abstract).—Experiments carried out with mirrors covered with an emulsion of silver bromide in gelatin washed with solutions of various salts have shown that the extinction curves for adsorbed silver or bromine ions are similar to those for hydrosols. The extinction coefficient of the emulsion containing silver ion in comparison with

that containing bromine ion is increased by about 17% in the near ultra-violet and blue, and by about 60–70% in the yellow-red, resulting in an extension of the absorption region by 500 Å. towards the longer-wave region. The thalious ion has a similar effect to the silver ion, but only half as great. Experiments on the spectral and photochemical sensitivity of emulsions with different adsorbed ions indicate that the hydroxyl, sulphite, and thalious ions extend the sensitivity towards the red, the sulphate and chlorate ions have no influence, and the bromine ion decreases it. The extension of sensitivity towards the red by the thalious ion amounts to 700 Å. These results are in agreement with corresponding observations on silver bromide sol alone and with absorption measurements.

M. S. BURR.

Theory of the solid-phase rule. A. VON BUZAGH (Kolloid-Z., 1928, 46, 178–185).—In continuation of previous work (A., 1927, 310), the relation between the amounts of colloid peptised and the amount of the disperse phase present in the massive state is discussed and the conclusion is reached that factors other than adsorption are involved in the so-called solid-phase rule. Experiments conducted with suspensions of animal charcoal, calcium carbonate, barium sulphate, zinc oxide, red lead, and mercuric oxide in water show that the solid-phase rule holds in such coarsely disperse systems in the absence of an additional peptising agent. The same effect is also observed in the preparation of sols (e.g., mastic) by the method of exchange of the dispersion medium. The relative amounts of dispersed material (or degree of peptisation) depends, not only on specific adsorption, but also on the concentration of the gel suspension; these factors determine whether or not peptisation in the narrow sense takes place. It is probable that the variation of particle size of the suspension with the concentration also plays a part.

E. S. HEDGES.

Effect of the spatial position of substituent groups on acidic strength. B. FLURSCHEIM (J.C.S., 1928, 3039–3040).—A claim for priority over the views of Hey (A., 1928, 1188).

F. J. WILKINS.

Ionisation of aromatic nitro-compounds in liquid ammonia. II. W. E. GARNER and H. F. GILLBE (J.C.S., 1928, 2889–2904; cf. A., 1925, ii, 792).—The velocity of ionisation of *m*-dinitro-compounds in liquid ammonia solution obeys a first-order law, even in cases where the ionisation does not proceed to completion. Measurements of the change in conductivity and extinction coefficients of these solutions show that at high dilution the ionic concentration is proportional to the conductivity. It is suggested that the ionisation is the result of two consecutive reactions, $R(NO_2)_2 + 2NH_3 \rightarrow R(NO_2)_2 \cdot 2NH_3 \rightleftharpoons R(NO_2)_2^{--} + (NH_3)^{++}$, the first of which governs the velocity of the process and proceeds to completion. The critical increment of the reaction is 7250 g.-cal. Vapour-pressure measurements give no indication of the existence of molecular complexes of the type $R(NO_2)_2 \cdot xNH_3$.

F. J. WILKINS.

Hydrolysis of tin chloride and the chlorostannates. L. SMITH [with A. PERSSON] (Z. anorg. Chem., 1928, 176, 155–180).—The concentration of chlorine ions and hydrogen ions in aqueous stannic chloride solutions have been determined, the latter by calorimetric, potentiometric, and polarimetric methods. Conductivity and *f.p.* determinations have also been carried out. In dilute solution the hydrogen and chlorine ions are present in equal concentrations, but for solutions of greater concentrations than 0.1 *M* an excess of chlorine ions is present. For old solutions the *f.p.* and conductivities are in good agreement with the values calculated on the assumption of the existence of univalent positive tin complexes, whereas for newly-prepared solutions the observed conductivities for 0.1–0.4 *M* solutions are 15–20% less than the calculated. Sodium salts lower the hydrogen-ion concentration appreciably more than do potassium salts. The influence of acids and salts at concentrations up to about 4 *N* has been studied by means of solubility measurements and determination of partition coefficients between ether and water. Even in *N*-hydrogen chloride solution the true concentration of stannic chloride and of chlorostannate ions must be small; complete inhibition of hydrolysis does not take place even in presence of 4 *N*-acid. It is probable that the stannic chloride and chlorostannate-ion concentrations are of similar magnitude. The percentage hydrolysis is influenced to a very variable extent by different chlorides; their repressive influence increases in the order ammonium, potassium, barium, sodium, magnesium.

H. F. GILLBE.

Transformation of hydrated ortho-ferric oxide into hydrated meta-ferric oxide. A. KRAUSE (Z. anorg. Chem., 1928, 176, 398–402; cf. A., 1928, 1202).—When kept under water, hydrated ortho-ferric oxide gradually changes into the meta-form, and the change is very much accelerated by the presence of hydroxyl ions. At the same time the isoelectric point changes from p_H 5.2 to 7.7. The dried meta-compound contains less water than the ortho-, is brownish-yellow instead of black, is more friable, and adheres more firmly to glass. The meta-oxide can also be readily peptised by either dilute acid or ammonia, whilst the ortho-oxide cannot.

M. S. BURR.

Decomposition pressures of nitrides. R. LORENZ and J. WOOLCOCK (Z. anorg. Chem., 1928, 176, 289–304).—The different methods employed in the investigation of the decomposition pressures of nitrides are reviewed. A method is described by which the formation of nitrides from the metal, or carbide, and nitrogen may be quantitatively studied, using a "Kurzschluss" vacuum furnace. The product formed by passing nitrogen over zirconium carbide gives up some gas again by heating above 1400°, but cannot be made to reabsorb nitrogen at a higher pressure. Although some nitrogen is absorbed by tantalum and titanium, no reversible equilibrium can be obtained. Between 750° and 1800°, and at a pressure of 1 atm. of nitrogen there is no appreciable absorption by molybdenum. The decomposition pressures of boron nitride have been observed between 1695° and 2045°. The results are reversible

and reproducible and the relation between $\log p$ and $1/T$ is approximately linear. The heat of formation of boron nitride per g.-mol. is calculated to be 28100 g.-cal. It has been shown by Shukov's method (A., 1910, ii, 254) that the nitrogen pressures in equilibrium with compounds of uranium and nitrogen increase continually with increasing nitrogen content. It is possible to obtain reversible equilibrium values, but these are not satisfactorily reproducible and a straight line is not obtained by plotting $\log p$ against $1/T$. The behaviour is similar to that of chromium and manganese (Shukov, *loc. cit.*), and may be due to the dissolution of nitrogen or nitride in the metal.

M. S. BURR.

System zinc oxide-water. A. GUTBIER and H. R. BARFUSS-KNOCHENDÖPPEL (Z. anorg. Chem., 1928, **176**, 363—371).—The preparation of three different samples of hydrated zinc oxide is described: A, the crystallised monohydrate $\text{ZnO} \cdot \text{H}_2\text{O}$; B, an amorphous zinc oxide hydrate subjected to ageing and having a composition corresponding with the formula $\text{ZnO} \cdot 0.342\text{H}_2\text{O} \cdot 0.027\text{CO}_2$; C, freshly-prepared amorphous zinc oxide hydrate, $\text{ZnO} \cdot 0.275\text{H}_2\text{O} \cdot 0.005\text{CO}_2$. The vapour pressure of preparation A is not measurable at the ordinary temperature but undergoes a marked rise at 73° . All but a very small fraction of the water, about 0.06 mol., can be readily removed, but the process is not reversible at the ordinary temperature, even in the presence of liquid water. This and other observations indicate that the crystallised monohydrate is not stable at the ordinary temperature (cf. Roth and Chall, A., 1928, 593). Preparation B gives up water less readily than C. The ratio of the adsorptive power of B to that of C for silver is 31 : 9, so that ageing diminishes the adsorptive power. On examination of the X-ray spectrograms C was found to give no interference, B showed broad diffused interference bands corresponding in position with those of zinc oxide and not with the crystallised monohydrate, whilst A showed sharp interference lines, the positions being different from those of zinc oxide lines. It is concluded that the ageing process in the system zinc oxide-water results in the formation of the oxide and liquid water, but that there is an intermediate stage consisting in the formation of the monohydrate.

M. S. BURR.

Fusion diagram of highly refractory oxides. H. VON WARTENBERG, H. LINDE, and R. JUNG (Z. anorg. Chem., 1928, **176**, 349—362).—The construction of a furnace made of zirconium oxide and heated by the oxy-hydrogen or oxy-coal gas flame is described. The furnace has been employed for the study of the m.-p. curves of the following binary mixtures of refractory oxides: $\text{CaO}-\text{Al}_2\text{O}_3$ (determined merely as a test of the behaviour of the furnace); $\text{ZrO}_2-\text{Al}_2\text{O}_3$; and $\text{CaO}-\text{ZrO}_2$. Softening points and m. p. of aluminium oxide mixtures were observed up to 20% of zirconium oxide. From 20% to 60%, at a little above 1900° , there was one m. p. only, evidently the eutectic. At 80% there was only a softening point. So much deformation took place that no m. p. could be observed. No evidence of compound formation was obtained. The m. p. of mixtures of calcium oxide and zirconium oxide of high zirconium

oxide content were rendered uncertain by the volatility of calcium oxide at the temperatures required for fusion, but there appears to be a well-defined eutectic at 2230° with less than 60% zirconium oxide. A second eutectic mixture with a higher zirconium content is formed at 2380° . Between these two there should be a compound, probably the meta-compound $\text{CaO} \cdot \text{ZrO}_2$, with 69% of zirconium oxide.

M. S. BURR.

Lithium chloride ammonia complexes. S. C. COLLINS and F. K. CAMERON (J. Physical Chem., 1928, **32**, 1705—1716).—Vapour-pressure measurements of the system lithium chloride-ammonia have been made at 0° , 33° , 45.2° , 54.5° , 58.3° , 66.4° , 74.9° , and 86.9° , and of the system lithium chloride-ammonia-water at 25° . In the former system, between 0° and 66° , either the mono-, tri-, or tetra-amminolithium chloride may be formed, but at 66.4° the only stable complex is the monoamino-chloride. Excepting the case of this complex, the measurements agree well with those of Bonnefoi (A., 1901, ii, 653), but, contrary to this worker, the existence of a diamino-complex could not be established. In the latter system, either the monohydrate, lithium mono-amminochloride, or triamminochloride may be a stable solid phase, but no diamino-complex was found.

L. S. THEOBALD.

Phase rule investigation of cupric bromide in aqueous and hydrobromic acid solutions. S. R. CARTER and N. J. L. MEGSON (J.C.S., 1928, 2954—2967).—The solubility of cupric bromide in water between 0° and 50° shows the existence of two solid phases, $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$ and CuBr_2 . The transition temperature is 17.97° (cf. Kurnakov and Sementshenko, A., 1899, ii, 287).

The system $\text{CuBr}_2-\text{HBr}-\text{H}_2\text{O}$ has been investigated at 0° and 25° . The results at 0° indicate two stable solid phases, $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$, and the violet $\beta\text{-CuBr}_2$. Up to a concentration of 59% of hydrobromic acid the stable solid phase is CuBr_2 , which exists in two forms, the transition between $\alpha\text{-CuBr}_2$ and $\beta\text{-CuBr}_2$ occurring at 26.0% hydrobromic acid. A metastable region exists which has a solid phase of composition corresponding with $3\text{CuBr}_2 \cdot 2\text{HBr} \cdot 6\text{H}_2\text{O}$. No evidence has been obtained of the existence of $\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$.

F. J. WILKINS.

Interaction of acids and neutral salts with stannic oxide and its relation to electrical charge. B. N. GHOSH (J.C.S., 1927, 3027—3038).—Solutions of neutral salts develop an acid reaction in contact with both α - and β -stannic acids. The concentration of the liberated hydrogen ions varies with the amount of stannic acid taken. The α -acid has a greater number of replaceable hydrogen ions than the β -acid, a result which is in accord with Mecklenburg's view that the former has a larger active surface than the latter. The capacity of cations to liberate hydrogen ions is in the order $\text{Mg}^{++} > \text{Ba}^{++} > \text{Sr}^{++} > \text{Li}^+ > \text{Na}^+ > \text{K}^+$. This is in agreement with Mukherjee's theory of the adsorption of ions (Phil. Mag., 1922, [vi], **44**, 321).

In the presence of acids, hydrated stannic oxide is positively charged and the adsorption of an acid is greater the smaller the positive charge on the surface. The capacity of an anion to diminish the positive

charge of the adsorbent increases with the adsorbability of the anion.

F. J. WILKINS.

System ammonium sulphate-sulphuric acid-ethyl alcohol. H. B. DUNNCLIFF, A. L. AGGARWAL, and R. C. HOON (J. Physical Chem., 1928, 32, 1697—1704).—An investigation of this system at 18.1° shows equilibrium to be established more rapidly than in the case of the corresponding system with sodium sulphate. The solid, $3(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$, formed by the action of alcohol on ammonium hydrogen sulphate is amorphous, but the solid phases resulting from the action of alcoholic sulphuric acid on this salt are crystalline. When the ratio of the weight of ammonium hydrogen sulphate to that of alcohol is unity or greater than unity the formation of a compound of the formula $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$ is indicated, but this solid phase is not formed when alcoholic sulphuric acids react with the ammonium salt. Solid phases of the composition $3(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$ are produced at various ranges of acid concentration, but when the total acidity reaches 80% or more, no solid phase results at -18° from the action of the alcoholic acid on the ammonium salt. The phase diagram indicates that equilibrium is controlled by factors other than the concentration of free sulphuric acid.

L. S. THEOBALD.

Equilibria of sulphides and silicates in fusions. W. JANDER [with K. ROTHSCHILD] (Metall-Wirtschaft, 1928, 7, 580—585; Chem. Zentr., 1928, i, 2897).—By fusion of the constituents in a graphite crucible, the contents being stirred with a magnesium rod, and analysis of the cooled mass, the following reactions were studied: $\text{FeS} + \text{PbSiO}_3 \rightleftharpoons \text{PbS} + \text{FeSiO}_3$; $\text{Cu}_2\text{SiO}_3 + \text{FeS} \rightleftharpoons \text{FeSiO}_3 + \text{Cu}_2\text{S}$; $\text{NiSiO}_3 + \text{FeS} \rightleftharpoons \text{FeSiO}_3 + \text{NiS}$; $\text{PbSiO}_3 + \text{Cu}_2\text{S} \rightleftharpoons \text{Cu}_2\text{SiO}_3 + \text{PbS}$; $\text{Cu}_2\text{SiO}_3 + \text{NiS} \rightleftharpoons \text{NiSiO}_3 + \text{Cu}_2\text{S}$; $\text{NiSiO}_3 + \text{PbS} \rightleftharpoons \text{PbSiO}_3 + \text{NiS}$. With lack of iron in the sulphide layer, larger amounts of the more noble metal pass into the silicate layer. Except for the lead-copper equilibrium the values of K obtained directly and by calculation from two equations are in accord.

A. A. ELDRIDGE.

Systematic doctrine of affinity. XLVII. Relationship of mercury to certain metals. W. BILTZ and F. MEYER. **XLVIII. Heats of formation of uranium tetrachloride, trichloride, and trioxide.** W. BILTZ and C. FENDIUS. **XLIX. Relationships of chlorine and other halogens with gold.** W. FISCHER and W. BILTZ. **L. Pneumatolytic transference of gold by chlorine.** W. BILTZ, W. FISCHER, and R. JUZA (Z. anorg. Chem., 1928, 176, 23—45, 49—63, 81—111, 121—142).—**XLVII.** The mercury vapour tensions of gold amalgams containing 7—25% of mercury have been measured at temperatures from about 250° to 350°. Several series of mixed crystals exist, together with one compound, HgAu_4 . The phase of composition HgAu_3 is a saturated mixed crystal; with a mercury percentage greater than 25 this phase exists in contact with an immiscible mercury phase. The amalgamation of gold by liquid mercury is feebly endothermic, the affinity of the process being less than 0.5 kg.-cal./g.-atom of mercury. Tensimetric measurements with cerium amalgams, which are extremely

pyrophoric, indicate the existence of CeHg_4 , which is but slightly soluble in mercury, and does not dissolve metallic cerium; the heat of formation, referred to solid cerium, is 5.8 kg.-cal./g.-atom of mercury. Calorimetric determinations yield for the heat of formation of Hg_5Ti_2 , referred to liquid mercury at 0°, 2.5 kg.-cal., and for solid mercury at -39°, -0.4 kg.-cal.; the density of the solid amalgam at 0° is 13.16, and of the liquid at 25°, 12.94; the zero molecular volume is nearly equal to the sum of those of the components. The heats of formation in kg.-cal./g.-atom of liquid mercury of the sodium amalgams are NaHg_4 1.9, NaHg_2 7.8, Na_7Hg_8 5.3, NaHg 13.2, Na_3Hg_2 11.4, and Na_3Hg 9.3. The relative magnitudes of the heats of amalgamation are in agreement with the hypothesis of a relationship between the stability of intermetallic compounds and the "nobleness" of the components.

XLVIII. By measurement of the heats of dissolution of uranium and its tetra- and tri-chlorides in hydrogen chloride solutions, the following heats of formation have been determined: $\text{U (solid)} + 2\text{Cl}_2(\text{gas}) = \text{UCl}_4(\text{solid}) + 251 \text{ kg.-cal.}$, and $\text{U (solid)} + 3/2\text{Cl}_2(\text{gas}) = \text{UCl}_3(\text{solid}) + 213 \text{ kg.-cal.}$ Uranium is thus, with regard to chlorine, a less noble metal than iron, and resembles thorium closely. The heat of formation of the trioxide, calculated from the heats of dissolution of the chlorides and oxide in iodine trichloride and ferric chloride solutions, is 292 kg.-cal.

XLIX. The dissociation pressures of aurous chloride and bromide and auric chloride have been determined at various temperatures. The heats of reaction, calculated from the van 't Hoff equation, are in close agreement with those obtained by calorimetric measurements. The values in kg.-cal. are $2\text{Au (solid)} + \text{Cl}_2(\text{gas}) = 2\text{AuCl (solid)} + 16.5$ (16.8), $\text{AuCl (solid)} + \text{Cl}_2(\text{gas}) = \text{AuCl}_2(\text{solid}) + 18.7$ (19.9), $2\text{Au (solid)} + \text{Br}_2(\text{gas}) = 2\text{AuBr (solid)} + 13.7$ (14.2), and $\text{AuBr (solid)} + \text{Br}_2(\text{gas}) = \text{AuBr}_3(\text{solid}) + (16.9)$; bracketed values refer to calorimetric values. These results differ widely, for the first and third reactions, from those of Thomsen, and the discrepancies cannot be ascribed to the existence of different modifications of the metal. The possibility of formation of gold dichloride has been investigated, but no evidence has been obtained for its existence or for the formation of double salts between the dichloride and potassium chloride.

L. The system gold-chlorine has been investigated at temperatures up to 1250° at 1 atm. pressure of chlorine, and at 900—1000° and up to 500° with varying pressures. At temperatures above 475° the vapour phase contains Au_2Cl_2 molecules having a heat of sublimation of about -36 kg.-cal. in the neighbourhood of 900°; the heat of formation of the double molecule of aurous chloride from solid gold is, at this temperature, -22 kg.-cal. Although isobars lead to the double formula for auric chloride at high temperatures, isothermal measurements indicate that more complex molecules are present, and the discrepancies cannot be explained by assuming the existence of a dissociation equilibrium such as $\text{Au}_4\text{Cl}_{12} \rightleftharpoons 2\text{Au}_2\text{Cl}_6$.

H. F. GILLBE.

Solubilities and transition points of the ferrous chloride hydrates in aqueous solution. F.

SCHIMMEL (Z. anorg. Chem., 1928, **176**, 285—288).—The system ferrous chloride–water has been investigated between -50° and $+117.5^{\circ}$. The di-, tetra-, and hexa-hydrates exist in contact with the solution as stable phases, the transition temperatures being for $\text{FeCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 76.5° , and for $\text{FeCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 12.3° . The b. p. of the saturated solution, which contains 50.4% of ferrous chloride, is 117.5° . Considerable supercooling may take place below the eutectic temperature of ice and the dihydrate, viz., -36.5° ; the eutectic mixture contains 30.4% of ferrous chloride. H. F. GILLBE.

Quaternary system $\text{Na}_2\text{C}_2\text{O}_4\text{--H}_2\text{SO}_4\text{--Na}_2\text{SO}_4$ (or $\text{H}_2\text{C}_2\text{O}_4\text{--H}_2\text{O}$ at 25°). E. ELOD and E. ACKER (Z. anorg. Chem., 1928, **176**, 305—324).—The above system has been examined at $24.71^{\circ} \pm 0.05^{\circ}$, and the existence of a new compound, acid sodium sulphate-oxalate with the empirical formula $\text{Na}_3\text{H}_3(\text{SO}_4)_2\text{C}_2\text{O}_4$, has been established. It is incongruently soluble in water with the separation of $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The compound appears in ten different crystallographic forms according to the conditions under which it is obtained. The range of existence of the sulphate-oxalate extends over a sulphuric acid concentration interval of 21—67%, and the hydrogen oxalate forms one of the solid components in equilibrium with solutions varying in composition through a wide range. This means that, by the action of sulphuric acid of different concentrations on sodium oxalate at 25° , the probability of the formation of hydrogen oxalate or sulphate-oxalate is very great. The results of the solubility determinations have been plotted on Jancke's four-co-ordinate diagram. By graphical analysis of the isothermal course of crystallisation on removing the products formed, two real crystallisation end-points may be observed. At one of these $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and $\text{Na}_2\text{C}_2\text{O}_4$ separate, whilst at the other is formed the stable salt pair $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}\text{--NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ with congruent solubility. There is a third point which might be regarded as a "virtual" crystallisation point, since crystallisation comes to an end before this is reached and only a syrupy liquid, consisting of strongly acid sodium sulphate and oxalic acid dissolved in concentrated sulphuric acid, is obtained. M. S. BURR.

Heat of formation of cementite. T. WATASE (Sci. Rep. Tohoku Imp. Univ., 1928, **17**, 1091—1109).—The heat of combustion of a mixture of sucrose and cementite obtained by the electrolysis of a steel containing 2% C has been determined and from this the heat of formation of cementite has been calculated using published data for the heat of formation of ferrosoferric oxide and carbon dioxide. The results obtained were: $\text{Fe}_3\text{C} + 3\text{O}_2 = \text{Fe}_3\text{O}_4 + \text{CO}_2 + 366.3 \text{ kg.-cal. at } 20^{\circ}$, whence $3\text{Fe} + \text{C} = \text{Fe}_3\text{C} - 4.8 \text{ kg.-cal. at } 20^{\circ}$.

A. R. POWELL.

Heterogeneous reactions between elements.

I. Action of chlorine on copper. L. FROMMER and M. POLANYI (Z. physikal. Chem., 1928, **137**, 201—208).—Determinations of the yields of cupric chloride obtained by the action of chlorine on copper under various conditions of temperature and pressure lead to the value 2 kg.-cal. as the heat of activation of the reaction. H. F. GILLBE.

Selenium cells as colorimeters. II. A. MICKWITZ (Z. anorg. Chem., 1928, **176**, 271—282).—The solubility of freshly-precipitated lead sulphide, expressed as percentage of lead, is given by the selenocolorimetric method as 68×10^{-6} , in good agreement with Weigel's conductimetric value, viz., 74×10^{-6} . The concentration–light absorption curves exhibit a break, due probably to the formation of submicroscopic aggregates of lead sulphide at higher concentrations. The method yields more accurate results than the usual colorimetric method, the average error of a determination being about $\pm 4.5\%$.

H. F. GILLBE.

Electrolytic conduction of crystal surfaces and the free ion conduction of solid salts. O. BLÜH and W. JOST (Z. physikal. Chem., 1928, **B**, **1**, 270—274).—The electrolytic conduction of α -silver iodide has been shown to be not markedly influenced by the presence of interfaces; the conclusion is therefore reached that the presence of internal interfaces is not the cause of the conductivity of such salts.

H. F. GILLBE.

Electrical conductivity of compressed salt mixtures. P. FISCHER (Z. Elektrochem., 1928, **34**, 756—758; cf. A., 1926, 478; 1927, **23**, 717).—By means of the method previously employed (*loc. cit.*), measurements have been made of the conductivities of the following ternary mixtures: lead, mercuric, and potassium iodide; lead, cadmium, and potassium iodide; lead, cadmium, and silver iodide. In many cases the conductivity of the ternary mixture is greater than that of a binary mixture of any two of the components. Values obtained with direct current and with alternating current agree closely. Measurements of the loss in weight of the silver anode show that Faraday's law holds, so that the conduction is electrolytic in nature. It is suggested that the results depend on deformations of the crystal lattices present.

L. L. BIRCUMSHAW.

The Ohm–Fourier law of conduction. S. RAY (Z. Elektrochem., 1928, **34**, 753—756).—A paper read before the Indian Science Convention, Calcutta, in 1919. Ohm's law is so modified that it can be treated by means of Fourier's law and compared in this way with the flow of heat through a conductor. Numerous relations are obtained and discussed. The author's suggestions have received support from subsequent work. L. L. BIRCUMSHAW.

Deviations from Ohm's law for electrolytes. M. WIEN (Physikal. Z., 1928, **29**, 751—755).—On account of uncertainties in the measurements of the relation between equivalent conductivity and concentration, the Debye–Hückel theory of strong electrolytes does not compel assent. New observations are necessary for rigid proof. The author's work (cf. A., 1928, 244) on the variation of conductivity with field strength is summarised. In strong fields the conductivity increases with the field strength, being proportional to the square of the field at the lower values. The proportionality constant varies approximately as the square of the product of the valencies of the ions, and is greatest at lower concentrations and lower dielectric constants. In very strong fields the conductivity approaches a limiting

value, the more readily so the lower the concentration. Within experimental error, this limiting value agrees with the conductivity at infinite dilution. When the field is at right angles to the *P.D.* used for measuring the conductivity, no increase is observed. The above phenomena require a modified theory of electrolytic dissociation for their explanation. R. A. MORTON.

Electrode potential of nickel. Effect of occluded hydrogen on the electrode potential of nickel. K. MURATA (Bull. Chem. Soc. Japan, 1928, 3, 253—261).—It was previously found that nickel electrodes prepared from powdered nickel oxide by reduction in hydrogen gave a reproducible electrode potential although they probably contained occluded hydrogen (cf. A., 1928, 596). Prolonged cathodic polarisation of the nickel electrode in dilute acid and in an atmosphere of hydrogen did not cause any increase but rather a slight decrease in the initial *E.M.F.* of the cell $\text{Ni}|\text{NiSO}_4(0.05M)|\text{KCl sat.}|\text{KCl}(0.1N), \text{Hg}_2\text{Cl}_2|\text{Hg}$. This slight decrease is ascribed to the presence of a trace of free acid used in the polarisation in the cell. Reduced nickel powder was not rendered less noble by cathodic polarisation, although previous authors have found that metals of the iron group become less noble when subjected to cathodic polarisation. The occluded hydrogen in nickel has no effect on the true electrode potential. Addition of a trace of oxygen to the cell causes the *E.M.F.* to fall often by as much as 30 millivolts. Subsequent treatment with hydrogen causes the electrode to return to its active state. During the measurement of the electrode potential of nickel oxygen must be rigorously excluded.

H. INGLESON.

Anodic behaviour of palladium in chloride solutions. F. MÜLLER (Z. Elektrochem., 1928, 34, 744—752).—It has been shown (A., 1928, 713) that the anomalous behaviour of palladium when used as an indicator electrode in oxidation-reduction reactions is connected with the presence of hydrogen chloride in the solutions. In solutions containing chlorine and hydrogen ions, of not too high p_{H} , the electromotive behaviour of palladium is found to be quite different from that of the other metals of the platinum group. By passing chlorine into the solution, or by anodic polarisation, the metal first dissolves quantitatively at relatively low potentials, but becomes suddenly passive on reaching a certain critical current density. The effect of increasing the concentration of the added hydrochloric acid is to cause complete passivity to occur at higher potentials, and in pure concentrated hydrochloric acid the metal remains active up to very high current densities. Palladium differs from other base metals, such as iron and nickel, in that it remains completely passive, like platinum, on anodic polarisation in solutions free from chloride, whereas iron and nickel in, e.g., sulphuric acid are at first active, and become passive only at higher current densities. Polarisation also renders a palladium anode active in solutions containing bromine and chlorine ions. In the transition from the active to the passive condition, characteristic pulsations sometimes occur. These are most marked in the case of iodide solutions, but are also sometimes observed in chloride solutions.

The observed phenomena are discussed, and it is suggested provisionally that they may be ascribed to the formation of a sparingly soluble film of unknown nature on the surface of the electrode.

L. L. BIRCUMSHAW.

Velocity coefficient of a homogeneous bimolecular gas reaction. R. G. W. NORRISH (Nature, 1928, 122, 923—924).—The thermal change $2\text{NO}_2 = 2\text{NO} + \text{O}_2$ affords by Hinshelwood's method a value of the critical increment of 33,200, in agreement with the value, 32,000, derived from the temperature coefficient. Thus further confirmation of the theory of kinetic activation is afforded.

A. A. ELDRIDGE.

Reactions of the third order. F. E. E. GERMANN (J. Physical Chem., 1928, 32, 1748—1750).—In the case of reactions of the type $\text{A} + 2\text{B} \rightarrow \text{R}_1 + \text{R}_2 + \dots$, errors have arisen in the derived mass-law equations through confusion in the use of equivalents per litre and mol. per litre as the units of concentration. Such cases are pointed out (Getman, "Outlines of Theoretical Chemistry," 1927, 433; Taylor, "Treatise on Physical Chemistry," 1924, 2, 872) and corrected equations are given.

L. S. THEOBALD.

Calculation of theoretical combustion temperatures. P. DROSSBACH (Z. Elektrochem., 1928, 34, 783).—In a previous communication (A., 1927, 940), certain data used for the calculation of the theoretical combustion temperatures of carbon monoxide and hydrogen were assumed to involve temperatures expressed as °C., whereas they were expressed as °Abs., and the combustion temperatures have therefore been recalculated. The values now obtained are: for carbon monoxide, 2640° (burning in oxygen) and 2000° (burning in air); for hydrogen, 3300° (oxygen) and 2250° (air).

L. L. BIRCUMSHAW.

Ignition temperature of mixtures of hydrogen and air. M. PRETTE and P. LAFFITTE (Compt. rend., 1928, 187, 763—765).—A modification of Mallard and Le Chatelier's pyrometric method for the determination of the ignition temperature of mixtures of hydrogen and air gave results in agreement with those obtained for hydrogen and oxygen by Dixon, who used the adiabatic compression method (A., 1926, 689). The temperature-composition curve is linear for 10—60% of hydrogen, but above the hydrogen content corresponding approximately with the upper limit of inflammability of hydrogen-air mixtures at the ordinary temperature (60—65%), the temperature rises very rapidly. The upper limit is 90.45% at 540° (cf. White, A., 1925, ii, 553).

J. GRANT.

Oxidation of hydrocarbons. DUMANOIS and MONDAIN-MONVAL.—See B., 1928, 917.

Decomposition of carbonyl bromide. E. H. REERINK (Rec. trav. chim., 1928, 47, 989—999).—Measurements have been made of the velocity of decomposition of carbonyl bromide at temperatures between 147° and 182°. The activation energy, calculated from the temperature coefficient of the reaction velocity, is 15,000 g.-cal. The results are explicable by the assumption that a first-order wall reaction occurs which is catalysed by a thin layer on the walls of the vessel of an organic substance, derived

probably from tap grease, and rendered active by the selective adsorption by it of bromine molecules.

F. G. TRYHORN.

Monochloroamine and hydrazine. I. Decomposition of monochloroamine in acid solution. M. BODENSTEIN (Z. physikal. Chem., 1928, 137, 131—141).—The decomposition of monochloroamine in a solution made initially slightly alkaline with ammonia has been studied: the first autocatalytic stage ceases almost entirely when the reaction has proceeded about half-way, and the reaction then recommences in a totally different manner, reaching its end very slowly. Raschig's equation $3\text{NH}_2\text{Cl} = \text{NH}_4\text{Cl} + \text{N}_2 + 2\text{HCl}$ is applicable only to the first half and to the extreme end of the reaction. It is probable, since in the second stage of the reaction hydrogen chloride is present in insufficient quantity to accord with the equation, that monochloroamine and hydrogen chloride react to form dichloroamine and nitrogen trichloride. In a solution saturated with boric acid and sodium borate the reaction is bimolecular.

H. F. GILLBE.

Kinetics of the hydrolytic decomposition of α -bromopropionic acid. J. ZAWIDZKI and J. G. ZAWIDZKI (Z. physikal. Chem., 1928, 137, 72—106).—The hydrolysis of the α -bromopropionic acid in aqueous solution at 90° has been studied by titration of the evolved hydrogen bromide. The velocity of the reaction is governed by the equation, typical of a negatively autocatalytic reaction, $dx/dt = K(a-x)/x^{\frac{1}{2}}$, where x is the concentration of hydrogen bromide and $a-x$ the instantaneous concentration of α -bromopropionic acid. At 90° , $K=0.000942$, whilst for the interval 80 — 90° the temperature coefficient is 2.99. In presence of a considerable quantity of hydrogen bromide or nitric acid, the equation $dx/dt = K(a-x)/(b+x)^{\frac{1}{2}}$, where b is the initial concentration of acid added, yields an almost identical value for K , whilst neutral salts in general produce not more than about 4% increase of the ordinary constant. Potassium sulphate, on account of the depression of the hydrogen-ion concentration in the solution produced by the reaction, $\text{CHMeBr}\cdot\text{CO}_2\text{H} + \text{K}_2\text{SO}_4 \rightarrow \text{CHMeBr}\cdot\text{CO}_2\text{K} + \text{KHSO}_4$, causes, when present at approximately equivalent concentration, a six-fold increase of the reaction velocity. The enormous accelerative action of potassium chloride is ascribed to an interchange of halogen atoms between the salt and the α -bromopropionic acid.

H. F. GILLBE.

Reduction of methylene-blue in mixtures of l  vulose and amino-acids. H. VON EULER and H. JOHANSSON (Svensk Kem. Tidskr., 1928, 40, 263—264).—Reduction of methylene-blue takes place more rapidly when both l  vulose and an amino-acid, e.g., alanine or glycine, are present than when either of these compounds is used separately. The rate of reduction increases with the p_H .

W. O. KERMAK.

Saponification of menthyl succinate, acetate, and isovalerate. V. A. NEKRASOVA (Arch. Pharm., 1928, 266, 595—599).—Menthyl succinate was prepared by heating menthol, succinic anhydride, and a trace of sulphuric acid at 110° for 30 hrs. The following data are given, k being the velocity coefficient for saponification with 0.5*N*-alcoholic potass-

ium hydroxide at the temperature indicated: menthyl succinate, m. p. 62° , k^{99-100} 3284×10^5 ; menthyl acetate, b. p. 226 — 228° , d^{20} 0.926, n_D^{20} 1.4668; menthyl isovalerate, b. p. 140 — 146° , d^{25} 0.907, k^{99-100} 49.77 — 50.54 . Menthyl hydrogen succinate could not be obtained.

S. COFFEY.

Chlorination of anilides. V. Significance of velocity measurements in relation to the problem of benzene substitution. A. E. BRADFELD and B. JONES (J.C.S., 1928, 3073—3081; cf. A., 1928, 628).—The isothermal condition $1/k_x^{\text{OR}} = 1/k_x^{\text{OR}'} + \text{const.}$ (where k_x^{OR} represents the velocity coefficient for the chlorination of $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{OR}$) derived in a previous paper has been interpreted as indicating the additivity of the energies of activation for the chlorination of ethers of the type $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{OR}$ by extending to these reactions the hypothesis that the product of the phase and steric factors is constant. Four other hypotheses are mentioned and expressions are derived from them which should, given sufficiently accurate experimental data, be able to be differentiated by the change in the ratio of the velocity coefficients with temperature. Some data for anisic acid and *p*-nitrophenetole are considered, but the experimental accuracy is not sufficient to admit of decision among the hypotheses. The problem of the nitration of ethers of the type $p\text{-RO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ is discussed.

H. INGLESON.

Kinetics of the reaction between calcium and nitrogen. A. VON ANTROPOFF and E. GERMANN (Z. physikal. Chem., 1928, 137, 209—237).—The reaction between pure crystalline calcium and nitrogen at 400 — 440° , which is the temperature of maximum velocity, takes place in three stages: the first is rapid and involves the actual calcium surface, the second is very slow and takes place through a thin and probably amorphous film of calcium nitride, whilst the third and rapid stage commences when the nitride film has reached a certain thickness and has probably become porous on account of the formation of a coarsely crystalline structure. The incidence of the reaction is retarded by the presence of traces of oxygen, but once the nitride film has formed the effect vanishes. Activation of the calcium surface is concerned with the elimination of the slow second stage and not with the nitride content of the metal. Minute quantities of lithium, sodium, or potassium in the calcium surface accelerate the reaction only at the beginning, probably by accelerating the crystallisation of the calcium nitride layer. Since lithium readily forms a nitride it must, to exert any such catalytic influence, be in intimate contact with the calcium surface. The activity of commercial calcium is due to the presence of sodium in minute enclosures in the metal; those near the surface have ordinarily no effect, owing to oxidation, and the acceleration of the reaction is therefore not apparent until the underlying sodium particles come into play. Variations commonly observed in the activity of commercial calcium are thus due to both the quantity of sodium present and its distribution, and to the degree of oxidation which it has undergone. Activation of calcium in practice is best produced by deposition of sodium on the surface immediately before use.

H. F. GILLBE.

Dissolution velocity of cadmium in hydrogen chloride solutions. M. CENTNERSZWER (Z. physikal. Chem., 1928, 137, 352—360).—In solutions of hydrogen chloride of concentration greater than 6*N* cadmium dissolves with measurable velocity. The process is characterised by an induction period, which diminishes as the acid concentration is increased, and during which the dissolution velocity increases rapidly. If the surface of the cadmium be activated by previous immersion in concentrated hydrogen chloride solution the induction period vanishes. Agitation of the acid produces noticeable effects only at concentrations above about 10*N*. The temperature coefficient of the reaction is approximately 2 for 10° rise. At the lower acid concentrations the process is almost entirely chemical, diffusion playing a relatively small part, but at higher concentrations and higher temperatures the latter becomes of increasing importance, as evidenced by the diminution of the temperature coefficient. H. F. GILLBE.

Corrosion of iron. H. ENDÔ.—See B., 1928, 929.

Catalytic preparation of copper sulphate. E. ABEL and O. REDLICH (Z. Elektrochem., 1928, 34, 740—744).—The possibilities of utilising the action of concentrated sulphuric acid on copper in the presence of oxygen (air), using nitric oxide or nitrosylsulphuric acid as a catalyst, for the technical preparation of copper sulphate have been explored, but the difficulties attendant on the process appear to be insurmountable. The most important of these are the sensitiveness of the reaction between copper and nitrosylsulphuric acid to the presence of water, which exerts an auto-anticatalytic influence, and the narrow temperature limits within which the reaction (which is strongly exothermic) can occur. The cause of the negative autocatalysis of the reaction $\text{Cu} + 2\text{HNSO}_5 = \text{CuSO}_4 + 2\text{NO} + \text{H}_2\text{SO}_4$ has been traced to the formation of an inactive surface film of the copper salt of nitrosylsulphonic acid. This may be partly or completely prevented by the addition of nitrogen peroxide or nitric acid, but the presence of excess of the acid exerts a retarding influence on the reaction.

L. L. BIRCUMSHAW.

Nitrite-nitrate formation from ammonia and oxygen at alkaline surfaces. K. A. HOFMANN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1928, 26, 461—465; cf. B., 1927, 600).—A further discussion of the view previously put forward that the formation of nitrite from ammonia and air proceeds through the intermediate stage of imide. Silver, which activates the above reaction at alkaline surfaces at about 350°, does not bring about an oxidation of ammonia in aqueous solution to nitrite. Silver, however, dissolves appreciably in ammonia solution in presence of air and forms ammino-silver hydroxide, $\text{Ag}(\text{NH}_3)_2\text{OH}$. This process ceases after several months, long before the saturation point of ammonia solution for silver oxide is reached, and the final concentration is dependent on the amount of silver in contact with the solution. O. J. WALKER.

Behaviour of zinc oxide and zinc oxide-chromium oxide catalysts in the decomposition and synthesis of methyl alcohol. H. H. STORCH (J. Physical Chem., 1928, 32, 1743—1747; cf. Smith

and Hawk, A., 1928, 488).—The catalytic activity of zinc oxide, prepared in various ways, and of zinc oxide-chromium oxide mixtures in the synthesis of methyl alcohol from hydrogen and carbon monoxide (4:1) under 3000 lb. pressure at 330° and 350° has been investigated. The addition of chromium oxide increases the activity of the zinc oxide in the synthesis, but has no effect on the decomposition of methyl alcohol (at 1 atm.). L. S. THEOBALD.

Synthesis of methyl alcohol. E. AUDIBERT and A. RAINEAU; also A. C. FIELDNER and R. L. BROWN.—See B., 1928, 920.

Partial oxidation of methane and ethane in presence of catalysts. T. E. LAYNG and R. OUKUP.—See B., 1928, 920.

Catalytic acceleration of the oxidation-reduction reaction between formic acid and methylene-blue. H. VON EULER and A. ÖLANDER (Z. physikal. Chem., 1928, 137, 29—44).—The reaction between methylene-blue and formic acid in presence of platinum sol has been studied by measurement of the time necessary for complete bleaching of the solution to occur. The reaction velocity, which is greatest at p_{H} 2—3, appears to be determined by the concentration of a complex which is formed between the formic acid and platinum. Increase of the methylene-blue concentration causes a decrease of the reaction velocity, the dye using up a certain quantity of the platinum sol. Investigation of the influence on the velocity of the acidity and formic acid concentration indicates that free formic acid, and not the formate ion, is concerned with the production of the complex catalyst. H. F. GILLBE.

Theory of molecular dislocation applied to homogeneous catalysis. J. BOESEKEN (Trans. Faraday Soc., 1928, 24, 611—620).—A summary.

Action of accelerators and inhibitors on the oxidation of liquid hydrocarbons. T. E. LAYNG and M. A. YOUNGER.—See B., 1928, 882.

Keto-enol isomerism and the mechanism of homogeneous reactions. F. O. RICE and J. J. SULLIVAN (Trans. Faraday Soc., 1928, 24, 678—682).—Determinations have been made of the rate of change of the tautomeric forms of ethyl acetoacetate, and of the effects of catalysts on this process. The percentage of enolic form was measured after different periods in mixtures which contained originally up to 40% of the enolic tautomeride. Concentrations of 4×10^{-5} mol. per litre of the catalysts piperidine, ammonia, bromine, pyridine, and quinoline increased the reaction velocity by factors between 11,400 for piperidine and 17 for quinoline. A unimolecular mechanism is suggested for the change, in which the enolic form, or a complex of this with the catalyst, undergoes a change dependent on the concentration and quite independent of the time between molecular collisions. The rate is determined by a process occurring inside the molecule or complex, and this in turn is determined by the number of internal degrees of freedom. F. G. TRYHORN.

Determination of the catalytic coefficient of the hydroxyl ion in the mutarotation of dextrose

and lactose. T. M. LOWRY and G. L. WILSON (Trans. Faraday Soc., 1928, 24, 683—687).—Careful determinations, in which the possibility of contamination by carbon dioxide was excluded, have been made of the velocity of mutarotation of lactose, dextrose, and tetramethylglucose in the presence of hydroxyl ions. The concentrations of hydroxyl ions in the solutions were computed from measurements of electrode potentials and on the basis of the assumption that the sugar forms a salt which is hydrolysed according to the law of mass action. The final values of the catalytic coefficients of the hydroxyl ion are, for lactose 5000, for dextrose 8000, and for tetramethylglucose 1600. The wide variation in these values is notable inasmuch as the mutarotation velocities of these sugars in pure water vary but little. F. G. TRYHORN.

Autoxidation and anti-oxygenic action. Catalytic properties of arsenic and its compounds. C. MOUREU, C. DUBRAISSE, and M. BADOCHÉ (Compt. rend., 1928, 187, 917—921).—The catalytic properties of arsenic and 21 of its compounds in concentrations of 1% are shown to have important positive or negative effects. Thus arsenic itself inhibits the oxidation of acetaldehyde for several hours and then accelerates it, whilst for *L*-pinene the order is reversed. An anti-oxygenic action is also shown towards styrene and benzaldehyde. Arsenic and its oxygenated derivatives, particularly the inorganic compounds, have relatively low activities on account of their insolubility, but the activities of the halogen derivatives are considerably higher. J. GRANT.

Acid and salt effects in catalysed reactions. XVII. Variation of catalytic activity of an acid with its concentration, and determination of ionisation constants. H. M. DAWSON, G. V. HALL, and A. KEY (J.C.S., 1928, 2844—2853; cf. A., 1928, 717).—The catalytic effects produced in the acetone-iodine reaction at 25° by acetic, chloroacetic, propionic, β -chloropropionic, succinic, and glycollic acids have been studied with reference to the variation of the catalysing power with the concentration. The connexion between reaction velocity and concentration gives a means of determining the ionisation constant of the acid as well as the catalytic activity of the undissociated acid. The constants so derived are in good agreement with those derived from conductivity measurements. In general, the catalytic activity of the undissociated acid increases with the ionisation constant. The relation between the catalytically determined constant K and the thermodynamic constant K_a (where $K = K_a/f^2$; f and f' is the mean activity coefficient of the ions) is discussed. H. INGLESON.

Catalytic activity of hydrogen ions in ethyl alcohol. H. GOLDSCHMIDT (Trans. Faraday Soc., 1928, 24, 662—666).—A résumé of evidence that catalytic effects are due to the undissociated acid molecules as well as to hydrogen ions in acid catalysis in ethyl alcohol solutions. F. G. TRYHORN.

Decomposition of nitrosotriacetoneamine in presence of hydroxyl ion. A. W. GOODALL and W. C. McC. LEWIS (Z. physikal. Chem., 1928, 137, 45—462).—The velocity of decomposition of nitroso-

triacetoneamine is in dilute alkali determined by the activity of the hydroxyl ion, and in concentrated alkali by that of the hydrogen ion. At intermediate concentrations (0.05—0.5*N*) the decomposition process consists of two reactions, having different critical increments, of which the one is catalysed by hydrogen ion and the other by hydroxyl ion. The mechanisms are represented by: (I) nitrosotriacetoneamine + OH' \rightarrow A + OH', and (II) A + H' \rightarrow B + H', where A represents a hypothetical intermediate compound and B the final decomposition products.

H. F. GILLBE.

Electrolysis of copper sulphate solutions separated by an animal membrane. CHANOTZ (Compt. rend. Soc. Biol., 1928, 98, 39—41, 42—43; Chem. Zentr., 1928, i, 3078).—With solutions less concentrated than 0.1*N* polarisation of the membrane results in a diminution of the current. The form of the separated copper is described. A. A. ELDRIDGE.

Electro-deposition of silver with special reference to the use of sodium cyanide. E. B. SANIGAR.—See B., 1928, 897.

Polymerisation distance between discharged ions in the preparation of persulphates. O. ESSIN (Z. Elektrochem., 1928, 34, 758—760).—In a previous investigation of the dependence of current efficiency on anodic current density in the preparation of ammonium persulphate (Essin and Krylow, A., 1927, 422) it was found that the sulphate ions must be discharged within a certain distance of each other in order that polymerisation (*i.e.*, persulphate formation) may take place. Assuming the presence of a layer of activated sulphate ions at the anode, the "polymerisation distance," l , is given by: $l = 1.68(eh/\tau)^{1/2}$, where e is the charge on the electron, h the thickness of the layer, and τ the life period of the activated ions. This is calculated to be of the order of 10^{-6} cm. (cf. Dhar and Mukerji, A., 1925, ii, 809).

L. L. BIRCUMSHAW.

Direct electrolytic preparation of potassium permanganate. G. RAPIN (Bull. Soc. chim., 1928, [iv], 43, 1174—1189).—A more detailed account of work already published (A., 1928, 969). In spite of the formation of potassium silicate, the use of an electrolyte of potassium hydroxide alone is recommended on the grounds of increased yield and efficiency. The temperature should not exceed 70—75°, and compact anodes of silicomanganese (60% Mn) are preferred.

Determination of the role of light in thermal chemical reactions. J. PERRIN (Compt. rend., 1928, 187, 913—916; cf. A., 1927, 527).—It is concluded that since one of the preliminary requirements of all reactions sensitive to temperature is the endothermic activation of the ordinary molecules, the part played by light as distinct from molecular agitation in a purely thermal reaction is for each reactant equal to the yield of fluorescence of this reactant under the conditions concerned. This yield is defined as the ratio of the number of luminous deactivations to the number of quanta absorbed, and may be measured without changing the temperature or medium by an exposure of sufficient intensity to the activating light absorbed by the substance concerned. J. GRANT.

Energetics, quantum action, and temperature coefficient of some photochemical reactions influenced by radiation of different frequency. A. K. BHATTACHARYA and N. R. DHAR (*Z. anorg. Chem.*, 1928, 176, 372—384; cf. A., 1928, 378).—The order of reaction, velocity coefficient, temperature coefficient, and number of molecules reacting per quantum absorbed have been determined in the dark, in sunlight, and in radiation of different wavelengths, for the following reactions: decomposition of sodium cobaltinitrite solution and potassium persulphate solution, and reactions between the persulphate and iodide of potassium, bromine and methyl or ethyl alcohol, oxalic and chromic acids, acetone and iodine in presence of hydrochloric acid, lactic acid and potassium permanganate in presence of manganese sulphate, and tartaric acid and potassium permanganate in presence of manganese sulphate. All are unimolecular except that between acetone and iodine, which is of zero order. More than one molecule always reacts for each quantum absorbed, so that Einstein's law of photochemical equivalence does not hold in any of these cases. The reaction per quantum increases with rising temperature of the reactants. In sunlight, the quantum efficiency is higher than for any other radiation. It also increases with increase in frequency of the radiation employed. The temperature coefficient of a photochemical reaction is always greater than 1 and less than that of the corresponding thermic reaction. The greater the observed acceleration by light the smaller is the temperature coefficient.

M. S. BURR.

Action of luminous rays on potassium chloride. J. RISLER and F. DE COURMELLES (*Compt. rend.* 1928, 187, 944—945).—In order to produce an impression on a photographic plate, films of potassium chloride required the following exposures (in days) to the sources mentioned: infra-red light (descence lamp with an ebonite filter) orange-red light (neon lamp with ruby filter) 44, λ 3650 Å (ultra-violet lamp with a nickel oxide filter) 36, sunlight 29, and unfiltered ultra-violet light 19. Activation of potassium chloride by ultra-violet light plays an important rôle in biological processes.

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Photochemical catalysis. Reaction between nitric oxide and cyanogen and its mechanism. R. G. W. NORRISH and F. F. P. SMITH (*Trans. Faraday Soc.* 1928, 24, 620—629).—Two reactions, of which the former is about six times as extensive as the latter, occur when mixtures of nitric oxide and cyanogen, each at 1/2—1/3 atm. pressure are illuminated by ultra-violet light of wave-length 360—220 μ : $4\text{NO} = \text{N}_2 + 2\text{NO}_2$; $4\text{NO} + (\text{CN})_2 = 3\text{N}_2 + \text{CO}_2$. In the former reaction, cyanogen acts as a catalyst, but neither reaction occurs in the absence of a trace of oxygen, and therefore of nitrogen peroxide. The total reaction is auto-catalytic as a result of accumulation of nitrogen peroxide. The existence of a comparatively stable intermediate compound is indicated by a dark reaction occurring over several days and continuing, with fall of pressure, ultra-violet illumination has ceased. This compound is believed to be nitrosyl cyanide, and is perhaps pro-

duced according to the two opposed photo-reactions $2\text{NO} + (\text{CN})_2$, 2NOCN . Of these reactions the former is catalysed or sensitised by nitrogen peroxide. Jointly, these reactions give rise to a photochemical stationary state associated with considerable equilibrium pressures (90 mm.) of nitrosyl cyanide. This latter compound, being unstable, decays spontaneously in the dark according to the reactions $2\text{NOCN} = \text{N}_2 + \text{O}_2 + (\text{CN})_2$ and $2\text{NO} + \text{O}_2 = 2\text{NO}_2$. These reactions, in combination with the process $2\text{NO} + (\text{CN})_2$, 2NOCN , give the total change represented by $4\text{NO} = \text{N}_2 + 2\text{NO}_2$. The reaction $4\text{NO} + (\text{CN})_2 = 3\text{N}_2 + 2\text{CO}_2$ results as a side reaction by the combination of the reactions $\text{NOCN} + \text{NO} = \text{NO} + \text{CO}_2 + \text{N}_2$ and $2\text{NO} + (\text{CN})_2 = 2\text{NOCN}$. A precisely similar series of changes, which can be explained by an analogous mechanism, has been observed in the system nitric oxide-cyanogen chloride. F. G. TRYHORN.

Photochemistry of iron-carbonyl compounds and the absolute absorption spectrum of the respiratory enzyme. O. WARBURG (*Naturwiss.*, 1928, 16, 856—861).—The photochemical decomposition of iron carbonyl with ultra-violet irradiation agrees with the equation $2\text{Fe}(\text{CO})_5 + h\nu \rightarrow 2\text{CO}$. Carbon monoxide is likewise set free by the action of light on the hæmoglobin "carbonyl," but on account of the high velocity of the back reaction the system does not lend itself to quantitative work. Carbon monoxide-pyridine-hæmin and carbon monoxide-ferrocysteine have, however, been studied in detail and the course of the photochemical change follows the equations $2\text{FeCO} + h\nu \rightarrow \text{Fe} + \text{CO}$ and $2\text{Fe}(\text{CO})_5 + h\nu \rightarrow 2\text{Fe} + 4\text{CO}$, respectively; i.e., in both cases two atoms of "carbonyl" iron are set free per quantum absorbed. The respiratory enzyme combines with 1 mol. of carbon monoxide per atom of iron, and its properties can be deduced from the respiration of the living cell under different conditions. From the changes which occur on irradiation the absorption spectrum of the enzyme has been deduced. The curve for the carbon monoxide-enzyme is very similar to that of the hæmin compound.

The absorption curve for the ferrocysteine-carbon monoxide is quite different, the maximum being at 490 μ and the intensity of absorption about 10⁻⁴ times as great, whilst the curve for iron pentacarbonyl is 10⁻⁴ times as great as that of the hæmin compound and shows only continuous absorption between 430 and 600 μ . The absorption spectra, therefore, indicate not merely the iron-carbonyl group as a part of the respiratory enzyme, but also show that it is attached to a hæmin-like molecule. The chemical constitution of the enzyme is therefore, in essentials, now known. R. A. MORTON.

Photochemical decomposition of glyoxal. R. G. W. NORRISH and J. G. A. GRIFFITHS (*J.C.S.*, 1928, 2829—2840).—The photochemical decomposition of gaseous glyoxal has been measured by observing the diminution in pressure during the illumination of the gas in a water-cooled glass bulb with the unfiltered light of a 3000-c.p. mercury-vapour lamp. The light

reaching the gas was probably in the regions 436, 405, and 365 μ and that active in promoting the decomposition at 3650 Å. The pressure-time curves conform approximately to a bimolecular law with respect to decomposing glyoxal. The final pressure even after prolonged heating is never exactly half the initial, as would be expected from the equation $2C_2H_2O_2 = CO + C_3H_4O_3 \rightarrow$ polymerised product, which reaction takes place to an extent of about 98.5%. A secondary reaction, $C_2H_2O_2 = 2CO + H_2$, probably occurs to a small extent. The mol. wt. of the glyoxal was determined from its vapour density as 58.7, so that thermal dissociation is excluded. A white solid produced during the decomposition of the gas appears to be the polymeride of the hitherto unknown glycerosone to which it is hydrolysed in aqueous and acid solutions. The properties of glycerosone suggest that it exists in aqueous solution in tautomeric equilibrium with an acidic hydroxy-methylene form, the change from neutral to acid taking place slowly at the ordinary temperature.

H. INGLESON.

Some properties of alkali metals. L. HACKSPILL (Helv. Chim. Acta, 1928, 11, 1003—1026).—A lecture delivered before the Swiss Chemical Society on Aug. 31, 1928.

R. N. KERR.

Hydrates of beryllium halides. V. ČUPR and H. ŠALANSKY (Z. anorg. Chem., 1928, 176, 241—257).

The preparation of considerable quantities of pure beryllium compounds is described. Beryllium chloride tetrahydrate, prepared by spontaneous evaporation of a clear solution of the oxide in hydrogen chloride solution, is extremely unstable in moist air, hydrogen chloride being readily evolved. The bromide tetrahydrate, precipitated in the analogous manner, does not lose hydrogen bromide in moist air; the corresponding iodide could not be prepared. The compounds $BeCl_2 \cdot 3H_2O \cdot Et_2O$ and $BeBr_2 \cdot 3H_2O \cdot Et_2O$ are described, but the analogous iodide has not been prepared, although evidence has been obtained for the existence of the compound $BeI_2 \cdot 2H_2O \cdot 2Et_2O$.

H. F. GILLBE.

Cadmium acetylides. K. GEBAUER (Z. anorg. Chem., 1928, 176, 283—284).—Slow passage of purified acetylene through an acetone solution of the compound $CdCl_2 \cdot NH_2Ph$ produces an orange, amorphous precipitate which when washed with acetone and dried at 110° has the composition $CdC_2 \cdot C_2H_2 \cdot CdI_2$. By washing this substance with alcohol or water the compound $CdC_2 \cdot C_2H_2$ is obtained. Both substances are stable in the air, and may be heated to about 200° without decomposition; neither is explosive.

H. F. GILLBE.

New fluoboric acid. A. TRAVERS and MALAPRADE (Compt. rend., 1928, 187, 765—767).—The curve of neutralisation of the mixture $H_3BO_3 + 4HF$ with potassium hydroxide solution indicates that boric acid reacts instantaneously with hydrofluoric acid to form a new fluoboric acid, the salt of which is easily decomposed by alkali. Tetrafluoboric acid, HBF_4 , is formed slowly, particularly in the cold, until equilibrium between the two fluoboric acids is established. The time taken and the amount of the latter formed at equilibrium increase with the concentration

of the reactants and with the initial acidity of the mixture (cf. Abegg, Fox, and Herz, A., 1903, ii, 540).

J. GRANT.

Existence of a new type of fluoborate. A. TRAVERS and MALAPRADE (Compt. rend., 1928, 187, 891—892; cf. preceding abstract).—In the determination of soluble or insoluble fluorides of the type MBF_4 by Travers' fluosilicate method (A., 1921, ii, 706) a preliminary alkaline fusion is required, since the reaction $H_3BO_3 + 3HF + nKF \rightarrow BF_3 \cdot nKF + 3H_2O$ increases the p_H value by destruction of the acids present, and there is no immediate precipitation of the insoluble potassium salt unless acid is added to increase the rate of formation of the acid HBF_4 . Fusion destroys the complex BF_4^- ion, and on acidification all the fluorine is converted into insoluble potassium fluosilicate, since the fluoborate produced is less stable and more soluble than KBF_4 . Further evidence for the existence of another fluoborate is provided by the action of boric acid on neutral concentrated solutions of potassium fluoride, and by the work of Abegg, Fox, and Herz (A., 1903, ii, 540).

J. GRANT.

Measurement of bi- and quadri-valent compounds of the rare earths. I. Samarium halides. W. KLEMM and J. ROCKSTROM (Z. anorg. Chem., 1928, 176, 181—199).—Isotherms of the system samarium trichloride-ammonia indicate the existence of complexes containing 13, 8, 5, 4, 2 $\frac{1}{2}$, 2, and 1 mols. of ammonia per mol. of trichloride. There is a considerable tendency to mixed crystal formation, especially above 8 mols. of ammonia. The existence of $SmCl_3 \cdot 9.5NH_3$ and $SmCl_3 \cdot 11.5NH_3$ could not be confirmed, whilst the triammine definitely does not exist. Samarium dichloride forms complexes having respectively 2 and 8 mols. of ammonia, which exhibit considerable tendency to formation of mixed crystals. Reactions such as the following take place with great ease: $SmCl_3 + NH_3 \rightarrow Sm(NH_3)Cl + H$ and $Sm(NH_3)Cl_2 + 2NH_3 \rightarrow Sm(NH_3)_2Cl + NH_4Cl$. At temperatures from 30° to 100° a sublimate of ammonium chloride is formed. There is a tendency for this type of reaction to occur with the trichloride at ammonia concentrations from 0 to 1M. The densities of samarium trichloride, tribromide, dichloride, and dibromide are 4.31 ± 0.01 , 5.40 ± 0.02 , 4.5 $\frac{1}{2}$, and 5.1 $\frac{1}{2}$, respectively; the m. p. of the trichloride, prepared by the action of chlorine and sulphur chloride on the oxide, is $677 \pm 1^\circ$, and that of the tribromide, prepared by the action of hydrogen bromide on the powdered trichloride, is $628 \pm 2^\circ$. The magnetic susceptibilities of the trioxide, tribromide, and dibromide, referred to 1 g., are 9900×10^{-6} , 15600×10^{-6} , and 71000×10^{-6} , respectively. H. F. GILLBE.

Hydrates and hydrogels. XI. Simplest silicic acids; aluminium hydroxide. R. WITTLSTÄTTER, H. KRAUT, and K. LOBINGER (Ber., 1928

[B], 2280—2293; cf. A., 1926, 36).—Solutions of monosilicic acid are obtained by passing the vapour of silicon tetrachloride into ice-cold water containing freshly-precipitated silver oxide, the success of the operation depending on the maintenance of a suitable hydrogen-ion concentration in the solution which is thus attained. When the brown colour of the silver

oxide has disappeared, the concentration of hydrochloric acid is adjusted to 0.01–0.005*N* by further addition of the oxide, the value of p_H (in presence of silicic acid) being 2.5–2.8. The clear solution contains more than 80% of the theoretical quantity of SiO_2 . The dissolved acid has the mol. wt. 72–75 and thus consists of 75–80% of monosilicic acid, the remainder being disilicic acid; the calculations are based on the unfavourable assumption that the total hydrochloric acid is free and completely ionised. Solutions of disilicic acid are obtained in a similar manner except that hydrogen chloride is not removed until addition of the silicon tetrachloride is complete and the acidity of the residual hydrochloric acid is adjusted to 0.01–0.001*N* (or the acid is removed quantitatively). In solutions 2–3 hrs. old, the mol. wt. of the silicic acid (as SiO_2) is 120–130 instead of 120, indicating the presence either mainly of disilicic acid or of a mixture of mono- and oligosilicic acids. The ability of the acid to pass rapidly and quantitatively through a fish-bladder membrane favours the former view. Solutions of monosilicic acid after preservation for 4–6 days contain mixtures of tetra- to hexa-silicic acids; the hexasilicic stage is only slowly passed during further preservation. Similar oligosilicic acids are obtained slowly from disilicic acid solutions with 0.01*N*-hydrochloric acid. Such preserved solutions with silicic acids of medium mol. wt. frequently do not give the Mylius reaction for β -silicic acids with egg-albumin. The volatility of silicic acid with water vapour when its solutions are distilled under diminished pressure is confined to the mono-acid. Solutions of the silicic acids can be titrated potentiometrically with sodium hydroxide. The graphs correspond with those of a very weak acid and the end-point is reached when silica and alkali are in the ratio 1 : 1. A second stage in the neutralisation cannot be recognised definitely. Hydrosols and gels of silicic acid behave exactly similarly to molecular solutions during titration, but the strength of the acid diminishes somewhat during condensation. Silicon dioxide, on the other hand, shows no indication of the combination with hydroxyl ions during titration and hence the gels do not behave as the dioxide with varying amounts of adsorbed water. For the titration, an antimony electrode is particularly suitable.

To α -aluminium hydroxide the structure $Al(OH)_3$ is assigned, whereas the γ compound is regarded as $Al_2O_3 \cdot 3H_2O$. The meta-compound may be regarded as $[Al_2O_3 \cdot H_2O]$ or as a polyaluminium hydroxide, $[-O-Al(OH)-]_n$. The gels *A* and *B* are polyaluminium hydroxides, *A* consisting of chains between the range $4Al(OH)_3 \cdot 3H_2O$ and $8Al(OH)_3 \cdot 7H_2O$, and *B* as their hydrates with higher water content than the simplest chain formula permits.

H. WREN.

Silicophosphoric acids. R. SCHWARTZ (Z. anorg. Chem., 1928, 176, 236–240).—Silicophosphoric acid, $H_8Si(PO_4)_4$, prepared by heating silica with the theoretical quantity of orthophosphoric acid at 120 until the product yields a clear solution with cold water (about 240–300 hrs.), is decomposed by warm water, acids, and alkalis, silica being precipitated. The lack of stability of the compound is evidenced

by conductivity and transport measurements. The dissociation $H_8Si(PO_4)_4 + 2H_2O \rightarrow 4H_3PO_4 + SiO_2$ is irreversible, since the liberated silica immediately assumes the colloidal state. Salts cannot be prepared from the aqueous solution, but thermal analysis of the system $Na_2O-SiO_2-P_2O_5$ indicates the existence of the sodium salt, of m. p. 961°. Attempts to produce the corresponding silicoarsenic acid or its salts have proved unsuccessful.

H. F. GILLBE.

Peroxides of titanium, zirconium, hafnium, and thorium. R. SCHWARTZ and H. GIESE (Z. anorg. Chem., 1928, 176, 209–232).—The hydrated peroxides of titanium, zirconium, hafnium, and cerium behave as peroxy-ortho-acids of the general formula $M(OOH)(OH)_3$. The formula of the thorium compounds is $Th_2O_7 \cdot 4H_2O$. Zirconium alone of the group forms a basic peroxy-sulphate, $Zr_2O_6 \cdot SO_4 \cdot 8H_2O$, obtained by the action of hydrogen peroxide on an acid zirconium sulphate solution. In contradiction to the results of Melikov and Pissarjevski, potassium pertitanate and perzirconate, prepared by this method, are found to have the formulae $K_2TiO_5 \cdot 6H_2O$ and $K_4ZrO_8 \cdot 6H_2O$, respectively, and are to be regarded as salts of tetraperoxy-ortho-acids. Similar compounds of thorium and hafnium have not been prepared. The compound first prepared by Mazzuchelli and Pantanelli has the formula $K_2TiO_5(SO_4) \cdot 3H_2O$, and analogous substances containing zirconium and hafnium, but not thorium, have now been prepared. The reactions underlying the new method of determining fluorine, based on the decolorisation of a solution of $K_2TiO_5(SO_4)_2$ by hydrogen fluoride, have been elucidated. Ammonium peroxytitanyl fluoride, $(NH_4)_3TiO_2F_5$, has been shown by conductivity measurements to yield on electrolytic dissociation four ions, and the production of the complex ion TiO_2F_5''' , in which the O-O linking occupies only one of the six co-ordination valencies, has thus been established. The substances discussed are to be regarded as true per-compounds.

H. F. GILLBE.

Active nitrogen. C. N. HINSHELWOOD (Nature, 1928 122 404–407).—A summary and discussion.

A. A. ELDRIDGE.

Active nitrogen. J. KAPLAN (Nature, 1928, 122, 771).—Polemical (cf. Hinshelwood, preceding abstract).

A. A. ELDRIDGE.

[Active nitrogen.] C. N. HINSHELWOOD (Nature, 1928, 122, 771).—A reply to Kaplan (preceding abstract).

A. A. ELDRIDGE.

Active nitrogen. VI. Formation of iron nitride in the iron-nitrogen arc. E. J. B. WILLEY (J.C.S., 1928, 2840–2844; cf. A., 1928, 3).—An arc using a current of 3–10 amp. at 35 volts struck between iron electrodes in a quartz bulb in an atmosphere of nitrogen gave iron nitride, Fe_3N_2 . From 12 to 15% of the iron withdrawn by aspiration from the inner blue cone of the arc was present as nitride. The proportion fell as the sampling point receded from the hottest zone. By visual inspection of the arc with a spectrometer it was not possible to observe the bands (in the yellow) characteristic of the nitrogen afterglow spectrum. It is possible that the rate of reaction of the active nitrogen with the iron is so

rapid that the quantity of the former in the free state is small. It is suggested that if the Rayleigh nitrogen be the active form in this case it is non-luminous or that under the conditions of experiment another and chemically more active form of nitrogen such as Lowry's (J.C.S., 1912, 101, 1152) is produced.

H. INGLESON.

Reaction between nitrogen peroxide and sulphur dioxide. E. BRINER, G. H. LUNGE, and A. VAN DER WIJK (Helv. Chim. Acta, 1928, 11, 1125—1144).—Reaction proceeds between the above two substances in the liquid state according to the equation $1.5\text{N}_2\text{O}_4 + 2\text{SO}_2 = \text{S}_2\text{N}_2\text{O}_9 + \text{NO}$. The pressure produced in the reaction has been measured; this is gradual at first, but at a certain point a sudden considerable increase takes place. The substance $\text{S}_2\text{N}_2\text{O}_9$ is a white, crystalline solid with the properties of an anhydride of nitrosylsulphuric acid. Whilst it is stable at the ordinary temperature, heat decomposes it into a solid S_2NO_7 and nitric oxide; this reaction appears to be reversible to a certain extent.

The heat of formation of $\text{S}_2\text{N}_2\text{O}_9$ has been calculated from its heat of dissolution in potassium hydroxide; $2\text{SO}_2 \text{ liq.} + 1.5\text{N}_2\text{O}_4 \text{ liq.} = \text{S}_2\text{N}_2\text{O}_9 \text{ sol.} + \text{NO gas} + 112 \text{ kg.-cal.}$ The same solid product is obtained by interaction of the two gases, but only very slowly at the ordinary temperature. Reaction is quicker at higher temperatures, but the product obtained has a nitrogen content lower than that corresponding with $\text{S}_2\text{N}_2\text{O}_9$. The course of the reaction has been investigated by measuring the decrease in pressure. The curve of pressure against time in all cases becomes almost parallel to the time axis at a point which corresponds with only part completion of the reaction. This abnormality is further emphasised by the fact that reaction does not take place at all between the gases if mixed at a sufficiently low pressure. The reaction is very much quicker in the presence of platinised asbestos as catalyst, but again reaction is incomplete, although it proceeds further than without catalyst. The properties of the substance $\text{S}_2\text{N}_2\text{O}_9$ are recorded and the mechanism of its formation is briefly discussed.

R. N. KERR.

Preparation of tantalum pentabromide. K. R. KRISHNASWAMI (Nature, 1928, 122, 845).—Bromine is distilled in an atmosphere of nitrogen or argon on to powdered tantalum at 260—300°.

A. A. ELDRIDGE.

Decomposition of trithionate solutions. A. HORNIG (Z. anorg. Chem., 1928, 176, 423—424).—Trithionate solutions are hydrolysed giving sulphate, thiosulphate, and hydrogen ions. The presence of the thiosulphate is difficult to detect in presence of the acid formed. On adding potassium trithionate, however, to a cold saturated solution of copper acetate, and leaving for a few days in the dark, a yellow, crystalline compound separates out in transparent monoclinic prisms. The composition corresponds with the formula $\text{K}_2\text{S}_2\text{O}_3 \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. Some long, thin, yellow needles of unknown composition have also been observed. The potassium cuprous thiosulphate is not stable in air or in boiling water, copper sulphide being formed.

M. S. BURR.

Reactions of hydrogen chloride with the dioxides of selenium and tellurium between 0° and 170°. T. W. PARKER and P. L. ROBINSON (J.C.S., 1928, 2853—2857).—By the action of hydrogen chloride on selenium dioxide two additive compounds are formed: (i) $\text{SeO}_2 \cdot 4\text{HCl}$, a yellow solid stable at 0°, and (ii) $\text{SeO}_2 \cdot 2\text{HCl}$, a yellow liquid, stable up to 170° and able to be distilled at this temperature with some decomposition into its constituents. This liquid dissolves hydrogen chloride in amounts varying with the temperature. There is no evidence that tellurium dioxide forms a definite additive compound within the range 0—150°. At 0°, hydrogen chloride is absorbed in varying amounts by the dioxide giving a heterogeneous product which loses water continuously in a stream of the gas as the temperature is raised.

H. INGLESON.

Molybdic acid-selenic acid. E. WENDEHORST (Z. anorg. Chem., 1928, 176, 233—235).—Treatment of selenic acid with molybdic acid on the water-bath for several days, followed by removal and evaporation to the liquid layer, yields a pure crystalline mass of the composition $\text{MoO}_3 \cdot \text{SeO}_3$, which with a little water yields a hydrate having when dried at 110° the formula $\text{MoO}_3 \cdot \text{SeO}_3 \cdot 2\text{H}_2\text{O}$. No other stable hydrate exists. The acid is extremely hygroscopic. Titration with potassium hydroxide, using phenolphthalein as indicator, shows it to be tetrabasic. Alcohol and ordinary acetone cause the production of a blue colour and a precipitate of selenium, whereas pure acetone has no such effect. Permanganate does not react with the acid, but with water the orange colour due to permolybdate is produced.

H. F. GILLBE.

Denigès' phospho-ceruleo-molybdenum compound. G. DENIGÈS (Pharm. Acta Helv., 1928, 3, 52—56; Chem. Zentr., 1928, i, 2920).—Polemical (cf. Verda, A., 1928, 1104).

A. A. ELDRIDGE.

Denigès' phospho-ceruleo-molybdenum compound. A. VERDA (Pharm. Acta Helv., 1928, 3, 56—59; Chem. Zentr., 1928, i, 2920).—A reply to Denigès (preceding abstract).

A. A. ELDRIDGE.

Chlorine fluoride. O. RUFF and E. ASCHER [with J. FISCHER and F. LAASS] (Z. anorg. Chem., 1928, 176, 258—270).—Chlorine fluoride has been prepared by passing chlorine into a copper vessel containing fluorine and heated at 250°, and fractionally condensing the product. The compound is an almost colourless gas of characteristic odour; in quartz vessels it becomes yellower in colour, probably on account of the formation of chlorine monoxide. The white solid melts at $-161 \pm 0.5^\circ$ to a yellow liquid of b. p. $-103 \pm 3^\circ$. The reaction is exothermal, and even in presence of a large excess of fluorine some free chlorine exists. In general, chlorine fluoride reacts in a similar manner to fluorine but exhibits greater activity towards most metals. A characteristic reaction is that with cellulose, which ignites in the cold, whereas with fluorine the reaction takes place only on warming. Glass is attacked at the ordinary temperature, the reaction being enormously accelerated by the presence of water vapour or hydrogen fluoride.

H. F. GILLBE.

New salts of the tervalent iodine cation. F. FICHTER and S. STERN (Helv. Chim. Acta, 1928, 11, 1256—1264).—The following salts of the tervalent iodine cation have been prepared by Fouque's method: *phosphate*, bright yellow crystals, *trichloroacetate*, *dichloroacetate*, *monochloroacetate*, light yellow powders. The *methanesulphonate*, light yellow crystals, has been prepared directly from the acetate. Double salts, *trichloroacetate-iodate* and *monobromoacetate-iodate*, have also been obtained. These salts have been shown to have the required composition by analysis of the products on decomposition with water. A saturated solution of iodine acetate in acetic anhydride was electrolysed, using a silvered platinum gauze as cathode; an amount of silver iodide was deposited equivalent to the current passed.

R. N. KERR.

Reactions and derivatives of iron carbonyl.
III. Iron carbonyls containing pyridine. W. HIEBER and F. SONNEKALB [with G. BADER] (Ber., 1928, 61, [B], 2421—2427; cf. A., 1928, 511).—The direct action of ethylenediamine on iron pentacarbonyl affords the additive compound, $\text{Fe}(\text{CO})_5 \cdot \text{en}$, without liberation of carbon monoxide. The substance is decomposed by dilute acid into its components together with iron tetracarbonyl, ferrous salt, and very small quantities of hydrogen and carbon monoxide. The substitution of carbon monoxide by ethylenediamine (*loc. cit.*) depends therefore on the presence of pyridine. The interaction of iron pentacarbonyl with a large excess of pyridine at 80° is accompanied by the maximal evolution of approximately 3 mols. of carbon monoxide; in the presence of 5 mols. of the base the disengagement occurs more rapidly, whereas it is invariably very slow at the atmospheric temperature. Light accelerates the change, causing the liberation of 2 mols. of carbon monoxide at the ordinary temperature. The compound $\text{Fe}(\text{CO})_5 \cdot \text{C}_5\text{H}_5\text{N}$ is the primary product which subsequently yields the substitution products $\text{Fe}(\text{CO})_4 \cdot \text{C}_5\text{H}_5\text{N}$ and $\text{Fe}(\text{CO})_3 \cdot 2\text{C}_5\text{H}_5\text{N}$. Substitution occurs only when the liberated carbon monoxide is allowed to escape. Decomposition of the compounds by dilute acids affords hydrogen, carbon monoxide, and ferrous salt; the proportion converted into the ferrous ion varies, the remainder of the metal appearing as iron tetracarbonyl. The carbon monoxide is partly reduced by the nascent hydrogen, which also hydrogenates the pyridine.

H. WREN.

Complex salts. I. Preparation and properties of some selenitopentammmincobalt salts. H. L. RILEY (J.C.S., 1928, 2985—2989).—Ions possessing an electrovalency of two show varying co-ordination valencies. The carbonate ion usually occupies two positions, but sometimes only one. Those of the sulphate or sulphite type possess a greater tendency to occupy one position in the complex. An explanation of this behaviour is advanced and evidence in its favour is obtained from the study of the properties of *selenitopentammmincobaltic chloride*, $[\text{Co}(\text{SeO}_3)(\text{NH}_3)_5]\text{Cl}$, occurring as brownish-red crystals which when dissolved in water dissociates as a binary electrolyte to the extent of 97% in 0.1N-solutions, and *selenitopentammmincobaltic selenite*, $[\text{Co}(\text{SeO}_3)(\text{NH}_3)_5]_2\text{SeO}_3 \cdot 3\text{H}_2\text{O}$ (?),

which could not be obtained in a pure state owing to its deliquescent nature.

H. INGLESON.

Metallic cyanates. III. Ammines of the simple cyanates with hexamethylenetetramine. R. RIPAN (Bul. Soc. Stiinte Cluj, 1928, 4, 29—41; Chem. Zentr., 1928, i, 2938—2939).—Compounds of the general formula $[\text{X}(\text{H}_2\text{O})_2\text{C}_6\text{H}_{12}\text{N}_4](\text{CNO})_2$, where $\text{X} = \text{Co}, \text{Ni}, \text{Mn}, \text{Fe}, \text{Cu},$ or Cd , have been prepared: their stability and insolubility are greater than those of the simple cyanates. The compounds $[\text{Cu}(\text{MeOH})_2\text{C}_6\text{H}_{12}\text{N}_4](\text{CNO})_2$ and $[\text{Cu}(\text{EtOH})\text{C}_6\text{H}_{12}\text{N}_4](\text{CNO})_2$ were also obtained.

A. A. ELDRIDGE.

Selenocyanammines. I. G. SPACU and R. RIPAN (Bul. Soc. Stiinte Cluj, 1928, 4, 3—22; Chem. Zentr., 1928, i, 2937—2938).—Selenocyanammines have been prepared (1) by adding the required base to a metallic salt solution, such that no precipitation takes place, and then precipitating the selenocyanamine by addition of alkali selenocyanate solution, (2) by causing potassium selenocyanate and a metallic nitrate to react in alcoholic solution, and addition of the required base after filtration from potassium nitrate. The following metallic *pyridine-* and *hexamethylenetetramine-selenocyanates* are described: $[\text{X}(\text{H}_2\text{O})_4\text{C}_6\text{H}_{12}\text{N}_4](\text{SeCN})_2$, where $\text{X} = \text{Co}, \text{Ni}, \text{Mn}, \text{Fe},$ or Zn ; $[\text{X}(\text{C}_5\text{H}_5\text{N})_4](\text{SeCN})_2$, where $\text{X} = \text{Co}, \text{Ni}, \text{Mn}, \text{Fe}, \text{Zn},$ or Cd ; $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_6](\text{SeCN})_2$, $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2](\text{SeCN})_2$; $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_2](\text{SeCN})_2$.

A. A. ELDRIDGE.

Sebor's method of quantitative spectral analysis. J. KNOP (Chem. Obzor, 1926, 1, 253 256; Chem. Zentr., 1928, ii, 371).—The method whereby it is sought to determine the concentration of dyes by measurement of the width of the absorption bands is inexact.

A. A. ELDRIDGE.

Gravimetric titrations and their application to microchemical determinations. B. ORMONT (Z. anal. Chem., 1928, 75, 209—228).—For microvolumetric analysis more accurate results can be obtained by weighing the standard solution in the burette before and after titrating to the end-point than by measuring the volume of solution used. The standard solution is prepared in such a way that it contains a definite fraction of the equivalent weight of the standard substance in 1 kg. of solution. A suitable burette for use in the work is described and illustrated, and the possible sources of error and the preparation of the solutions and indicators are discussed. Microchemical gravimetric titrations afford an accurate means of determining quantities between 6×10^{-4} and 2.6×10^{-7} g. of hydrogen chloride by acidimetry and 7.3×10^{-4} — 3.5×10^{-7} g. of arsenic trioxide by iodometry.

A. R. POWELL.

Apparatus for colorimetric titration. E. B. POWERS (Ecology, 1928, 9, 364).

CHEMICAL ABSTRACTS.

Systematic knowledge of indicators. XIII. Solvent errors. (1) Alcohol error with methyl-orange and related azo-indicators. XIV. New source of error in colorimetric measurements; the "light error" of some azo-indicators in presence of organic solvents. A. THIEL and SPRINGEMANN (Z. anorg. Chem., 1928, 176, 64 0,

112—120).—XIII. When alcohol is employed as solvent in titrations with azo-indicators two errors are liable to arise, one being purely optical and the other due to an alteration of the acid-sensitivity of the indicator. Measurements have been made of the extinction coefficients of methyl-orange, methyl-yellow, monomethyl-orange, and methyl-red in aqueous solutions containing 0—100% of ethyl alcohol. The p_H of 0.1*N*- and 0.01*N*-solutions of hydrogen chloride in various mixtures of alcohol and water has been determined, and the values of the half stages of the four indicators in the same mixtures have been ascertained.

XIV. Disubstituted *p*-aminoazobenzene derivatives in presence of methyl and ethyl alcohols and acetone are bleached by the action of light, the process reaching an equilibrium but reverting in the dark in accordance with the law for unimolecular reactions. The equilibrium is influenced by the alcohol concentration, and is liable to become a source of error in colorimetric determinations. H. F. GILLBE.

Simplified potentiometric analysis. E. MÜLLER and H. KOGERT (Z. anal. Chem., 1928, 75, 235—239).—Examples are given of the results obtained by the use of the capillary-wire electrode. From these it is inferred that the new electrode may be used satisfactorily in place of the *N*-calomel electrode for all potentiometric titrations.

A. R. POWELL.

Rapid determination of selenium. E. BENESCH (Chem.-Ztg., 1928, 52, 878—879).—Selenium precipitated as element by any of the usual methods is collected, washed roughly, and dissolved in cold saturated sodium sulphide solution. The red colloidal solution reacts quantitatively with potassium cyanide according to the equation $\text{Se} + \text{KCN} = \text{KSeCN}$. The end-point is marked by the change of colour from red to yellow.

S. I. LEVY.

Gas-volumetric determination of nitrogen in ammonia, carbamide, and ammonium salts. P. RISCHBIETH (Z. physikal.-Chem. Unterr., 1928, 41, 132—133; Chem. Zentr., 1928, i, 2973).—A lecture experiment. A. A. ELDRIDGE.

Determination of small quantities of nitrate nitrogen. B. G. SIMER (Chem. Listy, 1928, 22, 353—357, 473—476).—The reduction methods of Devarda and of Ulsch are unsuitable for the determination of small quantities of nitrate nitrogen (less than 2 mg.), whilst that of Arnd gives a mean error of only about 1% when duraluminium is used for reduction. The Gladstone-Tribe colorimetric method gives results on the average 10% below the actual values. The Marx-Trommsdorff titration method gives good agreement for quantities of nitrogen within the limits 0.1—0.5 mg.; this method cannot, however, be applied in the presence of sodium chloride.

R. TRUSZKOWSKI.

Volumetric method of determining phosphoric acid in alkali and alkaline-earth phosphates and in phosphates of iron and aluminium. DRAC-HOUSSOR and DOUCHY (Chim. et Ind., 1928, 20, 823—828).—A solution of a dihydrogen phosphate, neutral to methyl-orange and containing a sufficiency of calcium chloride, is titrated with standard sodium

hydroxide solution until neutral to phenolphthalein in the cold: $2\text{H}_3\text{PO}_4 + 3\text{CaCl}_2 + 6\text{NaOH} = \text{Ca}_3(\text{PO}_4)_2 + 6\text{NaCl} + 6\text{H}_2\text{O}$. Acid phosphates of iron or aluminium which would give precipitates are determined by the difference between titrations with methyl-orange and phenolphthalein. Errors due to the presence of carbon dioxide in the reagents are corrected by a blank. If calcium chloride is being used not more than small quantities of nitrates are admissible, and ammonia must be eliminated. Free lime in dicalcium phosphate may be determined in the same operation. Natural phosphates always contain iron and aluminium and must be treated accordingly. The method is sufficiently accurate for all industrial purposes. C. IRWIN.

Test for arsenic. DAUVÉ (Ann. Chim. analyt., 1928, [ii], 10, 320—321).—The solution is treated with sodium hydroxide and a piece of aluminium foil and the gases evolved are brought into contact with a paper saturated with mercuric chloride solution. A yellow stain on the paper indicates the presence of arsenic. Silver nitrate cannot be used in the test instead of mercuric chloride, as hydrogen silicide is evolved, and this gas, like hydrogen arsenide, blackens silver nitrate paper. A. R. POWELL.

Use of 8-hydroxyquinoline in silicate analysis. J. ROBITSCHEK—See B., 1928, 895.

Determination of carbon and hydrogen in organic substances by the dry method. D. BATESCU (Ber., 1928, 61, [B], 2336—2340).—The substance is burnt in air or oxygen, the contact agent being platinised asbestos held in position by oxidised copper gauze plugs containing the same catalyst. The tube, which is about 50 cm. long and 0.8 cm. internal diameter, is placed in a small sheet-iron furnace heated by three Teclu burners. A complete combustion requires only 0.75—1 hr. H. WREN.

Elementary micro-analysis. R. GOUBAU (Bull. Soc. chim. Belg., 1928, 37, 335—344).—A method of micro-combustion of organic substances is described which it is claimed possesses certain advantages over the ordinary Pregl method, particularly with regard to rapidity of working and simplicity of technique. The water and carbon dioxide formed by the combustion of the substance are not absorbed in the usual way, but are condensed in U-tubes cooled by means of an alcohol-carbon dioxide mixture and liquid oxygen, respectively. These tubes are sealed up after the combustion, and the actual weighing of the water and carbon dioxide formed can be postponed to any convenient time. Using 5 mg. of a substance, containing, e.g., 70% of carbon and 10% of hydrogen, the possible errors are $\pm 0.5\%$ C and $\pm 1.3\%$ H, but larger quantities may be conveniently employed, with a corresponding decrease in the possible error. The method is especially useful where small numbers of combustions are made from time to time.

O. J. WALKER.

Simultaneous determination of silver and cadmium by potentiometric titration. E. MÜLLER and H. HENTSCHEL (Z. anal. Chem., 1928, 75, 240—244).—The solution is first titrated with 0.1*M*-potassium bromide solution, using a silver indicator electrode and an opposed *E.M.F.* of

+0.173 volt against the normal calomel electrode, then with sodium ferrocyanide, using a platinum indicator electrode and an opposed *E.M.F.* of +0.15 volt. Both titrations are made at 75°.

A. R. POWELL.

Precipitation of zinc sulphide from solutions containing considerable quantities of sodium chloride. L. DEDE (Ber., 1928, 61, [B], 2248 2251).—The precipitation of zinc sulphide from neutral solutions of zinc salts by hydrogen sulphide in presence of a small quantity of sodium acetate is appreciably hindered by the addition of sodium chloride. In presence of even very small amounts of free acid, the effect of sodium chloride is so considerable that an exact determination of zinc is not possible. The deficit amounts to more than 30% when much sodium chloride is present. The zinc sulphide, precipitated by addition of colourless ammonium sulphide to solutions of zinc salts and ammonium acetate, settles more rapidly in the presence than in the absence of sodium chloride. In these cases, also, the separation of the sulphide is not quantitative, but the effect of the sodium chloride is less marked than in acid solution.

H. WREN.

Sensitivity of methods of detection of impurities in cadmium and copper. G. TAMMANN, A. HEINZEL, and F. LAASS (Z. anorg. Chem., 1928, 176, 143—146).—Microscopical examination of the residue remaining after cadmium containing 0.1–0.01% of lead, bismuth, antimony, or tin has been dissolved in 50% ammonium nitrate solution demonstrates that this procedure forms a sensitive test for the presence of these metals. The limits at which antimony, bismuth, and lead may be determined in copper by this method, after dissolving in 1.5% ammonium persulphate solution, is about 0.1%, the limit for gold being about 0.01%; the presence of cuprous sulphide, in quantity corresponding with about 0.001% of sulphur, may also be detected. In general, the sensitivity of the microscopical method is increased by first rolling the metal and then heating to above the eutectic temperature, as the phase rich in the impurity aggregates in the interstices between the crystals, and the foreign material remains after dissolution in the form of coarse particles.

H. F. GILLBE.

Rapid analysis of bronze and brass without electrolysis. H. KRUG.—See B., 1928, 930.

Determination of free aluminium oxide in silicate mixtures. L. A. SCHMELEV. See B., 19—8, 895.

Metallic cyanates. V. Separation of the metals of the third analytical group. R. RIPAN (Bul. Soc. Stiinte Cluj, 1928, 4, 104—109; Chem. Zentr., 1928, i, 2974).—The precipitate containing aluminium, zinc, manganese, chromium, iron, nickel, and cobalt is dissolved in 10% hydrochloric acid, treated with a few c.c. of "perhydrol", boiled, and filtered from sulphur; the filtrate is nearly neutralised with sodium carbonate, again boiled with ammonium nitrate (1–2 g.), and treated, with stirring, with repeated small quantities of a 2% potassium cyanate solution. Aluminium, chromium, and iron are thus precipitated; in their usual separation, aluminium

is again precipitated by means of cyanate. In the separation of the remaining metals, zinc is precipitated by means of pyridine and potassium bromide as the compound $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2]\text{Br}_2$. A. A. ELDRIDGE.

Gallium. II. R. FRICKE and K. MEYBING (Z. anorg. Chem., 1928, 176, 325—348; cf. A., 1925, ii, 417).—A method of determining gallium quantitatively as Ga_2O_3 is described. A platinum crucible is not suitable for this purpose. The electrical conductivity and f.p. depression of ammoniacal gallium hydroxide solutions have been determined, and it is concluded that the solubility of gallium hydroxide in ammonia solutions is largely due to the formation of salts and not of complex compounds. The hydrolysis of gallium chloride and sodium gallate has been investigated by the hydrogen electrode method. The results in the gallium chloride solution are complicated by the high hydration of the gallium ion, but, working in dilute solution, the first hydrolytic constant of gallium trichloride, $[\text{Ga}^{++}\text{OH}][\text{H}^+]/[\text{Ga}^{+++}] = 1.4 \times 10^{-3}$, giving for the third basic dissociation constant of gallium hydroxide $[\text{Ga}^{+++}][\text{OH}^-]/[\text{Ga}^{++}\text{OH}] = 4 \times 10^{-12}$. The second hydrolytic constant, $[\text{Ga}+(\text{OH})_2][\text{H}^+]/[\text{Ga}^{++}\text{OH}]$, is 3.5×10^{-4} and the corresponding basic dissociation constant 1.6×10^{-11} . The first hydrolytic constant of sodium gallate, $[\text{GaO}_2^-\text{OH}][\text{OH}^-]/[\text{GaO}_3^{---}] = 3 \times 10^{-3}$, from which the third acid dissociation constant is found to be $[\text{GaO}_3^{---}][\text{H}^+]/[\text{GaO}_2^-\text{OH}] = 2 \times 10^{-12}$. Similarly, the second hydrolytic constant and the second acid dissociation constant are 1.2×10^{-4} and 4.8×10^{-11} , respectively. It is evident that the acid and basic properties of gallium hydroxide are of practically the same order of magnitude. Further, the second dissociation constant, whether basic or acidic, is only a little greater than the third, which is to be explained on the basis of Bjerrum's theory of "Zwitterion" formation in ampholytes (A., 1923, i, 444). M. S. BURR.

Influence of cobalt on the determination of manganese in steel. I. WADA and S. SARITO.—See B., 1928, 930.

Sensitivity of methods of detection of small quantities of impurities in iron. G. TAMMANN and W. SALGE (Z. anorg. Chem., 1928, 176, 152—154).—Microscopical study of the residue left after the dissolution of iron in 15% ammonium persulphate solution enables the presence of 0.002% of sulphur, 0.05–0.02% of aluminium, 0.05% of antimony, 0.02% of zinc, or about 0.01% of silicon to be detected.

H. F. GILLBE.

Metallic cyanates. IV. Chromium. Gravimetric determination of chromium. R. RIPAN (Bull. Soc. Stiinte Cluj, 1928, 4, 57—61; Chem. Zentr., 1928, i, 2973).—When a neutral or slightly acid solution of a chromium salt (0.0002 g. Cr) is boiled with a 2% solution of potassium cyanate, granular chromium hydroxide is precipitated. Zinc and manganese, if present, are kept in solution by the addition of an ammonium salt, zinc being precipitated from the filtrate as $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2](\text{CNO})_2$ or the corresponding thiocyanate. For the determination of chromium (0.04–0.05 g.), the salt is dissolved in 200–250 c.c. of water and boiled until carbon dioxide is evolved with ammonium chloride (2 g.) and potassium

cyanate (0.3 g.), the precipitate being washed, dried, and ignited in the usual way. A. A. ELDRIDGE.

Analytical determination of uranium, thorium, and lead, as a basis for age-calculations. C. N. FENNER (Amer. J. Sci., 1928, [v], 16, 369—381).—Detailed directions are given for the determination of uranium, thorium, and lead in radioactive minerals such as euxenite, polycrase, samarskite, and monazite. C. W. GIBBY.

Control of a new method for the measurement of the temperature of a gas. M. CHOPIN (Compt. rend., 1928, 187, 935—937).—From 350° to 650° the temperature of a current of air calculated by the author's aerodynamic method (*ibid.*, 186, 1832) exceeds that indicated by an electric thermo-couple placed 6 mm. away from the orifice by 2.9° (mean), and is 3.5° (mean) below that obtained when the couple is 20—80 mm. from the orifice. Successive determinations at 600° gave values differing by less than 1°. J. GRANT.

Automatic apparatus for p_H measurement. A. LASSIEUR (Chim. et Ind., 1928, 20, 819—822).—The *E.M.F.* to be measured is made to charge a condenser which is then discharged through a ballistic galvanometer. The deflexion is a measure of the *E.M.F.*, further oscillations being damped out by a shunt. The condenser armatures are then short-circuited. A switch is described which makes these successive connexions by simple rotation. If driven by clockwork, one measurement per minute can be made. The apparatus is sensitive to 0.0045 volt or a p_H variation of 0.07. C. IRWIN.

[Apparatus for] ultrafiltration. P. DICKENS (Chem. Fabr., 1928, 633; cf. A., 1928, 728).—Attention is directed to the author's earlier publications describing the apparatus. A diagram of a modified form is given. S. I. LEVY.

Toy balloons and filtration. J. W. GARRETT and C. D. HURD (Ind. Eng. Chem., 1928, 20, 1130).—An inflated rubber toy balloon resting on top of a Buchner funnel is an aid in laboratory pressure filtration. It is put in position when most of the solvent has been withdrawn and prevents cracking of the precipitate. C. IRWIN.

Washing by decantation. G. E. MARSH (Ind. Eng. Chem., 1928, 20, 1241).—A chart gives the relationship between number of washings by decantation, initial and final concentrations of impurity, and the proportion of the volume occupied by the settled precipitate. C. IRWIN.

Projection of Brownian movement. N. H. BLACK (J. Chem. Education, 1928, 5, 868—873).—A projection apparatus for demonstration is described.

CHEMICAL ABSTRACTS.

Apparatus for working with exclusion of air or in a neutral atmosphere. P. DICKENS (Instru-ments, 1928, 1, 311—312).

Wing top oxygen-gas burner. G. R. ROBERTSON (Ind. Eng. Chem., 1928, 20, 1240—1241).—For glass working with natural gas oxygen is both necessary and safe, there being no tendency to light back to the mixing chamber owing to the slow rate of

flame propagation. The burner described employs a short horizontal tube as mixing chamber with a needle valve on each side from oxygen and gas supplies. C. IRWIN.

Laboratory humidity cabinet. I. C. MATTHEWS and A. M. BURGESS (Ind. Eng. Chem., 1928, 20, 1239—1240).—The cabinet is designed to maintain any temperature between 27° and 50° with humidity at any point between 80% and 100%. It is of stone with brass ducts and is fitted with a circulating fan and both water spray and steam jet. Wet- and dry-bulb thermometers operate automatic controls. C. IRWIN.

Protected reservoir and burette [for solutions affected by oxygen]. B. COHEN (Ind. Eng. Chem., 1928, 20, 1238).—The reservoir has an upper and lower three-way cock; the latter connects with the burette and the supply of solution. The upper cock connects with the inert gas supply and with a by-pass around the reservoir for flushing out. The reservoir is evacuated in order to charge it with solution. C. IRWIN.

Titration vessel with side container to avoid over-titration. J. LINDNER (Chem.-Ztg., 1928, 52, 868—869).—A side container is joined to the exterior of an Erlenmeyer flask midway between the base and the mouth. By inclining the flask a small portion of the liquid may be tipped into the side tube, and after titrating the bulk of the liquid, the rest is returned from the side tube, which is rinsed out and the titration completed. F. R. ENNOS.

Unbreakable explosion pipette. F. W. ISLES (Ind. Eng. Chem., 1928, 20, 1163).—An explosion pipette consists of a 1-in. tee with sparking plug in the side outlet and a 7.5-in. nipple screwed into the bottom. Top and bottom steel plugs carry capillary hose connexions with mercury as aspirating fluid. The joints are made with shellac. C. IRWIN.

Simplified cataphoriser. W. D. HORNE (Ind. Eng. Chem., 1928, 20, 1147).—A flattened capillary tube about 8 cm. long is enlarged at each end in a ground tapered tube in the form of a stopper. These are connected by rubber tubing to corks carrying glass tubes of 2 mm. diam. and platinum wires. The glass tubes serve for filling and emptying, and the platinum wires are only 12 cm. apart, thus enhancing the activity of the colloid particles. C. IRWIN.

Viscosimeter with double set of radiators. E. LASZLO (Chem.-Ztg., 1928, 52, 869).—A viscosimeter of the Engler type is provided with two sets of radiating vanes, one set being fixed to the inside of the outer heating bath and the other to the outside and base of the inner oil container, whereby the necessity for stirring is obviated. Other minor improvements are also described. F. R. ENNOS.

Universal siphon. G. BEETZ (Chem.-Ztg., 1928, 52, 868).—A glass siphon of the usual form is provided near the end of the lower limb with a tap, above which is a side tube also with a tap. The siphon is filled by closing the lower tap, opening that in the side tube, and blowing down a small water pump which is fixed temporarily to the side tube. F. R. ENNOS.

Geochemistry.

Phosphate content and hydrogen-ion concentration of the surface water of the English Channel and southern North Sea, June 18 2, 1928 H. R. SEWELL (Nature, 1928, 122, 91—922).—For the English Channel, the average phosphate content (excluding abnormal stations) was 8.64 mg. P_2O_5 per m.³, and the average (corr) was 8.03; corresponding values for the southern North Sea were 3.44 and 8.11, respectively, and for the Straits of Dover 3.65 and 8.05. There appears to have been a greater photo-synthetic activity in the surface water of the southern North Sea than in that of the English Channel. A. A. ELDRIDGE.

Meteoric iron of Savik, C. York, N. Greenland. O. B. BØGGILD (Medd. Grønland, 1927, 74, 9—30; Chem. Zentr., 1928, ii, 32).—The Savik meteorite (3401.7 kg.) contains 7.25% Ni, but no carbon, cobalt, or copper. A. A. ELDRIDGE.

Analysis of a eudialyte from Chibina steppes and its weathering products. G. P. TSCHERNIK (Bull. Acad. Sci., U.S.S.R. [Russia] 1928, ii, 720; Chem. Zentr., 1928, ii, 28—29).—The eudialyte, d 2.83—2.99, H 5—6, and its weathering product contain, respectively, TiO_2 1.81, 3.04; Fe_2O_3 1.54, 15.87; MnO 1.43, 2.20; H_2O 1.07, 3.25; 3.92; FeO 7.21, 3.85; Na_2O 12.97, 5.95; Cl 0.96, 0.14. A. A. ELDRIDGE.

Silicates. A. ENDRÉDY (Fold. Kozlony, 1927, 20—105; Chem. Zentr., 1928, ii, 29).—An attempt to elucidate the constitution of grossularite and adradite by "fractional" decomposition with hydrochloric acid. A. A. ELDRIDGE.

Karpholite. J. JAKOB and J. HESEMANN (Schweiz. Min. Petr. Mitt., 1928, 7, 134—137; Chem. Zentr., 1928, ii, 29).—Karpholite from Hettstedt, Harz Mts., and from Schlagenwald, Bohemia, corresponded, respectively, with the formulae $10SiO_2 \cdot 4Al_2O_3 \cdot Mn_2O_3 \cdot 2MgO \cdot 8H_2O$ and $4SiO_2 \cdot 2Al_2O_3 \cdot Mn_2O_3 \cdot 3H_2O$; n , 1.612, 1.617; n_z , 1.638, 1.639. A. A. ELDRIDGE.

Zirklerite. E. HARBORT (Kali, 1928, 22, 157—161; Chem. Zentr., 1928, ii, 30—31).—Zirklerite, from salt deposits of the N. German plain, is similar to rinneite; it contains large quantities of ferrous chloride and is coloured reddish-brown in the air. It has n 1.552, d 2.6, is optically uniaxial, and is rhombohedral hemihedral or tetartohedral hexagonal. The composition corresponds with the formula $2Al_2O_3 \cdot H_2O \cdot 9(Fe, Mg, Ca)Cl_2 \cdot 2H_2O$. A. A. ELDRIDGE.

Chemical composition of nepheline. J. MOROWICZ (Bull. Acad. Polonaise, 1928, 4, 111—125).—The data concerning the empirical formula of nepheline are discussed. It is concluded that the general formula is $K_2Al_2Si_2O_{10} \cdot nNa_2Al_2Si_2O_8$, where, in the majority of cases, $n=4$. J. W. SMITH.

Alumohydrocalcite. G. BILIRINE [with TSCHERYNKH] (Mem. Soc. Russe Min., 1928, 55, 243—258; Chem. Zentr., 1928, i, 2797).—The mineral d 2.231, H 2.5, contained SiO_2 0.67, Al_2O_3 28.60, Fe_2O_3 0.45, FeO 0.35, CaO 15.46, MgO , Na_2O , and K_2O

trace. P_2O_5 0.74, CO_2 25.20, H_2O 26.40. H O hygroscopic 2.48%. It is monoclinic, α 1.485 β 1.553, γ 1.570. The dehydration curve indicates the formula $CaH_2(CO_3)_2 \cdot 2Al(OH)_3 \cdot H_2O$. A. A. ELDRIDGE.

[Heterobrochantite, neptunite, rock salt, and syngenite.] H. BUTTGENBACH (Ann. Soc. Geol. Belg., 1926, 49, 164—180; Chem. Zentr., 1928, i, 2796).—Heterobrochantite (Chile), $CuSO_4 \cdot Cu(OH)_2$, H 2.5, d 3.757, is rhombic pyramidal; neptunite (Greenland) has $a:b:c=1.3164:1:0.8075$, $64^\circ 22'$. A scratch-test distinguishes between rock salt and potassium salts. The optical constants of syngenite are recorded. A. A. ELDRIDGE.

Schefferite and richterite. J. JAKOB (Schweiz. Min. Petr. Mitt., 1927, 7, 137—139; Chem. Zentr., 1928, ii, 30).—The manganiferous pyroxenes and amphiboles frequently, sometimes exclusively, contain tervalent manganese. Schefferite contains 4.00 and richterite 3.34—7.17% Mn_2O_3 . A. A. ELDRIDGE.

Micas containing rubidium and caesium. J. JAKOB (Schweiz. Min. Petr. Mitt., 1927, 7, 1, 141; Chem. Zentr., 1928, ii, 30).—Lepidohte (Nubeh, Usakos, S.W. Africa) and zinnwaldite (Zinnwald) contain, respectively: SiO_2 48.80, 48.55; TiO_2 trace, 0.0; Al_2O_3 24.44, 21.79; Mn_2O_3 1.48, 1.40; Fe_2O_3 2.34, 0.0; FeO 0.0, 9.51; MgO and CaO 0.0, 0.0; Li_2O 4.93, 3.73; Na_2O 2.15, 0.51; K_2O 9.26, 8.29; Rb_2O 1.73, 1.49; Cs_2O 0.60, 0.0; $H_2O(+)$ 1.88, 0.83; $H_2O(-)$ 0.0, 0.0; F 4.69, 6.67; α 1.529, 1.541; β 1.651, 1.571; $\gamma=\beta-$, 1.573. A. A. ELDRIDGE.

Harz mineral fields. IV. Occurrence of pyrrhotine and origin of antimony, nickel, and cobalt in the Rammelsberg minerals. G. FRIEDBOLD (Zentr. Min. Geol., 1928, 4, 161—167; Chem. Zentr., 1928, i, 3045—3046).—Pyrrhotine was found in zinc blende from the seventh Rammelsberg level. Calcite contained inclusions of antimonite; pyrrhotine contained pentlandite and cobalt glance. The conditions of the association of these minerals are discussed. A. A. ELDRIDGE.

Mineral constituents and origin of a certain kaolin deposit near Spokane, Washington. G. E. GOODSPEED and A. A. WEYMOUTH (J. Amer. Ceram. Soc., 1928, 11, 687—695).—In this region the rocks, which are at least pre-Tertiary, consist of metamorphics intruded by granite rocks. The kaolin deposits are classified into three types viz., (1) deposits of lacustrine origin, (2) material transported from the wash of felspathic rocks, (3) a residual deposit. The last type, in which no trace of the former existence of felspar is apparent, occurs in dykes cutting a sandy material. In this case the usual conception of the formation of kaolin by the weathering of felspathic rocks does not appear to be tenable. It is suggested that it may have been formed either (1) by effective endomorphic action, the whole of the pre-formed felspar being changed by the volatile constituents of an intrusion, or (2) by the direct action of a highly aqueous magmatic solution, the alumina directly forming kaolin instead of the intermediate felspar. The latter hypothesis is strengthened

by the absence of secondary silica. A list and description of the minerals found in the sandy matrix and kaolinitic dykes are given. A. T. GREEN.

Helium contents and ages of Japanese radioactive minerals from Ishikawa district. Y. KANO and B. YAMAGUCHI (Bull. Chem. Soc. Japan, 1928, 3, 244—252).—The minerals xenotime, samarskite, monazite, and ishihawaite (cf. A., 1922, ii, 861) have been examined for their helium content with the following results: 1 g. of the minerals heated to 1000° yields, respectively, 0.025, 1.42, 0.246, and 1.77 c.c. of helium. The uranium, thorium, and lead contents of ishihawaite were determined. Calculations based on the helium and lead contents give

values respectively for the age of this mineral as 72.3 and 127 million years. The ages of the samarskite and the monazite are calculated as 81.2 and 73.9 million years. These three minerals from Ishikawa belong to the same geological age, either Jurassic or Cretaceous. H. INGLESON.

Radioactive minerals from Divino de Ubá, Brazil. C. N. FENNER (Amer. J. Sci., 1928, [v], 16, 382—391).—A specimen of monazite from Divino de Uba contained 5.091% Th and 0.0927% Pb, from which its age is calculated to be 3.6×10^8 years. The age of samarskite from the same source is 3.4×10^8 years, reckoned from its content of 10.88% U, 1.64% Th, and 0.52% Pb. C. W. GIBBY.

Organic Chemistry.

Higher hydrocarbons from methane. F. H. CONSTABLE (Nature, 1928, 122, 882).—Carbon deposited on china clay is not capable of combining at any appreciable speed with hydrogen at 800—1200° (cf. Stanley and Nash, B., 1929, 7).

A. A. ELDRIDGE.

Slow combustion of triacontane. S. LANDA (Compt. rend., 1928, 187, 948—949).—The slow combustion of *n*-triacontane yields aliphatic acids (formic, butyric, and valeric acids identified), aldehydes (hexaldehyde and heptaldehyde identified), small amounts of unsaturated hydrocarbons, and carbon oxides, but no alcohols or ketones. This is in agreement with the theory that the last-named products arise only from branched-chain hydrocarbons. G. A. C. GOUGH.

Interaction of Δ^8 -pentenyl bromide and magnesium ethyl bromide. C. PRÉVOST (Compt. rend., 1928, 187, 946—948).— Δ^8 -Pentenyl bromide reacts with magnesium ethyl bromide to give Δ^7 -heptene, b. p. 94°, n_D^{22} 1.4017, d_4^{22} 0.701, which yields exclusively propionic and butyric acids in equimolecular proportions on oxidation with potassium permanganate, and γ -ethyl- Δ^4 -pentene, b. p. 85°, n_D^{22} 1.3966, d_4^{22} 0.6948, which yields diethylacetic acid on oxidation and a dibromide, b. p. 93.5°/15 mm., n_D^{24} 1.5006, d_4^{24} 1.5251. These results are in accord with the previously published theory (A., 1928, 152) and demonstrate the separation of Δ^8 -pentenyl ion. On treatment with alcoholic potassium hydroxide, the dibromide yields an acetylenic hydrocarbon, b. p. 87°, n_D^{22} 1.4023, d_4^{22} 0.7272, which gives a precipitate with aqueous or ammoniacal silver nitrate soluble in ether, alcohol, or an excess of the hydrocarbon. G. A. C. GOUGH.

Action of metallic tin on the dihalogen derivatives of methane. K. A. KOTSCHESCHKOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1191—1197)—See A., 1928, 1212.

Decomposition of organic compounds at high temperatures and pressures. L. R. HERNDON and E. E. REID (J. Amer. Chem. Soc., 1928, 50, 3066—3073).—36 Organic compounds, mainly alcohols, acids, and hydrocarbons, have been heated at constant volume in a metal bomb at temperatures

of 300—525° for periods of 2—48 hrs. For details of the very complicated results the original should be consulted. The quantities of gaseous, water-soluble, and water-insoluble products formed, the b. p. range of the last-named, and the reaction products which have been identified are tabulated. The composition of the gaseous mixture obtained from methyl, ethyl, *n*-propyl, isopropyl, benzyl, phenylethyl, and fenchyl alcohols is given. In general, hydroxylic compounds are dehydrated and the hydrocarbon residue is converted into an unsaturated product of wide b. p. range. Aromatic hydrocarbons yield complex mixtures of polymerisation and decomposition products. *n*-Heptane, benzene, toluene, benzoic and stearic acids, benzophenone, and phenol are only slightly decomposed at 400°. H. E. F. NOTTON.

Behaviour of alkoxide solutions towards nitric oxide. H. WIELAND [with J. J. CHAVAN and F. KLAGES] (Ber., 1928, 61, [B], 2382—2387; cf. Stechow, A., 1924, i, 1157; Traube, A., 1925, i, 110).—The production of the compound $\text{CH}_3[\text{N}(\text{NO})\cdot\text{ONa}]_2$ by the action of nitric oxide on a solution of sodium ethoxide in ethyl alcohol is not due to the production of acetone but of acetaldehyde, and sodium formate is formed instead of sodium acetate as assumed previously. The complete reaction is expressed: $3\text{EtONa} + 6\text{NO} \longrightarrow \text{CH}_3[\text{N}(\text{NO})\cdot\text{ONa}]_2 + \text{H}\cdot\text{CO}_2\text{Na} + 2\text{EtOH} + \text{N}_2\text{O}$. The rate of the complete reaction is controlled by that of the dehydrogenation of ethyl alcohol, which constitutes the main change; the formation of the sodium salt is a secondary process. Benzyl alcohol, in presence of sodium benzyl oxide, is much more rapidly dehydrogenated than ethyl alcohol, but the benzaldehyde produced cannot react further with nitric oxide with production of a salt. *iso*Propyl alcohol also reacts more readily than ethyl alcohol and a sodium salt is formed from the resultant acetone. Methyl alcohol does not appear to be affected by nitric oxide. H. WREN.

Preparation of α -dihydroxy-*n*-pentane (penta-methylene glycol) and α -di-iodo-*n*-pentane. A. MÜLLER and E. RÖLZ [with A. GERÖL (Monatsh. 1928, 50, 105—108; cf. A., 1928, 43, 270, 734).—Using the method previously described, α -dihydroxy-

n-pentane [diphenylurethane, m. p. 174—175° (corr.), 142—143° (corr.) on remelting] was prepared in 46% yield by reduction of ethyl glutarate. α -Dibromo-*n*-pentane was obtained in 62% yield by the action of dry hydrogen bromide and α -di-iodo-*n*-pentane in 76% yield by the action of red phosphorus and iodine on the glycol. R. K. CALLOW.

Carbohydrates and polysaccharides. XVII. Isomeric methyleneglycerols. H. HIBBERT and N. M. CARTER (J. Amer. Chem. Soc., 1928, 50, 3120—3127).—Benzoylation of the mixture of methyleneglycerols, prepared by an improved method (cf. Schulz and Tollens, A., 1896, i, 115; Nef, A., 1905, i, 3; Peacock, J.C.S., 1915, 107, 815), and fractional crystallisation of the product yields pure α -methyleneglycerol β -benzoate (I), m. p. 72°, and α -methyleneglycerol γ -benzoate, m. p. 26°. The latter is hydrolysed by 20% aqueous potassium hydroxide to pure α -methyleneglycerol (II), b. p. 84—85°/11 mm., d_4^{20} 1.2113, n_D^{20} 1.4477 (p-nitrobenzoate, m. p. 135°), the constitution of which is proved by its conversion by methyl iodide and silver oxide into γ -methyl- α -methyleneglycerol ether, b. p. 147°/760 mm., n_D^{20} 1.4213, d_4^{20} 1.0788, which is hydrolysed by dilute hydrochloric acid to α -methyl glyceryl ether. The benzoate I is similarly hydrolysed to α -methyleneglycerol (III), b. p. 82°/11 mm., n_D^{20} 1.4533, d_4^{20} 1.2256 (p-nitrobenzoate, m. p. 185°). This is methylated to β -methyl- α -methyleneglycerol ether, b. p. 152°/760 mm., 1.4295, which is hydrolysed to β -methyl glyceryl ether (A., 1928, 1213). The pure methyleneglycerols do not isomerise in presence of alkali hydroxide, but II is largely converted by a trace of hydrogen chloride into III, whilst III undergoes more complex changes. The original mixture contains about 60% of II and 40% of III. H. E. F. NOTTON.

Acetylation of diethylene oxide. M. MACLEOD (J.C.S., 1928, 3092).—From the interaction of diethylene oxide with acetic anhydride in the presence of anhydrous ferric chloride (cf. Knoevenagel, A., 1914, i, 163) small quantities of glycol diacetate and β -diacetoxyethyl ether, b. p. 110—135°/16 mm., d_4^{20} 1.123, n_D^{20} 1.4348, were isolated. A. I. VOGEL.

Reactivity of atoms and groups in organic compounds. VII. Influence of solvents on reaction velocity; adjuvance. J. F. NORRIS and S. W. PRENTISS (J. Amer. Chem. Soc., 1928, 50, 3042—3048).—The term "adjuvance" is proposed for that property of liquids whereby a reaction proceeds with different velocities in different "indifferent" solvents. Relative values for the adjuvance of some pure solvents in the combination of pyridine and ethyl iodide, as measured by the bimolecular velocity coefficients for this reaction at 25° in 0.2—1.0M-concentrations, are: benzene, 1.00; nitrobenzene, 25; acetone, 12.8; methyl alcohol, 2.5; ethyl alcohol, 1.4; *n*-propyl alcohol, 1.11; *n*-butyl alcohol, 1.11; isopropyl alcohol, 1.07; sec-butyl alcohol, 1.00, and *tert*-butyl alcohol, 0.93. The results are similar to those obtained by Menschutkin for the reaction between trimethylamine and ethyl iodide (cf. A., 1888, 901; 1890, 1366).

H. E. F. NOTTON.

Alkyl orthosilicates. A. W. DEARING and E. E. REIO (J. Amer. Chem. Soc., 1928, 50, 3058—3082).—The following alkyl orthosilicates have been obtained by adding silicon tetrachloride to the appropriate alcohols cooled below 0°: *n*-butyl, b. p. 160—165°/20 mm., d_4^{25} 0.9194; *n*-amyl, b. p. 145—150°/3 mm., d_4^{25} 0.8933; *n*-heptyl, b. p. 200—215°/3 mm., d_4^{25} 0.8958, and *n*-octyl, b. p. 240°/3 mm. (decomp.). Phenylethyl and β -chloroethyl orthosilicates could not be purified by distillation. The latter gives with aniline hydrochloride amorphous (?) β -anilinoethyl orthosilicate and similar products with dimethylaniline and pyridine. Silicon tetrachloride with isopropyl alcohol yields propylene and isopropyl chloride; it reacts very slowly with ethyl mercaptan, even at 200°. Ethyl orthosilicate converts phthalic and acetic anhydrides and sulphuric and benzoic acids into the corresponding ethyl esters, and benzene in presence of aluminium chloride into hexaethylbenzene. Silica gel free from strong electrolytes and moisture may be prepared by the action of water and acetic acid, respectively, on ethyl orthosilicate. The product has similar adsorptive properties to ordinary silica gel, but is a slightly better catalyst for contact esterification.

H. E. F. NOTTON.

Formation of allyl alcohol. Decomposition of glyceryl formates by heat. R. DELABY and P. DUBOIS (Compt. rend., 1928, 187, 949—951; cf. A., 1928, 1354).—The glyceryl monoformate (1 g.-mol.), obtained by esterification, decomposes smoothly at 235° to yield carbon oxides (total about 22.4 g.), hydrogen, saturated hydrocarbons, and 57% of allyl alcohol, partly as the formate. The monoformate containing 72% of the α -ester decomposes suddenly below 220° to afford a 4% yield of allyl alcohol. Hence the esterification product consists mainly of the β -formate. The α - and γ -diformates (1 g.-mol.) yield similarly carbon oxides (about 44.8 g.) at 255—310° and allyl alcohol (42.2—43.3 and 45—46.8 g., respectively). The diformate obtained by esterification contains probably a preponderance of the α -ester.

G. A. C. GOUGH.

Univalent iron, cobalt, and nickel. IV. Action of nitric oxide on ferrous mercaptide. W. MANCHOT and H. GALL (Ber., 1928, 61, [B], 2393—2394; cf. A., 1928, 35).—The production of nitrosylmercaptide, SET·NO, by the action of nitric oxide on ferrous mercaptide at a low temperature or in presence of the gas diluted with nitrogen, is established by its isolation (contrast Reihlen, A., 1927, 951). H. WREN.

Complex compounds of gold with mercaptanic radicals. II. Residual affinities of chloroauric acid. P. C. RAY and K. C. BOSE-RAY (J. Indian Chem. Soc., 1928, 5, 527—533).—When 1:4-dithian is treated with excess of aqueous gold chloride the compounds 2AuCl·HCl·(C₂H₄S)₂ (I) and 2HAuCl₃·3(C₂H₄S)₂·4H₂O (II) are obtained. Ammonia, pyridine, and benzylamine convert I into the substances Au₂Cl₆·6NH₃ (explodes when heated), 4AuCl₃·(C₆H₅S)₂·2C₅H₅N, and AuCl₃·CH₃·Ph·NH₂, respectively. If dithian is heated with aqueous gold chloride the products formed are II and the compound AuCl₃·(C₂H₄S)₂ (III). Pyridine converts III into the

substance $2\text{AuCl}(\text{C}_2\text{H}_4\text{S})_2$, but if the reaction is carried out in absence of light the product is $\text{AuCl}(\text{C}_5\text{H}_5\text{N})$. Treatment of II with potassium carbonate (0.5 mol.) gives potassium chloroaurate and the salt

$\text{KAuCl}_4 \cdot \text{HCl} \cdot 3(\text{C}_2\text{H}_4\text{S})_2 \cdot 2\text{H}_2\text{O}$, but with 1 mol. of the carbonate the complex salt $\text{KAuCl}_4 \cdot 3(\text{C}_2\text{H}_4\text{S})_2 \cdot 4\text{H}_2\text{O}$ is produced. The action of ammonia on II is to yield the explosive compound $\text{Au}(\text{NH}_3)_3 \cdot 1.5\text{H}_2\text{O}$, whilst pyridine gives dithian sulphone, and the substances $\text{AuCl}_3 \cdot 1.5\text{C}_5\text{H}_5\text{N}$, chars about 210° , and $\text{AuCl}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$.

Triethylene tetrasulphide and gold chloride afford the substance $\text{AuCl}(\text{C}_2\text{H}_4)_3\text{S}_2$. H. BURTON.

Properties of butyrates and isobutyrate. F. KJELSEBERG and A. MÜLLER (Deut. Parfümerieztg., 1928, 14, 235—236; Chem. Zentr., 1928, ii, 338).—*iso*Butyrates have smaller d and n than the corresponding butyrates; differences in the odours of esters and in the case of hydrolysis of esters are recorded. Terpinyl *isobutyrate* is specially resistant to hydrolysis. A. A. ELDRIDGE.

Oxidation of fats, nitrogenous substances, and their mixtures with carbohydrates by air, and metabolism in normal health and diabetes. C. C. PALIT and N. R. DHAR (J. Physical Chem., 1928, 32, 1663—1680; cf. A., 1926, 822).—Potassium stearate and oleate in the presence of sodium hydrogen carbonate or hydroxide are oxidised by the passage of air through their solutions at the ordinary temperature, and the amount of oxidation is increased by the addition of many of the metallic hydroxides. Mixtures of carbohydrates with potassium stearate or oleate are also oxidised by this treatment, but in these cases each component is oxidised to a smaller extent. Carbamide, hippuric acid, and glycine are also oxidised by air in the presence of reducing agents, and in alkaline solution the last two substances are oxidised even in the absence of a catalyst. When carbohydrates or fats are present, the extent of oxidation is decreased. In the presence of carbamide, the oxidation of the fat or of the carbohydrate is also diminished. Oxidation, in all cases, increases with an increase in amount of alkali present. Treatment with alkali should prove of value in metabolic diseases. L. S. THEOBALD.

Phenylstearic acid. C. M. DE MILT (Abstr. Theses, Univ. Chicago, Sci. Ser., 1925—1926, 4, 123—126).—Oleic acid and benzene, in presence of aluminium chloride, yield (?) *p*-phenylstearic acid, b. p. $250^\circ/4$ mm., n_D^{23} 1.4905 (sodium, potassium, lead, m. p. 86° , and silver salts; methyl ester, b. p. $228^\circ/4$ mm., n_D^{23} 1.4840; amide; anilide, b. p. $282^\circ/4$ mm.).

CHEMICAL ABSTRACTS.

Determination of small amounts of lactic acid. E. LEHNARTZ (Z. physiol. Chem., 1928, 179, 1—8).—A few changes are recommended in the Hirsch-Kauffmann (A., 1925, i, 96) and Embden (A., 1925, i, 719) modifications of the von Fürth-Charnass method for the determination of lactic acid. The error is not more than 2%. The presence of trichloroacetic acid is detrimental.

J. H. BIRKINSHAW.

Catalytic studies on acetoacetic ester. F. O. RICE and J. J. SULLIVAN (J. Amer. Chem. Soc., 1928, 50, 3048—3055).—Distillation of ethyl acetoacetate at the ordinary temperature and 10^{-5} mm. pressure in

quartz or Pyrex, but not in soft glass vessels, yields fractions containing 30—40% of enol, the half-life period of which is about 500 hrs. These are approximately ten times as stable as any previously obtained. The effects of measured amounts of 11 catalysts on the velocity of transformation have been determined. The results are, in general, in accordance with previous work (cf. Meyer and Hopff, A., 1921, i, 391; Rumeau, A., 1924, i, 939), but no substance has been found capable of stabilising the product, both oxalic acid and phthalic anhydride being accelerators. Attempts to increase the stability by removing traces of water by means of silica gel or acetyl chloride were unsuccessful. The temperature coefficient of the rate of change, k_{35}/k_{25} , is 4.9 or 6.3, and the heat of activation 31,200 g.-cal. H. E. F. NOTTON.

Reduction of the secondary hydroxyl group in ricinoleic acid. F. SIGMUND and F. HAAS (Monatsh., 1928, 50, 357—368).—Reduction of ethyl ricinoleate by sodium and boiling amyl alcohol yielded not more than a trace of the expected glycol (μ -hydroxyoleyl alcohol). The product was essentially oleyl alcohol, characterised by conversion into the acetate and preparation of stearyl alcohol and stearyl acetate by catalytic reduction in presence of platinum-black. The reduction of the hydroxyl group not vicinal to the double linking is anomalous, but was found also to occur in the reduction of ricinoleic acid or its derivatives by hydrogen in presence of Low's platinum-black (cf. also Grün and Woldenberg, A., 1909, i, 284; Grün and Czerny, A., 1926, 269).

Commercial ricinoleic acid was found to contain only 85% of free acid, and it was purified by heating with sodium hydroxide and separation of the barium salt. Reduction of the acid in acetic acid yielded stearic acid, or a mixture of ricinoleic and stearic acids when hydrogenation was incomplete. Similarly, methyl ricinoleate yielded methyl stearate under all conditions tried. The action of acetyl chloride on methyl ricinoleate yielded the acetyl derivative of about 84% purity, which could not be further purified without repeated fractionation. The hydrogenation of this crude acetyl derivative yielded impure methyl λ -acetoxystearate, b. p. 239 — 244° (corr.)/17 mm., from which λ -hydroxystearic acid was obtained by hydrolysis. λ -Hydroxystearic acid resisted catalytic hydrogenation, and in the reduction of ricinoleic acid the hydroxyl group must, therefore, be reduced before the double linking. R. K. CALLOW.

Second form of oxalic acid? A. E. TSCHITSCHIBABIN (J. pr. Chem., 1928, [ii], 120, 214—220; cf. Oberhauser and Hensinger, A., 1928, 505).—A theoretical paper in which the author's views concerning the existence of a *cis-trans* type of isomerism of oxalic acid (A., 1912, i, 149) are reviewed in the light of the reported isolation of an acid isomeric, but not identical, with oxalic acid by Wassilieff (A., 1902, i, 361) and other data from the literature.

J. W. BAKER.

The C_4 -saccharinic acids. IV. Preparation of β - γ -dihydroxybutyric acid. G. LEAVELL (Abstr. Theses, Univ. Chicago, Sci. Ser., 1925—1926, 4, 99—104).—The γ -lactone of α - γ -dihydroxybutyric acid is prepared in 54% yield from glycerol, by way of the

α -chlorohydrin and α -cyanohydrin. $\beta\gamma$ -Dihydroxybutyric acid phenylhydrazide has m. p. 109° . Reduction of the acid with sodium and alcohol gave a liquid, b. p. 188° , probably $\alpha\beta\delta$ -trihydroxybutane.

CHEMICAL ABSTRACTS.

Plant colouring matters. X. Crocetin and lycopin. P. KARRER, A. HELFENSTEIN, and R. WIDMER (Helv. Chim. Acta, 1928, 11, 1201—1209).— α -Crocetin (1 mol.) is reduced by titanous chloride (2.3 mols.) to *dihydro- α -crocetin* ($\gamma\eta\lambda$ -trimethyl- $\Delta^{8659\text{K}\mu}$ -tetradecaheptaene- $\alpha\epsilon$ -dicarboxylic acid), m. p. 192 — 193° after previous sintering, yellow, which on exposure to air absorbs oxygen (16.75%), and on treatment with ozone gives malonic acid. When the reduction is carried out with a large excess of titanous chloride the product is *hexahydro- α -crocetin*, an almost colourless oil, reduced by hydrogen in presence of platinum-black and acetic acid to tetradecahydro- α -crocetin. Colour reactions of these crocetins with several reagents are given. Pure γ -crocetin (A., 1928, 869) has m. p. 199 — 200° (uncorr.).

Phosphorus pentabromide converts dihydrophytol (Willstätter and Mayer, A., 1908, i, 383) into $\gamma\eta\lambda\sigma$ -tetramethylhexadecyl bromide, b. p. 185 — $188^\circ/0.6$ mm., which when treated with sodium in dry benzene yields a mixture of tetramethylhexadecene, b. p. $127^\circ/0.11$ mm., and the hydrocarbon $(\text{CHMe}_2\cdot[\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}]_3\cdot\text{CH}_2\cdot\text{CH}_2)_2$, b. p. 240 — $242^\circ/0.3$ mm. The former compound resembles phytene (Willstätter and Hocheder, A., 1907, i, 784), whilst the latter is similar to perhydrolycopin, $\text{C}_{40}\text{H}_{80}$, $d_4^{25} 0.8211$, 1.45837 (cf. A., 1928, 1016).

H. BURTON.

Preparation of potassium and sodium tetrabismuth tartrates. P. A. KOBER (J. Lab. Clin. Med., 1927, 12, 962—967).—Sodium and potassium tetrabismuth tartrates, obtained from alkaline tartrate solutions and bismuth hydroxide at a low temperature, are less toxic than other bismuth tartrates. The "tribismuth tartrates" are probably mixtures of di- and tetra-bismuth tartrates.

CHEMICAL ABSTRACTS.

Sulphopyrotartaric acids. III. H. J. BACKER and J. BURNING (Rec. trav. chim., 1928, 47, 1000—1010; cf. A., 1928, 46, 273).—Propane- $\alpha\alpha\beta$ -tricarboxylic acid is converted by heating with sulphur trioxide, fuming and concentrated sulphuric acids, and best with excess of chlorosulphonic acid into α -sulpho- β -methylsuccinic acid ($+2\text{H}_2\text{O}$), m. p. 115 — 120° (decomp.), isolated through its barium salt ($+6$ or $9\text{H}_2\text{O}$) [calcium salt ($+7\text{H}_2\text{O}$)]. Treatment of the acid with strychnine gives the *strychnine hydrogen salt* ($+4\text{H}_2\text{O}$), which on decomposition with sodium hydroxide affords a neutral sodium salt, $[M]_D +19^\circ$ in water (tervalent ion rotation). The free acid from this has $[M]_D +35^\circ$ in water (univalent ion rotation). Racemisation of the acid or its salts is not effected by heating at 100° . Ethyl sodiopropene- $\alpha\alpha\beta$ -tricarboxylate and ethyl chlorosulphonate afford *ethyl α -chloropropene- $\alpha\alpha\beta$ -tricarboxylate*, b. p. 160 — $168^\circ/20$ mm. The results now and previously obtained (*loc. cit.*) show that the addition of sulphite to itaconic, mesaconic, and citraconic acids does not give the same sulphomethylsuccinic acid (cf. Wieland, A., 1871, 132). The acid described by Andreasch (A., 1897, i,

327) is probably α -sulpho- β -methylsuccinic acid. The properties of the three isomeric sulphomethylsuccinic acids are appended.

H. BURTON.

[X-Ray examination of highly-polymerised organic substances.] G. MIE and J. HENGSTENBERG (Helv. Chim. Acta, 1928, 11, 1052).—Polemical against Ott (A., 1928, 465).

H. BURTON.

Highly-polymerised compounds. XI. [X-Ray examination of highly-polymerised organic substances.] H. STAUDINGER and R. SIGNER (Helv. Chim. Acta, 1928, 11, 1047—1051).—A criticism of Ott's conclusions (A., 1928, 465) regarding the structure of highly-polymerised polyoxymethylene compounds. Ott's conclusions appear to be based on the erroneous assumption that the elementary cell contains one molecule. It is suggested that complex molecules may be larger than the elementary cell. A determination of the methoxyl and acetyl content of complex polyoxymethylene dimethyl ethers and acetates, $\text{RO}\cdot[\text{CH}_2\cdot\text{O}]_n\cdot\text{R}$, indicates that n is on the average about 50. The physical properties of these compounds show that n is at least 20; the larger molecules must, therefore, have n —about 100. It appears that these highly-polymerised substances are not homogeneous, but are composed of molecules of varying length.

H. BURTON.

Action of metallic sodium on trimethylacetyl chloride. V. EGOROVA (J. Russ. Phys. Chem. Soc., 1928, 60, 1199—1210).—The action of metallic sodium on trimethylacetyl chloride in moist ether gave, instead of the expected hydroxyketone, $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CMe}_3$, the diketone, $\text{CMe}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CMe}_3$, b. p. 165 — 168° , together with some trimethylacetic ester of the hydroxyketone, m. p. 37° , and a trace of a polymeride of the diketone of high mol. wt., m. p. 180 — 181° . The formation of the diketone could not be due to oxidation, as it was obtained in the absence of air, and the hydroxyketone could not be oxidised to the diketone under the conditions of the experiment. When the diketone was treated with sodium, the hydroxyketone was obtained, together with some free trimethylacetic acid. Under the same conditions, benzil yielded only traces of benzoin and benzoic acid.

M. ZVEGINTZOV.

Sugars. J. MIKSIC (Vestnik Kral. Ces. Spol. Nauk., 1926, Cl. II, 18 pp.; Chem. Zentr., 1928, i, 2704—2705).—The following compounds of importance in sugar syntheses are described: *rhamnohexonamide*, m. p. 194° , $[\alpha]_D^{20} -47.26^\circ$, after 2 days unchanged, after 2 hrs. on the water-bath -21.48° ; *rhamnohexonic acid*, m. p. 151° (ammonium salt); *nitrile*, m. p. 145° , $[\alpha]_D^{20} -23.47^\circ$. *Mannoheptononitrile*, $\text{CH}_2\text{OH}\cdot[\text{CH}\cdot\text{OH}]_5\cdot\text{CN}$, m. p. 121 — 122° , $[\alpha]_D^{20} +31.4$ to $+23.11^\circ$ (final); *mannoheptonamide*, m. p. 188 — 189° (slow heating), 200° (rapid heating); *ammonium mannoheptonate*, m. p. 154° , $[\alpha]_D^{20} +31.31$ to $+7.22^\circ$ (final). α -Penta-acetylglucose, m. p. 111.5 — 112° , $[\alpha]_D^{20} +101.4^\circ$; *tetra-acetyl-d-gluconolactone*, m. p. 103° , $[\alpha]_D^{20} +13.46^\circ$. Acetylation of ammonium rhamnohexonate affords *tetra-acetyl-rhamnohexonolactone*, m. p. 128.5 — 129° , $[\alpha]_D^{20} +9.66^\circ$. *Hexa-*

acetyl- α -rhamnohexonamide has m. p. 71—72°; penta-acetyl- α -rhamnohexononitrile, m. p. 85—86° [α]_D²⁰ +76.43°; hepta-acetyl- α -galaheptonamide, m. p. 125.5—126°, [α]_D²⁰ +21.79° to +23.86° (after 24 hrs.); hexa-acetyl- α -mannoheptononitrile, m. p. 124.5—125°, [α]_D²⁰ +31.45°.

A. A. ELDRIDGE.

Mechanism of oxidation of some carbohydrates and polyhydric alcohols by hydrogen peroxide with iron salts as catalyst in acid media. A. T. KUCHLIN and J. BOESEKEN (Rec. trav. chim., 1928, 47, 1011—1026).—Oxidation of dextrose (1 mol.) with hydrogen peroxide (1 mol.) in presence of ferrous sulphate and a small amount of sulphuric acid proceeds more rapidly at 30° than at 0°, and glucosone is shown to be an intermediate product. Provided a low concentration of hydrogen peroxide is used, auto-decomposition is very small. With laevulose oxidation proceeds more quickly, the primary effect (cf. Wieland and Franke, A., 1927, 944) being much greater than for dextrose. When laevulose is oxidised in presence of ferric sulphate, reaction proceeds more slowly and the primary effect disappears; at the end of the reaction ferrous ions are present in solution. *d*-Arabinose is oxidised more slowly than either laevulose or dextrose. Erythritol is oxidised in presence of ferrous sulphate giving, in addition to acid products, an osone (isolated as impure disemicarbazone, m. p. 224°). The primary effect (maximum at about p_H 2.2) is much less in this case than for the sugars, and the amount of hydrogen peroxide reacted with at the beginning of the reaction is approximately equal to the amount of catalyst present.

Dihydroxyacetone osone (disemicarbazone, m. p. 221°) is oxidised by aqueous ferric chloride or sulphate. Increase of dilution causes a decrease in the initial velocity, which is not of the expected magnitude (in one case an increase was observed). This appears to be due to oxidation being effected by $FeOH^{++}$ or $Fe_2(OH)_2^{+++}$ ions, which are presumed to exist in relatively larger quantities at greater dilutions. Glucosone (shown to be formed by oxidation of dextrose and laevulose by copper acetate) is oxidised by ferric salts also.

The above experiments indicate that in the production of *d*-arabinose from dextrose, the reaction proceeds to a great extent through the intermediates glucosone and ketoglutaric acid. H. BURTON.

Determination of acetone groups in acetone [isopropylidene] sugars. H. ELSNER (Ber., 1928, 61, [B], 2364—2367).—The substance (50—100 mg.) is placed in a Claisen flask, the straight limb of which carries a narrow tube through which carbon dioxide is passed. The curved neck supports a tap funnel, which serves for the introduction of dilute sulphuric acid (4 c.c. of acid in 30 c.c. of water) and subsequently of 80 c.c. of water during the course of the distillation. The flask is connected by rubber stoppers to a condenser and receiver cooled in ice. The distillate is made up to 100 c.c. and 30 c.c. of *N*-potassium hydroxide are added. Simultaneously, a comparison solution containing a known weight of acetone, approximately equal to that expected, is prepared and similarly treated. The solutions are preserved in a closed flask for 1½ hrs. until the ordinary temperature

has been attained, after which equal quantities (about 40 c.c.) of 0.1*N*-iodine are added with brisk stirring. After exactly 4 min. the solutions are acidified with about 35 c.c. of *N*-sulphuric acid and excess of iodine is titrated with 0.1*N*-sodium thiosulphate.

H. WREN.

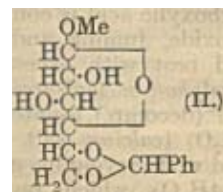
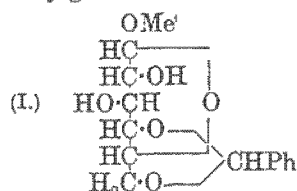
β -Arabinosan. H. VOGEL (Helv. Chim. Acta, 1928, 11, 1210—1213).—When α -arabinose is heated at 160°/15 mm. for 2 hrs. isomerisation into the β -form occurs, but after a further 2 hrs. β -l-arabinosan (annexed formula), m. p. 80—81°, [α]_D²⁰ +60.5° in water, is produced. This compound does not exhibit mutarotation; it reduces hot Fehling's solution, and is converted by boiling with water into arabinose. When it is heated with a small amount of zinc chloride at 150°/15 mm. for 1.5 hrs. di-arabinosan, $(C_5H_8O_4)_2$, m. p. 153—155°, [α]_D²⁰ +18.9° in water, is formed.

H. BURTON.

Transformations of β -pentabenzoyl-*h*-glucose. H. H. SCHLUBACH, F. TREFZ, and W. RAUCHENBERGER (Ber., 1928, 61, [B], 2368—2371; cf. A., 1927, 858).— β -Pentabenzoyl-*h*-glucose is converted by liquid hydrogen chloride or hydrogen bromide into halogenated derivatives of somewhat varying specific rotation. With hydrogen bromide in glacial acetic acid followed by treatment of the mixture with water and then of the solid product with silver carbonate and acetone, it gives tetrabenzoyl-*h*-glucose, [α]_D²⁰ +5.15° to +4.96° in chloroform, +11.9° to +3.5° in alcohol, characterised by re-benzoylation to β -pentabenzoyl-*h*-glucose. The tetrabenzoyl compound is converted by silver oxide and methyl iodide into β -tetrabenzoyl-*h*-methylglucoside, (+MeOH), [α]_D²⁰ -48.6° in chloroform, from which *h*-methylglucoside, [α]_D²⁰ -16.4° in water, is prepared by means of methyl-alcoholic ammonia.

H. WREN.

Derivatives of the benzylidenemethylglucosides. H. OHLE and K. SPENCKER (Ber., 1928, 61, [B], 2387—2392).—Mainly according to the work of Irvine and Scott (J.C.S., 1913, 103, 575) and Freudenberg, Toepffer, and Andersen, A., 1928, 1223), the constitution I or II is to be assigned to the benzylidenemethylglucosides.



The methylglucosides do not react with acetone in the presence of anhydrous copper sulphate, production of glucose diisopropylidene ether occurring only in the presence of mineral acid. The β -isomeride is affected by much lower concentrations of acid than the α -form. Glucose diisopropylidene ether in the presence of acetone and sulphuric acid under defined conditions is partly transformed into the mono-ether and a little free dextrose, but the furoid structure remains intact. If benzylidenemethylglucoside has the structure II, its partial conversion into glucose diisopropylidene ether or the hypothetical iso-

propylidenomethylglucoside under these conditions is to be expected, whereas this reaction cannot take place if it has the structure I, since the pyranoid α -methylglucoside remains unchanged. Experiment shows that benzylidene- α -methylglucoside is almost quantitatively converted into benzaldehyde and α -methylglucoside, thus establishing the constitution I.

The following new compounds are described: 2:3-dibenzoyl-4:6-benzylidene- α -methyl-d-glucoside, m. p. 148°, $[\alpha]_D^{20} +96.89^\circ$ in chloroform, from benzylidene- α -methylglucoside and benzoyl chloride in pyridine, and the corresponding β -compound, m. p. 185°, $[\alpha]_D^{20} +15.84^\circ$ in chloroform; 2:3-di-p-toluenesulphonyl-4:6-benzylidene- α -methyl-d-glucoside, m. p. 149°, $[\alpha]_D^{20} +66.5^\circ$ in chloroform, and the corresponding β -compound, m. p. 158°, $[\alpha]_D^{20} +54.70^\circ$ in chloroform.

H. WREN.

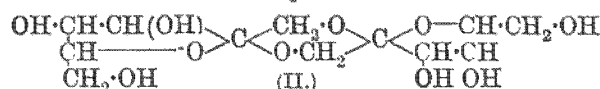
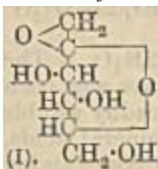
Formula of digitoxin. A. WINDAUS and G. STEIN.—See this vol., 71.

Constitution of solanine. G. ZEMPLÉN and A. GERECs (Ber., 1928, 61, [B], 2294—2300).—Solanine, $C_{44}H_{71}O_{15}N$, $[\alpha]_D^{20} -59.45^\circ$ in pyridine, is converted by sodium acetate and acetic anhydride into *trideca-acetylsolanine*, (?) $C_{70}H_{97}O_{23}N$, m. p. 204—205° after softening at 190°, $[\alpha]_D^{20} -34.96^\circ$ in alcohol, which is hydrolysed by hydrobromic and acetic acids in presence of chloroform to acetylated rhamnosidogalactose (see later) and acetylated solanidineglucoside, m. p. 115—120° (decomp.), $[\alpha]_D^{20} -8.01^\circ$ in alcohol, yielding on further hydrolysis solanidine and dextrose (identified as β -penta-acetylglucose). The bromoacetyl compound of rhamnosidoglucose is hydrolysed to the free *biose*, which could not be caused to crystallise. Its nature is deduced from the observation that it is converted by iodometric oxidation into a rhamnosidogalactonic acid which yields large amounts of methyl-furfuraldehyde when distilled with hydrochloric acid. In solanine, therefore, the solanidine residue is united to a trisaccharide; the sequence of monoses is dextrose-galactose-rhamnose, the dextrose being directly combined with the solanidine. Analyses of solanidine hydrochloride indicate the formula $C_{26}H_{41}ON$ for solanidine, which agrees with the composition $C_{44}H_{71}O_{15}N$ for solanine.

H. WREN.

Synthesis of the fundamental substance of inulin. H. H. SCHLUBACH and H. ELSNER (Ber., 1928, 61, [B], 2358—2363).—Treatment of laevulose with acetone and hydrochloric acid (cf. Irvine and Garrett, J.C.S., 1910, 97, 1282) yields α -fructose diisopropylidene ether and a non-crystalline syrup. The yields of the latter are improved if the second treatment with acetone is effected in the presence of anhydrous copper sulphate, whereby the isomerising effect of the acid is avoided, and are then at a maximum when 2% of water is present in the acetone, whereas with 0—0.5% of water the diisopropylidene ether is almost exclusively formed. By treatment with alcohol and ether, the syrupy product is caused to solidify; it contains only a small proportion of isopropylidene derivatives, which can be removed by further systematic treatment with alcohol and ether. The acetone-free solid has distinct reducing power even after treatment with yeast. It is separated by absolute alcohol into a *fructose anhydride*, $C_6H_{10}O_5$,

$[\alpha]_D^{20} -8.9^\circ$ in water, and a *difructose*, $C_{12}H_{22}O_{11}$, decomp. 198°, $[\alpha]_D^{20} -25.6^\circ$ in water. Exhaustive methylation of fructose anhydride by the method of Haworth and Learner (A., 1928, 510) affords *hexamethyldifructose anhydride*, b. p. 150°/0.1 mm., $n_D^{20} 1.4738$, $[\alpha]_D^{20} +31.1^\circ$ in chloroform, hydrolysed to a trimethylfructose, yielding a phenylosazone identical with the product obtained by Haworth and Learner from trimethylinulin. The synthetic fructose anhydride I represents, therefore, the fundamental substance of inulin. It is considered probable that this substance passes through the difructose (see above) to the difructose anhydride II, the molecules of which are associated to inulin by extra-molecular forces.



H. WREN.

Constitution of highly polymerised substances. XIII. H. STAUDINGER (Ber., 1928, 61, [B], 2427—2431).—A theoretical paper in which the structure of cellulose and caoutchouc is discussed in the light of the author's observations on polyoxymethylenes. Deductions as to the size of the molecule cannot be made from the size of the elementary cell, since the same structural principle can be repeated in a long molecule and thus a molecule may extend through many elementary cells. The soluble polyoxymethylene diacetates and dimethyl ethers, as well as the insoluble, highly polymerised polyoxymethylenes, have small elementary cells. The most convincing evidence of the highly polymerised nature of cellulose lies in the assumption that it is built on the same principle as the polyoxymethylenes.

H. WREN.

Cellulose. K. H. MEYER and H. MARK (Ber., 1928, 61, [B], 2432—2436).—A reply to Hess and Trogus (A., 1928, 1225). A protest is raised against the manner in which the authors have applied roentgenographic methods to the elucidation of the cellulose problem.

H. WREN.

Sulphuric esters of carbohydrates. E. GEBAUER-FULNEGG, W. H. STEVENS, and E. KRUG (Monatsh., 1928, 50, 324—327).—When cotton is treated with chlorosulphonic acid in the cold and kept for 24 hrs., hygroscopic crystals of chloroglucose tetrasulphate separate (cf. Claesson, A., 1879, 1033). If the reaction mixture is slowly added to acetic anhydride, α -penta-acetyl-d-glucose may be separated by treatment with brine or sodium acetate solution. The same product is obtained from dextrose by the same treatment. If, however, the reaction mixture from cotton or dextrose is added to acetyl chloride or bromide, β -aceto-chloroglucose is obtained, identified by conversion into penta-acetyl-d-glucose. Acetyl iodide is decomposed in this reaction. If the reaction between cotton and chlorosulphonic acid is stopped after 2 or 5 hrs., small quantities of octa-acetyl-cellobiose or tetra-acetylglucose, respectively, can be separated.

R. K. CALLOW.

Compounds of hexamethylenetetramine with silver and other metal salts and the influence

of anionic volume on the capacity for association by the central positive ion. P. RAY and J. DASGUPTA (J. Indian Chem. Soc., 1928, 5, 519—525).—Complex compounds of hexamethylenetetramine with the following silver salts are prepared in ammoniacal solution [in the following formulæ $B = (CH_2)_6N_4$]: $3AgCN, B$; $2AgCNO, B$; $2AgCNS, B$; $AgClO_4, B$; Ag_2CrO_4, B ; $4Ag_2Cr_2O_7, 5B, 4H_2O$; $Ag_2MoO_4, 2B, 2H_2O$; $Ag_2WO_4, 2B, H_2O$; $2Ag_2SO_4, 3B, 6H_2O$; $4Ag_2SO_4, 5B, 13H_2O$, and $AgSeO_4, 2B, 12H_2O$. The compounds $3CuCN, 2B$ and $3Cd(CN)_2, B$ have also been prepared. The substances are usually readily soluble in ammonia and are decomposed by mineral acids, yielding formaldehyde, and by alkali hydroxides giving the metal oxide. When heated they decompose with charring and give characteristic amine odours. In the above silver salt complexes increase in anionic volume is accompanied by an increased capacity of association of neutral molecules by the silver cation. In the silver halide-hexamethylenetetramine complexes the capacity of silver for association diminishes in the order F, I, Br, Cl, an anomaly similar to that observed by Ephraïm (A., 1918, ii, 313) for the corresponding amines. Since cadmium and silver have almost the same atomic volume, the composition of the complexes is similar, but the results are not strictly comparable, as cadmium is bivalent. The smaller atomic volume of copper causes an increase in the associating power.

Silver tellurate, borate, iodate, phosphate, arsenite, and arsenate do not form compounds with hexamethylenetetramine, probably because of the insolubility of these salts, whilst silver sulphite, benzoate, and salicylate give indefinite crystalline substances.

H. BURTON.

Molecular compound between glycine anhydride and silver nitrate. T. ASAHINA (Z. physiol. Chem., 1928, 179, 83—87).—A molecular compound, $NO_3Ag \cdot \begin{matrix} (C_2H_3O_2N)_2 \\ (C_2H_3O_2N)_2 \end{matrix} \cdot AgNO_3$, incipient decomp. 195° , is obtained when glycine anhydride and silver nitrate are mixed in concentrated aqueous solution.

J. H. BIRKINSHAW.

Substituted butyrolactams. S. S. G. SIRCAR (J. Indian Chem. Soc., 1928, 5, 549—554).—Substituted glutaric anhydrides are converted by ammonia and sodium hydroxide into the corresponding sodium glutaramates, which, after treatment with potassium hypobromite and subsequent acidification,

afford the butyrolactams $NH \cdot CH_2 \cdot CRR' \cdot CH_2 \cdot CO$ in 15—45% yield. These lactams are precipitated from aqueous solution by tannic and phosphotungstic acids, lead and mercuric acetates, and Meyer's and Dragendorff's reagents. With 3:5-dinitrobenzoyl chloride in alkaline solution they give deep violet colorations. The following are described: cyclohexanespirobutyrolactam, b. p. 180 — $181^\circ/13$ mm., m. p. 98° (benzoyl derivative, m. p. 138° ; nitroso-derivative, m. p. 82° ; mercurichloride, m. p. 158 — 160°); cyclopentanespirobutyrolactam, b. p. $164^\circ/16$ mm., m. p. 75° (benzoyl derivative, m. p. 70 — 71° ; nitroso-derivative, m. p. 51 — 52° ; mercurichloride, m. p. 135°); $\beta\beta$ -dimethylbutyrolactam, b. p. 146 — $147^\circ/12$ mm., m. p. 65 — 66° (benzoyl derivative, m. p. 69° ; nitroso-derivative, m. p.

45°); β -methyl- β -ethylbutyrolactam, b. p. 150 — $152^\circ/13$ mm., m. p. 74 — 75° ; $\beta\beta$ -diethylbutyrolactam, b. p. $163^\circ/12$ mm., m. p. 76 — 77° (mercurichloride, m. p. 130°); β -ethylbutyrolactam, b. p. 117 — $118^\circ/13$ mm., and β -methylbutyrolactam, b. p. $116^\circ/15$ mm. The lactam ring is more stable to alkali than the lactone, imide, or paraconic acid rings.

H. BURTON.

Product from β -alanine ester of high mol. wt., composed of β -alanyl groups united by linkings of amide character. E. ÅBDERHALDEN and F. REICH (Z. physiol. Chem., 1928, 178, 169—172).— β -Alanine methyl ester, when kept for a few days, yielded a white, amorphous solid, insoluble in ether, decomp. 310° , reacting alkaline in aqueous solution. The ratio of amino-nitrogen to total nitrogen was 1:10, but the mol. wt. determined by depression of the f. p. of acetic acid corresponded with the condensation of only 5 molecules. Hydrolysis by boiling 25% aqueous sulphuric acid gave a quantitative yield of β -alanine.

R. K. CALLOW.

Identity of the two possible isomeric methyl ethyl β -methyl- α -dicyanoglutaconates. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1928, 3, 261—265).—Proof of the identity of the sodium compounds obtained by either condensation (A., 1928, 1356) is obtained by converting each specimen into the crystalline silver derivative by the action of aqueous silver nitrate and examination of their refractive indices. X-Ray spectra of either specimen obtained by the Debye-Scherrer method with the $K\alpha$ molybdenum line are identical, the most intense line corresponding with a lattice distance 3.56 \AA . Either specimen, or one obtained by mixed crystallisation of the two, gives the same refractive indices, elongation occurring in the direction of the optical elasticity axis X , n_1 (the refractive index for the faster wave) being equal to α , the value of being 1.503 ± 0.001 , and the zone of elongation being negative. Similar results were obtained with the silver derivative of dimethyl β -methyl- α -dicyanoglutaconate, whilst the silver derivative of the diethyl ester elongates in the direction of the optical elasticity axis Z , the zone being positive and $\alpha_D = 1.580$. The results do not decide between the constitutions $C(CN)(CO_2Et) \cdot CMe \cdot CN \cdot (CN) \cdot CO_2Me$ and $C(CN)(CO_2Me) \cdot CMe \cdot CN \cdot (CN) \cdot CO_2Et$, but the fact that the presence of a β -methyl group causes no change in the course of the condensation favours the mechanism given previously (*loc. cit.*).

Methyl ethoxyethylidenecyanoacetate, m. p. 76 — 77° , is described.

J. W. BAKER.

Action of multivalent alcohols and phenols on arsenic compounds, especially arsenoacetic acid. B. ENGLUND (Svensk Kem. Tidskr., 1928, 40, 278—285; cf. A., 1928, 1364).—Arsenious acid dissolves in warm ethylene glycol and in solutions of pentaerythritol in glacial acetic acid or pyridine, but no definite chemical compounds could be prepared from these solutions. The action of arsenoacetic acid on some forty organic hydroxy-compounds has been investigated by the following method, which is based on the slight solubility of the acid in glacial acetic acid and the ready solubility of the compounds produced. A weighed quantity of the substance

together with arsenoacetic acid is introduced into a glass tube, and a known volume of acetic acid (containing about 1% of water) added. The tube is sealed and placed in a thermostat at 25°, where it is kept in rotation. After 24 hrs. 2 c.c. of the liquid are withdrawn and the dissolved arsenic is determined with 0.00*N*-potassium bromate solution. The extent to which interaction has taken place can be ascertained from the formula $L = (v - v_0)/80 - 1000g/MV$, in which v and v_0 — final and initial titration in c.c., g = weight of substance, V = volume of acetic acid, and M — mol. wt. of substances. Where the compound produced contains 1 mol. of hydroxy-compound to one atom of arsenic, L has a maximum value of 1. If 2 mols. of hydroxy-compound are combined with one atom of arsenic, its maximum is 0.5. The value of L is practically constant over a wide range of concentrations, but in cases where L is greater than 0.4 it diminishes with increasing concentration. A marked effect takes place in the case of substances containing two hydroxy-groups on adjacent carbon atoms, compounds with a five-membered ring being formed. α - γ -Glycols and m - and p -dihydroxybenzene derivatives give a much less marked effect, showing the tendency to form six- and seven-membered rings to be relatively small. Stereoisomerides exhibit a marked difference in reactivity, and the insertion of substituted groups in the substance under investigation also has a pronounced effect. The equilibrium constants of a number of these reactions have also been determined, but although the results were satisfactory the method is laborious, and the values obtained are affected by factors which have little influence on the value of L . The method as described is accordingly recommended for use in determining the configuration of polyhydroxy-compounds, as it requires only simple apparatus, and it is easy to determine if a reaction has taken place, L then giving a measure of its relative extent. H. F. HARWOOD.

Iron cacodylate and the determination of cacodylic acid. O. J. NOSKOWA and V. A. TERECHINA (Arch. Pharm., 1928, 266, 599—602).—Pure ferric cacodylate was obtained by treating dialysed ferric hydroxide with six equivalents of cacodylic acid, evaporating to dryness at 50°, and extracting unchanged acid with chloroform. Numerous attempts to prepare this compound in a more direct way afforded only basic salts. Arsenic was determined satisfactorily by the method described by Rupp and Siebler (B., 1924, 614) after conversion into arsenic trisulphide and arsenic acid. Cacodylic acid is not removed quantitatively from toxicological specimens by extraction with chloroform-alcohol mixtures.

S. COFFEY.

Organic salts of telluric acid. F. R. GREENBAUM (Amer. J. Pharm., 1928, 100, 630—635).—The following salts of telluric acid are described: *hexamethylenetetramine*, $(CH_2)_6N_4 \cdot H_2TeO_4 \cdot 4H_2O$; *carbamide*, $CON_2H_4 \cdot H_2TeO_4 \cdot 0.5H_2O$; *thiocarbamide*, $CSN_2H_4 \cdot 4H_2TeO_4$; *piperazine*, $C_4H_{10}N_2 \cdot 2H_2TeO_4 \cdot 4H_2O$. The first two salts are soluble in water, the others in alkali only. H. BURTON.

Nomenclature of parent ring systems. A. M. PATTERSON (J. Amer. Chem. Soc., 1928, 50, 3074—

3087; cf. A., 1925, i, 824).—Existing systems of nomenclature are reviewed and the general principles involved in the framing of a logical and comprehensive system are discussed. Additional methods of naming the more complicated ring systems are proposed, for details of which the original should be consulted.

H. E. F. NOTTON.

Highly-polymerised compounds. XIV. Constitution of dicyclopentadienes. H. STAUDINGER (Annalen, 1928, 467, 73—75).—A theoretical introduction (polemical against Diels and Alder, A., 1928, 1018) to the following abstract. J. W. BAKER.

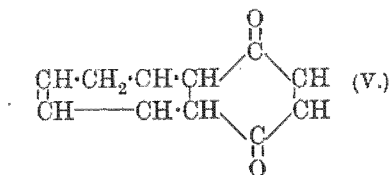
Constitution of dicyclopentadienes. F. BERGEL and E. WIDMANN (Annalen, 1928, 476, 76—91).—Evidence is adduced which is considered to render untenable the structures suggested by Diels and Alder (A., 1928, 1018) for dicyclopentadiene derivatives, and to confirm the 1:2-addition structures suggested by Staudinger (A., 1926, 719). The inter-conversion of the two isomeric acids,

$CH_2=CH \cdot CH \cdot CO_2H$ (I) 1 200° (decomp.),
 $CH_2 \cdot CH_2 \cdot CH \cdot CH \cdot CH_2 \cdot CO_2H$ (II) m. p. 133.5°, obtained by the oxidation of ketotetrahydrodicyclopentadiene and dihydrodicyclopentadiene glycol respectively with nitric acid (Wieland and Bergel, A., 1926, 56), has been investigated by the method of Hückel and Goth (A., 1925, i, 402). Diazomethane converts I into its *dimethyl* ester, m. p. 72.5—73°, which hydrolysis with methyl-alcoholic sodium methoxide yields a product, m. p. 170°, from which light petroleum (b. p. 90—115°) extracts an acid identical with II, leaving an acid, m. p. 178°, the *methyl* ester, b. p. 120°/15 mm., of which yields only resinous acids by a repetition of the hydrolysis. When similarly treated, II (best prepared in 70—80% yield by oxidation of dihydrodicyclopentadiene with a slight excess of potassium permanganate in acetone) yields an oily *dimethyl* ester, b. p. 134°/13 mm., which with sodium methoxide yields only an unidentified substance, m. p. 110°. Oxidation of ketotetrahydrodicyclopentadiene with potassium permanganate in aqueous-alkaline suspension, instead of with nitric acid, yields an acid, m. p. 232° (not identical with I or II), the *dimethyl* ester, m. p. 77.5—78°, of which by hydrolytic rearrangement yields the acid of m. p. 178°. Mild hydration by boiling with very dilute hydrochloric acid converts tetrahydrodicyclopentadiene dioxide into the hygroscopic, syrupy *glycol*,

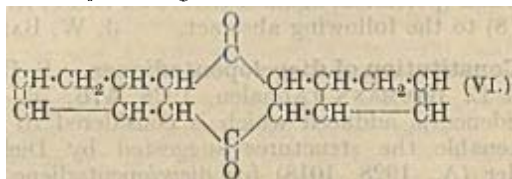
$CH(OH) \cdot CH_2 \cdot CH \cdot CH \cdot CH_2 \cdot CH \cdot OH$ (III), d *keto*-
 $CH(OH) \cdot CH \cdot CH \cdot CH \cdot CH \cdot OH$ (IV) Oxidation of
 $CH(OH) \cdot CH \cdot CH \cdot CH \cdot CH \cdot OH$ (IV) Oxidation of

these products and their parent substances under various conditions yields amorphous acids the composition of which agrees moderately well with that of the expected tetracarboxylic acid. Catalytic reduction (platinum oxide in chloroform) of the mono- and di-cyclopentadienebenzoquinones V and VI (Diels and others, *loc. cit.*; cf. Albrecht, A., 1906, i,

674) yields the corresponding *tetrahydro*-derivatives, m. p. 246° and 251° [without decomp.; Diels (*loc. cit.*)



gives m. p. 239—243° (decomp.), respectively. Since V readily undergoes fission into its components



by heating above its m. p. the formulæ proposed by Diels are rejected and the structures given above suggested.

J. W. BAKER.

X-Ray investigation of polymerised cyclopentadienes. J. HENGSTENBERG (*Annalen*, 1928, 467, 91—94).—Debye-Scherrer diagrams of tri-, tetra-, and poly-cyclopentadienes have been obtained and the distances between the planes for about 9 lines are tabulated. In every case the distance between the strongest reflecting planes is the same (5.3 Å.). The largest values for tri- and tetra-cyclopentadienes are 7.7 and 10.5 Å., respectively, the difference, 2.8 Å., being the size of the cyclopentadiene ring without double linkings, whence the value 2.45 Å. is obtained for each of the other rings. By sublimation of tetracyclopentadiene small (0.1 mm.) laminae are obtained from which by X-ray and optical examination it is deduced that the crystal is orthorhombic and either hexagonal or pseudo-hexagonal. With an assumed unit cell and the known density, 1.23 g./c.c., it is found that the unit cell contains 2 molecules. Thus, although the tri-, tetra-, and poly-cyclopentadienes have different lattices, the molecules are all the same size (2.8 Å.) in one direction, in agreement with the structures suggested by Staudinger.

J. W. BAKER.

Chromium powder in organic synthesis. S. N. CHAKRABARTY and S. DUTT (*J. Indian Chem. Soc.*, 1928, 5, 513—518).—A 42% yield of diphenylmethane is obtained when a mixture of benzene, benzyl chloride, and chromium powder is heated for 3—4 hrs. The chromium powder can be used in typical Ullmann and Friedel-Crafts reactions, but only with reactive chloro-compounds. It cannot be employed in the Reformatsky reaction, and it has no effect on bromo- or iodo-compounds. Freshly-powdered chromium is more reactive than an old specimen, but reactivation is effected to a certain extent by heating it in a current of pure, dry hydrogen to a red heat.

H. BURTON.

Titanium tetrachloride in organic synthesis. G. L. STADNIKOV and L. J. KASCHTANOV (*J. Russ. Phys. Chem. Soc.*, 1927, 60, 1117—1122).—Benzene does not react with titanium tetrachloride even at the b. p., but reacts with ethers and esters, both aliphatic

and aromatic. With benzyl ethyl ether, diphenylmethane, m. p. 25—26°, b. p. 259—261°, *p*-dibenzylbenzene, m. p. 85—86°, and *m*-dibenzylbenzene, m. p. 58—59°, were obtained. Oxidation with chromic anhydride yielded the corresponding diketones, m. p. 159.5—160° and 99°. Benzyl chloride gave the same products, the reactions going to completion in both cases. With benzoyl chloride and subsequent treatment with alkali, a quantitative yield of benzoic acid only was obtained, the benzene distilling over unchanged. If thiophen was added, however, a yield of benzothiophenone, m. p. 55—56° (oxime, m. p. 90—91°), was obtained. Diisoamyl ether did not react, whilst isoamyl acetate and isoamyl benzoate were hydrolysed to a slight extent.

M. ZVEGINTZOV.

Benzene theory. H. LOEWEN (*Z. Elektrochem.*, 1928, 34, 760—768).—Theoretical. It is considered that the most satisfactory benzene model is one in which six tetrahedra are grouped round a point in a plane, so that the apices of the tetrahedra lie alternately above and below the plane. This model will not explain the facts of enantiomorphism, but in all other respects is held to be in excellent agreement with the physical and chemical properties of benzene and the aromatic compounds. L. L. BIRCHMISHAW.

3 : 4-Dichloronitrobenzene. J. McMASTER and A. C. MAGILL (*J. Amer. Chem. Soc.*, 1928, 50, 3038—3041).—3 : 4-Dichloronitrobenzene (cf. Beilstein and Kurbatow, A., 1875, 450) is transformed by heating from 15° to 25° from a solid, m. p. 43°, to a liquid modification, equilibrium mixtures of the two forms being present at intermediate temperatures. It is converted by alcoholic potassium hydroxide into 3 : 3' : 4 : 4'-tetrachloroazoxybenzene and a little 2-chloro-4-nitrophenol and 3 : 4-dichloroaniline. With sodium alkoxides in the boiling alcohols it yields the following ethers of 2-chloro-4-nitrophenol : *ethyl*, m. p. 142°; *isopropyl*, m. p. 128°, and *n-butyl*, m. p. 136°, which have been converted by reduction, diazotisation, and coupling with β -naphthol into red or purple dyes.

H. E. F. NOTTON.

Constitution of the *m*-xylenesulphonic acids. J. POLLAK and F. VON MEISSNER (*Monatsh.*, 1928, 59, 237—250).—Previous work on the *m*-xylene-sulphonic acids is critically reviewed. In combination with the work now described, the results lead to the conclusion that the disulphonic acid (chloride, m. p. varying from 128° to 131°; amide, m. p. 248—249°) obtained by direct sulphonation of *m*-xylene is the 4 : 6-disulphonic acid, whilst the disulphonic acid with a liquid chloride (amide, m. p. 223—224°) which accompanies the former in small quantity in the preparation by certain indirect methods is the 2 : 4-disulphonic acid. The recognition of the true 2 : 4-disulphonic acid has been obscured by its ready transformation during the preparation of the chloride into *m*-xylene-4 : 6-disulphonyl chloride.

The constitution of *m*-xylene-4 : 6-disulphonic acid obtained by Wischin (A., 1891, 73) and, as the chloride, by Pollak and Lustig (A., 1924, i, 30) directly from *m*-xylene, is proved by its preparation from 6-amino-*m*-xylene-4-sulphonic acid by way of the diazo-compound (Pollak and Lustig, *loc. cit.*; Holleman and Choufoer, A., 1924, i, 1071) and also by

the work of Pollak and Schädler (A., 1918, i, 497) and of Pollak and Rudich (A., 1923, i, 27). It is now also confirmed by the formation of 4 : 6-dibromo-*m*-xylene in small quantity by treatment of the acid with bromine in aqueous solution at 60°, and by the failure to brominate the chloride. When *m*-xylene-4 : 6-disulphonyl chloride was treated with bromine in ether at the ordinary temperature, the substance was recovered unchanged, accompanied only by a little 4 : 6-dibromo-*m*-xylene-2-sulphonyl chloride, formed possibly by displacement and migration of the sulphonic acid group, or, more probably, derived from *m*-xylene-2-sulphonyl chloride present as an impurity. Wischin's proof (*loc. cit.*) of the constitution by conversion into 2 : 4-dichloro- and 2 : 4-dihydroxy-*m*-xylene is vitiated by the drastic nature of the reactions. The preparation of the same acid by Pfannenstill (Diss., Lund, 1894) from both *m*-xylene-2- and *m*-xylene-4-sulphonic acid is to be explained by migration of the sulphonic acid group in the former case. The possibility of such a migration, already demonstrated by Moody (Proc. C.S., 1888, 77), is now confirmed by the separation of *m*-xylene-4-sulphonamide, m. p. 136—137°, as a by-product in the preparation of *m*-xylene-2-sulphonamide, m. p. 112—113°, through the chloride, from the 2-sulphonic acid, even when the latter has been regenerated from the purified amide. *m*-Xylene-2-sulphonic acid, of the constitution of which there is no doubt (cf. Moody, *loc. cit.*), was prepared by debromination of 4 : 6-dibromo-*m*-xylene-2-sulphonic acid (Jacobsen and Weinberg, A., 1879, 61). It was also separated from the mother-liquors of the 4-sulphonic acid prepared by sulphonation of *m*-xylene by concentrated sulphuric acid at the ordinary temperature (Pollak and Lustig, *loc. cit.*). Further, Pfannenstill's liquid "2 : 5-disulphonyl chloride" (obtained solid, m. p. 85°, with difficulty) must be the 2 : 4-derivative, whilst his conclusion that the disulphonic acid which he prepared by way of the 6-amino-4-sulphonic acid was a new acid appears to be erroneous, since his supposed two series of compounds correspond closely in their properties, and he observed no mixed m. p. Wischin's preparation of a disulphonic acid by sulphonation of 6-bromo-*m*-xylene and debromination was examined. 6-Bromo-*m*-xylene-2 : 4-disulphonic acid yielded 6-bromo-*m*-xylene (characterised as the 4-sulphonyl chloride) when heated with hydrochloric acid at 150°, and, therefore, no migration has occurred in the first reaction. Debromination yielded a material which gave a mixture of solid 4 : 6- and liquid 2 : 4-disulphonyl chlorides, which were separated and converted into the amides. *m*-Xylene-2 : 4-disulphonyl chloride was prepared in best yield by treatment of sodium *m*-xylene-2-sulphonate with chlorosulphonic acid at 80—90° for 4 hrs., and elimination of the 4 : 6-derivative by crystallisation from ether. Reaction at 150° yielded the 4 : 6-derivative only. The 2 : 4-disulphonyl chloride yielded an amide, m. p. 223—224°, and its constitution was proved by converting it into 2 : 4-dibromo-*m*-xylene by bromination of the acid in aqueous solution at 70—80°. The occurrence of migration during preparation of the chloride was confirmed by treating the acid obtained from the

pure 2 : 4-disulphonamide with phosphorus pentachloride. Fractionation of the product yielded the 4 : 6-disulphonyl chloride. R. K. CALLOW.

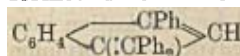
So-called "liquid distyrene." R. STOERMER and H. KOOTZ (Ber., 1928, 61, [B], 2330—2336).—Benzylacetone, b. p. 235—236°, conveniently prepared by reduction of styryl methyl ketone by hydrogen in presence of palladised calcium carbonate, is converted by magnesium phenyl bromide into $\alpha\gamma$ -diphenyl-*n*-butan- γ -ol, b. p. 180—190°/12 mm., converted by boiling 20% sulphuric acid into $\alpha\gamma$ -diphenyl- Δ^2 -butene, b. p. 169—170°/12 mm., d_4^{20} 1.0149 [nitroschloride, m. p. about 126° (decomp.)]. The hydrocarbon is transformed by ozonisation into acetophenone and phenylacetaldehyde; with bromine it vigorously evolves hydrogen bromide, leaving only non-crystalline products. It is not isomerised by exposure to the light of a mercury-vapour lamp.

Treatment of a preserved specimen of "liquid distyrene" which had yielded two dibromides, m. p. 102° and 129°, respectively (Stoermer and Thier, A., 1926, 160), yielded acetophenone and phenylacetaldehyde, showing that the double linking had become displaced from the α - to the β -position. The supposition that the change is due to traces of sulphuric acid not removed from the product is in harmony with the observation that protracted treatment of cinnamic acid with boiling, moderately dilute sulphuric acid gives a similar hydrocarbon which, like the preserved specimen, does not give a solid dibromide, but vigorously evolves hydrogen bromide when treated with bromine. The same isomerisation is observed when pure "distyrene" (which yields a crystalline bromide), dissolved in carbon disulphide containing a trace of iodine, is exposed to sunlight. The pure distyrene is transformed by ozonisation into benzoic acid and β -phenylpropaldehyde and is therefore $\alpha\gamma$ -diphenyl- Δ^2 -butene. Careful bromination of the latter hydrocarbon affords a new dibromide, C₁₈H₁₆Br₂, m. p. 79°, in addition to the dibromides, m. p. 102° and 129°, described previously. Since $\alpha\beta$ -dibromo- $\alpha\gamma$ -diphenylbutane contains three asymmetric carbon atoms, its existence in four racemic forms is to be presumed, but only indications of the fourth isomeride are observed. The dibromide, m. p. 102°, is separated by crystallisation from light petroleum (instead of alcohol) into the dibromide, m. p. 129°, and a new dibromide, m. p. 122°, so that the compound of m. p. 102° should be deleted from the literature. Debromination of the three dibromides with zinc affords in each case an unsaturated hydrocarbon of constant b. p. which is ozonised to benzaldehyde and β -phenylpropaldehyde and yields all three dibromides with bromine without evolution of hydrogen bromide. It appears that previous investigators have invariably used a distyrene contaminated with $\alpha\gamma$ -diphenyl- Δ^2 -butene. Pure distyrene is colourless and non-fluorescent.

H. WREN.

Action of hydrogen iodide on tetraphenylbutinenediol. J. SALKIND and A. KRUGLOV (Ber., 1928, 61, [B], 2306—2312; cf. A., 1926, 1121).— $\alpha\alpha\beta\beta$ -Tetraphenyl- Δ^2 -butinene- $\alpha\beta$ -diol is converted by hot aqueous hydriodic acid (10—12%) mainly into

the corresponding iodo-oxide, 3-iodo-2:2:5:5-tetra-phenyl-2:5-dihydrofuran, m. p. 139—140°, which does not contain a hydroxyl group and is oxidised by permanganate in acetone to benzophenone, carbon dioxide, and benzoic acid. In addition, $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\beta\gamma}$ -butatriene, m. p. 235°, is obtained in small amount; the hydrocarbon is the main product when the glycol or furan is treated with a saturated solution of hydrogen iodide in water or acetic acid at 0°. It is oxidised to benzophenone and carbon dioxide and reduced to $\alpha\alpha\delta\delta$ -tetraphenyl-*n*-butane (cf. Brand, A., 1921, i, 783). Under more drastic conditions, the glycol, furan, or hydrocarbon is transformed into 1:10:10-triphenylbenzofulvene,

], m. p. 204—205° (cf. Brand, *loc. cit.*), oxidised to benzophenone and *o*-benzoylbenzoic acid, and reduced in presence of spongy platinum to 1-phenyl-3-diphenylmethylidihydroindene, m. p. 135° (probably accompanied by a second form, m. p. 107°). Production of the fulvene is frequently accompanied by that of $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\beta\gamma}$ -butadiene.

H. WREN.

1-Chloronaphthalene. III. Sulphonation. P. FERRERO and G. BOLLINGER (Helv. Chim. Acta, 1928, 11, 1144—1151).—A detailed investigation has been made of the sulphonation of 1-chloronaphthalene by concentrated sulphuric acid at 20—160°. 1-Chloronaphthalene-4-sulphonic acid is formed in all cases with a maximum yield of 70% at 56°, using 2 parts of concentrated acid and a small amount of sulphuric acid monohydrate. No 1-chloronaphthalene-5-sulphonic acid was isolated in any experiment (cf. Armstrong and Wynne, Proc. C.S., 1890, 86), but at 160° some 1-chloronaphthalene-6-sulphonic acid was produced. In the experiments at 20—100° a small amount of an impure, apparently new chloronaphthalenesulphonic acid was isolated from the concentrated mother-liquors as its potassium salt. With chlorosulphonic acid at 30° 1-chloronaphthalene-4-sulphonyl chloride, m. p. 94°, is obtained (cf. Armstrong and Williamson, *ibid.*, 1886, 233; 1887, 145).

Numerous salts of 1-chloronaphthalene-4- and -5-sulphonic acids have been prepared, and the solubilities in water at 18° and 98° determined for the sodium, potassium, calcium, barium, and lead salt.

H. BURTON.

Electrochemical oxidation of α -methylnaphthalene. F. FICHTER and S. HERSZBEIN (Helv. Chim. Acta, 1928, 11, 1264—1267).—Oxidation of 1-methylnaphthalene in presence of acetone and dilute sulphuric acid at a lead anode at 20° and a current density of 0.018 amp./cm.² gives, in addition to unchanged material (38.7%), resinous products (36.6%) and crystalline material (10.5%). This last fraction when crystallised from acetone affords 4:4'-dimethyl-1:1'-dinaphthyl, m. p. 147°, which on nitration yields a mixture of dinitro-derivatives and on bromination gives a dibromo-derivative, m. p. 243°.

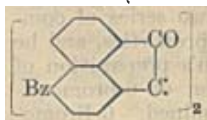
H. BURTON.

peri-Dibenzyl-naphthalene and two isomerides. K. DZIEWONSKI and J. MOSZEW (Bull. Acad. Polonaise, 1928, A, 283—291).—The action of benzyl chloride on naphthalene in presence of zinc chloride

at 100—120° gives, in addition to monobenzyl-naphthalenes (Roux, A., 1888, 1305; Dzeworski and Dziecielewski, A., 1928, 405), a viscous liquid from which have been isolated by fractional distillation 1:8-dibenzyl-naphthalene (I), m. p. 146.5° (cf. Boguski, A., 1906, i, 825), " β "-dibenzyl-naphthalene, m. p. 88° (*picrate*, m. p. 107°), and " γ "-dibenzyl-naphthalene, m. p. 132°. Benzyl chloride and 1-benzyl-naphthalene in presence of aluminium chloride at 100—120° give 15% of I, oxidised by boiling dilute nitric acid to 1:8-dibenzoyl-naphthalene, m. p. 189—190° (*bis-phenylhydrazone*, m. p. 270—271°). Nitration of I in acetic acid solution at 80—90° with a mixture of nitric acid (*d* 1.52) and sulphuric acid monohydrate gives the 4(?)*-nitro*-derivative, m. p. 141°, whilst sulphonation with chlorosulphonic acid in nitrobenzene solution at 100—110° affords 1:8-dibenzyl-naphthalene-4(?)*-sulphonic acid* (sodium salt). When the initial reaction is carried out with an excess of naphthalene in presence of aluminium chloride a considerable amount of 2:2'-dinaphthyl is obtained.

H. BURTON.

Phenyl- α - and - β -acenaphthylmethanes (5- and β -benzylacenaphthenes). K. DZIEWONSKI and K. LEONHARD (Bull. Acad. Polonaise, 1928, A, 99—110).—Benzyl chloride and acenaphthene react in presence of molten zinc chloride (cf. A., 1904, i, 390; 1926, 70), yielding 40% of 5-benzylacenaphthene (I), m. p. 110—111°, together with some β -(3 or 4)-benzylacenaphthene (II), b. p. 260—265°/20 mm., m. p. 45—46° (*dipicrate*, m. p. 101—102°). Oxidation of I with sodium dichromate in boiling acetic acid solution gives 5-benzylacenaphthenequinone, m. p. 170° (*monophenylhydrazone*, m. p. 177—178°), together with 5-benzoylacenaphthenequinone, m. p. 199°, and small amounts of 4-benzyl- and 4-benzoyl-naphthalic acids (*methyl esters*, m. p. 120—121° and 130°, respectively). When the oxidation is carried out first at 40—50°, and then at 100°, a mixture of 5:5'-*di*-benzyl-, m. p. 318—320°, and 5:5'-*di*-benzoyl-*di*-acendione (annexed formula), m. p. 305°, is produced.



Nitration of I with 30% nitric acid at 25—30° affords 6-nitro-5-benzylacenaphthene, m. p. 144°, whilst pyrogenic decomposition gives 5-benzylacenaphthylene, m. p. 104—105°. Oxidation of II with sodium dichromate in boiling acetic acid solution furnishes a benzoyl-naphthalic anhydride, m. p. 199—200° (*phenylhydrazone*, m. p. 248°).

4-Benzoylnaphthalic anhydride (*phenylhydrazone*, m. p. 260°) condenses with resorcinol in presence of zinc chloride at 190°, forming 4-benzoylnaphthylfluorescein, m. p. 160°. 4-Benzoylnaphthalic anhydride *phenylhydrazone* has m. p. 236°.

H. BURTON.

Perylene and its derivatives. XVII. A. ZINKE, A. DADIEU, K. FUNKE, and K. PONGRATZ (Monatsh., 1928, 50, 77—86).—If the products of chlorination of perylene, C₂₀H₁₁Cl₉ and C₂₀H₉Cl₇, previously described (A., 1928, 282) actually had those compositions, then reduction with amalgamated zinc and hydrochloric acid would be expected to yield mono- and tri-chloroperylene, respectively, since the nuclear halogen of 3:9-dichloroperylene is unaffected by this

treatment. Reduction of the product $C_{20}H_{11}Cl_9$ yielded, however, a product which changed in composition on repeated recrystallisation, and was shown, by examination of the absorption spectrum, to consist of a mixture of perylene and 3 : 9-dichloroperylene, and the product $C_{20}H_{11}Cl_9$ is, therefore, probably a mixture of the compounds $C_{20}H_{12}Cl_{10}$ and $C_{20}H_{10}Cl_8$. The product $C_{20}H_9Cl_7$ yielded 3 : 9-dichloroperylene when reduced, and is, similarly, a mixture of the compounds $C_{20}H_8Cl_8$ and $C_{20}H_{10}Cl_6$.

The products of bromination of perylene (cf. A., 1925, i, 383) were further investigated. An attempt to prepare 3 : 10-dicyanoperylene from the impure 3 : 10-dibromoperylene was unsuccessful. Treatment of the product from the mother-liquors of the dibromocompounds with cuprous cyanide in quinoline yielded impure *tricyanoperylene*, converted into *perylene-tricarboxylic acid* (sodium and pyridinium salts), the silver salt of which yielded with ethyl iodide the triethyl ester, m. p. 252° after sintering. Analogously to 3 : 9-dicyanoperylene (Pongratz, A., 1928, 177), tricyanoperylene yielded with hot concentrated sulphuric acid deep red crystals of 9 : 10-anhydroadicarbonylperylene-4-sulphon-3-carboxylimide.

R. K. CALLOW.

Fluosilicates of organic bases. C. A. JACOBSON and H. A. H. PRAY (J. Amer. Chem. Soc., 1928, 50, 3055—3058).—Aniline and fluosilicic acid in alcohol yield *aniline fluosilicate*, $(NH_2Ph)_2H_2SiF_6$, which, when heated, sublimes and decomposes liberating silicon tetrafluoride. The characteristically crystalline *methylaniline*, *o-toluidine*, *m-toluidine*, and *p-toluidine fluosilicates* are prepared similarly.

H. E. F. NOTTON.

Chlorination of anilides. V. Significance of velocity measurements in relation to the problem of benzene substitution. A. E. BRADFELD and B. JONES.—See this vol., 34.

Nitration of o-bromoacetanilide. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1928, 3092—3093).—Contrary to the statement of Franzen and Engel (A., 1921, i, 713), it is found that both mononitration products of *o-bromoacetanilide* are soluble in aqueous-alcoholic potassium hydroxide; the 2-bromo-4-nitroacetanilide is, however, more easily hydrolysed and 2-bromo-4-nitroaniline separates on keeping. Treatment of the filtrate with glacial acetic acid gave 2-bromo-6-nitroacetanilide, from which 2-bromo-6-nitroaniline, m. p. 74—75°, is obtained by hydrolysis with alcoholic hydrochloric acid. 2-Bromo-4-nitroaniline yields 2-bromo-4-nitroacetanilide, m. p. 132—133°, with acetyl chloride and acetic acid (cf. Chatterway, Orton, and Evans, A., 1901, i, 23; Korner, Atti R. Accad. Lincei, 1914, 22, i, 825). A. I. VOGEL.

Pentanitroaniline. B. FLURSCHEIM and E. L. HOLMES (J.C.S., 1928, 3041—3046).—Nitration of 3 : 5-dinitroaniline or of 3 : 5-dinitroacetanilide with a mixture of sulphuric and nitric acids yields *pentanitroaniline* containing 1 mol. of benzene of crystallisation, which is lost on exposure in a vacuum at the ordinary temperature to give *pentanitroaniline*, m. p. 192° (decomp.). The latter reacts with aqueous sodium acetate and acetone or with saturated sodium carbonate solution forming 2 : 4 : 6-trinitro-5-amino-

resorcinol, m. p. 236—237° (decomp.), which affords 2 : 4 : 6-trinitrophloroglucinol, m. p. 167°, with aqueous potassium hydroxide, whilst methyl and ethyl alcohol yield, respectively, 2 : 4 : 6-trinitro-5-aminoresorcinol dimethyl, m. p. 127·5°, and diethyl ether, m. p. 127·25—127·75°. With aqueous ammonia pentanitroaniline yields 2 : 4 : 6-trinitro-1 : 3 : 5-triaminobenzene, m. p. above 300°. A *tetranitrodiaacetamidophenol*, $C_{10}H_7O_{11}N_5$, m. p. 147—147·5°, was produced on acetylation with acetic anhydride and a little sulphuric acid. These reactions prove that all the nitro-groups are in the nucleus. Tetranitroaniline is converted into *tetranitroacetanilide*, m. p. 169°, on acetylation under similar conditions. A. I. VOGEL.

Interaction of chlorosulphonic acid with substituted cyanoacetamides. K. G. NAIK and M. B. AMIN (J. Indian Chem. Soc., 1928, 5, 579—583).—When cyanoacetanilide is treated with chlorosulphonic acid in presence of salicylide-chloroform (Anschütz, A., 1893, i, 121), *cyanoacetanilide- α -disulphonic acid* ($+4H_2O$), $CN \cdot C(SO_3H)_2 \cdot CO \cdot NHPh$, (I), is produced. *Cyanoacet-p-toluidide*- $(2H_2O)$, *-o-toluidide*- $(2H_2O)$, *-m-toluidide*- $(2H_2O)$, *- α -naphthylamide*- (H_2O) , *- β -naphthylamide*- (H_2O) , *-benzylamide*- $(2H_2O)$, and *-xylylide*- $(2H_2O)$, *- α -disulphonic acids* are prepared similarly. These compounds have no definite m. p. but char at about 260—280°. Treatment of I with bromine causes replacement of both sulphonic acid groups by the halogen. Cyanoacetamide does not react with chlorosulphonic acid, and the rate of sulphonation of the substituted cyanoacetamides appears to depend on the electronegative character of the groups attached to the methylene carbon atom.

H. BURTON.

Absorption spectra of thiocarbamides. Constitution of thiocarbamide. H. RIVIER and J. BOREL (Helv. Chim. Acta, 1928, 11, 1219—1228).—Absorption spectra of 0·1—0·0001M aqueous and alcoholic solutions of thiocarbamide, trimethyl-, *s*- and *iso*-tetramethyl-, *s*-diphenyldimethyl-, *isodiphenyldimethyl*-, b. p. 175°/0·5 mm., m. p. 30° (*picrate*, m. p. 131°; from methyl iodide and methylthiocarbamide), *s*-tetraphenyl-, *isotetraphenyl*-thiocarbamides, m. p. 70° (lit. 185°), and *s*- and *iso*-pentamethylthiobiurets have been measured between 232 and 580 μ . The *s*-derivatives show more marked absorption than the *iso*-derivatives, but the curves for thiocarbamide, trimethyl- and *isotetramethyl*-thiocarbamides are almost identical. It is concluded that thiocarbamide does not contain the C:S group, and Werner's internal salt formula is favoured. It is possible that thiocarbamide exists in a different form in solution from that in the crystal (cf. Demény and Nitta, A., 1928, 819).

H. BURTON.

Preparation and rearrangement of methylbenzhydryldichloroamine. A. McN. NEFF (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 141—149).—Hydrolysis of the product of heating methylbenzhydryldichloroamine with soda-lime at 200° afforded ammonia, aniline, and benzophenone, but not methylamine. Rearrangement experiments carried out below 150° indicate that the phenyl group is more easily removed from the $CMePh_2$

radical than the methyl group. An explanation is offered.

CHEMICAL ABSTRACTS.

Preparation, rearrangement, and reduction of β -methylbenzhydrylhydroxylamine. M. E. MAVER (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 111—116).—Methylbenzhydrylhydroxylamine, m. p. 112—113° (hydrochloride, m. p. 196°; chloroplatinate, decomp. 165°; benzoyl derivative, m. p. 183°), when heated with soda-lime at 230—250°, followed by hydrolysis, affords benzophenone and methylamine. It is concluded that only the methyl group migrated, a result which is not in accord with Neff's views (preceding abstract).

CHEMICAL ABSTRACTS.

Rearrangement of stereoisomeric hydrazones. J. XANTHOPOULOS (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 195—201).—Isomeric *p*-bromobenzophenonehydrazones, α , m. p. 166—167°, β , m. p. 102.5—103.5°, were separated by means of chloroform and petroleum. The ketazine was obtained as by-product. Isomeric *p*-chlorobenzophenonehydrazones, α , m. p. 154—155°, β , m. p. 105—106°, were separated by means of methyl alcohol, which dissolves the latter. The rearrangement of the four compounds when heated with zinc chloride was studied quantitatively; differences are due to the structural influence of the stereoisomerides. Two reactions are involved: $\text{CRR}'\cdot\text{N}\cdot\text{NH}_2 = \text{CR}:\text{N} + \text{NH}_2\text{R}'$; $\text{CRR}'\cdot\text{N}\cdot\text{NH}_2 = \text{CR}'\cdot\text{N} + \text{NH}_2\text{R}$.

CHEMICAL ABSTRACTS.

Substitution products of azobenzene. J. BURNS, H. McCOMBIE, and H. A. SCARBOROUGH (J.C.S., 1928, 2928—2936).—Nitration of 4-methylazobenzene, m. p. 72° (this and all other azobenzenes described in this paper were prepared by the condensation of nitrosobenzene with the appropriate amine), gives 4'-nitro-4-methylazobenzene, m. p. 183°; 3-methylazobenzene, b. p. 165°/15 mm., m. p. 18°, gives 4:4'-dinitro-3-methylazobenzene, m. p. 183°; and 2-methylazobenzene, b. p. 180°/20 mm., yields 4:4'-dinitro-2-methylazobenzene, m. p. 220°. Bromination of 4-methylazobenzene yields 4'-bromo-4-methylazobenzene, m. p. 152°, and 3-methylazobenzene affords 4-bromo-3-methylazobenzene, m. p. 69°, but 2-methylazobenzene yields a substance, $\text{C}_{13}\text{H}_9\text{NBr}_3$ (?), m. p. 210°, which is not an azo-derivative. Nitration, chlorination, and bromination of 4-chloroazobenzene, m. p. 92°, yield respectively 4-chloro-4'-nitroazobenzene, m. p. 169°, 4:4'-dichloroazobenzene, m. p. 188° (lit. 184°), and 4-chloro-4'-bromoazobenzene, m. p. 195°, whilst nitration and bromination of 3-chloroazobenzene, m. p. 68°, give 3-chloro-4'-nitroazobenzene, m. p. 129°, and 3-chloro-4'-bromoazobenzene, m. p. 128°. 4-Methoxyazobenzene, m. p. 64°, when chlorinated, gives 3:5-dichloro-4-methoxyazobenzene, m. p. 98°, whilst regulated bromination led to 3-bromo-4-methoxyazobenzene, m. p. 78°, and 3:4':5-tribromo-4-methoxyazobenzene, m. p. 130°; nitration yielded 3:4'-dinitro-4-methoxyazobenzene, m. p. 190°. Chlorination of 4-acetamidoazobenzene, m. p. 144°, gave 3-chloro-4-acetamidoazobenzene, m. p. 134° (3-chloro-4-aminoazobenzene, m. p. 99.5°), but attempts to introduce other substituents into the molecule failed. Bromination of 4-aminoazobenzene gave 3:5-di-

bromo-4-aminoazobenzene, m. p. 168°, but iodination and nitration were unsuccessful. The following are described: 4-bromomethylazobenzene, m. p. 115°, 4:4'-dichloroazobenzene, m. p. 157°; 2-bromo-4-nitroanisole, m. p. 108°; 3:5-dichloro-4-hydroxyazobenzene, m. p. 116°; 2-chlorobenzidine, m. p. 113°; 3:5-dibromoazobenzene, m. p. 104°; 3:5-dibromohydrazobenzene, m. p. 114°; 2:6-dibromobenzidine, m. p. 185°.

A. I. VOGEL.

Coupling reactions. J. POLLAK and E. GEBAUER-FÜLNEGG (Monatsh., 1928, 50, 310—323).—Previous work on the coupling of diazonium compounds with *o*-substituted phenols, particularly 1-substituted β -naphthols, is reviewed.

[With W. SPECHT and K. WINTER.]—Contrary to the statement of Wahl and Lantz (A., 1923, i, 209) and of Rowe and collaborators (A., 1926, 625), the coupling of diazotised *p*-nitroaniline with 1-bromo- or 1-chloro- β -naphthol does not immediately produce Para-red by displacement of the halogen atom. The substances formed are brown in colour and contain 85—90% of the amount of halogen calculated for the formula $\text{C}_{10}\text{H}_7\text{O}_2\text{N}_2\text{X}$ (X=Br or Cl). The substances may be formed on cotton by the usual method, and the brown shades produced are stable except to alkali. The substances are decomposed when recrystallisation is attempted, and Para-red is probably separated ultimately. Similar results are obtained with 1:6-dibromo- β -naphthol (on cotton only), 1-bromo-2-hydroxy-3-naphthoic acid, and 1-bromo-2-hydroxy-3-naphthanilide, m. p. 164° (prepared by bromination of 2-hydroxy-3-naphthanilide in acetic acid). The constitution of these products is uncertain, but it is possible that both diazo-oxides and β -naphthaquinone derivatives (Rowe, *loc. cit.*) are formed. 1-Nitro- β -naphthol yields an unstable product which decomposes at the ordinary temperature. No coupling takes place with nitroso- β -naphthol. 1-Methyl- β -naphthol couples readily (cf. Rowe, *loc. cit.*). 2:2'-Dihydroxy-1:1'-dinaphthylmethane couples slowly with diazotised *o*-nitroaniline on cotton, giving a shade different from Para-red. In this and other cases the "abnormal" product of coupling seems to be stabilised on the fibre.

[With R. MICHEL and P. POLLAK.]—Diazotised amines couple with thiol derivatives to form unstable diazo-sulphides, e.g., $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{S}\cdot\text{R}$, exclusively. These substances lose their diazo-nitrogen completely on attempting to recrystallise them, but are stabilised on the fibre. The diazo-sulphides obtained by coupling diazotised *o*-nitroaniline, aniline, and sulphanilic acid with dithioresorcinol, and diazotised *p*-nitroaniline with 2:4-dithiolphenol, 4:6-dithiol-*m*-cresol, 2-thiolnaphthalene, and 1:5-dithiolnaphthalene are described.

[With P. POLLAK and F. BECKER.]—1:5-Dithiolnaphthalene, m. p. 119° (Braun and Ebert, A., 1892, 1471, give 103°), is prepared by reduction of naphthalene-1:5-disulphonyl chloride by zinc dust and sulphuric acid, and separated by steam-distillation. The acetyl derivative, m. p. 187—189°, is obtained directly or by heating the disulphonyl chloride with zinc dust, acetic acid, acetic anhydride, and sodium acetate. The dibenzoyl derivative, m. p.

232°, and the *dimethyl ether*, m. p. 150°, are described.

R. K. CALLOW.

Compounds of arylenediamines [with zinc chloride etc.]. IMPERIAL CHEM. INDUSTRIES and A. RILEY.—Sec B., 1928, 886.

Alkaline fusion of anthracenemonosulphonic acids. P. FERRERO and A. CONZETTI (Helv. Chim. Acta, 1928, 11, 1152—1159).—Anthracene- α - and - β -sulphonic acids are obtained in 85% yield by reducing the anthraquinonesulphonic acids with zinc dust and ammonia. α -Anthrol is best obtained by fusing an alkali anthracenesulphonate with 3 parts of potassium hydroxide at 270° for 3 hrs. in a silver crucible (90% yield), or with 1 part of potassium or sodium hydroxides and 2 parts of water at 230° or 240° in an autoclave for 7 or 10 hrs., respectively. Optimum yields of β -anthrol are obtained with 3 parts of potassium or sodium hydroxides and 3 parts of water at 270° or 290° for 4 or 4.5 hrs. in an autoclave (95% yield), respectively.

H. BURTON.

Organic acids and bases in non-aqueous solutions. IV. Phenols and amines. F. HOLZL [with P. B. FIRCKS and M. MUCHITSCH] (Monatsh., 1928, 50, 291—309; cf. A., 1926, 1206; 1927, 310, 558).—The behaviour of (a) phenol, (b) pyrocatechol, (c) resorcinol, and (d) quinol towards organic bases in absolute alcoholic solution has been examined by conductivity measurements at 25° as in the previous investigations.

All compounds formed are largely dissociated by the action of the solvent, and, whilst the formation of a compound is easily shown, the ratios of the components are frequently determined with difficulty. The occurrence of maximum values of κ and of $\Delta = \kappa - (\kappa_3 + \kappa_\beta - \kappa_a)$ (where κ , κ_3 , κ_β , and κ_a are, respectively, the conductivities of the mixture, phenol, base, and alcohol) must be interpreted with due regard to the greater effect of the more highly dissociated basic component in repressing dissociation of the compound by the solvent, so that maxima corresponding with a compound tend to be displaced towards the basic side.

The compounds formed with (a), (b), (c), and (d) are as follows (A=1 mol. of phenol, B=1 mol. of base): ammonia: with (a), A_2B ; with (b), (c), and (d), AB; ethylamine: with (b), (c), and (d), AB; diethylamine: with (a), A_2B ; with (b), (c), and (d), AB; trimethylamine: with (a), A_2B ; with (b), AB; with (c) and (d), A_2B ; ethylenediamine: with (a), A_2B ; with (b), AB; with (c) and (d), A_2B ; benzylamine: with (a), (b), (c), and (d), AB; aniline: with (a), (b), (c), and (d), AB; *p*-toluidine: with (b), none; with (d), AB; *o*- and *m*-phenylenediamine: with (a), (b), (c), and (d), none; -phenylenediamine: with (a), none; with (b), (c), and (d), AB. The occurrence of other, more highly dissociated, compounds may be assumed in many cases. The exceptional behaviour of trimethylamine with resorcinol and quinol is analogous to the behaviour with dicarboxylic acids.

R. K. CALLOW.

Phenol- and cresol-sulphonyl chlorides. E. RIESZ, F. BERNDT, and G. HITSCHMANN (Monatsh., 1928, 50, 328—334).—The phenol- and cresol-sul-

phonyl chlorides previously prepared (Pollak, Gebauer-Fülneegg, and Riesz, A., 1926, 514) have been converted into sulphonanilides and, by the action of phosphorus pentachloride and a trace of phosphoryl chloride at 120—140°, into the corresponding chlorobenzene- and chlorotoluene-sulphonyl chlorides, with the exception of *p*-cresol-3:5-disulphonyl chloride, which reacts anomalously. Additional proof of the constitution of the phenol- and cresol-sulphonyl chlorides is thus obtained, and, in particular, the alternative formula for the trisulphonyl chlorides, in which the third group is attached to oxygen, already disproved by the preparation of trithiol derivatives (Pollak and Riesz, this vol., 60), is finally ruled out.

Phenol-2:4-disulphonyl chloride yields the *disulphonanilide*, m. p. 205°, and chlorobenzene-2:4-disulphonyl chloride. Phenol-2:4:6-trisulphonyl chloride yields the *trisulphonanilide*, m. p. 247°, and chlorobenzene-2:4:6-trisulphonyl chloride (cf. Davies and Wood, A., 1928, 746). *o*-Cresol-3:5-disulphonyl chloride yields the *disulphonanilide*, m. p. 154°, and 2-chlorotoluene-3:5-disulphonyl chloride, m. p. 78° [disulphonanilide, m. p. 183° (Wynne and Bruce, J.C.S., 1898, 73, 731, give 85° and 183°)]. *m*-Cresol-4:6-disulphonyl chloride yields the *disulphonanilide*, m. p. 185°, and 3-chlorotoluene-4:6-disulphonyl chloride, m. p. 125°. *m*-Cresol-2:4:6-trisulphonyl chloride yields the *trisulphonanilide*, m. p. 235°, and 3-chlorotoluene-2:4:6-trisulphonyl chloride, m. p. 161°. Toluene-3:4-sulphonyl chloride yields, with ammonium carbonate and ammonia, the *disulphonamide*, decomp. 300°, whilst when heated with aniline the sulphonyl ring is opened to give *m*-cresol-4:6-disulphonanilide. *p*-Cresol-3:5-disulphonyl chloride yields the *disulphonanilide*, m. p. 129° (Anschütz and Cürten, A., 1927, 1183, give 231°; cf. following abstract), and, with phosphorus pentachloride, (?) 3:4:5-trichlorobenzylidene chloride, m. p. 196°, which isomerised on keeping to *esopentachlorotoluene*, m. p. 218°.

R. K. CALLOW.

Constitution of cresoldisulphonyl chlorides.

E. RIESZ and F. PILPEL (Monatsh., 1928, 50, 335—340).—The constitutions of the cresoldisulphonyl chlorides previously described (Pollak, Gebauer-Fülneegg, and Riesz, A., 1926, 514; cf. preceding abstract) have now been verified. When *o*-cresol-3:5-disulphonyl chloride is hydrolysed by heating with 30% alcohol and heated with 2*N*-nitric acid, 3:5-dinitro-*o*-cresol is obtained. *m*-Cresol-4:6-disulphonyl chloride under the same conditions yields 2:4:6-trinitro-*m*-cresol, but nitration with fuming nitric acid gives 2-nitro-*m*-cresol-4:6-disulphonyl chloride, m. p. 183° [disulphonanilide, m. p. 212—215° (decomp.)], converted by heating with hydrochloric acid at 160° into 2-nitro-*m*-cresol, b. p. 60—68°/0.5 mm., m. p. 36°. Nitration in the 2-position is explicable only on the assumption that the sulphonyl chloride groups are initially in positions 4 and 6. *p*-Cresol-3:5-disulphonyl chloride yields on hydrolysis the disulphonic acid, m. p. 115° (Anschütz and Cürten, A., 1927, 1183), converted by successive treatment with acetic anhydride and phosphorus

pentachloride into acetyl-*p*-cresol-3:5-disulphonyl chloride, m. p. 121°, and m. p. 116° when mixed with the substance prepared by the method of Anschütz and Hodenius (A., 1918, i, 425) and Anschütz and Cürten (*loc. cit.*). The same acetate is obtained directly from *p*-cresol-3:5-disulphonyl chloride. When heated with aniline it yields *p*-cresol-3:5-disulphonanilide, m. p. 129° (cf. preceding abstract) (acetyl derivative, m. p. 105–110°). The constitution of *p*-cresol-3:5-disulphonyl chloride is sufficiently proved by its conversion into 3:5-dinitro-*p*-cresol by the usual method, and the m. p. 231° observed by Anschütz and Cürten for the disulphonanilide is unexplained.

R. K. CALLOW.

Oxidation products of 4:4'-dichloro-2:2'-dinitrodiphenyl sulphide and disulphide. E. RIESZ [with A. LORENZ, C. MYSCHALOV, and O. STRAKOSCH] (Monatsh., 1928, 50, 263–268).—Oxidation of 4:4'-dichloro-2:2'-dinitrodiphenyl sulphide (Beilstein and Kurbatow, A., 1879, 230) by fuming nitric acid at 150° yielded the *sulphoxide*, m. p. 236°. Further oxidation of the sulphoxide by the same method yielded the sulphone, m. p. 176°, identical with the by-product of oxidation of 4:4'-dichloro-2:2'-dinitrodiphenyl disulphide obtained by Blanksma (A., 1901, i, 460). The low m. p. of the sulphone and its decomposition by alcoholic alkali are anomalous. Treatment of the sulphide with chlorine in chloroform or acetic acid yielded the sulphoxide. Whilst treatment of the disulphide with chlorine in chloroform yields 4-chloro-2-nitro-1-chlorothiobenzene (Zincke, A., 1918, i, 537), in acetic acid 4-chloro-2-nitrophenylsulphonyl chloride (*sulphonanilide*, m. p. 138°; *sulphonamide*, m. p. 164°) was obtained. The reaction of hydrazobenzene with the sulphonyl chloride in equimolecular proportions yielded benzidine hydrochloride, azobenzene, 4-chloro-2-nitrobenzenesulphonic acid, m. p. 108° (lit. 127°), and unchanged sulphonyl chloride. The intermediate formation of a compound of the type $\text{NR}'(\text{SO}_2\text{R})\text{NHR}'$ is assumed in this and the analogous reaction with 4-chloro-2-nitro-1-chlorothiobenzene (Gebauer-Füllnegg and Riesz, A., 1928, 168).

R. K. CALLOW.

cycloHexanediois. I. *cis*- and *trans*-Quinitols. Separation and properties. L. PALFRAY and B. ROTHSTEIN (Bull. Soc. chim., 1928, [iv], 43, 1122–1131).—Separation of the *cis*- and *trans*-quinitols with a mixture of acetone and butyl alcohol gives unsatisfactory results, but separation is readily effected with acetone alone (cf. Willstätter and Lessing, A., 1901, i, 265) using a centrifuge, the *trans*-isomeride separating first. In acetone at 16° the solubility of the *trans*-isomeride is 1.91 g. per 100 c.c., of the *cis*-isomeride, 5.61; in commercial acetone, containing 3% of water, the corresponding values at 17.5° are 2.76 and 5.91. In either case the ratio of the solubilities varies inversely with the temperature and accordingly separation is more efficient at low temperatures. *trans*-Quinitol has m. p. 139° (cf. Baeyer, A., 1894, i, 174), and its *phenylurethane*, m. p. 262°; *cis*-quinitol has m. p. 102° (*cis*-*phenylurethane*, m. p. 188°). Crystallographic measurements are recorded for the four compounds. Mixtures of the quinitols containing 0–64% of the *trans*-isomeride have m. p. between

99.4° and 102°, and such mixtures can be approximately analysed by separation with acetone and m.-p. determinations on the three fractions, referred to the fusion curve. In this way quinitol prepared by Senderens and Aboulenc's method (A., 1922, i, 136) at 133° is found to contain 48–50% of *trans*-isomeride and 53–55% at 200°, temperature thus only slightly affecting the proportion of *trans*-isomeride. It is probable therefore that the quinitol, m. p. 102°, obtained by Sabatier and Mailhe (A., 1908, i, 529) was not the pure *cis*-isomeride but a mixture rich in the *trans*-form.

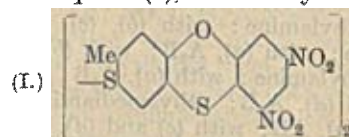
R. BRIGHTMAN.

Aromatic allyl and propenyl compounds. II. Geometrical isomerism of isosafrole. H. I. WATERMAN and R. PRIESTER (Rec. trav. chim., 1928, 47, 1027–1036).—The *cis*(α)-isosafrole obtained by the action of alcoholic potassium hydroxide on safrole (Nagai, A., 1921, i, 857; cf. Hoering and Baum, A., 1909, i, 788) is shown to be a mixture of safrole (43%) and *trans*(β)-isosafrole. The safrole is determined through its mercuriacetate compound, or the mixture is analysed by the authors' iodine addition method (A., 1928, 999).

H. BURTON.

Hydroxythiophenols. I. J. POLLAK and E. RIESZ (Monatsh., 1928, 50, 251–262).—Thiol derivatives of the three cresols and of resorcinol have been prepared by reduction of the corresponding sulphonyl chlorides (A., 1926, 514, 832).

[With R. FERKS.]—*o*-Cresol-3:5-disulphonyl chloride is reduced in acetone solution with zinc and 50% sulphuric acid, and the product, 3:5-dithiol-*o*-cresol, m. p. 51°, separated by steam-distillation. The *tri*-acetyl derivative, an oil, is prepared by combined reduction and acetylation of the disulphonyl chloride by the action of zinc, acetic anhydride, sodium acetate, and acetic acid. The *tribenzoyl* derivative, m. p. 96°, and *dipicryl* derivative, decomp. on heating, were also prepared. The latter yields a *phenoxthene* derivative with alcoholic potassium hydroxide. *m*-Cresol-4:6-disulphonyl chloride yields, similarly, 4:6-dithiol-*m*-cresol, m. p. 69° (derivatives: *tri*-acetyl, m. p. 56°; *tribenzoyl*, m. p. 120°; *dipicryl*, decomp. when heated). In this case treatment of the *dipicryl* derivative with alcoholic potassium hydroxide yields 2:4:2':4'-*tetranitro*-7:7'-*dimethyldibenzophenoxthene*-6:6'-disulphide (I), reduced by sodium sulphide

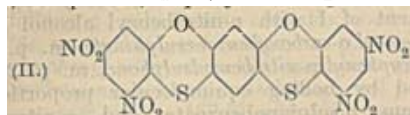


and alkali to a vat which dyes cotton a reddish-brown. *m*-Cresol-2:4:6-trisulphonyl chloride yields 2:4:6-trithiol-*m*-cresol, m. p. 35–36° (*tetra*-acetyl derivative, m. p. 76°).

[With F. PILFEL.]—*p*-Cresol-3:5-disulphonyl chloride yields 3:5-dithiol-*p*-cresol, m. p. 48° (derivatives: *tri*-acetyl, m. p. 98°; *tribenzoyl*, m. p. 138°; *dipicryl*, decomp. 109°; *trimethyl ether*, m. p. 77°; *phenoxthene disulphide*). By condensation with sodium monochloroacetate, 3:5-di(carboxymethylthiol)-*p*-cresol, m. p. 139°, was prepared.

[With W. FRANKFURTHER.]—Resorcinol-4:6-disulphonyl chloride yields 4:6-dithioresorcinol as an

oil, sparingly volatile in steam, isolated as the *lead* salt, $C_6H_4O_2S_3Pb$ [derivatives: tetramethyl ether, m. p. 83—86° (cf. A., 1915, i, 529); *tetra-acetyl*, m. p. 136—138°; *di(carboxymethyl)*, m. p. 174; *tetracarboethoxy*, m. p. 81°; *dipicryl*, decomp. on heating:



phenoxethene derivative (II), decomp. above 280°). Resorcinol-2:4:6-trisulphonyl chloride yields the very readily oxidised 2:4:6-trithiolresorcinol, isolated as the *lead* salt, $(C_6H_3O_2S_3)_2Pb_3$ (*penta-acetyl* derivative, m. p. 105—110°). R. K. CALLOW.

Manufacture of phenylthioglycollic acids containing halogen and alkyl groups in the nucleus. I. G. FARBERIND. A.-G.—See B., 1928, 921.

Mechanism of Salkovsky's colour reaction with cholesterol. V. J. NIKOLAEV and S. A. KRASTELEVSKAJA (J. Russ. Phys. Chem. Soc., 1928, 60, 1211—1216).—Cholesterol in chloroform solution gives with sulphuric acid an orange or red colour, depending on the concentration. When a solution of cholesterol in dry chloroform solution is treated with sulphuric acid and evaporated in a vacuum, ruby-red crystals of *cholesterol sulphate*, m. p. 160°, are obtained. The m.-p. diagrams of the system cholesterol-sulphuric acid also indicated the formation of an equimolecular compound, m. p. 160°. The colour reaction is due to the undissociated red cholesterol sulphate; moisture causes first dissociation into colourless ions, followed by hydrolysis, with fading of the colour, which returns on drying.

M. ZVEGINTZOV.

Yeast ergosterol. III. F. REINDEL (Annalen, 1928, 466, 131—147). [With H. WASENEGGER].—Oxidation of α -ergosterol (A., 1928, 295) in acetic acid solution at 70° with chromic oxide gives α -ergosterone (I), m. p. 131—133°, $[\alpha]_D +38.8^\circ$ in chloroform [*phenylhydrazone*, m. p. 127—128° (decomp.); *oxime*; *ketazine*, m. p. 225° (decomp.); *benzylidene* derivative, m. p. 162°], together with a small amount of a neutral compound, $C_{26}H_{42}O_3$, m. p. 219—221°. Catalytic reduction of I regenerates α -ergosterol [*benzoyl* derivative, m. p. 118—120° (cf. A., 1927, 241)], indicating that the ethylenic linking in I is not $\alpha\beta$ - to the keto-group. When a chloroform solution of I is treated with hydrogen chloride, β -ergosterone, m. p. 149—151°, $[\alpha]_D +37.1^\circ$ in chloroform (*oxime*, m. p. 214—216°), is produced. This ketone does not give a benzylidene derivative, suggesting that isomerisation is of the type $\cdot CO \cdot CH_2 \cdot \dot{C} \cdot CH \cdot \rightarrow \cdot CO \cdot CH \cdot \dot{C} \cdot CH_2 \cdot$.

[With A. DETZEL].—Oxidation of *allo*- α -ergostanol in acetic acid solution at 90° with chromic oxide gives, in addition to *allo*- α -ergostanone (34%), an acid, $C_{25}H_{44}(CO_2H)_2$, m. p. 217—219°, $[\alpha]_D +22.8^\circ$ in chloroform (26%; *methyl* ester, m. p. 81—83°), which when heated at 260—265° yields a cyclic ketone, $C_{26}H_{44}O$, m. p. 125—126°, $[\alpha]_D +107.7^\circ$ in chloroform (*oxime*, m. p. 215—216°). Catalytic reduction of *allo*- α -ergostanone gives *allo*- α -ergostanol together with an isomeric *sterol*, m. p. 206—207°, $[\alpha]_D +4.04^\circ$

in chloroform, not precipitable by digitonin, and having no antirachitic action even when irradiated. The *acetate*, m. p. 144—145°, of this new sterol is not identical with *allo*- α -ergostanyl acetate, m. p. 144—145°.

[With A. FROHLICH].—When a solution of ergosterol in hexahydrotoluene is shaken with potassium permanganate solution at the ordinary temperature, a small amount of an acid, b. p. 187°, resembling *n*-valeric acid, and a neutral compound (II),

$C_{26}H_{42}(or\ 40)O_4$, m. p. 199—201°, $[\alpha]_D -24.4^\circ$ in chloroform (*diacetate*, m. p. 148—152°, $[\alpha]_D +5.46$ in chloroform), are produced. This compound contains three active hydrogen atoms, and when its *di-p-nitrobenzoate*, m. p. 197° (decomp.), is hydrolysed with 5% alcoholic potassium hydroxide a compound (III), $C_{26}H_{40(38)}O_3$, m. p. 217—218°, is obtained. Catalytic reduction of II yields a compound, $C_{26}H_{44(42)}O_3$, m. p. 235—238° [*di-p-nitrobenzoate* m. p. 242° (decomp.)], formed by absorption of 3 mols. of hydrogen and subsequent elimination of water. When III is reduced catalytically 4 mols. of hydrogen are absorbed, and a substance, m. p. 131—132°, results.

Analogous oxidation of ergosteryl acetate gives the substance, $C_{27}H_{41}O_4Ac$, m. p. 174—175°.

H. BURTON.

***p*-Methoxycinnamyl alcohol.** P. KARRER (Helv. Chim. Acta, 1928, 11, 1209).—The alcohol has m. p. 79—80° (cf. A., 1922, i, 825).

H. BURTON.

Thiophenols. XII. Triphenylmethane series. K. BRAND and H. PABST (J. pr. Chem., 1928, [ii], 120, 199—213).—The synthesis of various 2-methoxy-5-chlorotriphenylcarbinols has been effected and the stability of their salts compared with that of the corresponding 2-methoxy-, 2-thiol-, and their 5-chloro-derivatives. 4-Chloro-*o*-anisidine is converted by the appropriate Sandmeyer reaction into 4-chloro-2-bromoanisole (I), m. p. 29—30°, b. p. 127 130/12 mm., $d_4^{20} 1.6170$, $n_D^{20} 1.58592$ (yield 65%), and 4-chloro-2-cyanoanisole, m. p. 99° (yield 60—70%), which is hydrolysed by dilute alcoholic potassium hydroxide to 5-chloro-2-methoxybenzoic acid, the methyl ester (II), b. p. 235—240°, of which is also obtained by the action of methyl sulphate on 5-chlorosalicylic acid. By the action of magnesium 5-chloro-*o*-anisyl bromide (from I) on benzophenone is obtained 5-chloro-2-methoxytriphenylcarbinol, m. p. 124° (yield 50—60%), which is converted by zinc dust and acetic acid or alcohol and anhydrous hydrogen chloride into 5-chloro-2-methoxytriphenylmethane, m. p. 120°. The action of the same Grignard reagent on ethyl benzoate furnishes 5:5'-dichloro-2:2'-dimethoxytriphenylcarbinol, m. p. 190° (yield 60 70%), similarly reduced to 5:5'-dichloro-2:2'-dimethoxytriphenylmethane, m. p. 144—145°, whilst from II is obtained 5:5':5''-trichloro-2:2':2''-trimethoxytriphenylcarbinol, m. p. 165°, converted into the corresponding methane, m. p. 212°. The colours of these carbinols and of the corresponding 2-methoxy-, 2-methylthiol, and their 5-chloro-derivatives in a mixture of acetic and sulphuric acids and in liquid sulphur dioxide are tabulated, and the stability of the various carbonium sulphates and perchlorates is

determined by the method of Baeyer and Villiger (A., 1902, i, 769). The stability of the 2-methoxy-triphenylcarbonium salts to hydrolysis is greater, but that of the 5-chloro-2-methoxy-derivatives is less, than that of the parent triphenylcarbonium salts. In general the introduction of a methoxy- (and, to a smaller extent, a methylthiol) group in the 2-position increases the stability, whilst the presence of chlorine in the 5-positions decreases it to a value less than that of the unsubstituted derivatives themselves, with the exception that the 5:5'-dichloro-2:2'-dimethoxy-compound has the lowest and the 5:5':5''-trichloro-2:2':2''-trimethoxy-compound the greatest stability of this group of derivatives (cf. Brand and Groebe, A., 1925, i, 397). J. W. BAKER.

Preparation of compounds of the type of malachite-green and of phenolphthalein by means of the Grignard reaction. J. S. CHAMBERLAIN and M. F. DULL (J. Amer. Chem. Soc., 1928, 50, 3088—3092).—Michler's ketone and magnesium *p*-dimethylaminophenyl bromide (cf. Baeyer and Villiger, A., 1903, i, 811; Sachs and Ehrlich, A., 1904, i, 196) yield *pp'*-hexamethyltriaminotriphenylcarbinol (crystal-violet). Magnesium *p*-carboxyphenyl bromide was obtained in sufficient quantity to form with Michler's ketone a trace of *pp'*-tetramethyldiamino-*p''*-carboxytriphenylcarbinol (chrome-green). Benzoylbenzoic acid and 2 mols. of magnesium phenyl bromide afford diphenylphthalide (cf. Osterseizer, A., 1913, i, 729). H. E. F. NOTTON.

Constitution of isocampholic acid. II. J. VON BRAUN and A. HEYMONS (Ber., 1928, 61, [B], 2276—2280).—The constitution assigned previously (A., 1928, 753) is confirmed. Ethyl isocampholate is reduced by sodium and alcohol to β-2:2:3-trimethylcyclopentylethyl alcohol, $\text{CHMe} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, b. p. 109—112°/13 mm., d_4^{20} 0.9046, n_D^{20} 1.4591, from which β-2:2:3-trimethylcyclopentylethyl bromide, b. p. 102°/12 mm., and trimethyl-β-2:2:3-trimethylcyclopentylethylammonium bromide, decomp. 277° (corresponding chloroplatinate, decomp. 244°), are successively derived. The bromide is transformed by silver oxide into the corresponding hydroxide, converted by distillation after addition of 3—4 mols. of potassium hydroxide into a mixture of dimethyl-β-2:2:3-trimethylcyclopentylethylamine, b. p. 94—95°/14 mm. (picrate, m. p. 100—111°; hydrochloride, m. p. 226°), and 2:2:3-trimethylcyclopentylethylene, b. p. 155—156°, d_4^{24} 0.8024, n_D^{25} 1.4439. Ozonisation of the hydrocarbon and subsequent decomposition of the ozonide with zinc dust and water gives norisocampholic acid (2:2:3-trimethylcyclopentanecarboxylic acid), b. p. about 130°/12 mm., (chloride, b. p. about 85°/13 mm.; ethylamide, m. p. 68—69°), and 2:2:3-trimethylcyclopentane-1-aldehyde, b. p. 75—77°/13 mm., d_4^{19} 0.9158, n_D^{20} 1.4486 (semicarbazone, m. p. 188°; non-crystalline oxime). H. WREN.

***o*-Sulphinobenzoic acid.** W. B. PRICE and S. SMILES (J.C.S., 1928, 2858—2863).—When dry chlorine is passed into a mixture of carbon tetrachloride and *o*-thiolbenzoic acid until the latter is dissolved, an unstable dichloride of *o*-sulphinobenzoic acid,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{SCl}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$ (I), m. p. 62°, is formed, which when decomposed with ice gives a 70% yield of *o*-sulphinobenzoic acid, m. p. 126° (cf. Gattermann, A., 1899, i, 516; Davis and Smiles, J.C.S., 1910, 97, 1290). Treatment of I with *p*-nitrobenzyl alcohol affords *p*-nitrobenzyl *o*-carboxybenzenesulphinate, m. p. 121°; *o*-carboxyphenyl-*p*-nitrobenzylsulphone, m. p. 226°, is obtained by boiling equimolecular proportions of potassium *o*-sulphinobenzoate and *p*-nitrobenzyl bromide. The *p*-nitrobenzyl ester of *o*-carboxyphenyl-*p*-nitrobenzylsulphone, m. p. 190°, was produced with 2 mols. of *p*-nitrobenzyl bromide, and gave 3-keto-2-*p*-nitrophenyl-2:3-dihydrothionaphthen 1:1-dioxide, m. p. 186°, when boiled with alcoholic sodium hydroxide followed by treatment with dilute sulphuric acid. The *p*-nitrobenzyl ester of *m*-carboxyphenyl-*p*-nitrobenzylsulphone, prepared in a similar manner, has m. p. 203°. The interaction of ethyl chloroacetate and potassium *o*-sulphinobenzoate led to 3-keto-2-carbethoxy-2:3-dihydrothionaphthen 1:1-dioxide, identical with the "anhydro"-derivative obtained by Feist (A., 1926, 74; cf. Arndt, Kirsch, and Nachtwey, *ibid.*, 843) from the reaction between fuming sulphuric acid and ethyl benzoylacetate. The dichloride I reacts with solutions of phenols (2 mols.) in carbon tetrachloride or in dry ether with the formation of hydroxy-derivatives of *o*-carboxydiphenyl sulphide in good yield; thus phenol gave 2-carboxy-4'-hydroxydiphenyl disulphide, m. p. 193°; resorcinol yielded 2-carboxy-2':4'-dihydroxydiphenyl disulphide, m. p. 190° [interaction in equimolecular proportions gave bis-2'-carboxyphenylthiol-2:4-dihydroxybenzene, $\text{C}_6\text{H}_4(\text{OH})_2(\text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2$, m. p. 272°], and β-naphthol furnished *o*-carboxyphenyl 2-hydroxy-α-naphthyl sulphide, m. p. 237°. A. I. VOGEL.

***p*-Cymene.** XI. *p*-Cymyl-2-carbithionic acid. A. S. WHEELER and C. L. THOMAS (J. Amer. Chem. Soc., 1928, 50, 3106—3109).—The Grignard reagent from 2-bromo-*p*-cymene (Bogert and Tuttle, A., 1916, i, 601) yields with carbon disulphide at −10° red, oily *p*-cymyl-2-carbithionic acid (yellow zinc salt, m. p. 92°; methyl ester, b. p. 167—168°/8 mm.; ethyl ester, b. p. 141—142°/3 mm.) (cf. Houben, A., 1906, i, 847). Complex, amorphous, yellow zinc, m. p. 196° (decomp.), copper, m. p. 75° (decomp.), mercuric, m. p. above 300°, and cadmium, m. p. 125° (decomp.), salts of the type $\text{C}_{10}\text{H}_{13} \cdot \text{CS}_2 \cdot \text{M} \cdot \text{OAc}$ are formed from the acid and metallic acetates. With phenylhydrazine the acid gives a colourless substance, m. p. 112°, and with phosphorus pentachloride a liquid, b. p. 141°/8 mm. H. E. F. NOTTON.

Liquid crystals of stereoisomeric cinnamic acids. R. STOERMER and F. WODARG (Ber., 1928, 61, [B], 2323—2330).—In extension of the observation that *trans*-*p*-methoxycinnamic acid has liquid-crystalline properties which are not shared by the corresponding *allo*-acid (Stoerner, A., 1911, i, 295), it is found that the stable, linear forms of *p*-alkoxycinnamic acids give enantiotropic crystalline-liquid phases which do not occur with the angular, labile forms. Extreme lengthening of the alkyl chain causes disappearance of this property, as does also its branching. The esters,

amides, anisidides, and *p*-toluidides of the liquid-crystalline alkoxybenzoic acids do not exhibit enantiotropic phases, but liquid-crystalline esters are obtained by esterification with anisoleazophenol even in the case of the labile acids.

The following substances are described: the *p*-anisidide, m. p. 184°, *p*-toluidide, m. p. 161°, and *p*-anisoleazophenyl ester, m. p. 162° and about 320°, of *p*-methoxycinnamic acid; *p*-anisoleazophenyl *p*-methoxyallocinnamate, m. p. 157.5° and 301°; *p*-ethoxybenzaldehydesemicarbazone, m. p. 202° (decomp.); *p*-ethoxycinnamic acid, m. p. 190° and 196° (methyl ester, m. p. 68—69°; ethyl ester, m. p. 36°; amide, m. p. 195°; *p*-anisidide, m. p. 179°; *p*-toluidide, m. p. 164°; *p*-anisoleazophenyl *p*-ethoxycinnamate, m. p. 178° and about 317°; *p*-ethoxyallocinnamic acid, m. p. 86°, its chloride (prepared by means of phosphorus pentachloride in presence of ether) and amide, m. p. 118°; *p*-anisoleazophenyl *p*-ethoxyallocinnamate, m. p. 172° and about 300°; *p*-propoxybenzaldehyde, b. p. 268°, and its semicarbazone, m. p. 178—179° (decomp.); *p*-propoxycinnamic acid, m. p. 166° and 182° (methyl ester, m. p. 65°; ethyl ester, m. p. 37°; amide, m. p. 188—189°; *p*-anisidide, m. p. 161°; *p*-toluidide, m. p. 166—167°); *p*-propoxyallocinnamic acid, m. p. 90—91°, and its amide, m. p. 115°; *p*-butoxybenzaldehyde, b. p. 285°; *p*-n-butoxycinnamic acid, m. p. 154° and 185—186° (methyl ester, m. p. 77°; ethyl ester, m. p. 38°; amide, m. p. 184°; *p*-anisidide, m. p. 148°; *p*-toluidide, m. p. 146—147°); *p*-anisoleazophenyl *p*-n-butoxycinnamate, m. p. 177° and about 320°; *p*-n-butoxyallocinnamic acid, m. p. 74° (amide, m. p. 110°; *p*-anisidide, m. p. 114°; *p*-anisoleazophenyl ester, m. p. 138° and about 300°); *p*-isobutoxybenzaldehyde, b. p. 258°; *p*-isobutoxycinnamic acid, m. p. 159°; *p*-benzyloxybenzaldehyde, m. p. 72°, which is not suitable for Perkin's reaction; methyl *p*-benzyloxy-cinnamate (from methyl *p*-hydroxycinnamate, benzyl bromide, and potassium hydroxide) and *p*-benzyloxy-cinnamic acid, m. p. 199°; *p*-cetyloxybenzaldehyde, m. p. 19° (phenylhydrazine, m. p. 89°); *p*-cetyloxy-cinnamic acid, m. p. 200—202° (decomp.); *p*-anisoleazophenyl benzoate, m. p. 161° and 173°. H. WREN.

Theory of the Perkin synthesis. Mechanism of the reaction. P. KALNIN (Helv. Chim. Acta, 1928, 11, 977—1003).—When a mixture of benzaldehyde (1 mol.), acetic anhydride (1 mol.), and pyridine (optimum 0.67 mol.) is heated at 180° for 32 hrs. a 5.4% yield of cinnamic acid is obtained. If the anhydride is replaced by sodium acetate the yield is nil. When a stronger tertiary base is used in place of pyridine, the yield increases with the strength of the base and the maximum yield is obtained with a smaller mol. proportion of bases. Thus, benzyldiethylamine gives 6.87% of acid, whilst triethylamine affords 29.27% using 0.33 mol. of base. The action of the base is to cause enolisation of the anhydride. The mechanism of the Perkin reaction is explained in five stages: (1) enolisation of the anhydride by sodium acetate, (2) addition of benzaldehyde to the enol, (3) further enolisation of the intermediate benzoyl derivative, (4) elimination of acetic acid from the enol additive product, (5) rearrangement of the intermediate compound

...CPh:CH·CH(OH)·O... to cinnamic acid. The following evidence is advanced to substantiate the mechanism. (1) Acetic anhydride reacts in the enol form with sodium, since decomposition of the resulting product with dilute acetic acid gives appreciable amounts of acetone. The yield of unsaturated acid is greater with increased ability of the anhydride used to exist in enol form. Thus, the firmly-bound methyl and phenyl groups in propionic and phenylacetic anhydrides activate the methylene hydrogen atom, resulting finally in correspondingly larger amounts of condensation products. (2) Small amounts of cinnamic acid are obtained with sodium as condensing agent at 180°, or from benzyldiethylaniline and acetic anhydride in presence of potassium carbonate. Addition to the double linking occurs thus: $\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot + \text{Ph}\cdot\text{CHO} \longrightarrow \text{CH}_2\text{Bz}\cdot\text{CH}(\text{OH})\cdot$, because of the strong valency requirement of the phenyl group (cf. Scheibler and Friese, A., 1925, i, 1417). (3) Most benzoyl derivatives of similar constitution to the intermediate exist in enol forms (K. H. Meyer, A., 1912, i, 940). (4) When the Perkin reaction is carried out in presence of a relatively large amount of acetic acid the yield of cinnamic acid is almost nil.

When sodium or potassium acetate is replaced by sodium or potassium carbonates, sodium or potassium phosphates, and potassium sulphite, 20.4—58.9% yields of cinnamic acid are obtained.

The results of Meyer and Beer (A., 1913, i, 617; cf. Michael, A., 1901, i, 358), and the condensation of *o*-chlorobenzaldehyde with potassium acetate at 240°, are explained by assuming the intermediate production of acetic anhydride during the experiment (cf. Campardou and Séon, A., 1928, 393). H. BURTON.

Preparation of dimethyl phenylethylmalonate. T. W. RAY (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 151—156).—An attempt to prepare dimethyl phenylethylmalonate from propylbenzene failed because this on attempted α -dibromination afforded an unsaturated compound, probably γ -phenyl- Δ^8 -propylene. In an attempt to prepare it from phenyl ethyl ketone, treatment of this substance with hydrogen chloride and cyanide afforded methylatropic acid, m. p. 134—136°. Attempted preparation from benzyl cyanide failed because methyl α -bromo- α -phenylbutyrate, decomp. 95—100°/2 mm., with potassium cyanide gave very little methyl α -cyano- α -phenylbutyrate b. p. 120—130°/0.1 mm. Ethyl α -cyano- α -phenylbutyrate has b. p. 100—140°/0.2 mm. CHEMICAL ABSTRACTS.

Addition of halogens to unsaturated acids and esters. II. Addition of "bromine chloride" to phenylpropionic acid. N. W. HANSON and T. C. JAMES (J.C.S., 1928, 2979—2985; cf. A., 1928, 1004).—An equimolecular mixture of bromine and chlorine dissolved in carbon tetrachloride (bromine chloride solution) reacts in the dark with phenylpropionic acid in carbon tetrachloride solution at 0° to give a mixture of two chlorobromocinnamic acids which were separated by means of light petroleum into two forms, m. p. 129° (plates) and 112° (needles), respectively. These two forms are considered to be geometrical isomerides, since (a) exposure of a chloroform solution of the less fusible acid mixed with a

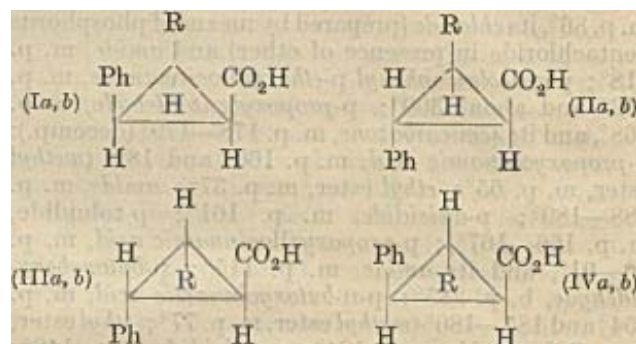
little bromine gave almost entirely the more fusible acid, and (b) the more fusible form is unaffected by such treatment (cf. Roser and Haselhoff, A., 1888, 1314; Stoermer and Heymann, A., 1913, i, 618). When the compound of m. p. 112° is treated with cold concentrated sulphuric acid 3-chloro-2-bromo-1-ketoindene (I), m. p. 105° [anilido-derivative, m. p. 170°; piperidyl derivative, m. p. 117° (decomp.); oxime, m. p. 194°; mixed m. p. with 2-chloro-3-bromo-1-ketoindene, m. p. 105°, 65—100°; the oxime of 2-chloro-3-bromo-1-ketoindene has m. p. 184° (decomp.); cf. Roser and Haselhoff, *loc. cit.*], is formed, whilst the isomeride, m. p. 127°, is unaffected by this treatment: indeed I may be conveniently prepared from the product of interaction of phenylpropionic acid and "bromine chloride," since the indone was readily separable from the residual acid by dissolving in hot light petroleum. This establishes the compound of m. p. 112° as the *cis*- and that of m. p. 127° as the *trans*-isomeride. "Bromine chloride" reacts much more rapidly with phenylpropionic acid than either bromine or chlorine, the reaction being of the bimolecular type without an inhibition period (cf. A., 1928, 1004). The action of bromine and chlorine dissolved in carbon tetrachloride with the *cis*-forms of β -chloro- α -bromo-, $\alpha\beta$ -dibromo-, and $\alpha\beta$ -dichloro-cinnamic acids was studied in the manner described by Williams and James (A., 1928, 412). With bromine, the amount of halogen which disappeared was extremely small even after several weeks. With chlorine, $\alpha\beta$ -dichloro-cinnamic acid formed an additive product, $\alpha\alpha\beta\beta$ -tetrachloro- β -phenylpropionic acid, m. p. 130°; $\alpha\beta$ -dibromocinnamic acid led to some replacement of the bromine by chlorine but to no recognisable product, whilst β -chloro- α -bromocinnamic acid gave mainly $\alpha\beta\beta$ -trichloro- α -bromo- β -phenylpropionic acid, m. p. 127°, together with a small quantity of $\alpha\alpha\beta\beta$ -tetrachloro- β -phenylpropionic acid (produced by partial replacement of bromine by chlorine). A. I. VOGEL.

Reactions of nitroso-derivatives with unsaturated compounds. VI. Catalytic action of nitroso-derivatives on *o*-nitro-substituted [aryl]-acetylenes; behaviour of *p*-nitrosoanisole. L. ALESSANDRI (Gazzetta, 1928, 58, 551—560).—Owing to the complexity of the reaction between nitrosobenzene and *o*-nitrophenylacetylene (A., 1927, 572), the reactions of the former with *o*-nitrophenylpropionic acid, which might be expected to behave more simply, have been examined. Since, however, this acid readily loses carbon dioxide, it gives the same products as does *o*-nitrophenylacetylene, viz., isatin, *N*-hydroxyisatin, and a trace of α -isatinoxime *N*-phenyl ether, together with azoxybenzene and unchanged acid. Ethyl *o*-nitrophenylpropionate is converted by nitrosobenzene into ethyl isatogenate; similar changes have been observed under the influence of sulphuric acid or of pyridine; nitrosobenzene (which remains unaltered) gives a greater yield than these, with also a colourless secondary product, m. p. 121°. Methyl *o*-nitrophenylpropionate similarly isomerises to methyl isatogenate and a substance, m. p. 139°. These colourless by-products have the same percentage composition as the initial materials, and are produced whether these are treated with nitrosobenzene or

with *p*-nitrosoanisole; it must therefore be assumed that these latter substances have only a catalytic action.

p-Nitrosoanisole acts on safrole, ethyl phenylpropionate, or toluene in a similar manner to nitrosobenzene. E. W. WIGNALL.

Ring fission in the cyclopropane series. XIV. R. STÖRMER and F. SCHENCK [with H. BUSCHMANN] (Ber., 1928, 61, [B], 2312—2323; cf. A., 1928, 174).—The requisite 2-phenyl-3-hydroxybenzylcyclopropane-1-carboxylic acids are obtained from γ -truxillic acid (cf. *loc. cit.*) or from ϵ -truxillic acid through ϵ -truxillamic acid and 3'-amino-2'-4'-diphenylcyclobutane-1'-carboxylic acid, which is transformed by ethereal nitrosyl bromide into the lactone IIb (R = CHPh.OH), to-



gether with diphenylbutadiene. The lactone is converted into the corresponding acid, oxidised to the ketonic acid II (R = Bz), m. p. 174—175° (*semicarbazone*, m. p. 194—195°; *methyl ester*, m. p. 93°). The ketonic acid, like the stereoisomeric acids I, II, and III (*loc. cit.*), is converted by catalytic hydrogenation into α -phenacyl- β -phenylpropionic acid.

The hydroxy-acid IIb is converted by hydrogen chloride in cold ether into γ -phenyl- α - α' -chlorobenzyl- Δ^{β} -butenoic acid, m. p. 155—156°, converted by sodium hydroxide into benzaldehyde, diphenylbutadiene, and regenerated hydroxy-acid and by aluminium amalgam into γ -phenyl- α -benzyl- Δ^{β} -butenoic acid; the *methyl ester*, m. p. 98—99°, is described. Hydrogen chloride, like hydrogen bromide, is therefore added at the carbon atoms 2 and 3 of the cyclopropane ring. Fission of the ring by glacial acetic and sulphuric acids occurs in a precisely similar manner, giving γ -phenyl- α - α' -acetoxybenzyl- Δ^{β} -butenoic acid, CHPh:CH·CH(CO₂H)·CHPh·OAc. Since the acid contains two asymmetric carbon atoms it can exist in two racemic modifications (each of which may give two *cis-trans*-isomerides). The hydroxy-acids IIa, IIb, and IIIa give an acid, m. p. 152—152.5° (*methyl ester*, m. p. 87°), whereas the hydroxy-acid Ia yields an isomeric acid, m. p. 152—154° (*methyl ester*, m. p. 92—92.5°). The methyl ester of the hydroxy-acid Ia gives both esters simultaneously. The difference of the two unsaturated acids is caused by the arrangement of the groups around the asymmetric carbon atoms, since it persists in the products of their hydrogenation, the γ -phenyl- α - α' -hydroxybenzyl-*n*-butyric acids [isomeride I (from acid of m. p. 152—152.5°), m. p. 112—113° (*methyl ester*, m. p. 62—62.5°; non-crystalline *acetyl derivative*, and its *methyl ester*, m. p. of 50—51°); isomeride II (from acid of m. p. 152—154°),

m. p. 93—94.5° (methyl ester, m. p. 64—64.5°; methyl ester of acetyl derivative, m. p. 69—70°). The methyl esters are oxidised to the same methyl α -benzoyl- γ -phenyl-*n*-butyrate, converted by hydrolysis into α , δ -diphenylbutan- α -one, m. p. 56—57° (oxime, m. p. 101—102°; semicarbazone, m. p. 126.5—127.5°), obtained directly by oxidation of the corresponding acids. The syntheses of the ketone by addition of benzaldehyde to an ethereal solution of magnesium γ -phenyl-*n*-propyl bromide with subsequent oxidation of the α , δ -diphenylbutan- α -ol, m. p. 45—46°, or directly by addition of the Grignard reagent to the aldehyde, is recorded. The identity of the non-crystalline methyl α -benzoyl- γ -phenyl-*n*-butyrates from the different hydroxy-acids is further established by the conversion of each preparation by means of semicarbazide into 3-phenyl-4- β -phenylethyl-5-pyrazolone-1-carboxylamide, m. p. 131.5—132.5°. The fission of the cyclopropane ring between the carbon atoms 2 and 3 in the production of the γ -phenyl- α - α' -acetoxybenzyl- Δ^2 -butenoic acids is established by the production of α , δ -diphenylbutadiene and the formation of α , β -dibenzylidenepropionic acid by the hydrolysis of the methyl esters. The position of the α -acetyl group follows from the conversion of the free acetylated acids by boiling sodium carbonate into phenylisocrotonic acid, benzaldehyde, and acetic acid. The isomeric γ -phenyl- α - α' -hydroxybenzyl-*n*-butyric acids are transformed by 75% sulphuric acid into 1-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid, m. p. 150—151°.

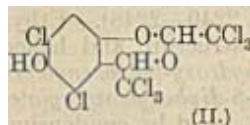
Addition of formic acid takes place in the same manner as that of acetic acid. The hydroxy-acids IIb and IIa give a formyl product, m. p. 160° (methyl ester, m. p. 96°), whereas the methyl ester of the hydroxy-acid Ia yields mainly an isomeric methyl ester, m. p. 93—94°.

The results thus obtained appear to justify the previous assumption that, after contraction of the ring, the carboxyl and phenyl groups remain on the same side of the ring as in the truxillic and truxinic acids.

H. WREN.

Condensation of chloral with anisic acid, with *p*-nitroanisole, and with 2 : 6-dichloroquinol. F. D. CHATTAWAY and F. CALVET (J.C.S., 1928, 2913—2918; cf. A., 1927, 458, 967).—Anisic acid condenses with chloral in the presence of a large excess of concentrated sulphuric acid at the ordinary temperature, forming 5-carboxy-2-methoxy-1- $\beta\beta\beta$ -trichloro- α -hydroxyethylbenzene (I), m. p. 198—199°; if the condensation be prolonged (8 days) or if dry hydrogen chloride be passed into a solution of I in concentrated sulphuric acid, 5-carboxy-2-methoxy-1- $\alpha\beta\beta\beta$ -tetrachloroethylbenzene, m. p. 247—249°, is formed, whereas if I be heated with concentrated sulphuric acid 4-methoxyisophthalaldehydic acid, m. p. 244—245° (2 : 4-dichlorophenylhydrazones, m. p. 303—305° [decomp.]), is obtained. The constitution of I was established by oxidation with alkaline potassium permanganate to a mixture of *o*-carboxy-2-methoxyphenylglyoxylic acid, m. p. 254—255° (phenylhydrazones, m. p. 231° [decomp.]), and 4-methoxyisophthalic acid, m. p. 275—276°. *p*-Nitroanisole condenses similarly with chloral in the presence of concentrated sulphuric acid at the ordinary

temperature, giving 5-nitro-2-methoxy-1- $\alpha\beta\beta\beta$ -tetrachloroethylbenzene, m. p. 131—132°, which was converted into $\alpha\beta\beta$ -trichloro-5-nitro-2-methoxystyrene, m. p. 94—95°, when boiled with alcoholic potassium hydroxide, and into 5-nitro-2-methoxybenzoic acid, m. p. 161°, when oxidised with potassium permanganate in acetone solution. 2 : 6-Dichloroquinol condenses readily with 2 mols. of chloral in the presence of a large excess of concentrated sulphuric acid, forming 5 : 7-dichloro-6-hydroxy-2 : 4-bis(trichloromethyl)-1 : 3-benzdioxin (II), m. p. 114—115° which gave an acetyl derivative, m. p. 179—180°, and 5 : 7-dichloro-6-hydroxy-2 : 4-bis(dichloromethylene)-1 : 3-benzdioxin, m. p. 137—138°, when boiled with alcoholic potassium hydroxide.



A. I. VOGEL.

Dependence of rotatory power on chemical constitution. XXXIII. Resolution of *dl*-*m*-carboxyphenyl ethyl sulphoxide and of *dl*-*m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine. J. HOLLOWAY, J. KENYON, and H. PHILLIPS (J.C.S., 1928, 3000—3006).—*m*-Ethylthiolbenzoic acid, m. p. 99—100°, prepared from *m*-thiolbenzoic acid and ethyl *p*-toluenesulphonate, gave *dl*-*m*-carboxyphenyl ethyl sulphoxide, m. p. 104—106°, when oxidised with nitric acid. The *l*-brucine salt, m. p. 125—126°, $[\alpha]_{D}^{25} + 69^\circ$ in chloroform, was decomposed with aqueous sodium hydroxide to *d*-*m*-carboxyphenyl ethyl sulphoxide, m. p. 71°, $[\alpha]_{D}^{25} + 236^\circ$ in chloroform. A table of specific rotatory powers of this substance in various solvents for different wave-lengths is given; they are all greater than those of *d*-*m*-carboxyphenyl methyl sulphoxide (Clarke and others, A., 1927, 243). The quinidine salt, m. p. 198—199°, $[\alpha]_{D}^{25} + 102^\circ$ in chloroform, when decomposed gave *l*-*m*-carboxyphenyl ethyl sulphoxide, $[\alpha]_{D}^{25} - 232^\circ$ in chloroform. *m*-Carboxyphenylethylsulphine, m. p. 162—164°, prepared by oxidation of *m*-methylthiolbenzoic acid or *d*-*m*-carboxyphenyl ethyl sulphoxide with hydrogen peroxide, and also *m*-carboxyphenyl ethyl sulphide dibromide, m. p. 102°, prepared from *m*-ethylthiolbenzoic acid and bromine in carbon disulphide solution, are optically inactive.

“Chloramine-T” and *m*-ethylthiolbenzoic acid react, yielding *dl*-*m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine, m. p. 149°, giving a brucine salt, m. p. 161°, $[\alpha]_{D}^{25} - 157^\circ$ in ethyl alcohol; decomposition of the latter with hydrochloric acid yielded *l*-*m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine, (I) m. p. 149—150°, $[\alpha]_{D}^{25} - 368^\circ$ in ethyl alcohol. The *d* + *dl*-sulphilimine isolated from the mother-liquors of I gave the pure *d*-*m*-carboxyphenylethylsulphine-*p*-toluenesulphonylimine, m. p. 150—151°, $[\alpha]_{D}^{25} + 373^\circ$ in ethyl alcohol, through the strychnine *d*-salt, m. p. 174° (decomp.), $[\alpha]_{D}^{25} + 152^\circ$ in ethyl alcohol, and a slightly less pure compound, m. p. 149—150°, $[\alpha]_{D}^{25} + 364^\circ$ in ethyl alcohol, through the cinchonidine salt, m. p. 198—199°, $[\alpha]_{D}^{25} + 50^\circ$ in chloroform. The rotatory dispersion is less complex than that exhibited in the corresponding solvents by the sulphoxide; the sulphilimine exhibits simple rotatory dispersion in ethyl-alcoholic solution. The *l*-*dl*-sulphilimine is converted into a mixture of

p-toluenesulphonamide, *m*-carboxyphenyl ethyl sulphide, and *dl*-*m*-carboxyphenyl ethyl sulphoxide when hydrolysed with hydrochloric acid, whilst the *dl*-sulphilimine gives *p*-toluenesulphonamide and *m*-carboxyphenylethylsulphone with hydrogen peroxide. These results provide further evidence for the existence of semipolar double linkings (cf. Harrison and others, A., 1926, 1031). A. I. VOGEL.

So-called "fluoreneoxalic ester." R. KUHN and E. LEVY (Ber., 1928, 61, [B], 2240—2248).—Ethyl fluoreneoxalate has the enolic structure and hence must be regarded as ethyl α -hydroxy- β -diphenyleneacrylate. Methyl α -hydroxy- β -diphenyleneacrylate, m. p. 117.5°, is prepared in 65% yield by condensing fluorene with methyl oxalate in presence of methylalcoholic potassium methoxide. It is converted by ozone into fluorenone and methyl oxalate and by hydrogenation in presence of platinum oxide into methyl α -hydroxy- β -diphenylenepropionate. With alkaline hypiodite it yields 9-iodofluorene. It affords fluorenone-*p*-nitrophenylhydrazine, m. p. 209°, with *p*-nitrophenyldiazonium hydrate. It is converted by diazomethane and *p*-nitrobenzoyl chloride into the corresponding methyl ether, C₁₇H₁₄O₃, m. p. 60°, and *p*-nitrobenzoate, C₂₃H₁₅O₆N, m. p. 255°. As ketone, it is transformed by bromine in glacial acetic acid into methyl β -bromo- β -diphenylenepyrivate, m. p. 94.5°. Methyl α -oximino- β -diphenylenepropionate, m. p. 190°, is described. When methyl α -hydroxy- β -diphenyleneacrylate is titrated with bromine by Meyer's method, results varying from 75 to 95% of enol are obtained owing to the unusually slow reaction between the bromoketone and hydriodic acid. At the end of 1—2 hrs. after addition of β -naphthol and potassium iodide, an enol content of 100% is indicated if the crystalline ester is covered with bromine dissolved in glacial acetic acid. If solutions of the ester in glacial acetic acid are employed which have been preserved for about 20 hrs., titration shows 58.8% of enol. H. WREN.

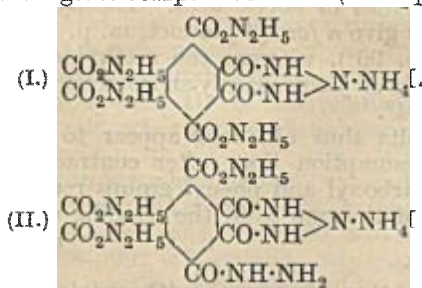
Syntheses with radiant energy. II. Photosynthesis of $\alpha\beta$ -triphenyl-lactic acid. R. DE FAZI.—See A., 1928, 1341.

Colour on the basis of molecular strain. VI. Effect of sulphur on colour. A. N. DEY and S. DUTT (J. Indian Chem. Soc., 1928, 5, 639—641).—When sulphur replaces oxygen in a series of dyes the colour is deepened, presumably because of the greater loading effect of the sulphur atom. A similar increase of colour is to be expected when carbon is replaced by sulphur, and to test this hypothesis a series of dyes has been prepared from thiodiglycollic acid analogous to those obtained from glutaric acid (Dutt and Thorpe, A., 1925, i, 140; Dutt, A., 1926, 830). Resorcinol condenses with thiodiglycollic acid in presence of a small amount of concentrated sulphuric acid at 150°, yielding resorcinolthiodiglycollein, not melted at 310°. Similar condensations using phloroglucinol, phenol, *m*-diethylaminophenol, and *m*-phenylenediamine afford phloroglucinolthiodiglycollein, phenolthiodiglycollein, m. p. 129°, tetraethylthiodiglycollyrhodamine, m. p. 172—173°, and 2:7-diaminothiodiglycollylacridine, m. p. 241°, respectively. These compounds

have deeper colours than the corresponding glutaric acid derivatives. H. BURTON.

Succinic acid derivatives from acylphenylacetonitrile. G. HELLER, H. HERRMANN, and G. SPIELMEYER (J. pr. Chem., 1928, [ii], 120, 193—198).—Oxidation of α -acetylphenylacetonitrile (*anil*, m. p. 102—103°; phenylhydrazone, m. p. 114°) with sodium nitrite and acetic acid at 0° for 24 hrs. yields $\alpha\alpha$ -diacetyl- $\alpha\alpha$ -diphenylsuccinodinitrile, m. p. 173—174°, together with isomeric and other substances which could not be purified. The same product is obtained when absolute nitric acid diluted with 2 parts of acetic acid at 0° or nitric acid (d 1.36) at the ordinary temperature (accompanied, in this case, with 30% of *p*-nitrobenzoic acid) is used as oxidising agent, or by the action of iodine and sodium methoxide on the original nitrile. Similarly, oxidation of α -benzoylphenylacetonitrile either with nitrous acid at 0°, 20% hydrogen peroxide in acetic acid solution, or sodium methoxide and iodine, yields $\alpha\alpha'$ -dibenzoyl- $\alpha\alpha'$ -diphenylsuccinodinitrile, m. p. 207°, which is converted by treatment with concentrated sulphuric acid for 2 months into $\alpha\alpha'$ -dibenzoyl- $\alpha\alpha'$ -diphenylsuccinic anhydride, m. p. 243°. J. W. BAKER.

Mellitic acid. E. LURIA (Quim. e Ind., 1928, 5, 35—38; Chem. Zentr., 1928, i, 2501).—The neutral metallic mellitates (uranyl, +12H₂O; cerium, +9H₂O; cadmium; lithium, +9H₂O) crystallise with 3*n*H₂O, where *n*=0 to 8, in accordance with the tribasicity of the acid towards methyl-orange, and other properties. Evaporation of a solution containing mellitic acid and hydrazine gives compounds I and (subsequently) II:



A. A. ELDRIDGE.

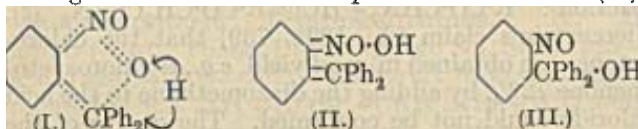
Manufacture of cyclic ketones [from naphthalene etc. and maleic anhydride]. I. G. FARBENIND. A.-G.—See B., 1928, 887, 922.

Manufacture of compounds of the perylene series [perylene-carboxylic acids]. I. G. FARBENIND. A.-G.—See B., 1928, 921.

Intermediate compounds and azo dyes therefrom [aminohydroxyarylsulphonecarboxylic acids]. BRIT. DYESTUFFS CORP. and M. MENDOZA.—See B., 1928, 887, 921.

Tautomerism of *o*-nitrobenzaldehyde. II. Reply to H. Gilman, R. Fothergill, and F. Arndt. I. TANASESCU (Bull. Soc. chim., 1928, [iv], 43, 1117—1122).—In reply to Gilman and Fothergill's criticism (A., 1928, 64) of the theory previously advanced (A., 1928, 178) to account for the tautomerism of *o*-nitrobenzaldehyde, the author points out that the hypothesis is not based exclusively on the presence of a mobile hydrogen atom and that such

mobile hydrogen atoms have been observed in other nitro- and nitroso-benzene derivatives. The formation of unsaturated hydrocarbons by the action of magnesium organohalides is readily attributed to the reducing powers of the latter compounds. With magnesium methyl iodide methane only was formed. In reply to Arndt (A., 1928, 759) it is asserted that photochemical reasons render the dynamic equilibrium (I) very probable in the case of *o*-nitrotriphenylmethane. If the oxygen atom remains attached to nitrogen there results the *o*-quinonoid derivative (II)



already described (A., 1927, 139), whilst if the oxygen atom comes within the sphere of attraction of the carbon atom the *o*-nitrosocarbinol (III) (*loc. cit.*) results. The fact that *p*-nitrobenzaldehyde is slightly soluble in alkali is attributed to the formation of hydrates, which is an insufficient explanation of the much greater solubility of the *o*-isomeride. Although *o*-nitroacetophenone cannot react in a tautomeric form, the formation of *C*-methylantranil on reduction may be preceded by the formation of the intermediate

phase $C_6H_4 \begin{smallmatrix} \text{CMe} \\ \text{NO} \end{smallmatrix} O$: in the case of *o*-nitrobenzaldehyde a corresponding structure (OH for Me) gives a ready interpretation of the reaction with aromatic hydrocarbons in presence of sulphuric acid.

R. BRIGHTMAN.

"Oxidising" action of alkalis. I. G. LOCK (Ber., 1928, 61, [B], 2234—2240).—The potassium salt of salicylaldehyde reacts quantitatively with potassium hydroxide at 105—110°, giving potassium salicylate and hydrogen. The presence of moisture is not necessary, but advantageous, since it depresses the temperature of reaction by facilitating the formation of an intimate mixture. The reaction is not preceded by a Cannizzaro change, since the potassium compound of salicyl alcohol does not react with potassium hydroxide under these conditions. Sodium and lithium hydroxides behave similarly to the potassium compound but require a higher temperature. Barium hydroxide, dehydrated at 120°, also effects the change; the absence of "oxidising action" is not a specific property of the alkaline-earth hydroxides but merely a consequence of their use in aqueous solution. Sodamide does not react with the potassium derivative of salicylaldehyde. The "oxidising action" of potassium hydroxide cannot be ascribed to dissociation of water, since it may occur at a relatively low temperature and with anhydrous materials. It must be regarded as a dehydrogenation with replacement of the typical hydrogen atom of the aldehydic group by the OK radical.

H. WREN.

1:2-Dialkylcyclopentane derivatives. F. H. CASE and E. E. REID (J. Amer. Chem. Soc., 1928, 50, 3062—3065).—The 2-methyl, b. p. 106—107°/17 mm. (all b. p. corr.) (*semicarbazone*, m. p. 152—153°), 2-ethyl (I), b. p. 100°/7 mm., d_4^{25} 1.0310 (*semicarbazone*, m. p. 148—149°), and 2-isopropyl derivatives of ethyl cyclopentanone-2-carboxylate have been obtained from

the sodio-derivative (cf. Rysselberge, A., 1926, 1238) and the appropriate alkyl iodide in boiling benzene or xylene. The ester I is hydrolysed by dilute sulphuric acid to 2-ethylcyclopentanone, b. p. 160—161°/755 mm., d_4^{25} 0.9260 (cf. Best and Thorpe, J.C.S., 1909, 95, 713). This is converted in poor yield by magnesium *n*-propyl bromide into 2-ethyl-1-propylcyclopentan-1-ol, b. p. 115—116°/42 mm., d_4^{25} 0.8949, and by magnesium ethyl bromide into 1:2-diethylcyclopentan-1-ol, b. p. 101—102°/46 mm., d_4^{25} 0.9041, the iodide of which yields with zinc dust mainly a 1:2-diethylcyclopentene, b. p. 147—149°/761 mm., d_4^{25} 0.8136 (cf. Kijner, A., 1911, i, 967).

H. E. F. NOTTON.

Alkylation of hydroxymethylenecyclohexanones. H. K. SEN and K. MONDAL (J. Indian Chem. Soc., 1928, 5, 609—630).—When the sodium salts of hydroxymethylenecyclohexanones are treated with alkyl iodides *O*-ethers are not produced, but *C*-alkylation occurs, and after hydrolysis of the intermediate products (when isolated) 2-alkylcyclohexanones are obtained. The intermediate product is a reducing agent and is postulated as a 2-alkylcyclohexanone-2-aldehyde. Thus, when 2-hydroxymethylenecyclohexanone is treated with sodium in benzene and then heated at 100° with methyl iodide, the resulting product is a liquid, b. p. 130—150°/45 mm. (slight decomp.), hydrolysed by cold, dilute sodium hydroxide to 2-methylcyclohexanone. With sodium ethoxide at 100° under pressure, no intermediate is isolated. 2-Methyl-6-hydroxymethylenecyclohexanone gives 2:6-dimethylcyclohexanone (*oxime*, m. p. 118°; *semicarbazone*, m. p. 193—194°) in benzene or ether solution, but in presence of alcohol a small amount of the monomethyl derivative is also formed. From the requisite alkylhydroxymethylenecyclohexanones and alkyl iodides the following substituted cyclohexanones were prepared: 2-ethyl-; 2:5-dimethyl- (*oxime*, m. p. 96°); 6-benzyl-2-methyl- (impure *semicarbazone*, m. p. 140° after sintering at 132°); 2:3:4-trimethyl- (*semicarbazone*, m. p. 212°). 3-Methyl-6-hydroxymethylenecyclohexanone and isopropyl iodide yield a mixture of 3-methylcyclohexanone and menthone. The action of acetyl chloride on the sodium salt of hydroxymethylenecyclohexanone is to form the corresponding *O*-acetate (*semicarbazone*, m. p. 182—184°). Similarly, 2- and 4-methyl-6-hydroxymethylenecyclohexanone benzoates (*semicarbazones*, m. p. 175° and 183—184°, respectively) are prepared using benzoyl chloride. Alkylation of hydroxymethyleneacetophenone gives impure *O*-ethers.

Determinations of the amounts of enol form present in 2-hydroxymethylene-, 2-, 3-, and 4-methyl-6-hydroxymethylene-cyclohexanones, hydroxymethylenecamphor, and hydroxymethyleneacetotoluene by K. H. Meyer's titration method shows that the percentage of enol falls considerably when an alcoholic solution is kept for some time. In benzene or ether the reverse change takes place. Since these hydroxymethylene derivatives can exist in the aldehyde form the sodium compounds are postulated as $>CNa \cdot CHO$.

H. BURTON.

Carbon rings. XIII. Oxidation of thirteen- to seventeen-membered monocyclic ketones with Caro's acid to fourteen- to eighteen-ring lactones.

L. RUZICKA and M. STOLL (Helv. Chim. Acta, 1928, 11, 1159—1173).—Oxidation of exaltone (cyclopentadecanone) in light petroleum solution at 30—35° with Caro's acid gives a mixture of cyclopentadecanone peroxide (I), m. p. 179—180°, ξ -hydroxypentadecanoic acid (II), m. p. 82—82.5°, ξ -hydroxypentadecanoic acid lactone (exaltolide) (III), b. p. 171—174°/14 mm., m. p. 31—32°, d_4^{25} 0.9383, n_D^{25} 1.4633, etholide, $C_{30}H_{58}O_5$, m. p. 75—77°, formed by loss of 1 mol. of water from 2 mols. of II, and resinous products. If the oxidation is carried out at 50° or 65° no peroxide is produced. In acetic acid solution at 20—40° similar mixtures are also formed. Hydrolysis of III with cold 5% sodium hydroxide solution and subsequent oxidation with chromic oxide and acetic acid yields tridecane- α -dicarboxylic acid. Reduction of I with zinc dust and acetic acid or treatment with warm 90% sulphuric acid regenerates exaltone. Similar oxidation of cyclo-tridecanone furnishes the lactone, b. p. 147—148°/14 mm., m. p. 25—26°, d_4^{25} 0.9590, n_D^{25} 1.4649, of μ -hydroxy-tridecanoic acid, m. p. 77—78°. From cyclotetradecanone the lactone, b. p. 164—165°/16 mm., m. p. 27—28°, d_4^{25} 0.9528, n_D^{25} 1.4644, of ν -hydroxytetradecanoic acid, m. p. 93—95°, is obtained. ω -Hydroxyhexadecanoic acid lactone, b. p. 188°/15 mm., m. p. 33—34°, d_4^{25} 0.9348, n_D^{25} 1.4644, from cyclohexadecanone, is the pure dihydroambrettolide of Kerschbaum (A., 1927, 541). Dihydrocivetone yields the lactone, m. p. 40—41°, d_4^{25} 0.9231, n_D^{25} 1.4615, of π -hydroxyheptadecanoic acid, m. p. 84—85°, oxidised further to pentadecane- α -dicarboxylic acid.

The lactones described show a fairly regular increase of m. p. with increase of carbon atoms, but a corresponding decrease in the values of d . The hydroxy-acids show an alternation in the m. p., the odd-numbered acids being the more fusible. The lactones have pronounced odours.

H. BURTON.

Carbon rings. XIV. Ketones with nineteen-, twentyone-, and twenty-nine-membered rings. L. RUZICKA, M. STOLL, and H. SCHINZ (Helv. Chim. Acta, 1928, 11, 1174—1180).—Distillation of the thorium salt of octadecane- α -dicarboxylic acid, m. p. 124—125° (prepared by electrolysis of ethyl hydrogen nonane- α -dicarboxylate and subsequent hydrolysis), gives 2.5% of cyclononadecanone, m. p. 72° (semicarbazone, m. p. 184°), oxidised by chromic oxide and acetic acid to heptadecane- α -dicarboxylic acid. From yttrium eicosane- α -dicarboxylate 3.8% of cycloheneicosanone, b. p. 176—177°/0.3 mm., m. p. 45—46°, d_4^{25} 0.8746, n_D^{25} 1.4617 (semicarbazone, m. p. 177—178°), is obtained. The benzylidene derivative of this ketone is oxidised to nonadecane- α -dicarboxylic acid. cyclononacosanone, m. p. 45—47°, d_4^{25} (supercooled) 0.8802, n_D^{25} 1.4702 (semicarbazone, m. p. 152—154°), is prepared from the yttrium salt of octacosane-1:28-dicarboxylic acid, obtained by electrolysis of methyl hydrogen tetradecane- α -dicarboxylate, m. p. 65—67°. Methyl hydrogen decane- α -dicarboxylate has m. p. 39—41°. H. BURTON.

Ionone. F. HERNÁNDEZ, J. JAUMA, and L. VERDERAU (Quim. e Ind., 1927, 4, 301—309; Chem. Zentr., 1928, i, 1954).—Descriptive. The b.-p. curves of α - and β -ionone between 3 and 19 mm. are given.

A. A. ELDRIDGE.

Acylation of diazomethane. Formation of chloroacetophenone from benzoyl chloride. W. BRADLEY and G. SCHWARZENBACH (J.C.S., 1928, 2904—2912; cf. Dale and Nierenstein, A., 1927, 564; Arndt and Eistert, A., 1928, 739; Bradley and Robinson, A., 1928, 759, 1009).—The interaction between an acid chloride (1 mol.) and an ethereal solution of diazomethane (2 mols.) led primarily to a diazoketone: $R\cdot COCl + CH_2N_2 = R\cdot CO\cdot CHN_2 + HCl$ (a); $CH_3N_2 + HCl = CH_3Cl + N_2$ (b), small quantities of the chloro-ketone being produced from the diazoketone by a side reaction: $R\cdot CO\cdot CHN_2 + HCl = R\cdot CO\cdot CH_2Cl + N_2$ (c). Nierenstein's claim (A., 1928, 739) that the chloro-ketones are obtained in good yield, e.g., ω -chloroacetophenone 72%, by adding the diazomethane to the acid chloride could not be confirmed. The course of the reaction between benzoyl chloride and diazomethane under various experimental conditions is interpreted as follows: when benzoyl chloride is in excess, (a) is the primary reaction and (c) occurs to a small extent; rapid mixing or mixing during 25 min. of equimolecular quantities in ether dried over phosphoric oxide or calcium chloride gives about 50% of ω -diazacetophenone and 10—13% of ω -chloroacetophenone.

Phenylacetyl chloride and diazomethane gave an oily diazomethyl ketone, which yielded benzyl *p*-nitrobenzoyloxymethyl ketone, m. p. 120°, when treated with *p*-nitrobenzoic acid in acetone. *p*-Nitrobenzoyl chloride and diazomethane react, giving ω -diaz-*p*-nitroacetophenone, m. p. 116—117°, which was converted into *p*-nitro- ω -acetoxycetophenone, m. p. 121—122°, when heated in glacial acetic acid solution (Dale and Nierenstein, A., 1927, 564, describe *p*-nitro- ω -acetoxycetophenone, m. p. 132°). The interaction between the chloride of *o*-diacetylprotocatechuic acid, m. p. 48—50° (Malkin and Nierenstein, A., 1928, 646, give m. p. 55°), and diazomethane yielded ω -diaz-3:4-diacetoxycetophenone, m. p. 76—77°, which furnished ω -3:4-triacetoxycetophenone, m. p. 92—93°, when heated with glacial acetic acid at 65—70° and ω -chloro-3:4-diacetoxycetophenone, m. p. 107.5—108°, when treated with hydrogen chloride in dry ether (cf. Voswinckel, A., 1910, i, 42, m. p. 110°; Malkin and Nierenstein, *loc. cit.*, m. p. 94°). Cinnamoyl chloride and diazomethane react to give a diazo-compound, m. p. 77—78°, which is probably the pyrazoline related to styryl diazomethyl ketone.

A. I. VOGEL.

Aromatic hydroxymethylene ketones and their derivatives. E. BENARY (Ber., 1928, 61, [B] 2252—2255; cf. A., 1926, 500; 1927, 573).—Nuclear-substituted hydroxymethylene ketones are converted by ammonium acetate and glacial acetic acid into imino-compounds, basic substances being produced, at the most, in traces. *p*-Bromophenyl β -hydroxyvinyl ketone, m. p. 71—72° (copper salt, decomp. about 268°; anilide, m. p. 178°), is prepared from *p*-bromoacetophenone, ethyl formate, and sodium in the presence of ether. It is converted by phenylhydrazine into 1-phenyl-5(3)-*p*-bromophenylpyrazole, m. p. 127°, and by ammonium acetate and glacial acetic acid into di-*o*-*p*-bromobenzoylvinylamine, $C_{18}H_{15}O_2NBr_2$, m. p. 217°. *p*-Chlorophenyl β -hydroxyvinyl ketone, m. p. 48—49°, similarly yields an anilide, m. p. 163—164°, di-*p*-chlorobenzoylvinylamine, m. p. 204°, and 1-phenyl-

5(3)-*p*-chlorophenylpyrazole, m. p. 118°. *m*-Nitrophenyl β -hydroxyvinyl ketone, m. p. 85°, its anilide, m. p. 151° after darkening, and di- β -*m*-nitrobenzoylvinylamine, m. p. 215—216°, are described. *m*-Cyanophenyl β -hydroxyvinyl ketone, m. p. 103—104°, yields di- β -*m*-cyanobenzoylvinylamine, m. p. 165°. Di- β -*p*-toluoylvinylamine, m. p. 155—156°, and di- β -*p*-methoxybenzoylvinylamine, m. p. 188—189°, are prepared from *p*-tolyl β -hydroxyvinyl ketone and *n*-methoxyphenyl β -hydroxyvinyl ketone, respectively. H. WREN.

Stereoisomeric bromoketimines. H. D. YOUNG (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 203—207).—Of the six bromoketimines prepared: $\text{CRR}'\text{NH} + \text{HOBr} = \text{CRR}'\text{NBr} + \text{H}_2\text{O}$, only *p*-chlorobenzophenonebromimine (α -form m. p. 109°, β -form m. p. 85°) and *p*-bromobenzophenonebromimine (α -form m. p. 104°, β -form m. p. 80°, third form m. p. 102—103°) were obtained in stereoisomeric forms. Bromimines of benzophenone, m. p. 41°, *p*-methoxybenzophenone, m. p. 95°, β -naphthophenone, m. p. 102°, and *p*-chloro-*p*-methoxybenzophenone, m. p. 77·5°, are described.

CHEMICAL ABSTRACTS.

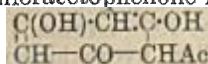
Isomerism of styryl methyl ketones. J. PASCUAL (Anal. Fis. Quim., 1928, 26, 222).—An isomeride of isobenzylidenedeoxybenzoin, m. p. 78—79°, is obtained from β -bromobenzylidenedeoxybenzoin by treatment with potassium acetate and acetic acid and extraction with ether. The new substance, which is white, gradually changes to the yellow isomeride (cf. A., 1925, i, 144). H. F. GILLBE.

Interaction of ethyl acetoacetate with distyryl ketones. IV. Selective addition to unsymmetrical chlorodistyryl ketones. I. M. HEILBRON and R. HILL (J.C.S., 1928, 2863—2870; cf. A., 1927, 565).—Interaction of styryl methyl ketone with *o*-chlorobenzaldehyde in the presence of 0·01 mol. of aqueous sodium hydroxide led to 2-chloro- β -hydroxy- β -phenylethyl styryl ketone, m. p. 79—80°, which with acetic anhydride gave 2-chlorodistyryl ketone, m. p. 82—83°; the latter could be obtained directly by increasing the alkali concentration to 0·03 mol. 3-Chlorodistyryl ketone, m. p. 108—109°, was similarly prepared. 4-Chloro- β -hydroxy- β -phenylethyl styryl ketone has m. p. 108—109°. Condensation of 2-chlorostyryl methyl ketone with *m*-chlorobenzaldehyde in the presence of dry hydrogen chloride at 0° gave 2:3'-dichlorodistyryl ketone, m. p. 67—68°; 2:4'-dichlorodistyryl ketone, m. p. 109°, and 3:4'-dichlorodistyryl ketone, m. p. 134° (3-chlorostyryl methyl ketone, b. p. 171°/20 mm., m. p. 28—29°, from *m*-chlorobenzaldehyde and acetone in the presence of aqueous sodium hydroxide), were prepared similarly. All the above distyryl ketones condense readily with ethyl acetoacetate in the presence of alcoholic sodium ethoxide. Thus, 2-chlorodistyryl ketone yielded ethyl 3-phenyl-5-*o*-chlorostyryl- Δ^5 -cyclohexen-1-one-2-carboxylate, (I), m. p. 137° [also obtained by warming ethyl (γ -keto- α -phenyl- ϵ -2-chlorophenyl- Δ^5 -pentenyl)acetoacetate, m. p. 112°, produced by condensation of the ketone and ethyl acetoacetate in the presence of piperidine, with alcoholic sodium ethoxide], and ethyl 3-phenyl-5-*o*-chlorostyryl- Δ^4 -cyclohexen-1-one-2-carboxylate (?)

(II), m. p. 107°, both of which gave *o*-chlorobenzoic acid when oxidised with potassium permanganate in acetone solution. When treated with sulphuric and acetic acids I afforded 3-phenyl-5-*o*-chlorostyryl- Δ^5 -cyclohexen-1-one, m. p. 142°, whilst II gave 3-phenyl-5-*o*-chlorostyryl- Δ^4 -cyclohexen-1-one(?), m. p. 136—137°. 4-Chlorodistyryl ketone condenses similarly to give ethyl 3-phenyl-5-*p*-chlorostyryl- Δ^5 -cyclohexen-1-one-2-carboxylate, m. p. 124—125° (oxidised to *p*-chlorobenzoic acid). Ethyl 3-*o*-chlorophenyl-5-*m*-chlorostyryl- Δ^5 -cyclohexen-1-one-2-carboxylate has m. p. 108—109° and yields *m*-chlorobenzoic acid, and ethyl 3-*o*-chlorophenyl-5-*p*-chlorostyryl- Δ^5 -cyclohexen-1-one-2-carboxylate, m. p. 143°, affords *p*-chlorobenzoic acid on oxidation. 3:4'-Dichlorodistyryl ketone gives ethyl 3-*m*-chlorophenyl-5-*p*-chlorostyryl- Δ^5 -cyclohexen-1-one-2-carboxylate, m. p. 122° (*p*-chlorobenzoic acid on oxidation). The mechanism of the reaction is discussed and an explanation of the results based on electronic conceptions is given. 2-Chlorostyryl methyl ketone condenses with *m*-chlorobenzaldehyde in the presence of aqueous sodium hydroxide with the formation of 2:2'-dichlorodistyryl ketone, m. p. 124°. A. I. VOGEL.

Phloracetophenone monomethyl ether and the so-called "hydroxypæonol." A. SONN (Ber., 1928, 61, [B], 2300—2302).—The constitutions assigned previously (A., 1925, i, 1267) to 2:6-dihydroxy-4-methoxyacetophenone, m. p. 136—137°, and 4:6-dihydroxy-2-methoxyacetophenone, m. p. 205—207°, are confirmed. Both compounds are converted by diazomethane into 2-hydroxy-4:6-dimethoxyacetophenone, which is transformed by ethyl iodide and potassium hydroxide into 4:6-dimethoxy-2-ethoxyacetophenone, m. p. 69—70°. This substance is also derived from the compound, m. p. 136—137°, by the successive action of diazoethane (giving 2-hydroxy-4-methoxy-6-ethoxyacetophenone, m. p. 133—134°) and methyl iodide and potassium hydroxide, whereas the isomeric ether, m. p. 205—207°, is transformed successively into 2-hydroxy-6-ethoxy-4-methoxyacetophenone, m. p. 56—57°, and 2:6-dimethoxy-4-ethoxyacetophenone, m. p. 81—82°. The "hydroxypæonol" of Rennie, Cooke, and Finlayson (J.C.S., 1920, 117, 338) and of Finlayson (B., 1927, 27) cannot be a monomethyl ether of phloracetophenone, since its m. p. is too low and the monoethers are not volatile with steam; it is probably the dimethyl ether. H. WREN.

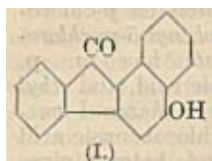
Tautomerism of phloracetophenone and related substances. A. SONN and K. WINZER (Ber., 1928, 61, [B], 2303—2306).—Phloracetophenone, its 2- and 4-monomethyl ethers, its dimethyl ether, di- and tri-acetyltriketohexamethylene, phloroglucinol and its trimethyl ether, resorcinol, and dimethyldihydroresorcinol have been titrated with bromine in methyl alcohol and chloroform according to Meyer's method. The behaviour of phloracetophenone is best expressed by the constitution



Ethyl 4-hydroxy-2:6-diethoxybenzoate, m. p. 180—181°, 4-methoxy-2:6-diethoxybenzoic acid, m. p. 166° (decomp.) (methyl ester, m. p. 95°), and methyl 2-hydroxy-4-methoxy-6-ethoxybenzoate, m. p. 97—98°, are described. H. WREN.

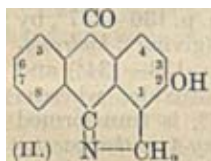
Constitution of a new hydroxybenzfluorenone.

H. E. FIERZ-DAVID and G. JACCARD (Helv. Chim. Acta, 1928, **11**, 1042—1047).—Condensation of α -naphthyl methyl ether with benzoyl chloride in presence of carbon disulphide and aluminium chloride gives phenyl α -4-methoxynaphthyl ketone, m. p. 82—83°, which when heated with 6 parts of dry aluminium chloride at 100—145° affords 85% of 5-hydroxy-chrysofluorenone (I), m. p. 305°, and 2% of 2-hydroxybenzanthrone (Perkin, J.C.S., 1922, **121**, 478, 917). The hydroxybenzanthrone described by Scholl and Seer (A., 1913, i, 56) is therefore I. Zinc dust distillation of I gives chrysofluorene, m. p. 188° (cf. Graebe, A., 1905, i, 83). β -Naphthyl methyl ether and benzoyl chloride yield mainly phenyl α -2-methoxynaphthyl ketone (25% of the methoxyl group is hydrolysed), which in turn gives 4-hydroxybenzanthrone. 1:5-Dimethoxy-4:8-dibenzoylnaphthalene, m. p. 356—358°, does not yield a benzanthrone derivative when heated with aluminium chloride.



H. BURTON.

Derivatives of hydroxyaminomethylanthraquinones and dihydroxydianthraquinonyl ethylenes. H. DE DIESBACH and P. GUBSER [with R. DE LANDERSET and H. LEMPEN] (Helv. Chim. Acta, 1928, **11**, 1098—1125).—2-Hydroxyanthraquinone reacts with *N*-methyloltrichloroacetamide (cf. Einhorn, A., 1906, i, 245) in cold concentrated sulphuric acid, yielding 2-hydroxy-1-trichloroacetamidomethylanthraquinone (I), m. p. 215° (decomp.), hydrolysed by boiling 10% sodium hydroxide solution in an atmosphere of hydrogen to 2-hydroxy-1:9(N)-isopyrroleanthrone (II) (annexed formula) (cf. Scholl, A., 1927, 675) (benzoyl derivative). This compound is decomposed by boiling with solvents, and dissolves in sulphuric acid and alkalis giving red solutions. One of the methylene hydrogen atoms



is very labile (cf. Scholl, *loc. cit.*). When II is boiled with acetic acid, preferably in absence of air, *s*-di-(α -2-hydroxyanthraquinonyl)ethylene glycol (tetrabenzoyl derivative + 12H₂O) is formed, oxidised to 2-hydroxyanthraquinone-1-carboxylic acid, m. p. 237° with loss of carbon dioxide. Oxidation of I or II with gaseous oxygen in alkaline solution, or with nitrous acid after previous hydrolysis, gives *s*-di-(α -2-hydroxyanthraquinonyl)ethylene (III) (dibenzoyl derivative + 3H₂O), also oxidised to 2-hydroxyanthraquinone-1-carboxylic acid. *N*-Methylolbenzamide and *N*-methylolphthalimide yield similarly 2-hydroxy-1-benzamidomethyl-, m. p. 250° (decomp.), and 2-hydroxy-1-phthalimidomethyl-anthraquinone (IV), m. p. 265° (decomp.), respectively. Accompanying IV is some 2-hydroxy-1-anthraquinonylmethylphthalamic acid, which loses water at 190°, forming IV. When IV is treated with hot sodium hydroxide solution and then acidified, the phthalate of 2-hydroxy-1-aminomethylanthraquinone (dibenzoyl derivative, m. p. 196°) is produced, which when boiled with acetic acid furnishes the acetate. When the above phthalate is heated with acetic acid at 170° *s*-di-(α -2-hydroxyanthraquinonyl)ethylenediamine (tetra-

benzoyl derivative) is formed. This is converted by boiling with nitrobenzene into III. 1-Hydroxyanthraquinone and the three *N*-methylol compounds yield 1-hydroxy-4-trichloroacetamidomethyl-, m. p. 197°; a mixture of 1-hydroxy-4-benzamidomethyl-, m. p. 208° (decomp.), and -2:4-di(benzamidomethyl)-, m. p. 276° (decomp.), and a mixture of 1-hydroxy-2:4-di(phthalimidomethyl)-anthraquinones, m. p. about 178°, respectively. 1-Hydroxy-2-methylanthraquinone affords 1-hydroxy-2-methyl-4-trichloroacetamidomethyl- (V), m. p. 239°, and -4-phthalimidomethyl-anthraquinone (VI), m. p. 285°. Hydrolysis of V with 10% sodium hydroxide solution in an atmosphere of hydrogen gives 4-hydroxy-3-methyl-1:9(N)-isopyrroleanthrone, more stable than II but oxidised in alkaline solution by gaseous oxygen to *s*-di-(α -4-hydroxy-3-methylanthraquinonyl)ethylene (VII). Hydrolysis of VI affords the phthalate of 1-hydroxy-2-methyl-4-aminomethylanthraquinone, which with acetic acid at 170° gives *s*-di-(α -4-hydroxy-3-methylanthraquinonyl)ethylenediamine, converted by boiling nitrobenzene into VII. 2-Hydroxy-3-methyl-1-trichloroacetamidomethyl- and -1-phthalimidomethyl-anthraquinones have m. p. 227° and 244°, respectively.

2-Hydroxy-1-trichloroacetamidomethylanthraquinone-3-carboxylic acid, decomp. 260° [-1-phthalimidomethyl derivative, m. p. 290°], is hydrolysed by sodium hydroxide solution to an unstable acid (2-hydroxy-isopyrroleanthrone-3-carboxylic acid?) which readily loses nitrogen, furnishing *s*-di-(α -2-hydroxy-3-carboxyanthraquinonyl)ethylene oxide. Oxidation of the unstable acid with nitrous acid gives *s*-di-(α -2-hydroxy-3-carboxyanthraquinonyl)ethylene. Both these compounds are oxidised by potassium permanganate or hydrogen peroxide to 2-hydroxyanthraquinone-1:3-dicarboxylic acid, decomp. about 250°.

2:3-Dihydroxy-1:4-di(trichloroacetamidomethyl)-anthraquinone, m. p. 253° [-1:4-di(phthalimidomethyl) derivative, m. p. 272°], is converted by warm 10% sodium hydroxide solution into β -amino- α -*bis*-(α -2:3-dihydroxy-4-aminomethylanthraquinonyl)ethyl alcohol isolated as its dihydrochloride.

Anthrarufin reacts with *N*-methylolphthalimide, yielding 1:5-dihydroxy-4(?)-phthalimidomethylanthraquinone, decomp. 230°, but with *N*-methyloltrichloroacetamide 1:5-dihydroxy-2:4:6:8-tetra(trichloroacetamidomethyl)anthraquinone, decomp. about 275°, is produced. Similarly, chrysazin gives 1:8-dihydroxy-2:4:5:7-tetra(phthalimidomethyl)-, -2:4:5:7-tetra(trichloroacetamidomethyl)-, decomp. 260°, and -2:4:5-tri(benzamidomethyl)-anthraquinones, decomp. about 250°, respectively.

H. BURTON.

Munjistin. I. P. C. MITTER and A. K. SEN (J. Indian Chem. Soc., 1928, **5**, 631—638).—Munjistin (Stenhouse, Annalen, 1864, **130**, 325; Schunk and Romer, A., 1877, ii, 788), probably 1:3-dihydroxyanthraquinone-2-carboxylic acid, should be formed by oxidation of rubiadin (A., 1928, 763). A further attempt has been made to prepare rubiadin in order to test the above hypothesis. When *o*-cresol and phthalic anhydride are condensed in presence of aluminium chloride (cf. Bentley and others, J.C.S., 1907, **91**, 1631; Ullmann, A., 1920, i, 53), a mixture of *o*-2'-hydroxy-3'-methylbenzoylbenzoic acid, m. p.

196°, and *o*-4'-hydroxy-3'-methylbenzoylbenzoic acid (I), m. p. 223°, is obtained. When I is heated with concentrated sulphuric acid on the water-bath, 2-hydroxy-1-methylanthraquinone, m. p. 211—212° (acetyl derivative, m. p. 125°), is produced (cf. Bentley, *loc. cit.*). Oxidation of this with alkaline potassium ferricyanide gives an ill-defined acid product. *o*-4'-Methoxy-3'-methylbenzoylbenzoic acid, m. p. 176°, is converted by heating with sulphuric acid at 155° into a mixture of 2-hydroxy-3-methylanthraquinone (II), m. p. 299° (acetyl derivative, m. p. 176°), and its methyl ether, m. p. 184°. Zinc dust distillation of II affords 2-methylanthracene, thus establishing the constitution. When II is heated with potassium hydroxide at 200—205°, 3-methylalizarin, m. p. 245—246° (acetyl derivative, m. p. 262°), is formed, and this is oxidised by manganese dioxide and concentrated sulphuric acid to 3-methylpurpurin, m. p. 234° (acetyl derivative, m. p. 287°). It was not possible to reduce 3-methylpurpurin to rubiadin by alkaline stannous chloride. Oxidation of munjistin gives no definite product.

H. BURTON.

Cannizzaro's reaction in pinacolin and benzil transformations. B. L. VANZETTI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1298—1301; Chem. Zentr., 1928, i, 2823—2824).—A neutral, reddish-brown oil obtained in the preparation of veratrilic acid from veratril and potassium hydroxide is believed to be a tetramethoxyanthraquinone. A. A. ELDRIDGE.

Orcein-like dyes. II. F. HENRICH and W. HEROLD (Ber., 1928, 61, [B], 2343—2349; cf. A., 1928, 632).—*p*-Amino-*m*-cresol is oxidised by silver oxide in dry ether to toluquinonemonimine, m. p. 59°, which may be preserved for a considerable period, particularly in the dark. Amino-orcinol, in ether or benzene, does not appear to be affected by silver oxide. 6-Amino-5-methoxy-*m*-cresol is readily transformed into the corresponding quinoneimine, m. p. 111° (hydrochloride, nitrate, sulphate, picrate), which gradually gives a blue, indophenol-like coloration with alkaline solutions of phenol, immediately with those of resorcinol, orcinol, or cresorcinol. Similarly, 2-amino-*o*-methoxy-*m*-cresol yields the corresponding quinone-monimine, m. p. 61°. The orcein-like dye, obtained previously (*loc. cit.*) by oxidation of an alcoholic solution of amino-orcinol with air, can be separated into a part soluble and a portion almost insoluble in alcohol. The insoluble portion does not yield amino-orcinol when treated with stannous chloride and hydrochloric acid, but this is obtained from the part soluble in alcohol.

H. WREN.

Derivatives of dibenzanthronyl. K. ZAHN and P. OCHWAT, Assrs. to GRASELLI DYESTUFF CORP.—See B., 1928, 808.

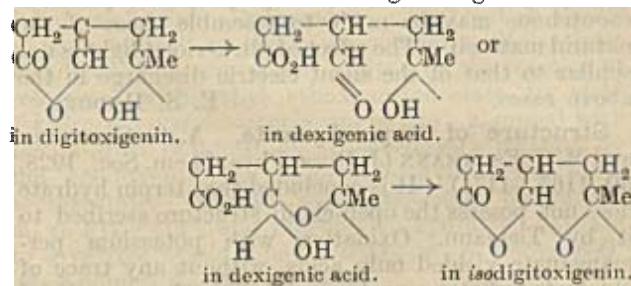
Manufacture of α -anthraquinonyl ketones. I. G. FARBENIND. A.-G.—See B., 1928, 887.

Manufacture of benzantrones and intermediate products. I. G. FARBENIND. A.-G.—See B., 1928, 922.

Manufacture of derivatives of pyrazolanthrone. I. G. FARBENIND. A.-G.—See B., 1928, 922.

Formula of digitoxin. A. WINDAUS and G. STEIN (Ber., 1928, 61, [B], 2436—2440).—New

analyses of digitoxin and many of its derivatives indicate the formula $C_{41}H_{64}O_{13}$ for the substance and its hydrolysis to 1 mol. of digitoxigenin, $C_{23}H_{34}O_4$, and 3 mols. of digitoxose. Digitoxigenin is a simply unsaturated, dihydroxy-lactone containing a system of four carbocyclic rings. One of the two hydroxyl groups is secondary and readily acetylated; the other is tertiary and is readily eliminated as water by combination with a neighbouring hydrogen atom. The following revised data are recorded (cf. Cloetta, A., 1921, i, 39; Windaus and Freese, A., 1926, 153): digitoxigenin, $C_{23}H_{34}O_4$, m. p. 250°, $[\alpha]_D^{25} + 19.1^\circ$ in methyl alcohol; acetyldigitoxigenin, $C_{25}H_{36}O_5$, m. p. 217°; anhydrodigitoxigenin, m. p. 193°, $[\alpha]_D^{25} - 4.68^\circ$ in methyl alcohol; tetrahydroanhydrodigitoxigenin, $C_{23}H_{36}O_3$, m. p. 167—168°, $[\alpha]_D^{25} + 24.60^\circ$ in methyl alcohol; tetrahydroanhydrodigitoxigenone, $C_{23}H_{34}O_3$, m. p. 245°, $[\alpha]_D^{25} + 37.3^\circ$ in chloroform, converted by Clemmensen's method into the lactone, $C_{23}H_{36}O_2$, m. p. 185°, $[\alpha]_D^{25} + 33.7^\circ$ in chloroform; the lactonedicarboxylic acid, $C_{23}H_{34}O_6$, has m. p. 296°, and its dimethyl ester, $C_{25}H_{38}O_6$, m. p. 128°. Further study of the isomerisation of digitoxigenin by alkali hydroxide considered in conjunction with the observations of Jacobs and Gustus (A., 1928, 1120) permits the identification of the following arrangements:



New or revised data are given for the following compounds: isodigitoxigenin, m. p. 272° (acetyl derivative, m. p. 243°); digitoxigenone, m. p. 200°, $[\alpha]_D^{25} + 33.3^\circ$ in chloroform; isodigitoxigenone, m. p. 264°, $[\alpha]_D^{25} + 19.5^\circ$ in chloroform.

H. WREN.

Amyrins. I. Dehydrogenation of amyirin. O. BRUNNER (Monatsh., 1928, 50, 284—290).—Since the isomerism of the amyrins probably disappears on dehydrogenation, the investigation was carried out with the mixture of the two isomerides. When heated with sulphur a violent reaction took place with foaming and carbonisation, but dehydrogenation occurred smoothly by heating with palladised animal charcoal (cf. Diels and Gadke, A., 1925, i, 1062) at 290° for 100 hrs. and finally at 320° for 24 hrs. The product was extracted with ether and fractionated. The fraction of b. p. 120—150°/12 mm. yielded the picrate, m. p. 131—132°, of an oily hydrocarbon (C, 91.43; H, 9.20%; mol. wt. 179). The fraction of b. p. 150—190°/12 mm. yielded the picrate of a hydrocarbon, m. p. 87° (C, 90.97; H, 10.36%; mol. wt. 197). The higher-boiling fractions yielded no crystalline compound.

R. K. CALLOW.

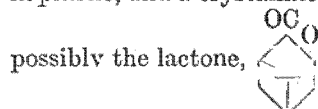
Osmotic experiments with caoutchouc solutions. H. KROEPFELIN and W. BRUMSHAGEN (Ber., 1928, 61, [B], 2441—2443).—Measurements of the osmotic pressure of benzene solutions of sol caoutchouc

obtained from crêpe rubber extracted with acetone at concentrations of 10–20 g. per litre give results for the micellar weight of the same order of magnitude as those of Meyer and Mark (A., 1928, 1252). H. WREN.

Effect of silent electric discharge on caoutchouc and decalin. P. FROMANDI (Kolloidchem. Beihefte, 1928, 27, 189–222).—When the silent electrical discharge acts on decahydronaphthalene, hydrogen is eliminated and this process is followed by condensation of the resulting unsaturated molecules. The exact course of the reaction depends on the atmosphere in which the experiment is conducted; thus, the unsaturated compound forms an ozonide in an atmosphere of oxygen, and in a nitrogen atmosphere an entry of nitrogen into the molecule takes place. The experiments on caoutchouc were carried out in decahydronaphthalene as solvent. Natural caoutchouc passes into a cyclic isomeride under the influence of the silent electric discharge. Meanwhile, the iodine value, viscosity, softening point, and mol. wt. are lowered. Synthetic isoprene caoutchouc, which from its iodine value already appears to have a cyclic structure, behaves similarly, with the exception that in the first stages of the process the charge is in the reverse direction. This latter fact seems to suggest that the physical and chemical properties of synthetic caoutchouc may be made to resemble those of the natural material. The effect of ultra-violet light is not similar to that of the silent electric discharge in the above cases. E. S. HEDGES.

Structure of terpin hydrate. A. S. GINZBERG and M. S. ESCHMANN (J. Russ. Phys. Chem. Soc., 1928, 60, 1165–1171).—It is concluded that terpin hydrate does not possess the open-chain structure ascribed to it by Tiemann. Oxidation with potassium permanganate yielded only acids, without any trace of aldehyde or ketone, such as might have been expected had a primary carbinol group been present. Metallic sodium gave only terpin and sodium hydroxide in equivalent amounts. The determination of the number of hydroxyl groups by the Tschugäev-Zerevitinov method (with magnesium alkyl halides) showed conclusively that two hydroxyl groups and one molecule of water of crystallisation were present. This was further confirmed by the formation in the cold of *s*-diphenylcarbamide with phenylcarbimide, instead of a phenylcarbamate. The absence of a primary alcohol grouping was further demonstrated by the negative action of benzoyl chloride, methyl sulphate, or Nessler's reagent. Terpin hydrate, accordingly, is concluded to be, like many tertiary alcohols, a crystallohydrate. M. ZVEGINTZOV.

Nopinene ozonide. G. BRUS and G. PEYRES-BLAUQUES (Compt. rend., 1928, 187, 984–986).—When nopinene is ozonised in chloroform solution at 0° and the solvent is evaporated, the ozonide, $C_{10}H_{16}O_3$, is obtained as a viscous liquid, which slowly and partly crystallises at 0°. This when hydrolysed by acid or alkali furnishes hydrogen peroxide, formaldehyde, nopinone, and a crystalline substance, m. p. 125–126°,

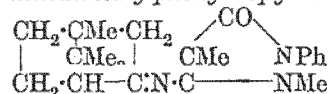


As the yield of nopinone (characterised by the formation of a compound $C_{18}H_{20}OCl_3$, m. p. 145–146°, by the action of hydrogen chloride in alcoholic solution) is 50%, the present is the best method of preparation. Determination of the formaldehyde obtained furnishes an accurate determination of nopinene (cf. Dupont and Brus, A., 1923, i, 934); the sample used was found to contain 93% of a substance containing the CH_2 grouping.

E. W. WIGNALL.

Configuration of tervalent nitrogen. M. FRÈREJACQUE (Compt. rend., 1928, 187, 894–896).—Various amines have been condensed with camphor- α -sulphonyl chloride, m. p. 88° (amide, m. p. 143°, $[\alpha]_{5461} + 94^\circ$ in water; cf. A., 1926, 1251), and thus are obtained the camphorsulphonyl derivatives of aniline, m. p. 124°, $[\alpha]_{5461} - 42.5^\circ$ (alcohol); *o*-toluidine, m. p. 117°, $[\alpha]_{5461} - 49.5^\circ$ (alcohol); *p*-toluidine, m. p. 197°, $[\alpha]_{5461} - 52.5^\circ$ (alcohol); and ethylaniline, m. p. 89°, $[\alpha]_{5461} - 68^\circ$ (benzene). In neutral solvents these derivatives are strongly laevorotatory, whilst the sulphonic acid, its methyl ester, amide, and chloride are dextrorotatory, but in alkaline solution the anilides are dextrorotatory, this being explained by the conversion of the camphor portion of the molecule into the enol form. The rotation of the anilides increases proportionately to the amount of alcoholic potassium hydroxide added until an equimolecular proportion has been added and then remains constant. All attempts to isolate enantiomorphous forms of these compounds of tervalent nitrogen were unsuccessful, the rotation remaining unchanged after fusion for several hours, or after reprecipitation by acids from their solutions in dilute alkalis. J. W. BAKER.

Compounds of camphor with amines. E. ROMAGNOLI (Annali Chim. Appl., 1928, 18, 465–468; cf. Saccardi and Romagnoli, A., 1927, 1196).—*Camphor-2-aminodimethylphenylisopyrazolone*,



m. p. 194°, prepared from pernitrosocamphor and aminoantipyrine, is readily split into the component molecules by hydrochloric acid, and forms with hydroferrocyanic acid an additive compound, charring at about 160°, T. H. POPE.

Constituents of campherol. M. ISHIDATE (J. Pharm. Soc. Japan, 1928, No. 555, 410–415; cf. A., 1928, 526).—By repeated fractional crystallisation from light petroleum, *d*-campherol is separated into 5-hydroxycamphor, m. p. 217–218°, $[\alpha]_D^{20} + 41.3^\circ$ (acetyl derivative, b. p. 159–160°/27 mm., $[\alpha]_D^{20} + 24.8^\circ$; semicarbazone, m. p. 233–235°), and 3-hydroxycamphor, m. p. 193–195°, $[\alpha]_D^{20} + 15.2^\circ$ (semicarbazone, m. p. 183–184°). K. ISHIMURA.

Synthesis of tetrahydrofurylpropylamine. R. TAKAMOTO and T. HIROHASHI (J. Pharm. Soc. Japan, 1928, No. 555, 446–450).— β -2-Furylacraldioxime is reduced with sodium amalgam to γ -2-furylpropylamine, b. p. 172.5–173°/754 mm., 34–35°/20 mm. (platinum double salt, m. p. 179–180°; picrate, m. p. 165–166°; picrolonate, m. p. 231–232°), which

is converted by hydrogen and platinum into γ -2-tetrahydrofurylpropylamine, b. p. 186—187°/754 mm., 46—47°/20 mm. (platinum double salt, m. p. 171—172°; picrate, m. p. 136—137°; picrolonate, m. p. 176—177°). K. ISHIMURA.

$\alpha\alpha'$ - and $\alpha\alpha'$ -Disubstituted- $\alpha\alpha'$ -dihydro- $\beta\beta'$ -benzofurans. F. SEIDEL (Ber., 1928, 61, [B], 2267—2276).—2 : 2-Diphenyl-1 : 2-diphenyl-1 : 2-dihydroisobenzofuran, described by Guyot and Catel (A., 1905, i, 226, 540; 1906, i, 761; 1907, i, 76), and *o*-benzoyldiphenylmethane are completely independent compounds which cannot be transformed into one another. Phthalide is converted by magnesium phenyl bromide in ether into *o*-hydroxymethyltriphenylcarbinol, m. p. 159°, transformed by boiling hydrochloric and acetic acids into 2 : 2-diphenyl-1 : 2-dihydroisobenzofuran, m. p. 95°, which does not react with phenyl- or benzoyl-hydrazine or *p*-nitroaniline and is not reduced by zinc and acetic acid, hydriodic acid, tin and hydrochloric acid, sodium amalgam, or sodium. It is oxidised by potassium dichromate in acetic acid to diphenylphthalide, m. p. 115—116°. Boiling, dilute nitric acid transforms it into the ether,

$(C_6H_4 \begin{smallmatrix} \text{CPh} \\ \text{CH} \end{smallmatrix} O)_2O$, m. p. 259—260°, oxidised by potassium dichromate and acetic acid to diphenylphthalide and converted by hydrochloric acid and ethyl alcohol at 135° into 1-ethoxy-2 : 2-diphenyl-1 : 2-dihydroisobenzofuran, m. p. 97°. Addition of a solution of phenylphthalide in benzene to ethereal magnesium phenyl bromide affords 1-hydroxy-1 : 2-diphenyl-1 : 2-dihydroisobenzofuran, reduced by sodium amalgam and methyl alcohol to 1 : 2-diphenyl-1 : 2-dihydroisobenzofuran, m. p. 93—95°, which does not react with hydrazine or 2 : 4-dinitrophenylhydrazine and is oxidised by nitric acid to *o*-dibenzoylbenzene, m. p. 148°. *o*-Benzoyldiphenylmethane, b. p. 220—225°/15—17 mm., m. p. 47—50° (phenylhydrazone, m. p. 139°), prepared from *o*-cyanodiphenylmethane and magnesium phenyl bromide, is oxidised by nitric acid to *o*-dibenzoylbenzene. *o*-Aminobenzyl chloride hydrochloride is converted by benzene in the presence of aluminium chloride into *o*-aminodiphenylmethane hydrochloride, m. p. 180°, from which *o*-iododiphenylmethane, b. p. 175—180°/14—17 mm., is derived. H. WREN.

7-Hydroxy-6-methoxycoumarin and its glucoside. E. GLASER [with M. SCHNECK] (Arch. Pharm., 1928, 266, 573—582).—Partial methylation of α -sculetin (7 : 6-dihydroxycoumarin) with methyl iodide affords α -methyl α -sculetin, m. p. 184° (Tiemann and Will, A., 1883, i, 199), which is shown to be 6-hydroxy-7-methoxycoumarin. Methyl sulphate and potassium hydroxide in methyl-alcoholic solution, however, furnish 7-hydroxy-6-methoxycoumarin, yellow, m. p. 199°, in 75% yield, identical with β -methyl α -sculetin, scapoletin, gelsemic acid, and chrysotropic acid, for which the following colour reactions are described: ferric chloride, green; potassium permanganate, dark green, turning indigo-blue with dilute sulphuric acid; boiling concentrated hydrogen sulphite solution followed by ferric chloride, blue, changing to red on addition of ammonia solution.

Its solutions in alkali or alcohol fluoresce more strongly than those of α -sculetin. Condensation of acetobromoglucose with β -methyl α -sculetin (7-hydroxy-6-methoxycoumarin) in presence of alkali gives 6-methoxy-7-coumarinyl tetra-acetylglucoside, m. p. 104—105°, $[\alpha]_D^{25}$ -39° in methyl alcohol. This is a β -glucoside according to the emulsin test, and is hydrolysed by absolute methyl-alcoholic ammonia to 6-methoxy-7-coumarinyl β -glucoside, m. p. 127—128°, $[\alpha]_D^{25}$ -37.5° in water. The parent glucoside and, incidentally, also methyl α -sculetin give a clear green coloration with ferric chloride, whilst the tetra-acetate remains colourless in the cold but becomes red on boiling. Colour reactions with potassium permanganate and nitric acid are similar in both cases. The fluorescence of these substances in acid solution has been studied: methyl α -sculetin > α -sculetin > methyl α -sculetin. S. COFFEY.

New synthesis of coumarin derivatives. R. WEISS and E. MERKSAMMER (Monatsh., 1928, 50, 115—122).—The reaction previously described (Weiss and Woidich, A., 1927, 250), in which resacetophenone is condensed with ethyl ethoxyacetoacetate by heating with alcoholic sodium ethoxide, has been further investigated, and the product is now found to be 7-hydroxy : 6-diacetylcoumarin. The reaction affords a new general synthesis of coumarin derivatives. Proof of this interpretation is given by the reaction of resorcinol with ethyl ethoxyacetoacetate to yield 7-hydroxy-3-acetylcoumarin, m. p. 236°, identical with the product obtained by Knoevenagel's method by the condensation of resorcyaldehyde with ethyl acetoacetate. It yields a *p*-bromobenzoyl derivative, m. p. 212—214°, and reacts with hydrazine hydrate to give resorcylaldazine (+H₂O), m. p. above 300° (cf. Knöpfer, A., 1909, i, 188).

7-Hydroxy-3 : 6-diacetylcoumarin is accompanied by a substance, C₁₆H₁₄O₆, m. p. 192—197°, in small amount. The substance previously described as 2-resorcyl-5-benzoyl-1 : 4-pyrone is actually 7-hydroxy-3-benzoyl-6-acetylcoumarin. The following compounds, prepared by the same method, are described: 7-hydroxy-3 : 6-diacetyl-5-methylcoumarin, m. p. 211—212° (from oracetophenone); 7-hydroxy-6-benzoyl-3-acetylcoumarin, m. p. 215—217° (from 2 : 4-dihydroxybenzophenone); 7 : 8-dihydroxy-3-acetylcoumarin, m. p. 254—255° (from pyrogallol). Methyl methoxyacetoacetate, also used in these reactions, was obtained crystalline, m. p. 56—58°. R. K. CALLOW.

Production of thiophen by the interaction of acetylene and carbon disulphide. H. V. A. BRISCOE, J. B. PEEL, and P. L. ROBINSON (J.C.S., 1928, 2857—2858).—Thiophen obtained from acetylene and sulphur (cf. Peel and Robinson, A., 1928, 1112) is produced probably by a direct reaction of acetylene with sulphur, and not by a secondary reaction between acetylene and carbon disulphide. Thiophen is produced in quantity by the latter reaction only when temperatures considerably higher than those required with sulphur are used. Acetylene saturated with carbon disulphide vapour was passed through a tube packed with broken porous pot and heated electrically. At 350° a trace of thiophen

appeared; at 700° maximum formation occurred, the condensate containing 10% by volume of thiophen and 10% of hydrocarbons. R. J. W. LE FEVRE.

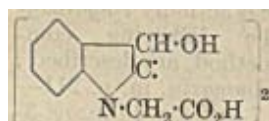
Primary tar oils [thiophens]. R. WEISSGERBER.
—See B., 1928, 917.

Alkylation and acylation of thiophen in presence of tin tetrachloride. G. STADNIKOV and I. GOLDFARB (Ber., 1928, 61, [B], 2341—2342; cf. A., 1928, 427).—The yields of acylated thiophens obtained by the action of acid chlorides on thiophen in presence of tin tetrachloride depend considerably on the solvent employed. The yield of acetylthiophen increases from 50—58% to 96% when petroleum, b. p. 120—140°, is replaced by benzene. Benzoylthiophen m. p. 55°, is prepared in 92% yield in presence of benzene. Benzhydryl ethyl ether, thiophen, and stannic chloride in carbon disulphide afford diphenylthienylmethane, m. p. 65°, and *dibenzhydrylthiophen*, m. p. 85—85.5° (oxidised by chromic acid to benzophenone). H. WREN.

Thiophenols. Formation of rings containing sulphur. C. FINZI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1312—1314; Chem. Zentr., 1928, i, 2178).—The formation of thioresorcinol-*o*-benzoic acid, dithioxanthone, dithioxanthhydrol, thioresorcinoldipropionic acid, dithiochromanone, ketodihydrothiazinethiopropionic acid, thioresorcinol-*o*-phenylpropionic acid, and dithioflavanone is described.

A. A. ELDRIDGE.

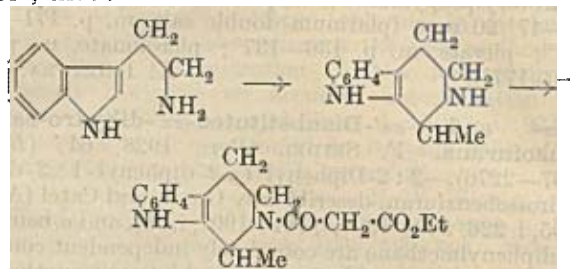
Derivatives of isatin. A new example of isomerism. N. J. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1179—1190).—The condensation of sodio-isatin with ethyl chloroacetate and chloromalonate and with ethylene dibromide was investigated. Sodio-isatin and ethyl chloroacetate gave a good yield of *ethyl isatin-N-acetate*, m. p. 114° which could be hydrolysed only with extreme difficulty by aqueous hydrogen iodide, with partial reduction, to give a compound, m. p. 219—220°, of the annexed formula.



With ethyl chloromalonate, sodio-isatin yielded *diethyl isatin-N-malonate*, m. p. 82°. Interaction of sodio-isatin with ethylene dibromide was very slow the final products being *isatin N-ethyl bromide*, m. p. 130°, and *ethylenedi-isatin*, m. p. 190°. Further condensation of isatin *N*-ethyl bromide with ethyl sodiomalonate yielded a mixture of unidentified products together with *n*-propylaniline. When ethylenedi-isatin was distilled with lime, an oil containing aniline and quinoline was obtained. The quinoline was separated from aniline by means of silver nitrate, which formed with it a compound, m. p. 128°, from which the silver can be removed by ammonium sulphate. M. ZVEGINTZOV.

Synthesis of carboline derivatives. G. TATSUI (J. Pharm. Soc. Japan, 1928, No. 555, 453—459).— β -(3-Indolyl)ethylamine reacts with paraldehyde yielding *tetrahydroharman*, m. p. 179—180° [*hydrochloride*, m. p. 265° (decomp.)]; *benzoyl* derivative, m. p. 168—169°, which with ethyl sodiomalonate at 110—

120° gives *tetrahydroharmanmalonate*, m. p. 134—135°, thus:



Tetrahydroharmanmalonic acid loses carbon dioxide at 155°, giving *acetyl tetrahydroharman*.

K. ISHIMURA.

Acridone derivatives. R. WEISS (Monatsh., 1928, 50, 109—114).—An account is given of unsuccessful attempts to synthesise a heterocyclic analogue of trimethylenetriphenylmethane triketone (Weiss and Korezyn, A., 1925, i, 560) derived from triphenylamine.

[With L. KATZ.]—3-Nitro-4-methylbenzophenone, m. p. 130—132°, was prepared from 2-nitro-*p*-toluoyl chloride and benzene by the Friedel-Crafts reaction. The 3-amino-derivative, m. p. 108—110°, obtained by reduction with stannous chloride, yielded with *o*-chlorobenzoic acid by the Ullmann reaction *N*-(5'-benzoyl-*o*-tolyl)anthranilic acid (+0.5H₂O), m. p. 190—192° (methyl ester, m. p. 95—100°). Condensation of *o*-chlorobenzoic acid with 2-amino-*p*-toluic acid hydrochloride yielded 2-methyldiphenylamine-5:2'-dicarboxylic acid [*N*-(5-carboxy-*o*-tolyl)anthranilic acid], m. p. 257° (decomp.). Attempts to prepare acridone derivatives from either of these anthranilic acids were unsuccessful.

[With W. HANDL and J. L. MELZER.]—Condensation of *o*-iodotoluene with *N*-*o*-tolylantranilic acid yielded *NN*-di-*o*-tolylantranilic acid, m. p. 206—209°. When heated with concentrated sulphuric acid it yielded *N*-*o*-tolyl-4-methylacridone, m. p. 197—199°. Similarly, *N*-phenyl-*N*-*o*-tolylantranilic acid, m. p. 166—168°, yielded a mixture, m. p. 180—195°, of *N*-*o*-tolyl- and *N*-phenyl-4-methylacridones. Attempts to oxidise the methyl groups of the anthranilic acids or to bring about further ring-closure in the acridones were unsuccessful. R. K. CALLOW.

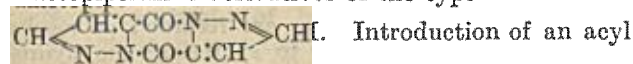
Pyridine and quinoline derivatives. III. New synthesis of 2-aminonicotinic acid and its behaviour with nitric acid. C. RATH and G. PRANGE (Annalen, 1928, 467, 1—10).—2:5-Diaminopyridine (obtained by electrolytic reduction of 3-nitro-2-aminopyridine) is converted (yield 50%) by the Sandmeyer reaction into 5-cyano-2-aminopyridine, b. p. 240—250°/15 mm., m. p. 163—164°, which is hydrolysed to 2-aminopyridine-5-carboxylic acid + 2H₂O (I), decomp. 312° [nitrate, m. p. 242° (decomp.)]. This is converted by the action of a mixture of sulphuric and nitric (*d* 1.35) acids not, as Marckwald (A., 1894, i, 381) states, into the nitrate, but into 2-nitroaminopyridine-5-carboxylic acid (II) decomp. explosively 233° (sodium salt), which is reduced by tin and hydrochloric acid to I, and, also contrary to Marckwald (*loc. cit.*), is converted by 10% sodium hydroxide into the disodium salt of 3-nitro-2-hydroxypyridine-5-carboxylic acid, m. p. 277°

(decomp.); the free acid is converted by the action of iodine, potassium hydroxide, and sodium hydrogen carbonate at 150—160° into 5-iodo-3-nitro-2-hydroxypyridine. If I is nitrated under Tschitschibabin's conditions (cf. A., 1915, i, 591) and the whole reaction mixture subsequently heated to 100°, the main product is 2-hydroxypyridine-5-carboxylic acid, converted by iodine and sodium hydrogen carbonate into 3:5-di-iodo-5-hydroxypyridine. J. W. BAKER.

Dyes derived from quinoline-2-aldehyde. A. N. DEY and S. DUTT (J. Indian Chem. Soc., 1928, 5, 535—537).—Condensation of quinoline-2-aldehyde with dimethylaniline in presence of zinc chloride, and subsequent oxidation of the product formed with manganese or lead dioxide, affords pp-tetramethyldiaminodiphenyl-β-quinolinylcarbinol, m. p. 196—198°. The corresponding tetraethyldiamino-, m. p. 144—145°, dibenzyl dimethyldiamino-, m. p. 172—174°, and dibenzyl diethyldiamino-derivatives, m. p. 252—254° are obtained from diethyl-, benzylmethyl-, and benzylethyl-aniline, respectively. If 2-methylquinoline tribromide is used instead of the aldehyde the carbinols can be obtained directly. The dyes described are green or blue-green and are devoid of photosensitising properties. H. BURTON.

Derivatives of diketopiperazine. Synthesis of o- and m-tyrosine. H. UEDA (J. Biochem. Japan, 1928, 8, 397—407).—3:6-Di-(o-acetoxybenzylidene)-2:5-diketopiperazine, obtained by condensation of glycine anhydride with salicylaldehyde, was diacetylated and reduced to o-tyrosine anhydride. Condensation of glycine anhydride with o-methoxybenzaldehyde afforded 3:6-di-(o-methoxybenzylidene)-2:5-diketopiperazine, or with m-hydroxybenzaldehyde, the corresponding m-compound. The latter, on deacetylation and reduction, gave m-tyrosine anhydride. Reduction before hydrolysis produced the amino-acids. CHEMICAL ABSTRACTS.

Pyrazole derivatives of the type of diketopiperazine. K. VON AUWERS and E. CAUER (Ber., 1928, 61, [B], 2402—2411).—Pyrazolecarboxylic acids generally lose carbon dioxide when heated above their m. p. and pass into the corresponding pyrazoles, but in certain cases amorphous products of high m. p. are formed in greater or smaller amount. These substances are also produced by attempts to acylate certain pyrazolecarboxylic acids. They are doubtless diketopiperazine derivatives of the type



Introduction of an acyl group into an aliphatic α-amino-acid scarcely affects the behaviour of the compound when heated. If an acid residue is attached to one of the nitrogen atoms of a pyrazolecarboxylic acid, the tendency to lose carbon dioxide when heated may be greatly or completely repressed. The approximate yields of diketopiperazine and acylpyrazole obtained when the various acids are heated are given in parentheses: N-carbethoxy-4-methylpyrazole-3-carboxylic acid (0%, 80%); N-o-nitrobenzoyl-4-methylpyrazole-3-carboxylic acid (60%, 40%); N-o-nitrobenzoyl-5-methylpyrazole-3-carboxylic acid (90%, 10%); N-acetyl-o-methylpyrazole-3-carboxylic acid (100%, 0%),

N-acetyl-4-bromo-5-methylpyrazole-3-carboxylic acid (100%, 0%); N-carbethoxy-4:5-dimethylpyrazole-3-carboxylic acid (50%, 50%); N-acetyl-4-phenylpyrazole-3-carboxylic acid (100%, 0%). The production of diketopiperazines by the acylation of pyrazolecarboxylic acid does not depend greatly on the mode of operation (heating with acyl chloride or treatment in pyridine), but the influence of the structure of the pyrazole and nature of the acyl chloride is very marked. The yields of diketopiperazine and acyl derivative obtained by the two processes are given below: pyrazole-3-carboxylic acid and o-nitrobenzoyl chloride (little, much, 50%, 50%); 4-methylpyrazole-3-carboxylic acid with ethyl chloroformate (0%, 100%), acetyl chloride (0%, 100%, 0%, 100%) or o-nitrobenzoyl chloride (0%, 100%, 5%, 95%); 5-methylpyrazole-3-carboxylic acid with acetyl chloride (5%, 95%, 10%, 90%), or o-nitrobenzoyl chloride (95%, 5%, 100%, 0%), 4-o-dimethylpyrazole-3-carboxylic acid with ethyl chloroformate (—, 80%), with acetyl chloride (10%, 90%) or o-nitrobenzoyl chloride (100%, 0%, 100%, 0%), 4-chloro-5-methylpyrazole-3-carboxylic acid with o-nitrobenzoyl chloride (100%, 0%); 4-bromo-o-methylpyrazole-3-carboxylic acid with acetyl chloride (10%, 90%) or o-nitrobenzoyl chloride (100%, 0%, 100%, 0%); 4-phenylpyrazole-3-carboxylic acid with acetyl chloride (0%, 100%) or o-nitrobenzoyl chloride (100%, 0%, 100%, 0%); 4-phenylpyrazole-3-carboxylic acid with o-nitrobenzoyl chloride (100%, 0%, 100%, 0%); tetrahydroindazole-3-carboxylic acid with o-nitrobenzoyl chloride (0%, 100%). Thionyl chloride is the most suitable acid chloride for the transformation of pyrazolecarboxylic acids into diketopiperazines. Glycine and o-nitrobenzoyl chloride react vigorously at 135° without giving a piperazine derivative, but the acid is not affected by thionyl chloride. Boiling acetic anhydride, which converts α-amino-acids into diketopiperazines, mainly acetylates pyrazolecarboxylic acids. Whereas esters of α-amino-acids are usually converted more or less readily into diketopiperazines at the ordinary temperature, pyrazolecarboxylic esters are stable under these conditions but lose carbon dioxide when heated without production of anhydridised compounds.

The following compounds appear to be new: N-o-nitrobenzoylpyrazole-3(5)-carboxylic acid, m. p. 195—196°; ethyl N-chloroacetyl-5-methylpyrazole-3-carboxylate m. p. 127.5—129.5°; 3-methyl-5-ethylpyrazole, b. p. 118°/12 mm. (picrate, m. p. 137.5—139°; an isomeric picrate, m. p. 126—128°, is described); 3(5)-propylpyrazole, m. p. 117°/13 mm. (picrate, m. p. 150—152°), diketopiperazine, C₁₂H₁₂O₂N₄, m. p. 285—286°, from 4:5-dimethylpyrazole-3-carboxylic acid and o-nitrobenzoyl chloride; N-acetyl-4-phenylpyrazole-3-carboxylic acid, m. p. 162.5—164.5° (decomp.).

Relative tenacity of alkyl groups towards nitrogen. K. VON AUWERS and W. MAUSS (Ber., 1928, 61, [B], 2411—2420; cf. A., 1925 i, 1100; 1928 306).—Thermal decomposition of the iodides of NN'-dialkylbenzimidazoles, (C₆H₄ < $\begin{array}{c} \text{NR} \\ \text{NR} \end{array} > \text{CH})\text{X}$, requires somewhat protracted heating at an elevated temperature and yields a considerable proportion of

resinous matter, whilst the decomposition products are mixed with unchanged original material. The compounds are therefore not so suitable as the indazolium salts for the comparison of the tenacities of alkyl groups. Nevertheless such tenacity is found to increase in the order methyl, ethyl, propyl, and to diminish with benzyl. With simple iminazoles (cf. Sarasin, A., 1923, i, 710), von Braun's rule is followed by the methylethyl and methylpropyl but not by the ethylbutyl and propylbutyl derivatives. The ethylpropyl compound behaves unexpectedly by yielding ethyliminazole. Somewhat similar irregularities are observed with tetra-alkylammonium salts, so that it appears that the thermal decomposition of quaternary salts can be applied to the constitution of tenacity series only in very definite circumstances.

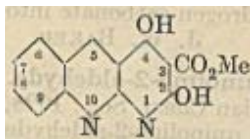
The following compounds are described: 1:3-diethylbenziminazolium iodide, m. p. 225—227°, and the corresponding picrate, m. p. 254—257°; 1-ethylbenziminazole, b. p. 160—162°/12 mm. (picrate, m. p. 219°); 1-methyl-3-ethylbenziminazolium iodide, m. p. 192—193°; 1-benzylbenziminazole, m. p. 115—115.5° (picrate m. p. 161—163°); 1-methyl-3-benzylbenziminazolium iodide, m. p. 158°; 1:3-dipropylbenziminazolium iodide, m. p. 202—203°; 1-propylbenziminazole, b. p. 170—172°/14 mm. (picrate, m. p. 204—206°); 1-ethyl-3-propylbenziminazolium iodide, m. p. 171.5—172°; 1-benzyl-3-ethylbenziminazolium iodide, m. p. 173.5—174.5°; 1-n-butylbenziminazole, b. p. 114—116°/12 mm. (picrate, m. p. 79.5—81.5°); 1-ethyl-3-butyliminazolium iodide; 1-propyl-3-butyliminazolium iodide.

Triethylpropylammonium iodide, m. p. 255—256° decomposes at 260—270° into ethyl iodide and diethylpropylamine. Ethyltripropylammonium iodide affords propyl iodide and ethyldipropylamine. Diethyldipropylammonium iodide, m. p. 238—240° gives ethyl and propyl iodides and diethylpropylamine and ethyldipropylamine. H. WREN.

Preparation of histidine. F. CHEMNITZ (Pharm Zentr., 1928, 69, 741—742).—Ox blood is hydrolysed with boiling hydrochloric acid (*d* 1.19) and the product distilled in a vacuum at 50°. The syrupy residue is neutralised with 0.1*N*-sodium hydroxide and sodium carbonate without allowing the temperature to rise, filtered, and heated with 0.2*N*-sodium hydroxide until all the ammonia is expelled. After filtering off small quantities of leucine and tyrosine which separate, histidine is precipitated as its double mercurichloride by alternate addition of a hot solution of mercuric chloride and a cold solution of sodium carbonate so that the reaction mixture remains alkaline. The precipitate, purified by reprecipitation with sodium carbonate from its solution in dilute hydrochloric acid, is decomposed by hydrogen sulphide, and the filtrate concentrated to yield histidine hydrochloride, which may be purified by crystallisation from 60% alcohol or by conversion into the picrate. J. W. BAKER.

Synthesis of methyl 2:4-dihydroxybenz 1:10-naphthyridine-3-carboxylate. G. KELLER and E. STRANG (Monatsh., 1928, 50, 144—148).—Quinoline-2:3-dicarboxylic acid (cf. A., 1928, 1024) was converted into the anhydride, m. p. 223°

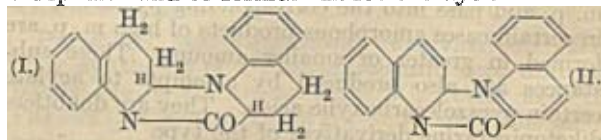
(cf. Konopnicki and Sucharda, A., 1928, 73), by heating with acetic anhydride. Treatment of the anhydride with ammonia in benzene solution yielded the amorphous *quinoline-2-carboxylamide-3-carboxylic acid*, sintering at 175°, m. p. 189—190°, which, by the action of sodium hypobromite, yielded 2-aminoquinoline-3-carboxylic acid, m. p. 290—292° (decomp.), from



which 2-aminoquinoline was obtained by distillation. Methyl 2-aminoquinoline-3-carboxylate, m. p. 140—141°, ethyl malonate, and sodium ethoxide when heated at 145—150° gave methyl 2:4-dihydroxybenz-1:10-naphthyridine-3-carboxylate (annexed formula), m. p. 240°, gelatinous from alcohol. R. K. CALLOW.

Manufacture of derivatives of pyrazolanthrone and of vat dyes. I. G. FARBERIND.—See B., 1928, 922, 923.

Red quinoline dye of Besthorn. H. WIELAND, O. HETTICHE, and T. HOSHINO (Ber., 1928 61 [B] 2371—2381; cf. A., 1904, i, 527; 1905, i, 612).—The dye obtained by Besthorn by heating quinoline-2-carboxylic acid with acetic anhydride or from quinoline-2-carboxyl chloride and quinoline is readily hydrogenated in the presence of Adams' platinum catalyst to the compound $C_{19}H_{18}ON_2$, m. p. 155°, which is readily re-converted into the dye. It is isomerised by boiling methyl-alcoholic potassium hydroxide to the β -compound, $C_{19}H_{18}ON_2$, m. p. 133—134°, reconverted by lead peroxide into the dye. Either the α or β -form the hydro-compound is transformed by 20% hydrochloric acid at 150° into a mixture of dihydrocarbostyryl, m. p. 163—164°, 1:2:3:4-tetrahydroquinoline, quinoline, and 1:2:3:4-tetrahydroquinoline-2-carboxylic acid (isolated as the hydrochloride dihydrate, m. p. 115—125°, decomp. 200°), and a yellow resin probably containing polymerised dihydroquinoline. The non-appearance of tetrahydrocarbostyryl is due, probably, to its instability. The results are interpreted as giving confirmation to the constitution I of the hydro-compound and to formula II for the dye:

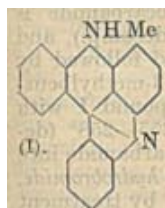


The following observations are recorded as results of unsuccessful attempts to synthesise the hydro-derivative. Quinoline-2-carboxyl chloride condenses with tetrahydroquinoline to 2-quinolyl 1-tetrahydroquinolyl ketone, m. p. 115—116° (hydrochloride, m. p. 160—162°), which could not be hydrogenated or oxidised directly to Besthorn's dye. 1:2:3:4-Tetrahydroquinoline-2-carboxylic acid, m. p. 112—113° (hydrochloride, m. p. 115—120° with loss of water of crystallisation, m. p. [anhyd.] 200° [decomp.]; methyl ester, b. p. 180°/15 mm., and its hydrochloride, m. p. 191°; nitroso-derivative, decomp. 132°), is prepared by hydrogenation of quinoline-2-carboxylic acid in glacial acetic acid in presence of Adams' platinum catalyst. Hydrogenation of the methyl ester with

palladium-black affords *methyl di-4:4'-tetrahydroquinolyl-2:2'-dicarboxylate*, m. p. 175—176°, in addition to the simple ester, but this complication is not observed when the Adams catalyst is employed. The acid hydrochloride is converted by ethyl chloroformate in weakly alkaline solution into *1-carbethoxy-1:2:3:4-tetrahydroquinoline-2-carboxylic acid*, m. p. 96—97°, converted by hot thionyl chloride into the corresponding *anhydride*, m. p. 155—156°. *1:2:3:4-Tetrahydroquinoline-2-carboxylic acid hydrochloride* is transformed by acetic anhydride in pyridine into *1-acetyl-1:2:3:4-tetrahydroquinoline-2-carboxylic acid*, m. p. 175—176°, and by benzoyl chloride and sodium hydroxide into *1-benzoyl-1:2:3:4-tetrahydroquinoline-2-carboxylic acid*, m. p. 187—188° (decomp.), which with thionyl chloride yields a labile compound containing sulphur and ultimately decomposing into quinoline-2-carboxyl chloride and sulphur.

H. WREN.

Triphenylmethane compounds with linked benzene nuclei. IV. Preparation of an iminophenyleneacridine derivative; dependence of colour on the nature of the atoms completing the ring. R. WEISS and J. L. KATZ (*Monatsh.*, 1928, 50, 225—230).—*N-(5'-Anilino-o-tolyl)anthranilic acid*, m. p. 190—193°, was obtained when *o*-chlorobenzoic acid was heated with 3-amino-4-methyldiphenylamine in amyl alcohol in presence of potassium carbonate and copper powder. When heated with zinc chloride in acetic acid, it yielded *1-anilino-4-methylacridone*, m. p. 140—160° (+AcOH or +EtOH), which was converted by heating with



phosphoryl chloride or zinc chloride into *methyliminophenyleneacridine* (I), dark blue crystals, m. p. above 355°, yielding a blue solution in hydrochloric acid. Coeramidonine derivatives (in which NH is replaced by CO) are reddish-brown and fluorescent. In the course of attempts to synthesise com-

pounds of this class by other methods, *5-nitro-2-methyldiphenylamine-2'-carboxylic acid*, m. p. 220—221° (methyl ester, m. p. 152—155°), was prepared by an Ullmann reaction from 4-nitro-*o*-toluidine and *o*-chlorobenzoic acid. Closure of the ring could not be effected, only amorphous products being obtained. When reduced by stannous chloride, carbon dioxide was lost simultaneously, yielding *5-amino-2-methyldiphenylamine*, m. p. 89—91°. R. K. CALLOW.

New synthesis of benztriazole derivatives. S. N. CHAKRABARTY and S. DUTT (*J. Indian Chem. Soc.*, 1928, 5, 555—559).—*o*-Nitrobenzeneazophenol is reduced by alcoholic ammonium sulphide to *2-4'-hydroxyphenyl-1:2:3-benztriazole*,

$C_6H_4 \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ N \end{smallmatrix} N-C_6H_4 OH$, m. p. 231°, oriented by oxid-

ation with alkaline potassium permanganate, when triazoledicarboxylic acid (Bladin, A., 1893, i, 375) is produced. The following 2-substituted-1:2:3-benztriazoles have been prepared: *4'-methoxyphenyl*, m. p. 138°; *2':4'-dihydroxyphenyl*, m. p. 191°; *4'-hydroxynaphthyl*, m. p. 201°; *2'-hydroxynaphthyl*, m. p. 119°; *4'-hydroxy-3'-carboxyphenyl*, m. p. 300; *4'-hydroxy-3'-carboxynaphthyl*, m. p. 189°; *3'-hydr-*

oxy-4'-carboxyphenyl, m. p. 109°; *2':3':4'-tri-hydroxy-6'-carboxyphenyl*, m. p. 191°; *4'-hydroxy-3'-aldehydophenyl*, m. p. 132°; *4'-aminophenyl*, m. p. 135°, and *4'-dimethylaminophenyl*, m. p. 187°. Reduction of 4-benzeneazo-*m*-nitroaniline gives *5-amino-2-phenyl-1:2:3-benztriazole*, m. p. 182°. *5-Amino-2-4'-sulphophenyl*, *5-amino-2-naphthyl*, m. p. 169°, and *5-amino-2-β-naphthyl-1:2:3-benztriazole*, m. p. 114°, are prepared similarly.

It is suggested that the introduction of a group into one of the benzene nuclei in *o*-nitroazobenzene (reduced normally to the *o*-amino-derivative) causes the two rings to move nearer to each other in space. The intermediate reduction product, *o*-hydroxylaminohydrazobenzene, can then eliminate water, and subsequently loses hydrogen forming the benztriazole.

H. BURTON.

isoOxazole ψ -bases and salts. II. E. P. KOHLER and N. K. RICHTMYER (*J. Amer. Chem. Soc.*, 1928, 50, 3092—3106).—Further evidence is adduced for the structures previously ascribed (A., 1928, 652) to the ψ - and anhydro-bases derived from fully substituted isooxazolinium salts. The additive product from 3:4:5-triphenylisooxazole and ethyl sulphate is converted by ferric chloride and hydrochloric acid into 3:4:5-triphenyl-2-ethylisooxazolinium ferrichloride, m. p. 165—167°. This is not attacked by ozone, but with permanganate it gives acetaldehyde, benzoic acid, and benzil. It is reduced by Grignard reagents to *ethyl-β-benzoyl-αβ-diphenylvinylamine*, m. p. 118—119°, the constitution of which is confirmed by its synthesis from the substance $CPhBz:CPh:N:CH_3$, (I) (*loc. cit.*) and magnesium methyl iodide. The ferrichloride affords with aqueous sodium hydrogen carbonate a solution of the isooxazolinium hydroxide, which readily isomerises to the ψ -base (II), *5-hydroxy-3:4:5-triphenyl-2-ethylisooxazoline*, m. p. 120° (decomp.) with rapid heating. This forms with methyl alcohol 5-methoxy-3:4:5-triphenyl-2-ethylisooxazoline (III), m. p. 100°, with acids, the corresponding 3:4:5-triphenyl-2-ethylisooxazolinium salts, and with sodium in dry ether, a yellow *sodio*-derivative. 3:4:5-Triphenyl-2-ethylisooxazolinium chloride and sodium cyanide yield 5-cyano-3:4:5-triphenyl-2-ethylisooxazoline (IV), m. p. 89°, which, unlike the isooxazolinium salts, is oxidisable by ozone.

When II, III, and IV are heated above their m. p. they lose water, methyl alcohol, and hydrogen cyanide, respectively, forming the *anhydro-base*, $CPhBz:CPh:N:CHMe$, m. p. 112°. In presence of traces of bases this gives with methyl alcohol yellow *oxyethyl-β-benzoyl-αβ-diphenylvinylamine*, m. p. 140°, with hydrogen cyanide, *α-cyanoethyl-β-benzoyl-αβ-diphenylvinylamine*, m. p. 130°, which is hydrolysed by concentrated hydrochloric acid to dibenzoylphenylmethane and alanine, and with magnesium methyl iodide, yellow *isopropyl-β-benzoyl-αβ-diphenylvinylamine*, m. p. 115°, which yields *isopropylamine hydrochloride* on hydrolysis. The anhydro-base is hydrolysed by traces of acid in the air to *β-benzoyl-αβ-diphenylvinylamine*, m. p. 162°, the ozonide of which is hydrolysed to benzil and benzamide. On one occasion a (? stereo-)isomeric *amine*, m. p. 208°, was obtained

from the base I. Both isomerides are hydrolysed by acid to dibenzoylphenylmethane, but the former reacts with 2 mols. and the latter with 1 mol. of Grignard reagent. The former is also formed from magnesium phenyl bromide and either 3:4:5-triphenylisooxazole or benzoylphenylacetone nitrile (cf. Claisen, A., 1926, 406).

α -Nitrostilbene and *p*-bromophenyl nitromethane in methyl alcohol are converted by sodium methoxide into a mixture of isooxazoles, which was ethylated and treated with ferric chloride. Pure 3:4-diphenyl-5-bromophenyl-2-ethylisooxazolinium ferrichloride, m. p. 172—174° (greenish-yellow and brown modifications), obtained by recrystallisation of the product, was identified by decomposition of the corresponding chloride at 170° to 3:4-diphenyl-5-bromophenylisooxazole, m. p. 172—173°. This is ozonised to β -benzilmonoxime *p*-bromobenzoate, m. p. 145—146°, which is formed from *p*-bromobenzoyl chloride and β -benzilmonoxime in pyridine. With alkali, the ferrichloride yields 5-hydroxy-3:4-diphenyl-5-*p*-bromophenyl-2-ethylisooxazoline, m. p. 105° (decomp.), which is ozonised to *p*-bromobenzil, m. p. 89—90°, and benzoic acid. This decomposition establishes the constitutions ascribed to these ψ -bases, the tautomeric open-chain formulæ, such as CPhBz:CPh·NEt·OH, being rendered improbable by the differences in colour between the isomeric derivatives of the ψ - and anhydro-bases. β -*p*-Bromobenzoyl- $\alpha\beta$ -diphenylvinylamine, m. p. 172°, and its ethylidene derivative, m. p. 102°, are also described.

H. E. F. NOTTON.

Curtius' decomposition of acid azides. H. LINDEMANN (Helv. Chim. Acta, 1928, 11, 1027—1028).—The author objects to the term "modified Curtius reaction" (Naegeli and Stefanovitch, A., 1928, 881) for the preparation of azides from acid chlorides and sodium azide. Examples using this method are quoted, namely, the formation of 2-chloro-3:5-dinitro-*p*-toluidine, m. p. 173° (from the corresponding toluoyl chloride and sodium azide, with subsequent action of hot 50% acetic acid), and the conversion of indoxazen-3-carboxylazide into 3-amino-indoxazen, m. p. 110°.

H. BURTON.

Amino-3-hydroxy-1:4-benzisooxazines. G. NEWBURY and M. A. PHILLIPS (J.C.S., 1928, 3046—3050).—The synthesis of three remaining amino-3-hydroxy-1:4-benzisooxazines is described. 3-Nitro-2-aminophenol, obtained by nitration of *ON*-diacetyl-*o*-aminophenol, gave, with chloroacetyl chloride, 3-nitro-2-chloroacetamidophenol, m. p. 153—154°. This, when treated with 2*N*-sodium hydroxide, yielded 5-nitro-3-hydroxy-1:4-benzisooxazine, m. p. 115—116°, which by reduction with iron and water led to 5-amino-3-hydroxy-1:4-benzisooxazine, m. p. 236° (hydrochloride; acetyl derivative, m. p. 255°; derived triazole, m. p. 204°).

Reduction of 2:4-dinitrophenoxyacetic acid (iron and dilute hydrochloric acid) gave 6-amino-3-hydroxy-1:4-benzisooxazine, (I), m. p. 300° (decomp.) [acetyl derivative, m. p. 298—299° (bath at 240°)]. 4-Nitro-2-aminophenol gave 4-nitro-2-chloroacetamidophenol, m. p. 245° (decomp.), which led to 6-nitro-3-hydroxy-1:4-benzisooxazine, m. p. 233—234°. 4-Acetamidophenoxyacetic acid when nitrated formed 2-nitro-

4-acetamidophenoxyacetic acid, m. p. 205—206°, which when treated with tin and hydrochloric acid gave I. 5-Nitro-2-chloroacetamidophenol, m. p. 233° (decomp.), yielded 7-nitro-3-hydroxy-1:4-benzisooxazine, m. p. 232°, and 7-amino-3-hydroxy-1:4-benzisooxazine, m. p. 220° [hydrochloride, m. p. 275—278° (decomp.); acetyl derivative, m. p. 250°]. De-arsenication of 3:5-dinitro-4-hydroxyphenylarsinic acid gave 2:6-dinitrophenol, from which 6-nitro-2-aminophenol (acetyl derivative, monohydrate, m. p. 102—103°, anhydrous, m. p. 122°) was obtained. 6-Nitro-2-chloroacetamidophenol had m. p. 126° and formed, successively, 8-nitro-3-hydroxy-1:4-benzisooxazine, m. p. 255°, and 8-amino-3-hydroxy-1:4-benzisooxazine, m. p. 180° [hydrochloride, m. p. 272° (decomp.); acetyl derivative, m. p. 257°]. R. J. W. LE FÈVRE.

Aminobenzthiazoles. X. Mobility of the 1-amino-3-methylbenzthiazole system. R. F. HUNTER and E. R. STYLES (J.C.S., 1928, 3019—3027).—The mobility of 1-amino-3-methylbenzthiazole is established by application of the symmetry test (Ingold and Piggott, *ibid.*, 1922, 121, 2381) and also the substitution test (*ibid.*, 1923, 123, 1470). 1-Acet-amido-3-methylbenzthiazole, (I), m. p. 258° [from stable acetyl-*o*-tolylthiocarbamide by conversion into a tetrabromide, m. p. 140° (decomp.), followed by reduction with sulphurous acid], and 1-imino-2-acetyl-3-methyl-1:2-dihydrobenzthiazole, m. p. 170° [obtained by the action of bromine on labile acetyl-*o*-tolylthiocarbamide (at higher temperatures the tetrabromide derived from stable acetyl-*o*-tolylthiocarbamide is formed) to a tribromide, m. p. 173° (decomp.), and treatment of this with sulphurous acid followed by ammonia], gave (tautomeric) 1-amino-3-methylbenzthiazole when hydrolysed. The compound I with bromine gives a hexabromide, m. p. 255—258° (decomp.). Bromine converts *o*-tolylthiocarbamide into 1-amino-3-methylbenzthiazole dibromide hydrobromide, m. p. 129° (decomp. and efferv.), which by treatment with (1) ethyl alcohol gives 5-bromo-1-amino-3-methylbenzthiazole hydrobromide, m. p. 280—290° (with charring); (2) sulphurous acid, gives 1-amino-3-methylbenzthiazole; (3) air, gives 1-amino-3-methylbenzthiazole hydrobromide, m. p. 220°. 1-Amino-3-methylbenzthiazole tetrabromide has m. p. 302°.

Methylation of 1-amino-3-methylbenzthiazole by means of methyl iodide gives a mixture of 1-methylamino-3-methylbenzthiazole and 1-imino-2:3-dimethyl-1:2-dihydrobenzthiazole. These are synthesised as follows: *s*-*o*-tolylmethylthiocarbamide, m. p. 161°, gives with bromine either a tetrabromide, m. p. 75° (decomp.), or a tribromide, m. p. 113°, both of which give 1-methylamino-3-methylbenzthiazole, m. p. 130° (acetyl derivative, m. p. 133°), by reduction with sulphurous acid; the bromo-compound from *as*-*o*-tolylmethylthiocarbamide yields, when treated with sulphurous acid, 1-imino-2:3-dimethyl-1:2-dihydrobenzthiazole, m. p. 86° (acetyl derivative, m. p. 147°). 5-Bromo-1-amino-3-methylbenzthiazole gives a dibromide hydrobromide, m. p. above 250°, leading to 5-bromo-1-amino-3-methylbenzthiazole. The following are prepared by the usual methods: 5-bromo-1-amino-3-methylbenzthiazole, m. p. 212° (dibromide hydrobromide, m. p. above 250°); *s*-*o*-tolyl-*n*-propyl-

thiocarbamide, m. p. 66°; 1-n-propylamino-3-methylbenzthiazole tetrabromide, m. p. 71° (efferv. at 130°); 1-n-propylamino-3-methylbenzthiazole, m. p. 62° [hydrobromide, m. p. 179° (decomp.); acetyl derivative, m. p. 61°], (?) -bromo-1-n-propylamino-3-methylbenzthiazole hydrobromide, m. p. 259°; s-5-bromo-o-tolyl-n-propylthiocarbamide, m. p. 79°; 5-bromo-1-n-propylamino-3-methylbenzthiazole, m. p. 82°; s-o-tolyl-n-heptylthiocarbamide, m. p. 98° (hexabromide, m. p. 53°); 1-n-heptylamino-3-methylbenzthiazole, m. p. 57° (acetyl derivative, m. p. 73°); (?) -bromo-1-n-heptylamino-3-methylbenzthiazole hydrobromide, m. p. 220°; s-5-bromo-o-tolyl-n-heptylthiocarbamide, m. p. 71°, and 5-bromo-1-n-heptylamino-3-methylbenzthiazole, m. p. 75°.

R. J. W. LE FEVRE.

Benzidine rearrangement in heterocyclic series. II. P. K. BOSE and B. K. SEN (J. Indian Chem. Soc., 1928, 5, 643—655).—Phenacyl bromide and 1-o-tolylthiosemicarbazide, m. p. 163—164° (from o-tolylhydrazine, potassium thiocyanate, and alcoholic hydrogen chloride), react in alcohol, forming 2-o-tolylhydrazino-4-phenylthiazole, m. p. 175—180° (decomp.; acetyl derivative, m. p. 152°), which is oxidised by alcoholic ferric chloride to 2-o-toluenazo-4-phenylthiazole, m. p. 110°, and converted by boiling dilute hydrochloric acid by a benzidine rearrangement (cf. A., 1928, 188) into 2-amino-4-phenyl-o-p-amino-m-tolylthiazole, m. p. 165° [hydrochloride, m. p. 197°; picrate, m. p. 227° (decomp.); diacetyl derivative, m. p. 182°; chloroplatinate, not melted at 300°]. 2-o-Tolylhydrazino-4-p-tolylthiazole, m. p. 179° (decomp.; acetyl derivative, m. p. 160—161°; azo-derivative, m. p. 148°), gives similarly 2-amino-4-p-tolyl-5-p-amino-m-tolylthiazole, m. p. 181° [hydrochloride, m. p. 278° (decomp.); diacetyl derivative, m. p. 208°; picrate, m. p. 201° (decomp.); chloroplatinate]. 2-o-Tolyl-4-methylthiazole, m. p. 162° (decomp.; acetyl derivative, m. p. 96°), affords 2-amino-5-p-amino-m-tolyl-4-methylthiazole, m. p. 144° [hydrochloride, m. p. 261° (decomp.); picrate, m. p. 247° after decomp. at 200°; diacetyl derivative, m. p. 266°; chloroplatinate]. From 1-m-tolylthiosemicarbazide, m. p. 134—135°, and the appropriate halogenoketone there were prepared 2-m-tolylhydrazino-4-phenyl-, m. p. 188° (decomp.; acetyl derivative, m. p. 145°), -4-p-tolyl-, m. p. 191° (decomp.; acetyl derivative, m. p. 121°), and -4-methyl-thiazole, m. p. 135° (decomp.; acetyl derivative, m. p. 119°), which are converted into 2-amino-4-phenyl-5-p-amino-o-tolyl-, m. p. 135° [hydrochloride, m. p. 265—270° (decomp.); picrate, m. p. 215° (decomp.); diacetyl derivative, m. p. 235°], 2-amino-4-p-tolyl-5-p-amino-o-tolyl-, m. p. 175° [hydrochloride, m. p. 247° (decomp.); picrate, m. p. 202° (decomp.); diacetyl derivative, m. p. 236°], and 2-amino-5-p-amino-o-tolyl-4-methyl-thiazole, m. p. 157° [hydrochloride, m. p. 263° (decomp.); picrate, m. p. 212° (decomp.); diacetyl derivative, m. p. 236°], respectively.

p-Tolylthiosemicarbazide, m. p. 174° (lit. 150°), and phenacyl bromide afford 3-p-toluidino-2-imino-4-phenyl-2:3-dihydrothiazole, m. p. 193° (decomp.; acetyl derivative, m. p. 147°), hydrolysed by hydrochloric acid to the corresponding 2-keto-derivative, m. p. 210—211°. The analogous 2-imino-4-methyl derivative, m. p. 168—169° (p-tolylthiocarbimide

derivative, m. p. 143°), affords the corresponding 2-keto-compound, m. p. 177°. 3-p-Toluidino-2-imino-4-p-tolyl-2:3-dihydrothiazole (acetyl derivative, m. p. 155°; p-tolylthiocarbimide derivative, m. p. 152°) has m. p. 184° (decomp.). 2-Benzeneazo-4-phenyl-, m. p. 117°, -4-p-tolyl-, m. p. 161°, and -4-methyl-thiazole, m. p. 120°, are prepared by oxidising the corresponding phenylhydrazino-derivatives (*loc. cit.*) with ferric chloride.

The rearrangements now and previously described support the view that a system of conjugated double linkings must be present in the heterocyclic ring (Fargher and Pyman, J.C.S., 1919, 115, 222) before isomerisations can occur.

H. BURTON.

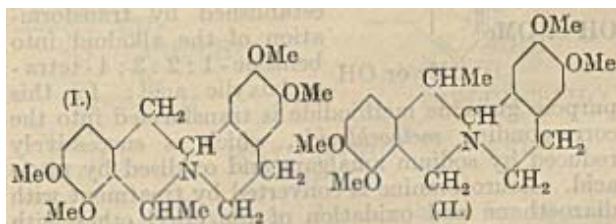
Microchemical reactions of homatropine. M. WAGENAAR (Pharm. Weekblad, 1928, 65, 1213—1216).—The crystal forms and optical properties of the precipitates obtained by addition of gold chloride, picrolonic acid, picric acid, iodine, and bromine solutions are described. The bromine test will detect 2 mg. in 20 c.c. of solution, the iodine test 5 mg. in 25 c.c.

S. I. LEVY.

Determination of the absorbing capacity of the ergot alkaloids in the ultra-violet and a practical application. A. HARMSMA (Pharm. Weekblad, 1928, 65, 1114—1134).—The absorption spectra of ergotin, ergotoxin, ergotamine, and ergotaminin have been mapped for wave-lengths from 360 to 260 μ . The maximum in each case is at 316 μ . Quantitative spectrum determinations of the alkaloid content of *Secale cornutum* agreed well with chemical determinations carried out by the Keller-Fromme method. Similar determinations on extracts prepared in various ways also showed good agreement with the chemical determinations. Physiological methods of examination are discussed, and some results given.

S. I. LEVY.

Synthesis of oxydehydrocorydaline. J. B. KOEFFLI and W. H. PERKIN, jun. (J.C.S., 1928, 2989—3000).—A literature review suggests that corydaline is preferably represented by II rather than by I (Dobbie and Lauder, *ibid.*, 1902, 81, 148).



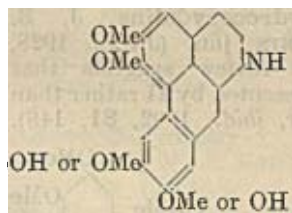
The synthesis of oxydehydrocorydaline described supports this conclusion. β -Veratrylcrotonic acid, m. p. 138—140° (from ethyl bromoacetate and zinc by dehydration of ethyl β -veratryl- β -hydroxybutyrate giving ethyl β -veratrylcrotonate, b. p. 195—196°/10 mm.), was reduced by sodium amalgam to β -veratrylbutyric acid, m. p. 84—85° (monohydrate, m. p. 60—61°, with loss of 1H₂O at 100°), which, when treated with sulphuric acid yielded 5:6-dimethoxy-3-methyl-1-hydrindone, m. p. 90—91° [oxime, m. p. 128—129°; isonitroso-derivative, m. p. 225—226° (decomp.)], and when brominated in acetic acid gave 6-bromo- β -veratrylbutyric acid, m. p. 106—107°. This

acid readily gave with sulphuric acid 4-bromo-6:7-dimethoxy-3-methyl-1-hydrindone, m. p. 82—83°, the isonitroso-derivative, m. p. 217° (decomp.), of which underwent the Beckmann transformation with toluene-*p*-sulphonyl chloride, giving 6-bromo-2-carboxy-3:4-dimethoxy- α -phenylpropionitrile. This by hydrolysis led to 6-bromo-3:4-dimethoxy- α -methylhomophthalic acid (*anhydride*, m. p. 128—129°). Debromination by sodium amalgam gave 3:4-dimethoxy- α -methylhomophthalic acid; the *anhydride*, m. p. 131—133°, of this acid combined with β -veratrylethylamine to give *N*- β -veratrylethyl-3:4-dimethoxy- α -methylhomophthalamic acid, the methyl ester of which lost water when treated with phosphoryl chloride giving 6:7:3':4'-tetramethoxy-9-methyl-2'-carboxymethoxy-3:4-dihydroprotopapaverine, m. p. 136—137° (with previous softening), which when heated eliminated methyl alcohol giving oxydehydrocorydaline, m. p. 235—236° (lit. 228—228.5°).

An acid, m. p. 90—95°, is described as probably a stereoisomeride of β -veratrylerotonic acid.

R. J. W. LE FEVRE.

Constitution of laurotetanine. E. SPATH and F. STRAUHAL (Ber., 1928, 61, [B], 2395—2402; cf. Greshoff, A., 1891, 334; Filippo, A., 1899, i, 312; Gorter, A., 1921, i, 587).—Methylation of laurotetanine in alcohol-ether yields an amorphous product which mainly retains the secondary character of the nitrogen atom. It is divided by treatment with acetic anhydride at the ordinary temperature into *N*-acetyl-laurotetanine *O*-methyl ether, $C_{22}H_{25}O_5N$, m. p. 188—189°, and a tertiary base identical with glaucine. Gorter's *isoglaucine* (*loc. cit.*) is therefore a mixture of laurotetanine *O*-methyl ether and glaucine, and laurotetanine must possess the ring system of the latter substance. Oxidation of laurotetanine affords 4:5-dimethoxybenzene-1:2:3-tricarboxylic acid, which passes at 260° into carbon dioxide and *m*-hemipinic



anhydride. The annexed formula is therefore suggested for laurotetanine. The presence of the phenanthrene nucleus is established by transformation of the alkaloid into benzene-1:2:3:4-tetracarboxylic acid; for this purpose glaucine methiodide is transformed into the corresponding *methochloride*, which is successively reduced by sodium amalgam and oxidised by nitric acid. Laurotetanine is converted by treatment with diazoethane and oxidation of the ethyl ether with potassium permanganate into 4-methoxy-5-ethoxybenzene-1:2-dicarboxylic acid, identified as the anhydride and ethylimide. Attempts to convert laurotetanine into corydaldine were unsuccessful. Glaucine is not appreciably affected by treatment with tin and hydrochloric acid and laurotetanine does not suffer electrolytic reduction at a lead cathode; it may therefore be assumed that the pyridine nucleus is tetrahydrogenated. The accumulated data do not permit a decision as to the positions of the hydroxyl and methoxyl groups indicated in the formula.

1-Keto-5:6-dimethoxy-1:2:3:4-tetrahydroiso-

quinoline, m. p. 154—155°, is obtained by the action of phosphoric oxide in toluene on carbethoxy- β -2:3-dimethoxyphenylethylamine.
H. WREN.

Constitution of laurotetanine. G. BARGER and R. SILBERSCHMIDT (J.C.S., 1928, 2919—2927).—A study of the products obtained by exhaustive methylation (Hofmann) has shown that, contrary to the opinions of Gorter (A., 1921, i, 587), the *N*-methyl methyl ether of laurotetanine (Gorter's *isoglaucine*) and glaucine are identical; therefore laurotetanine has the constitution suggested for it independently by Spath and Strauhal (preceding abstract). Hydrated laurotetanine (m. p. 124—134°; lit. 125°, 134°) gave, by methylation with diazomethane followed by addition of methyl iodide, *dimethyl-laurotetanine methiodide*, m. p. 210°. Treatment of this with alcoholic potassium hydroxide and subsequent acidification gave *dimethyl-laurotetaninemethine hydriodide*, m. p. 265°. The free *methine* was an uncrystallisable oil, but *dimethyl-laurotetaninemethine methiodide* (obtained from the components in ethereal solution) had m. p. 276°. The last compound, when heated with methyl-alcoholic potassium hydroxide, gave trimethylamine (isolated as the chloroplatinate) and 2:3:5:6-tetramethoxy-8-vinylphenanthrene, m. p. 142°, which was oxidised by cold neutral permanganate to 2:3:5:6-tetramethoxyphenanthrene-8-carboxylic acid, m. p. 215°.

Attempts are described to decide between the two formulæ by exhaustive methylation of laurotetanine ethyl ether and comparison of the products with two synthetic ethoxytrimethoxyethylphenanthrenes. Both laurotetanine and glaucine gave a vinylphenanthrene and phenanthrenecarboxylic acid; attempts to decarboxylate the acid were unsuccessful. 2:3:5:6-Tetramethoxy-8-ethylphenanthrene was therefore prepared by reduction of the vinyl compound with hydrogen-palladium chloride-gum arabic.

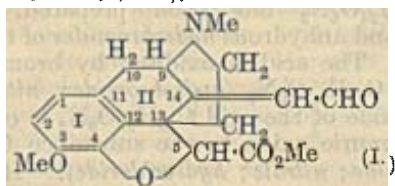
3:4-Dimethoxyethylbenzene, b. p. 110—112°/9 mm. (obtained by the reduction of 3:4-dimethoxyvinylbenzene or of acetoveratrone, the latter being the better method), gave by Gattermann's reaction 3:4-dimethoxy-6-ethylbenzaldehyde, b. p. 150—159°/9 mm., m. p. 28—30° (*semicarbazone*, m. p. 197—199°). Oxidation by alkaline permanganate gave 3:4-dimethoxy-6-ethylbenzoic acid, m. p. 138°. The above aldehyde condensed with hippuric acid under the conditions of a Perkin reaction to give the *azlactone* of 3:4-dimethoxy-6-ethylbenzylidenhippuric acid, m. p. 155° (hydrolysis with dilute potassium hydroxide gave the free acid, m. p. 212°), which, by boiling with 30% potassium hydroxide yielded 3:4-dimethoxy-6-ethylphenylpyruvic acid, m. p. 181°. Oxidation of this by alkaline hydrogen peroxide led to 3:4-dimethoxy-6-ethylphenylacetic acid, m. p. 67°, the potassium salt of which condensed with 6-nitro-3:4-dimethoxybenzaldehyde, giving α -3:4-dimethoxy-6-ethylphenyl- β -6-nitro-3:4-dimethoxyphenylacrylic acid, m. p. 208° (previous sintering at 203°), which by ammoniacal ferrous hydroxide reduction gave the corresponding *amine*, m. p. 192°. This was treated with nitrous acid and the resulting crude 2:3:5:6-tetramethoxy-8-ethylphenanthrene-9-carboxylic acid decarboxylated to 2:3:5:6-tetramethoxy-

oxy-8-ethylphenanthrene identical with the corresponding compound obtained from laurotetanine.

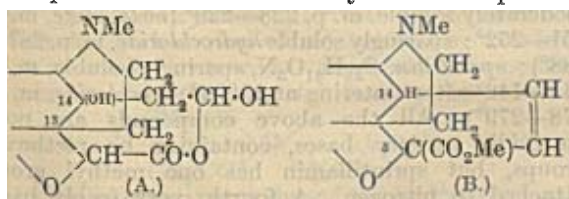
6-Nitro-3-methoxy-4-ethoxybenzaldehyde (nitro-vanillin ethyl ether) has m. p. 159–160°. Improved methods for the methylation of vanillin and guaiacol are described.

R. J. W. LE FÈVRE.

Morphine alkaloids. VI. Thebaine and other products of ozonolysis. H. WIELAND and L. F. SMALL (Annalen, 1928, 467, 17–52).— α -Thebaine (hydriodide, m. p. 185–187°; hydrochloride), obtained by the ozonolysis of thebaine (Pschorr and Einbeck, A., 1907, i, 958), has formula I if the Schöpf-

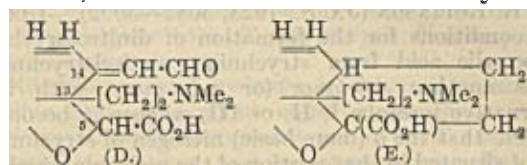


Robinson formula for thebaine (cf. A., 1927, 472) is accepted. It is converted by bromine in dilute hydrochloric acid, and subsequent treatment with alkali, into bromothebaine, m. p. 147°, the bromine probably entering ring I, and by 30% hydrogen peroxide in acetic acid into thebaine dicarboxylic acid, m. p. 189–190° (decomp.), the ester group being hydrolysed. Hydrolysis with cold 0.33N-barium hydroxide yields the aldehyde acid, thebaine acid, decomp. 235°, but concentrated hydrochloric acid at 95–98° gives rise to the hydrochloride, m. p. 210° (decomp.) (also obtained by the action of excess of N-hydrochloric acid on thebaine acid), of hydroxydihydrothebaine acid (A), decomp. 230–240°, the free acid being liberated by the action of methyl-alcoholic sodium methoxide, whilst thallium hydroxide yields a different substance, decomp. 231–235°, containing an additional mol. of water and yielding a different hydrochloride, decomp. 260°. Catalytic reduction of α -thebaine with platinum oxide in methyl alcohol opens the

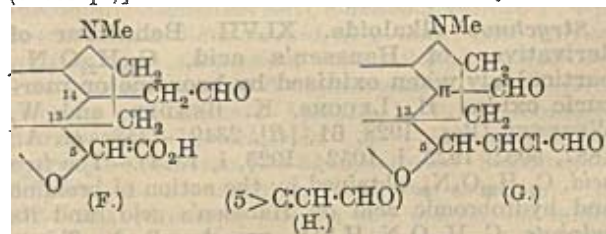


oxygen bridge, leaving the 8:14 double linking unattacked, and yields the phenolic derivative dihydrothebaine, m. p. 140° (indefinite) [methiodide, m. p. 239–240° (decomp.)]; acetyl derivative of methiodide, m. p. 250° (decomp.)]. Reduction of α -thebaine with aluminium amalgam in moist ether (and, in poor yield, with zinc and hydrochloric acid) yields deoxythebaine (B), m. p. 147° (decomp.) (hydrochloride), which retains the oxygen bridge but has no aldehydic properties, and is reduced catalytically after hydrolysis with N-hydrochloric acid, to dihydrodeoxythebaine acid (C), m. p. 163–165° (decomp.), isolated as its hydrochloride, m. p. 236–237° (decomp.). The Hofmann degradation of the methiodides of these various compounds has been investigated. The methiodide, m. p. 163° (decomp.), of A eliminates only

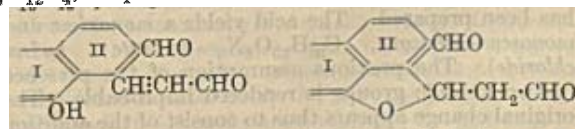
methyl alcohol, the product again treated with methyl iodide yielding the original methiodide; α -thebaine methiodide, decomp. 250–255°, yields de-N-methylthebaine acid (D), amorphous [methiodide, decomp. 250–255°; hydrochloride, m. p. 270° (decomp.)]; the methiodide, m. p. 175–177°, of dehydrodeoxythebaine acid (E), m. p. 195–197° (decomp.) (methiodide, m. p. 156–158°). When C is heated with methyl iodide



at 100° it yields a substance, $C_{37}H_{45}O_8N_5I \cdot H_2O$, m. p. 217–218° (decomp.), which by decomposition with thallium hydroxide and further treatment with methyl iodide yields the simple methiodide, m. p. 167–168° (decomp.). By short heating at 200° α -thebaine is converted into β -thebaine, m. p. 151° (probably stereoisomeric about the 8:14 double linking), which yields the same deoxythebaine by reduction with aluminium amalgam, but by reactions similar to those applied to the α -compound it yields hydroxydihydro- β -thebaine acid, m. p. 230° (decomp.) (hydrochloride, decomp. 260°); ethyl hydrogen β -thebaine dicarboxylate decomposes at 220° (the ester group is less readily hydrolysed than in the α -compound). Ozonolysis of dihydrothebaine in hydrochloric acid yields isodihydrothebaine acid (F), m. p. 248–249° (decomp.) [hydrochloride; methiodide, m. p. 179–180° (decomp.)]; reduced with hydrogen and platinum oxide in water to the tetrahydro-acid, m. p. 230–235° (decomp.), and isodihydrothebaine, m. p. 103–105° [methiodide, m. p. 147–148° (decomp.)]. Ozonolysis of chlorocodizone yields chlorocodizone (G), m. p. 104° [hydrochloride, m. p. 212° (decomp.)]; oily methiodide], which is reduced by zinc and acetic acid to deoxycodizone, m. p. 161° [hydrochloride, m. p. 223–224° (decomp.)]. The action of hot methyl-alcoholic



potassium hydroxide on chlorocodizone for 15 min. yields anhydrocodizone (H), m. p. 110°. Longer treatment (1 hr.) yields two nitrogen-free substances, $C_{15}H_{12}O_4$, m. p. 88° and 159°, for which the structures

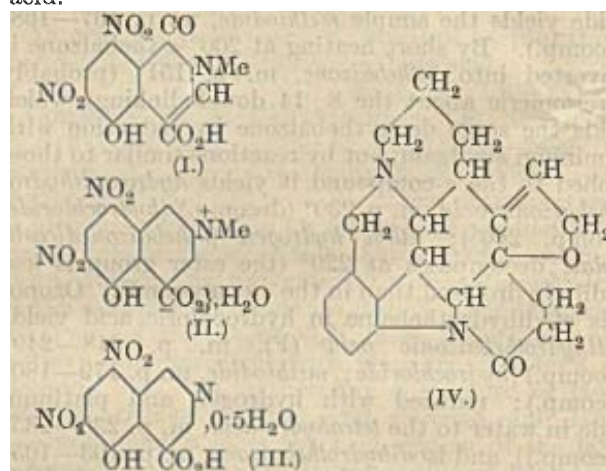


are suggested, the phenol yielding a methyl ether, m. p. 105–108°. Alcoholic potassium acetate converts chlorocodizone into a substance, $C_{28}H_{19}O_2N$, m. p. 189°. These results are in agreement with the Schöpf-

Robinson formula for thebaine, similar revision being necessary to Freund's formulæ for phenyldihydrothebaine methyl ether and *O*-methylthebainone, neither of which reacts with ozone.

J. W. BAKER.

Strychnine and brucine. VII. Constitution of the alkaloids discussed in relation to the hypothesis that dinitrostrychnol is an *isoquinoline* derivative. R. C. FAWCETT, W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1928, 3082—3092).—Under the conditions for the formation of dinitrostrychnol-carboxylic acid from strychnine, methylstrychnine gives another *substance* (or *substances*) with the alternative formulæ I, II, or III, whence it becomes evident that the *b* (more basic) nitrogen of strychnine is not situated in that portion of the molecule which is broken up during oxidation, but is actually the heterocyclic nitrogen of dinitrostrychnol-carboxylic acid.



The logical consequences of this view are discussed, and a formula, IV (where, however, the possibility of bridged rings is left open), which satisfactorily explains the known reactions of strychnine is advanced.

R. J. W. LE FÈVRE.

Strychnos alkaloids. XLVII. Behaviour of derivatives of Hanssen's acid, $C_{19}H_{22}O_8N_2$, particularly when oxidised by bromine or mercuric oxide. H. LEUCHS, K. BENDER, and W. WEGENER (Ber., 1928, 61, [B], 2349—2358; cf. A., 1887, 505; 1922, i, 1052; 1925, i, 1314).—The free acid, $C_{19}H_{22}O_8N_2$, obtained by the action of bromine and hydrobromic acid on Hanssen's acid, and its *sulphate*, $C_{19}H_{22}O_8N_2 \cdot H_2SO_4$, are described. Treatment of its hydrobromide with methyl alcohol and hydrogen chloride gives the *dimethyl ester*, $C_{12}H_{26}O_8N_2$, m. p. 225—227° (decomp.) [anhydrous *nitrate*], and the *monomethyl ester nitrate*. The *monosilver salt* has been prepared. The acid yields a *monoxime* and *monosemicarbazone*, $C_{20}H_{25}O_8N_5$ (*nitrate*; *hydrochloride*). The previous assumption of the presence of two ketonic groups is rendered improbable. The original change appears thus to consist of the addition of two hydroxyl groups at the $C=C$ linking reducible by sodium amalgam and the conversion of the (non-demonstrable) $>CH-OH$ group of brucine and cacotheleine into $>CO$. The acid $C_{19}H_{22}O_8N_2$ is

oxidised by yellow mercuric oxide suspended in water to the acid $C_{19}H_{22}O_9N_2 \cdot 2H_2O$ [*hydrobromide* (+ $3H_2O$); *hydrochloride*]. Reduction of the acid $C_{19}H_{22}O_8N_2$ by sodium amalgam affords the compound, $C_{19}H_{24}O_8N_2$, isolated as the *nitrate* or *hydrobromide*; the latter substance is oxidised by mercuric oxide to the *hydrobromide*, $C_{19}H_{22}O_9N_2 \cdot HBr$. The free, reduced Hanssen acid, $C_{19}H_{24}O_8N_2$, yields a *silver salt* from which the *methylbetaine*, $C_{20}H_{26}O_8N_2 \cdot MeOH$, *methobromide*, $C_{20}H_{27}O_8N_2Br$, and *methiodide*, $C_{20}H_{27}O_8N_2I$, are obtained. The methobromide is transformed by silver carbonate and water into the betaine. The *dihydrazide*, $C_{19}H_{28}O_4N_6$, m. p. 265—268° (decomp.), of the acid $C_{19}H_{24}O_8N_2$ has been prepared. The trihydrated and anhydrous *hydrobromides* of the acid are described. The acid is oxidised by bromine to the compound $C_{19}H_{26}O_9N_2$ (*hydrobromide*; *nitrate*). The hydrobromide of the acid $C_{19}H_{26}O_9N_2$ is oxidised by yellow mercuric oxide to the substance $C_{19}H_{24}O_9N_2$ (*hydrobromide*; *nitrate*; *hydrochloride*). H. WREN.

Helleborus group. VII. Constituents of the roots of *Helleborus niger* and *H. viridis*; new alkaloids from *H. viridis*. O. KELLER [with W. SCHOBEL] (Arch. Pharm., 1928, 266, 545—572; cf. A., 1927, 799).—Previous investigators are not agreed as to the composition of the two glucosides helleborin and helleborein. The two substances, m. p. 269° and 270°, respectively, previously isolated by Keller, are identical with helleborin, to which the formula $C_{28}H_{36}O_6$ is now ascribed. The benzene extract from the roots of *H. viridis* acidified with aluminium sulphate solution affords helleborin, 1% of fat, brown colouring matters, resin, and a pungent oil volatile in steam, but no alkaloids. The latter, which are present to the extent of 0.1—0.2%, are obtained by repeating the extraction after basifying the roots with ammonia, the following substances being isolated, chiefly by means of their different solubilities in ether: *celliamin*, $C_{21}H_{35}O_2N$, readily soluble, m. p. 127—131° after sintering at 115°; *sprintillamin*, $C_{28}H_{45}O_4N$, moderately soluble, m. p. 228—229° (*methiodide*, m. p. 251—252°; sparingly soluble *hydrochloride*, m. p. 287—288°); *sprintillin*, $C_{25}H_{41}O_3N$, sparingly soluble, m. p. 141—142° after sintering at 132° (*hydrochloride*, m. p. 278—279°). All the above compounds are non-glucosidic tertiary bases, containing no methoxyl groups, but sprintillamin has one methyl group attached to nitrogen. A fourth, very feebly basic *alkaloid*, $C_{25}H_{43}O_6N$, m. p. 267—268° after darkening at 210°, is described. In addition to the above the roots of *H. viridis* contain sucrose. The roots of *H. niger* are free from alkaloids. Celliamin, sprintillamin, and sprintillin have a characteristic action on the heart.

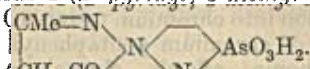
S. COFFEY.

Unsymmetrical arseno-compounds from *p*-arsinoanilinoethyl alcohol and *p*-arsinoanilinoacetamide. C. S. PALMER and E. B. KESTER (J. Amer. Chem. Soc., 1928, 50, 3109—3119; cf. A., 1924, i, 109).—Water-soluble, unsymmetrical derivatives of 4-carbamylmethylaminoarsenobenzene and 4-β-hydroxyethylaminoarsenobenzene have been prepared by reducing equimolecular mixtures of one of the above arsenic acids with another suitably substituted arsenic acid by means of stannous chloride or hypo-

phosphorous acid and potassium iodide at 5—10°. It is shown that reduction takes place first to the two symmetrical arsenobenzenes, which then rearrange. The following derivatives of 4'- β -hydroxyethylamino-arsenobenzene are described: 4-amino-(dihydrochloride; N-methylenesulphoxylic acid); 4-hydroxy- (hydrochloride); 3-amino-4-hydroxy- (dihydrochloride; N-methylenesulphoxylic acid); 4-carboxymethylamino- (dihydrochloride) and 4-carboxymethoxy-; also the following derivatives of 4'-carbanylmethylamino-arsenobenzene: 4-amino- [dihydrochloride; di-(N-methylenesulphoxylic acid)]; 4-hydroxy- (hydrochloride); 3-amino-4-hydroxy- (dihydrochloride; N-methylenesulphoxylic acid); and 4-carboxymethoxy-. Equal mols. of *p*-arsinoanilinoacetic acid and *p*-arsinoanilinoacetamide are reduced by stannous chloride to 4-carboxymethylamino-4'-carbanylmethylaminoarsenobenzene dihydrochloride and by hypophosphorous acid at the ordinary temperature to 4-carboxymethylamino-4'-carbanylmethylaminotetra-arsenobenzene dihydrochloride. Other arsenobenzenes prepared include 4-carboxymethylamino-4'-hydroxy-, hydrochloride; 3-amino-4-hydroxy-4'-carboxymethoxy-; 3:4'-diamino-4-hydroxy-, dihydrochloride; and 4-amino-4'-hydroxy-, hydrochloride; but the 3-amino-4-hydroxy-hydrochloride could not be obtained in a similar way from a mixture of phenylarsinic and 3-amino-4-hydroxyphenylarsinic acids, only the symmetrical arseno-derivatives being formed.

H. E. F. NOTTON.

Pyridine and quinoline derivatives. IV. Pyridine-3-arsinic acid. A. BINZ, C. RATH, and J. GANTE (Annalen, 1928, 467, 11—16).—The difficulty encountered in the preparation of pyridine-3-arsinic acid (A., 1927, 890) has been overcome by using 5-aminopyridines with a negative substituent in the 2-position, which is readily eliminated after conversion into the arsinic acid. 2-Chloropyridine-5-arsinic acid (*loc. cit.*) is converted by heating with hydrazine hydrate in aqueous solution for 3.5 hrs. into 2-hydrazinopyridine-5-arsinic acid (I), not melting below 240° (*p*-nitrobenzylidene derivative, reduced to *p*-aminobenzylidene derivative), which by condensation with ethyl acetoacetate and heating the product in toluene, yields 1-(2'-pyridyl)-3-methyl-5-pyrazolone-

5'-arsinic acid,  Oxidation

of I with hydrogen peroxide and 5% hydrochloric acid yields (10—12%) pyridine-3-arsinic acid, m. p. 112—113° (copper salt), from which are obtained 3-pyridyl-dichloroarsine, decomp. 137°, 3-pyridylarsenious oxide, decomp. 187°, and 3-pyridylarsine, decomp. 102°, and, by reduction with hypophosphorous acid before isolation, 3:3'-arsenopyridine. J. W. BAKER.

Heterocyclic arsenic compounds. II. Derivatives of 1:4-benzisooxazine. G. NEWBERY, M. A. PHILLIPS, and R. W. E. STICKINGS (J.C.S., 1928, 3051—3073).—3-Hydroxy-1:4-benzisooxazine-5-arsinic acid, m. p. 245—248° (decomp.) (calcium, barium, and magnesium salts), was prepared from 2-nitro-3-carboethoxyaminophenylarsinic acid. 3-Acetamido-4-hydroxyphenylarsinic acid with chloroacetic acid gave 2-acetamidophenoxyacetic acid, m. p. above 280°

(magnesium salt); 2-acetamidophenoxyacetamide-4-arsinic acid, m. p. 236° (decomp.) (magnesium salt), was prepared similarly, and was reduced by sulphurous acid and hydrochloric acids in presence of potassium iodide to 2-nitrophenoxyacetic acid 4-dichloroarsine. Reduction of the corresponding arsinic acid gave impure 3-hydroxy-1:4-benzisooxazine-4-dichloroarsine, which dissolved in sodium hydroxide to give 3-hydroxy-1:4-benzisooxazine-6-arsenoxide. 3-Hydroxy-1:4-benzisooxazine-6-arsinic acid was reduced by hyposulphite to 3:3'-dihydroxy-6:6'-arseno-1:4-benzisooxazine.

Nitration of 3-hydroxy-1:4-benzisooxazine-6-arsinic acid gave about equal yields of 5-nitro-3-hydroxy-1:4-benzisooxazine-6-arsinic acid (calcium, barium, magnesium, and monoammonium salts) and 7-nitro-3-hydroxy-1:4-benzisooxazine-6-arsinic acid. Ferrous hydroxide reduced the former to 5-amino-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, m. p. above 300° [calcium, barium, magnesium, and sodium salts; acetyl derivative; corresponding triazole, m. p. 247° (decomp.), and its calcium, barium, and magnesium salts], which underwent de-arsenication when boiled with hydrochloric acid to 5-amino-3-hydroxy-1:4-benzisooxazine hydrochloride, whilst the latter was reduced by ferrous hydroxide (or dextrose and alkali) to 7-amino-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, m. p. 258—260° (decomp.) (barium, calcium, and magnesium salts; acetyl derivative, m. p. 275°; urethane), de-arsenication of which gave 7-amino-3-hydroxy-1:4-benzisooxazine. 3:7-Dihydroxy-1:4-benzisooxazine-6-arsinic acid, m. p. above 300° (barium, calcium, and magnesium salts), was obtained from 5-amino-2:4-dihydroxyphenylarsinic acid by chloroacetylation in alkaline solution.

The following compounds are also described: 8-nitro-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, 3-nitro-5-chloroacetamido-4-hydroxyphenylarsinic acid, m. p. 200° (decomp.) (magnesium salt), 8-nitro-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, decomp. 320° (calcium and magnesium salts), 2:6-diacetamidophenoxyacetic acid 4-arsinic acid, m. p. 212° (decomp.) (magnesium salt), 8-amino-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, m. p. above 300° (barium, calcium, and magnesium salts), 8-amino-3-hydroxy-1:4-benzisooxazine-6-hydroxychloroarsine hydrochloride, 8-amino-3-hydroxy-1:4-benzisooxazine-6-arsenoxide hydrochloride, 8:8'-diamino-3:3'-dihydroxy-6:6'-arseno-1:4-benzisooxazine, 8-acetamido-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, m. p. 275—280° (decomp.) (barium and magnesium salts), 8-acetamido-3-hydroxy-1:4-benzisooxazine-6-dichloroarsine (corresponding arsenoxide), 8:8'-diacetamido-3:3'-dihydroxy-6:6'-arseno-1:4-benzisooxazine, 3-hydroxy-1:4-benzisooxazine-6-arsinic acid 8-glycineamide (corresponding arsenic acid), 8-glycylamino-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, 8-chloro-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, m. p. above 280° (magnesium salt), 3-hydroxy-8-methyl-1:4-benzisooxazine-6-arsinic acid, 3:3'-diacetamido-4:4'-dihydroxy-5:5'-dimethylarsenobenzene, 3-hydroxy-8-methyl-1:4-benzisooxazine-6-arsenic acid, 3:3'-dihydroxy-8:8'-dimethyl-6:6'-arseno-1:4-benzisooxazine, 8- β -hydroxyethylamino-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, 3-hydroxy-8-carboxy-1:4-benz-

isooxazine-6-arsinic acid, 3-nitro-4-hydroxy-5-carboxyphenylarsinic acid [monohydrate, m. p. 282—284° (decomp.); magnesium, barium, and calcium salts], 3-amino-4-hydroxy-5-carboxyphenylarsinic acid, m. p. above 300° (calcium, barium, magnesium, mono- and di-sodium salts), 3-acetamido-4-hydroxy-5-carboxyphenylarsinic acid, m. p. 250—254° (decomp.) (magnesium and calcium salts), 3-hydroxy-8-carboxy-1:4-benzisooxazine-6-arsinic acid, m. p. 300—305° (decomp.), 3-hydroxy-2-methyl-1:4-benzisooxazine-6-arsinic acid, m. p. above 300° (calcium and magnesium salts), 3-hydroxy-2-ethyl-1:4-benzisooxazine-6-arsinic acid, m. p. above 280° (magnesium salt), 8-acetamido-3-hydroxy-2-methyl-1:4-benzisooxazine-6-arsinic acid, decomp. 265° (magnesium salt), 8-acetamido-3-hydroxy-2-ethyl-1:4-benzisooxazine-6-arsinic acid, 3- ω -chlorocarbethoxyamino-4-hydroxyphenylarsinic acid, m. p. 209° (decomp.) (magnesium salt), 2:3-dihydro-1:4-benzisooxazine-6-arsinic acid, m. p. above 300° (magnesium salt), 2:3-dihydro-1:4-benzisooxazine-6-arsenoxide, 6:6'-arseno-(2:3-dihydro-1:4-benzisooxazine), 3- ω -chlorocarbethoxyamino-5-acetamido-4-hydroxyphenylarsinic acid, m. p. 189° (decomp.) (magnesium salt), 3:3'-di-(β -hydroxyethylamino)-5:5'-diacetamido-4:4'-dihydroxyarsenobenzene, 3-hydroxy-1:4-benzisooxazine-8-arsinic acid, m. p. 298° (decomp.) (magnesium, calcium, barium, and sodium salts), 6-amino-3-hydroxy-1:4-benzisooxazine-8-arsinic acid, m. p. above 300° (barium, calcium, and magnesium salts), 6-acetamido-3-hydroxy-1:4-benzisooxazine-8-arsinic acid, m. p. above 300° (magnesium salt), and 6:6'-diacetamido-3:3'-dihydroxy-8:8'-arseno-1:4-benzisooxazine.

R. J. W. LE FEVRE.

Heterocyclic arsenic compounds. III. Derivatives of 4-amino-3-hydroxyphenylarsinic acid. I. E. BALABAN (J.C.S., 1928, 3066—3073).—The preparation of the following arsenicals from 4-amino-3-hydroxyphenylarsinic acid (cf. Brit. J. Venereal Dis., 1927, 3, 1) is described: 3-hydroxy-1:4-benzisooxazine-7-arsinic acid (calcium, magnesium, and barium salts), 8-nitro-3-hydroxy-1:4-benzisooxazine-7-arsinic acid, decomp. 280°, 6(?) -nitro-3-hydroxy-1:4-benzisooxazine-7-arsinic acid, decomp. 280° (magnesium, calcium, and barium salts), 8-amino-3-hydroxy-1:4-benzisooxazine-7-arsinic acid (hydrate 0.75H₂O; barium, calcium, and magnesium salts), 8-acetamido-3-hydroxy-1:4-benzisooxazine-7-arsinic acid (magnesium and calcium salts), 2-nitro-4- ω -hydroxyacetamido-3-hydroxyphenylarsinic acid, efferv. 210°, 2-amino-4- ω -hydroxyacetamido-3-hydroxyphenylarsinic acid (magnesium, calcium, and barium salts), 4- ω -hydroxyacetamido-2-acetamido-3-hydroxyphenylarsinic acid, 8-acetamido-3-hydroxy-1:4-benzisooxazine-5-arsinic acid (magnesium and calcium salts), 8-amino-3-hydroxy-1:4-benzisooxazine, m. p. 180° (hydrochloride, chars at 270° and decomp. about 300°, efferv.; acetyl derivative, m. p. 257°), 8-amino-3-hydroxy-1:4-benzisooxazine-5-arsinic acid (hydrate 0.5H₂O; magnesium, calcium, and barium salts), benzoxazolone-5-arsinic acid (magnesium salt), 5-nitro-4-amino-3-hydroxyphenylarsinic acid (hydrate 1H₂O; calcium salt), 6-nitrobenzoxazolone-5-arsinic acid (magnesium and barium salts), 6-aminobenzoxazolone-5-arsinic acid (hydrate 1H₂O; barium, calcium, and magnesium salts),

6-acetamidobenzoxazolone-5-arsinic acid (magnesium and calcium salts), 6-acetamidobenzoxazolone-3-arsinic acid (magnesium, calcium, and barium salts).

R. J. W. LE FEVRE.

Organo-selenium compounds. M. TAKAMATSU (J. Pharm. Soc. Japan, 1928, No. 555, 450—453).—Phenol gives with selenious acid selenophenol (dihydroxydiphenyl selenide), Se(C₆H₄·OH)₂ (cf. Michaelis and Kuncell, A., 1898, i, 136), and similarly phenoxyacetic acid gives diphenoxyacetic acid selenoxide (dianisylselenoxide- $\omega\omega'$ -dicarboxylic acid), SeO(C₆H₄·O·CH₂·CO₂H)₂, decomp. 210°.

K. ISHIMURA.

Mercuration of neutral-red and its sulphonic acid. I. M. LEVINE (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926 (1928), 4, 105—110).—The following compounds were prepared (the constitutions indicated being doubtful): 2:5-Diacetoxymercuri-neutral-red acetate; 2:5-dichloromercuri-neutral-red chloride; neutral-red-2-sulphonic acid (mercury salt); sodium 5-hydroxymercuri-neutral-red-2-sulphonate.

CHEMICAL ABSTRACTS.

Chromium triphenyl, chromium tetraphenyl, and thallium diethyl. F. HEIN and E. MARKERT (Ber., 1928, 61, [B], 2255—2267; cf. A., 1926, 534).—Chromium triphenyl is prepared as a brownish-yellow, friable powder by the electrolysis of chromium triphenyl iodide dissolved in liquid ammonia at a platinum cathode or by mixing solutions of the iodide and sodium in liquid ammonia. The electrolytic product invariably contains ammonia either adsorbed or chemically combined. The compound is unstable, readily losing diphenyl. By suitable treatment with alcohol and water it is converted quantitatively into chromium triphenyl hydroxide. The metal in chromium triphenyl cannot normally be tervalent, since it passes readily into chromium triphenyl hydroxide, in which it is quadrivalent. It is assumed that the operative valency electrons are derived from groups other than the usual and that the 4₁₁ electron ("potassium electron"; cf. Hund, A., 1925, ii, 912) is not involved and thus causes the similarity of chromium triphenyl to the alkali metals as shown by its ready conversion into a base. The same hypothesis is applicable to chromium tetraphenyl and its transformation into chromium tetraphenyl hydroxide. Electrolysis of chromium pentaphenyl hydroxide in liquid ammonia affords chromium tetraphenyl identical with the product derived from the tetraphenyl iodide. Solutions of chromium tetraphenyl in pyridine are stable when shielded from light and preserved in an atmosphere of nitrogen and the substance is unimolecular at concentrations 0.062—0.086N, according to the results of Rast's capillary method. The similarity of chromium tetraphenyl to the tetra-alkylammonium radicals, indicated by the ready transition into strong bases, is not paralleled by any power of yielding amalgams or of formation of blue solutions in liquid ammonia. Measurements of the decomposition tension and the cathodic polarisation potential of chromium tetraphenyl hydroxide in methyl alcohol do not indicate metallic properties of the radical. Chromium tetraphenyl is deposited on the mercury as a compact precipitate which shows no tendency to penetrate into the metal and does not

possess the characteristic metallic conductivity. The cathodic potential curve shows no similarity to that of metals. The ion, CrPh_4' , does not therefore appear to be formed during the transformation of chromium tetraphenyl into the corresponding hydroxide and the change is expressed: $\text{CrPh}_4 + \text{HOH} \longrightarrow \text{CrPh}_4\text{H}\cdot\text{OH}$ or $\text{CrPh}_4 + \text{H}' \longrightarrow \text{CrPh}_4\text{H}'$. Hydrogen is not evolved but remains attached to the basic molecule. Superficially, the chromium tetraphenyl radical may be regarded as a basic anhydride analogous to ammonia, but the properties of the CrPh_4 group are not markedly influenced by the addition of hydrogen and the reaction with water is irreversible.

Electrolysis of thallium diethyl hydroxide or iodide in liquid ammonia or methyl alcohol at platinum or mercury cathodes gives only thallium at temperatures down to -70° . H. WREN.

Aspartic and glutamic acids in various proteins. D. B. JONES and O. MOELLER (J. Biol. Chem., 1928, 79, 429—441).—Figures are given for the content of aspartic and glutamic acids of various proteins, the determinations being made by direct isolation of the amino-acids by the method of Foreman (A., 1914, ii, 826) except that barium salts were utilised instead of calcium salts. The percentages of these acids found were in all cases greater than those recorded in the literature, the difference being especially marked in the case of aspartic acid. C. R. HARRINGTON.

Alkaline decomposition of cystine. J. C. ANDREWS (J. Biol. Chem., 1928, 80, 191—210).—The yield of sulphide obtained on keeping cystine in cold 4*N*-sodium hydroxide is increased by the presence of lead and by exclusion of oxygen; the result is due to the fact that accumulation of sulphide in solution leads to some reduction of the cystine to cysteine. The speed of racemisation of cystine in alkaline solution is greater than the speed of decomposition, although here again fictitiously large results are obtained for the change in optical rotation, owing to formation of cysteine. The rate of liberation of sulphide from cystine depends on the concentration of alkali. The speed of deamination of cystine is greatly increased by the presence of lead, an effect which is apparently specific for this metal, since it is not exhibited by other metals (*e.g.*, copper and zinc) which form insoluble sulphides; deamination proceeds at the same rate whatever be the degree of racemisation of the cystine. C. R. HARRINGTON.

Cystine content of proteins. Y. TERUUCHI and L. OKABE (J. Biochem. Japan, 1928, 8, 459—467).—A modification of Okuda's method gave the following results: serum-albumin 1.58, egg-white, 2.01, serum-globulin 1.64, fibrin 1.48, beef 0.66, chicken 0.64, salmon 0.58, edestin 1.13, legumin 0.90, gliadin 2.19, zein 0.58, globin 0.61, gelatin 0.04, human hair 14.26, horse hair 11.07, wool 9.12, casein 0.33.

CHEMICAL ABSTRACTS.

[Structure of silk fibroin.] R. O. HERZOG (Ber., 1928, 61, [B], 243).—The author's treatment of silk fibroin with resorcinol at 120° was limited to 30 min., not 30 hrs. as stated by Meyer and Mark (A., 1928, 1229). H. WREN.

Carbon and hydrogen determinations using a metal tube. S. AVERY (Ind. Eng. Chem., 1928,

20, 1232—1234).—A copper tube protected by an outer nickel tube held in place by friction is suitable for organic combustions. The copper tube projects beyond the nickel tube, at each end of which water jackets are soldered to protect the stoppers. The progress of the combustion can be followed by counting gas bubbles. C. IRWIN.

Elementary organic analysis. A. WAHL and J. P. SISLEY (Bull. Soc. chim., 1928, [iv], 43, 1279—1282).—See A., 1928, 909.

Determination of nitrogen in nitro-compounds by reduction with stannous chloride and subsequent titration. G. WALLERIUS (Tekn. Tidskr., 1928, 58, Kemi, 33—35; Chem. Zentr., 1928, ii, 372).—Colver and Prideaux's method (A., 1917, ii, 340, 512) is improved. The stannous chloride solution is prepared by dissolving 130—140 g. of the dihydrate in a mixture of 200 g. of water and 880 g. of hydrochloric acid (*d* 1.19), filtering, and keeping in an atmosphere of carbon dioxide; its titre falls 0.5% per week. The nitro-compound (0.02 g.-equiv.) is boiled under reflux for 20 min. with 20 c.c. of the *N*-stannous chloride solution, decomposition of particles being avoided by the use of asbestos sheet. The mixture is rapidly cooled, starch solution added, and the liquid titrated with 0.1*N*-iodine solution. Nitro-compounds which are volatile in steam must first be sulphonated by means of fuming sulphuric acid. A. A. ELDRIDGE.

Volumetric determination of reducing sugars. R. BIAZZO (Annali Chim. Appl., 1928, 18, 447—453).—The difficulty of determining cuprous oxide formed by the action of a small quantity of a reducing sugar on Fehling's solution may be overcome by allowing the oxide to react with silver oxide in ammoniacal solution and determining the amount of metallic silver produced. After the sugar solution has been boiled for 2 min. with 10 c.c. of Fehling's solution diluted to 50 c.c. with water, the flask is closed by a rubber stopper traversed by a cylindrical separating funnel charged with 15 c.c. of a solution containing 220 g. of ammonium sulphate and 300 c.c. of concentrated ammonia solution per litre. After a short time, almost the whole of this solution is run into the flask and the tap of the funnel is then closed. The flask is shaken until the cuprous oxide is completely dissolved, and 10 c.c. of 3.5% silver nitrate solution are introduced; air is then admitted to the flask, which is left in the dark for some time. The silver is then washed by decantation, the filter-paper being afterwards returned to the flask and the silver dissolved in nitric acid and determined by titration with thiocyanate. Using 10.84, 21.79, 32.53, 43.62, and 51.50 mg. of invert-sugar, the above procedure gave 11.14, 21.16, 31.93, 42.33, and 50.68 mg.

Methylene-blue forms a convenient indicator in the determination of reducing sugars by Ionescu and Vargolici's method (A., 1921, ii, 283). T. H. POPE.

Polarimetric determination of small amounts of dextrose. C. LUNDSGAARD and others.—See this vol., 91.

Determination of aniline by Lehmann's method. A. V. PAMFILOV and V. E. KISSELEVA.—See B., 1928, 885.

Jaffe's reaction for creatinine. V. Isolation of the red compound. I. GREENWALD (J. Biol. Chem., 1928, 80, 103—106; cf. A., 1928, 744).—A hot solution of picric acid (2 mols.) was treated with creatinine (1 mol.) and, after cooling, with excess of sodium hydroxide, the solution was filtered and poured into 10 vols. of alcohol, yielding a precipitate of a red substance, $C_4H_7ON_3 \cdot C_6H_3O_7N_3 \cdot 2NaOH$. On treatment with dilute acetic acid this yielded creatinine picrate, whilst, when dissolved in water in presence of sodium picrate, it gave immediately the red colour of Jaffe's reaction equivalent to its content of creatinine. C. R. HARRINGTON.

Colorimetric microdetermination of furfuraldehyde. K. SUMINOKURA and Z. NAKAHARA (Trans. Totteri Soc. Agric. Sci., 1928, I, 158—159).—Xylidine in presence of acetic acid gives with furfuraldehyde a red colour stronger and more stable than the corresponding colour with aniline. The colour with xylidine has the added advantage of being specific for furfuraldehyde, and enables accurate determinations of the latter to be made in aqueous or ethereal solution. B. W. ANDERSON.

Detection of colouring matter by separation [of fluid layers]. J. J. HOFMAN (Pharm. Weekblad, 1928, 65, 1190—1198).—The method consists in adding 5 c.c. of the aqueous liquid containing the colouring matter to mixtures of (a) 5 c.c. each of ethyl and benzyl alcohols, (b) 5 c.c. each of ethyl and amyl alcohols, and (c) 10 c.c. of acetone and 1 c.c. of benzene, and then causing separation into two layers by adding

5 c.c. of water. Tables are given showing the colorations of the two layers for a large number of natural and synthetic colouring materials when water, dilute hydrochloric acid, dilute sodium hydroxide solution, and solutions of sodium hydrogen sulphite and hydrogen peroxide are added to cause separation. The method may be used to identify an unknown colouring material, and also to detect the presence of synthetic colouring matter in foods, essences, etc.

S. I. LEVY.

Detection of gallic acid and tannin. S. A. CELSI (Rev. Centr. Est. Farm. Bioquim., 1928, 16, 642—650; Chem. Zentr., 1928, i, 2850).—Gallic acid, tannin, etc., which yield pyrogallol when heated, are detected by the production of a cherry-red colour when a trace of the latter in concentrated acetic acid is heated with a few drops of formaldehyde solution and concentrated hydrochloric acid.

A. A. ELDRIDGE.

Reactions of colchicine. L. EKKERT' (Pharm. Zentr., 1928, 69, 662—663).—Colchicine gives a yellow colour with concentrated sulphuric acid and when heated the solution changes colour through golden-yellow, saffron-yellow, brownish-red, blood-red to deep garnet-red. A yellow colour is also formed by colchicine and dilute sulphuric acid, dilute and concentrated hydrochloric acid, dilute nitric acid, acetic acid, and hot phosphoric and lactic acids. A mixture of 0.01 g. of colchicine, 0.003—0.005 g. of tartaric acid, and 1 c.c. of concentrated sulphuric acid on heating becomes green and if either salicylic or citric acid be used instead of tartaric acid a garnet-red solution is formed. E. H. SHARPLES.

Biochemistry.

Gas tensions in tissues affected by local temperatures. H. C. BAZETT and L. SRIBYATTA (Amer. J. Physiol., 1928, 86, 565—577).—Carbon dioxide tension is under normal conditions lower in the subcutaneous tissue than in alveolar air. The high oxygen saturation of blood at lower temperatures is dependent on a failure of the tissues to utilise oxygen rather than on the physical effects of temperature on hæmoglobin dissociation. B. A. EAGLES.

Mode of combination of carbon dioxide in the blood. K. HAYASI, Y. NISHIMURA, and M. OKUYAMA (J. Biophysics, 1927, 2, 293—303).—Samples of oxalated goat's blood have been equilibrated with carbon dioxide at a definite pressure and the quantities of carbon dioxide contained in the plasma and in the whole blood have been determined separately as well as the p_H of the whole blood. At the same carbon dioxide tension the corpuscles take up more carbon dioxide than does the plasma. The results are at variance with the view that carbon dioxide in the plasma exists only as free carbon dioxide or hydrogen carbonate, but suggest that a part of it exists in an unknown form. W. O. KERMACK.

Production of carbon monoxide by the oxidation of dextrose in alkaline solution by oxygen

or air. **Biological consequences of this reaction.** M. NICLOUX (Bull. Soc. Chim. biol., 1928, 10, 1135—1163).—When a solution of dextrose (0.25 g.) in 0.1N-potassium hydroxide (50 c.c.) is shaken with oxygen (50 c.c.) or an equivalent amount of air at 84°, carbon monoxide (1.62 c.c.) and dioxide (5.13 c.c.) are liberated. Carbon monoxide is not liberated in the absence of oxygen, but an excess of oxygen tends to diminish the amount formed. Sodium and lithium hydroxides act in a similar way and barium and calcium hydroxides and sodium carbonate more slowly; sodium hydrogen carbonate is without action. Lævulose, galactose, lactose, and maltose behave similarly to dextrose; sucrose yields carbon monoxide only subsequent to its inversion by the alkali.

Carbon monoxide is found in the blood of mammals, birds, and fish; dog's blood contains about 1.5 c.c. per litre. The amount present in the blood is too great to be accounted for by the small amount possibly existing in the atmosphere (Gautier, A., 1900, ii, 720) and it is therefore suggested that it arises from oxidation of the sugars in the blood-stream.

G. A. C. GOUGH.

Correlation between oxygen capacity and the total hæmoglobin content. E. BAUER, K. LAWROWSKY, and E. SKUJIN (Z. ges. exp. Med., 1927, 58, 586—595; Chem. Zentr., 1928, i, 3086).—A

large hæmoglobin content corresponds in man with a small degree of oxygen saturation.

A. A. ELDRIDGE.

Hydrogen-ion equilibrium in the blood. III. Temperature effect on the amphoteric property of oxyhæmoglobin. S. KATO (J. Biophysics, 1927, 2, 243—249).—When blood-serum and defibrinated blood from the same animal are equilibrated at 18° at a carbon dioxide tension of 51.6 mm. the p_H of the two fluids is 6.97. At higher tensions of carbon dioxide at this temperature the p_H of the serum is below that of the defibrinated blood, whilst at lower carbon dioxide tensions the p_H of the defibrinated blood is less than that of the serum. The oxyhæmoglobin therefore acts as a buffer at any p_H other than 6.97, which is therefore the isoelectric point of oxyhæmoglobin at 18°. By the use of the same method the isoelectric point of oxyhæmoglobin is found to be 6.82 at 25°, 6.75 at 30°, whilst at 37° the isoelectric point was not attained at a carbon dioxide tension of 200 mm. These results have been confirmed by experiments on cataphoresis of oxyhæmoglobin at various hydrogen-ion concentrations. By this method the isoelectric point of oxyhæmoglobin at 37° was found to be 6.57.

W. O. KERMACK.

Spectrophotometric studies on oxyhæmoglobin. E. KÈVE (Biochem. Z., 1928, 201, 439—453).—Determinations of the extinction coefficient ϵ and of the constant A , where c (concentration) = $A\epsilon$, were carried out on various samples of crystallised oxyhæmoglobin from the horse and dog. The ratio $\epsilon_{511.6-533.1}/\epsilon_{565.8-555.9}$ has the value 1.61–1.62 for once-crystallised oxyhæmoglobin; further crystallisation lowers the value eventually to 1.55. For once-crystallised horse oxyhæmoglobin $A_{411.6-533.1} = 1.16$, $A_{565.8-555.9} = 1.88$. In the spectrophotometric determination of the hæmoglobin content of blood, the value as determined from the values for ϵ and A may differ by 3%.

J. H. BIRKINSHAW.

Hæmochromogen. M. L. ANSON and A. E. MRSKY (J. Gen. Physiol., 1928, 12, 273—288).—Hæmochromogens contain reduced hæm combined with a nitrogenous base, a reversible equilibrium existing between the hæmochromogen on the one hand and its constituents on the other. One of the two compounds formed by reduced hæm with cyanide is a typical hæmochromogen to which the name cyanohæmochromogen has been given. This compound probably contains one cyano-group per mol. of hæm. The hæmochromogen formed from hæmoglobin is a compound of denatured globin and reduced hæm, 1 mol. of denatured globin (M 16,700) being able to convert 10 mols. of reduced hæm into hæmochromogen. Edestin and zein are less efficient as bases in the formation of hæmochromogen than is denatured globin.

W. O. KERMACK.

Conversion of blood pigment into bile pigment. —F. SCHWERTTEL (Biochem. Z., 1928, 201, 435—438; cf. Pollak, A., 1928, 1270).—The substance $C_{16}H_{16}O_4N_4$ was prepared in crystalline form from quinone (1 mol.) and pyrocatechol (2 mols.) by the action of ammonia. It had m. p. 194—195° and corresponded in all respects with the product obtained by

Pollak (*loc. cit.*) from pyrocatechol and hæmin. Pollak's product is therefore not of pyrrole nature.

J. H. BIRKINSHAW.

Differentiation of the labile iron of blood by means of its reaction with carbon monoxide and oxygen. G. BARKAN and E. BERGER (Arch. exp. Path. Pharm., 1928, 136, 278—299; cf. A., 1928, 537).—Saturation of blood with carbon monoxide or complete reduction with hydrogen prevents the separation by acid of 65% of the total labile iron. This action is partly reversible in the former case and completely in the latter by reoxygenation. Application of a distribution equation for the reaction of this labile iron with carbon monoxide and oxygen yields a distribution constant one fourth to one tenth of that for hæmoglobin. The remainder of the labile iron (35%) can be separated by acid after saturation of blood with carbon monoxide or complete reduction with hydrogen. Hydrocyanic acid is without action on the labile iron of blood. This action of carbon monoxide on part of the labile iron shows itself in the case of the blood of living rabbits.

H. R. ING.

Blood-cell metabolism. I. Effect of methylene-blue and other dyes on the oxygen consumption of mammalian and avian erythrocytes. G. A. HARROP and E. S. G. BARRON (J. Exp. Med., 1928, 48, 207—223).—The respiratory metabolism of non-nucleated mammalian erythrocytes is greatly increased by the addition of methylene-blue and certain other dyes; the effect on avian blood is less marked. The role of an oxygen-carrier is ascribed to the dye.

CHEMICAL ABSTRACTS.

Permeability of membranes. VI. Mensuration of the dried collodion membrane (calculation of dimensions and relations to certain biological membranes). A. A. WEECH and L. MICHAELIS (J. Gen. Physiol., 1928, 12, 221—230).—Measurements are given of the area, thickness, density, and water content of collodion membranes used in experiments previously described (A., 1927, 727). The results are discussed in relation to the behaviour of certain membranes of animal origin and in particular to the membrane of the red blood-corpuscle.

W. O. KERMACK.

Colloidal osmotic pressure of the blood fluid. I. Conditions which influence the colloidal osmotic pressure of the blood-serum. II. Restitution of the blood fluid after hæmorrhage. K. HIROTA (J. Biochem. Japan, 1928, 9, 71—85, 87—102).—I. When the colloidal osmotic pressure of blood-serum is measured by the use of a collodion membrane, the results obtained depend on the nature of the aqueous solution against which the serum is equilibrated, being reduced with increasing concentration of the salts in this liquid and with increasing acidity. When isotonic salt solutions are used, higher results are obtained with potassium chloride and ammonium chloride and lower results with disodium hydrogen phosphate, potassium sulphate, magnesium chloride, calcium chloride, and potassium dihydrogen phosphate than with sodium chloride. Serum shows the same colloidal osmotic pressure as does plasma from the same blood.

II. In rabbits bled up to 30% of their blood-volume,

fluid passes into the blood-stream and at the same time the colloidal osmotic pressure is almost but not quite maintained. The liver plays an important part in regulating the process. The conditions favouring rapid restoration of the blood-volume are low blood-pressure and high colloidal osmotic pressure in the blood. The results support Bayliss and Starling's theory of lymph production. W. O. KERMACK.

Importance of the membrane in the measurement of the osmotic pressure of plasma-protein. A. NITSCHKE (Z. ges. exp. Med., 1928, 59, 298—302; Chem. Zentr., 1928, i, 3099).—The osmotic pressure of serum-protein towards isotonic Ringer's solution is higher with a collodion membrane or a parchment membrane coated internally with collodion than with a parchment membrane, uncoated or coated externally with collodion. An explanation is offered.

A. A. ELDRIDGE.

Colorimetric determination of serum-proteins by means of phenol reagent. H. WU and S. M. LING (Chinese J. Physiol., 1928, 2, 399—402).—It is suggested that the standard for use in Wu's method (A., 1922, ii, 406) should be made by the addition of 50 c.c. 0.1*N*-sodium carbonate and 200 c.c. 95% alcohol to 250 c.c. of an approximately 0.5% solution of dialysed egg-albumin, the actual concentration of the protein being determined by Kjeldahl's method.

F. C. HAPFOLD.

Protein spreading as method for determination of serum-albumin and -globulin. E. GORTER and F. GREDEL (Biochem. Z., 1928, 201, 391—411).—The general principles of the spreading of proteins on water are discussed. In maximum spreading (on 0.1*N*-acid or -alkali) the linked amino-acids which form the protein molecule assume an approximately horizontal position. A second maximum occurs at the isoelectric point due to the free amino- and carboxyl groups. On 0.001*N*-acid or alkali the spreading is much less; the cause of this is uncertain.

A method is described for the determination of albumin and globulin in serum, using the principle of spreading on 0.1*N*-hydrochloric acid. The proteins were separated by precipitation of the globulin with half-saturated ammonium sulphate. A number of determinations were made on the sera of man and various animals and compared with gravimetric data. In a micro-method for the determination of globulin and albumin, the globulin and total protein are determined and the albumin by difference.

J. H. BIRKINSHAW.

Examination of sera of mountain-dwellers by electrodialysis. A. TÓTH (Biochem. Z., 1928, 201, 412—423).—Globulin and albumin determinations were made on the sera of animals and man living at high and low altitudes. Rats showed a lower globulin content at high than at low altitude. In the case of the guinea-pig, rabbit, and man there was no marked difference. Repeated removal of blood from rabbits led to a diminution of the globulin content of the serum.

J. H. BIRKINSHAW.

Micro-determination of the ether-soluble organic acids in blood. S. L. ORSKOV (Biochem. Z., 1928, 201, 22—33).—The rocking extraction method of Widmark, used for urine (A., 1928, 96), is adapted

as a micro-method and is successfully applied to the determination of the organic acids of 0.1—0.2 c.c. of human and rabbit's blood and of added benzoic acid.

P. W. CLUTTERBUCK.

Cholesterol ester content of blood-serum and plasma. Cholesterol esterase in animal tissues. Hypercholesterolaemia of fasting. Effect of age on cholesterol of blood-serum. R. E. SHOPE (J. Biol. Chem., 1928, 80, 125—126, 127—132, 133—140, 141—148).—Blood-serum contains a higher proportion of cholesterol in the form of esters than does plasma. An enzyme capable of hydrolysing cholesteryl esters is widely distributed throughout animal tissues; the action of this enzyme probably accounts for the low cholesteryl ester content of *post-mortem* blood. The hypercholesterolaemia of fasting is relieved equally by the administration of any one primary foodstuff or of a mixed diet; exclusive feeding with fat for 48 hrs. causes no increase in blood-cholesterol. The cholesterol content of the blood increases from birth during the early life of the animal and slowly decreases again in old age; cholesteryl esters are absent from the blood at birth and appear when the increase in total cholesterol begins.

C. R. HARRINGTON.

Solvent action of normal and pathological human serum on cholesterol. M. LOPER, A. LEMAIRE, and A. LESURE (Compt. rend. Soc. Biol., 1928, 98, 101—103; Chem. Zentr., 1928, i, 3086).—The solvent action of serum on cholesterol is not dependent on the cholesterol content, the flocculation, or the cholesterol skin-reaction, although this is usually negative when the cholesterololysis is increased.

A. A. ELDRIDGE.

Colorimetric determination of lipin-phosphorus in blood. S. L. LEIBOFF (J. Biol. Chem., 1928, 80, 211—214).—Blood is poured into a mixture of alcohol and ether, an aliquot portion of the filtrate is evaporated, and the residue incinerated with sulphuric acid and hydrogen peroxide; phosphate is then determined by the author's method (A., 1928, 1391).

C. R. HARRINGTON.

Relationship between phosphoric acid and glycolysis in blood. W. A. ENGELHARDT and A. E. BRAUNSTEIN (Biochem. Z., 1928, 201, 48—65).—Two opposed and independent processes contribute to the phosphoric acid balance of blood *in vitro*, first, a separation of inorganic phosphorus from organic compounds, and second, the processes directly related to glycolysis in which phosphoric acid becomes combined, the former, in distinction to the latter, being insensitive to the action of ions and to the displacement of p_H . The inorganic phosphorus content of rabbit's defibrinated blood does not change on keeping in a thermostat at 37°, but increases considerably on dilution with isotonic saline, the increase being greater the greater is the dilution. If diluted with anisotonic saline, the increase is greater the more strongly hyper- or hypo-tonic is the saline. Addition of a series of chlorides showed that univalent cations do not exert any specific effect on the amount of inorganic phosphorus formed, but calcium ions caused a greater increase than the univalent ions. Dilution with isotonic solutions of salts of monobasic acids showed that different anions cause different increases of

inorganic phosphorus, the following being arranged in order of the intensity of their action: $I, NO_3, CNS < Br < Cl < F$. Erythrocytes contain both the substrate from which inorganic phosphorus is derived and the phosphatase necessary to release it, but serum contains only the enzyme. If in place of whole blood washed red cells or serum to which has been added a boiled suspension of corpuscles are used, a constant increase of inorganic phosphorus occurs which is independent of dilution and of the action of different ions and of displacement of p_H . The difference between the two sets of experiments is due to the fact that in the latter glycolysis cannot occur. When washed cells are suspended in Ringer's solution containing dextrose, a glycolysing system is again obtained and the increase of inorganic phosphate is greatly decreased in comparison with controls of the same cells in Ringer's solution without dextrose, whilst the effect of ions becomes similar to that in whole blood. All the factors which, with a glycolysing system, bring about an increase of inorganic phosphorus inhibit glycolysis to the same extent. Addition of arsenate either to whole blood or to the cells-dextrose system causes an even greater increase of inorganic phosphorus than addition of sodium fluoride (cf. A., 1928, 1269).
P. W. CLUTTERBUCK.

Nature of the sugar combined with protein of blood-plasma. Z. DISCHE (Biochem. Z., 1928, 201, 74—86).—The total carbohydrate of horse blood-plasma is about 0.3%, of which 0.08—0.11% exists as free sugar, and the rest, which is combined with protein (cf. Glassmann, A., 1926, 192, 1169), consists of about equal amounts of *d*-mannose and a non-fermenting sugar resembling glucosamine. Mannose was isolated by autoclaving the dialysed plasma with 3% sulphuric acid at 120°, precipitating the protein decomposition products with phosphotungstic acid, and identifying as the phenylhydrazone.

P. W. CLUTTERBUCK.

Total sugar of blood and urine. II. Hydrolysable sugar of blood. M. R. EVERETT and F. SHEPPARD (J. Biol. Chem., 1928, 80, 255—268).—Hydrolysis with sulphuric acid does not increase the nitrogenous reducing substances in protein-free blood-filtrates, nor does it affect the reducing power of solutions of dextrose; technical errors are also excluded, so that the real existence of hydrolysable sugar (A., 1927, 1102) is confirmed. This substance is present also in plasma, but to a smaller extent than in corpuscles; it is not removed by treatment with yeast, and it is for the most part resistant to alkaline hydrolysis. It is present in increased amount in leucæmic blood, and may consist, in part, of glycogen.

C. R. HARRINGTON.

Variations of the results of sugar determinations in relation to dilution of the blood after the mercurial proteinisation of blood. G. FONTÈS and L. THIVOLLE (Bull. Soc. Chim. biol., 1928, 10, 1164—1178).—The more dilute the blood the greater is the apparent sugar content after deproteinisation by mercuric sulphate or chloride. The plasma and, to a greater extent, the corpuscles are both subject to this effect, which is not due to the acidity of the mercuric salts, since deproteinisation

with tungstic acid gives figures for the "immediately reducing" sugar independent of dilution. The effect is not produced after the action of yeast. The facts may be explained by supposing that the mercuric salt combines with an unknown blood-constituent, thus setting free at certain dilutions a reducing substance, probably a carbohydrate.
G. A. C. GOUGH.

Oscillations of blood-sugar values within brief periods and the blood-sugar curve on uniform ingestion of dextrose. O. J. NIELSEN (Biochem. J., 1928, 22, 1490—1498).—A number of determinations of the blood-sugar in fasting individuals at complete rest made at intervals of 1—5 min. for a period of $\frac{1}{2}$ —2 hrs. did not divulge the previously described oscillations of the blood-sugar curve. In normal individuals an almost horizontal curve was found, in insulin- and diet-treated diabetics a rising curve, in diabetics treated with diet only a falling curve, and in a diet-treated diabetic with advanced kidney insufficiency a horizontal curve. There were no oscillations in the blood-sugar in non-diabetics after ingestion of dextrose or in diabetics at different times of the day after ingestion of food or administration of insulin. No uniform blood-sugar curves were obtained on different days after ingestion of the same amount of dextrose with a plentiful and fairly uniform mixed diet. On the other hand, the amount of dextrose eliminated in the urine in 2 hrs. was the same each day. In one case uniform blood-sugar after ingestion of dextrose on three different days was obtained in a patient receiving during this time the same amount of food, salts, and liquid.

S. S. ZILVA.

Micro-determination of the water-content of blood. L. BRACALONI (Arch. Farm. speriment., 1928, 46, 115—118).—Modifications in Bang's method are suggested.

T. H. POPE.

Ultra-violet absorption spectra of uric acid and of the ultra-filtrate of serum. F. C. SMITH (Biochem. J., 1928, 22, 1499—1503).—Uric acid when dissolved in water shows two sharp bands in the ultra-violet absorption spectrum; when dissolved in sodium carbonate only one band is obtained. The values for the concentration of uric acid in serum obtained from the spectroscopical examination are in very fair agreement with those obtained by chemical methods. The absorption spectrum of uric acid present in the ultra-filtrate of blood-serum is similar to that of uric acid dissolved in water or in the buffer solution and not to that of the acid dissolved in carbonate. A blood-filtrate from a pathological case showed marked general absorption.

S. S. ZILVA.

Theory of blood coagulation. E. WALDSCHMIDT-LEITZ, P. STADLER, and F. STEIGERWALDT (Naturwiss., 1928, 16, 1027).—The capability of a substance to be decomposed by trypsin-kinase is connected with its power of inhibiting blood-clotting. The conclusion is reached that blood-clotting is a proteolytic process and thrombin a proteolytic enzyme. Of the proteolytic enzymes examined, trypsin-kinase alone is able to hasten blood-clotting. It is probable that thrombin is related to trypsin-kinase, if not identical with it.
J. H. BIRKINSHAW.

Imitation of organic forms by means of albumin and hydrofluoric acid. L. A. HERRERA (Atti R. Accad. Lincei, 1928, [vi], 8, 15—19).—An extension of previous work (cf. A., 1928, 913).

Microscopical tests for glutathione in cells. P. JOYET-LAVERGNE (Compt. rend. Soc. Biol., 1928, 98, 658—660; Chem. Zentr., 1928, i, 2946).—The red colour-reaction with sodium nitroprusside solution given by reduced glutathione in fresh tissue is rendered more sensitive by placing the material in a 10% sodium cyanide or saturated aqueous sodium sulphite solution for 10 min. Sodium sulphate and trichloroacetic acid solutions exercise a similar effect.

A. A. ELDRIDGE.

Membrane of the egg of *Voluta brasiliensis* as dialyser. A. H. ROFFO and L. M. CORREA (Bol. Inst. Med. Exp., 1927, No. 16, 5 pp.; Chem. Zentr., 1928, ii, 364).—The membrane of the egg of *Voluta brasiliensis*, a La Plata mollusc, is insoluble in water, but soluble in acetic acid and concentrated alkalis. It contains 2.45% of ash, traces of carbohydrate, and no lipins. Its properties resemble those of keratin. The membrane is suitable for ultra-filtration.

A. A. ELDRIDGE.

Chemistry of brain. II. Phosphatides of the normal human brain soluble in light petroleum. K. SINGER and O. DEUTSCHBERGER. III. Phosphatides of the brain, soluble in light petroleum, in progressive paralysis and marasmus. K. SINGER (Biochem. Z., 1928, 198, 328—339, 340—349).—II. The total light petroleum extract of human adult brain (per g. moist weight) is constant, but the amount extractable from different slices varies irregularly. The nitrogen distribution of these extracts is the same as that obtained for horse brain (A., 1927, 371) with the exception of the galactoside-nitrogen, which is much smaller. The foetal brain contains only a small amount of substance extractable by light petroleum, the nitrogen content of which, however, is 1.5—2 times that of the extracts of adult brain. As development proceeds, the total light petroleum extract increases and the amount of nitrogen decreases, the decrease being initially rapid and later more gradual.

III. The amount of the light petroleum extract of brain in five cases of progressive paralysis is increased and the nitrogen content is decreased, in comparison with the normal. The choline-nitrogen is decreased to one third of the normal, the amino-nitrogen is slightly decreased, and only traces of galactoside-nitrogen are detectable. The ratio total amino-nitrogen : choline-nitrogen is 3:1:1 instead of the normal value 1.4:1. This decrease in lecithin is not, however, specific for progressive paralysis.

P. W. CLUTTERBUCK.

Combination of the protein of brain with alkaloids and organic bases. A. PETRUNKINA and M. PETRUNKIN (Biochem. Z., 1928, 201, 185—189).—Alkaloids (strychnine, morphine, cocaine, and quinine) and guanidine combine with the denatured protein of brain only when the p_H is higher than 4 (cf. A., 1928, 190).

P. W. CLUTTERBUCK.

Physical chemistry of the epidermis. H. SCHADE and A. MARCHIONINI (Arch. Dermat. Syph., 1928, 154, 690—716; Chem. Zentr., 1928, ii, 71—

72).—The p_H of the epidermis is between 1.78 and 5.17, the average value being 3.78; the values vary at different points. Perspiration is associated with an increase of acidity; wounding or restricted evaporation is attended by an alkaline reaction.

A. A. ELDRIDGE.

Cholesterol in tissues. E. N. CHAMBERLAIN (J. Physiol., 1928, 66, 249—261).—Tables are given showing the cholesterol content of the suprarenals, spleen, brain, liver, kidneys, lungs, muscle, and blood in normal rabbits. Cholesterol injected intravenously causes a large increase in the cholesterol content of the spleen. It is suggested that the spleen may be concerned normally in maintaining the blood-cholesterol at a fixed value by continually removing small excesses.

B. A. EAGLES.

Cholesterol of protoplasm. I. Ox-heart. G. PFEIFFER (Biochem. Z., 1928, 201, 424—434).—The isolation of the total cholesterol of heart tissue by extraction with solvents was found not to give quantitative results. The best method was the hydrolysis of the tissue with 2% sodium hydroxide solution followed by ether extraction according to Fex's method (A., 1920, i, 697). The ether extract was fractionally crystallised after a digitonin precipitation of cholesterol and oxysterol. The saponification of the cholesteryl esters with 5% metallic sodium in absolute alcohol required 24—30 hrs. The bound cholesterol was 34% of the total cholesterol.

J. H. BIRKINSHAW.

Distribution of potassium in the animal organism. A. LEULIER, L. VELLUZ, and H. GRIFFON (Compt. rend., 1928, 187, 957—959).—The potassium contents, determined by a modification of the cobaltinitrite method, of the small intestine, heart, and leg muscle of the guinea-pig are 1.84, 2.02, and 2.31%, respectively (average for dry tissue). The amounts vary very little from animal to animal.

G. A. C. GOUGH.

Composition of the enamel of teeth. A. BERNARDI (Annali Chim. Appl., 1928, 18, 454—460).—Analyses of the dental enamel of cattle gave: For animals of 2—5 years, (1) soluble ash, 99.87; Ca, 32.74; Mg, 2.50%; (2) soluble ash, 99.87; Ca, 37.28; Mg, 2.42; PO_4 , 52.44; Cl, 0.33%. For animals of 7—10 years or older, (1) soluble ash, 99.81; Ca, 40.89; Mg, 0.40%; (2) soluble ash, 99.63; Ca, 41.54; Mg, 0.89; PO_4 , 52.05; Cl, 0.25%. In two of a number of cases traces of fluorine were detected.

T. H. POPE.

Determination of silica in tissues. E. J. KING (J. Biol. Chem., 1928, 80, 25—31).—The dried tissue is incinerated with nitric acid in presence of boric acid, the ash is extracted with sodium hydroxide, and the solution almost neutralised with sulphuric acid; phosphates are precipitated with magnesia mixture, the filtrate is treated with molybdic acid, and the yellow colour of the silicomolybdic acid formed is compared with a picric acid standard. Figures are given for the silica content of various tissues.

C. R. HARRINGTON.

Is ozone a normal constituent of cod-liver oil? J. A. DE LOUREIRO (Compt. rend. Soc. Biol., 1928, 97, 879—880; Chem. Zentr., 1928, ii, 301).—Ozone

was detected in all crude oils examined; it is considered to originate from autoxidation, and not to be an original constituent. A. A. ELDRIDGE.

Arsenic in fish. E. SADOLIN (Biochem. Z., 1928, 201, 323—331).—The arsenic of fish occurs principally in the fat-soluble compounds. The arsenic compounds appear to be acidic, since they are extracted by a weakly alkaline solution along with the fatty acids.

The concentration of arsenic is higher in the liver of fish than in muscular tissue. The oil extracted from tissue contains more arsenic than the tissue itself. The arsenic content of fish bears no relation to their oil content. J. H. BIRKINSHAW.

Biochemistry of mixed human saliva. I. Dextrose content. D. ENTIN and A. A. SCHMIDT (Deut. Monatsschr. Zahnheilkunde, 1927, 710—712; Chem. Zentr., 1928, i, 2955).—The Hagedorn-Jensen method is not applicable to saliva. Dextrose and fermenting substances are absent from fasting mixed human saliva. The quantity of substances which reduce thiocyanate (average 9.7 mg.-%) is fairly constant for the individual. A. A. ELDRIDGE.

Chemical mechanism of hydrochloric acid secretion. I. Electrolyte variations in human gastric juice. H. A. BULGER, C. M. STROUD, and M. L. HEIDEMAN. **II. Blood passing through the stomach of dogs.** H. A. BULGER, D. ALLEN, and L. B. HARRISON (J. Clin. Invest., 1928, 5, 547—560, 561—571).—Acid secretion is accompanied by little change in the chlorine concentration of blood, although the total base falls proportionally to the increase in acid. The concentration of phosphate in gastric contents is usually greater than in serum. As blood flows through a secreting portion of a dog's stomach, the total base increases, whilst the chlorine is little changed. CHEMICAL ABSTRACTS.

Composition of human milk. M. BELL (J. Biol. Chem., 1928, 80, 239—247).—Figures are given for the composition of human milk at various stages of lactation; in general the ash and protein content decreased and the lactose and fat increased with the time after delivery. The volume of milk was increased by increase in the carbohydrate of the diet, and decreased by supplementing the fat; in neither case was the composition of the milk significantly affected. C. R. HARRINGTON.

Effect of heat on certain constituents of milk. Adult utilisation of heated milk. K. DAUM (Abstr. Theses, Univ. Chicago, Sci. Ser., 1925—1926, 4, 423—430). CHEMICAL ABSTRACTS.

Polarimetric determination of small amounts of dextrose. C. LUNDGAARD, C. N. J. GRAM, S. A. HOLBØLL, and E. RUD (Biochem. Z., 1928, 201, 341—352).—A comprehensive series of polarimetric determinations of dextrose on solutions of unknown composition was carried out by three observers. Three different polarimeters were used. The results indicate that when the amount of dextrose is small a considerable percentage error is encountered. In 95% of the cases this did not exceed the absolute value of 0.020% of dextrose. Previous determinations of dextrose in biological fluids employing the polarimetric method and conclusions therefrom need confirmation. J. H. BIRKINSHAW.

Optical activity of cerebrospinal fluids. C. N. J. GRAM, O. J. NIELSEN, and E. RUD (Biochem. Z., 1928, 201, 353—368).—Polarimetric determinations of dextrose in samples of cerebrospinal fluid were carried out under special precautions (see preceding abstract). The values were consistently lower than the figures obtained by copper reduction. After precipitation of proteins with lead acetate the polarimetric value coincided with the reduction value. After partial removal of the sugar by dialysis, negative rotations were obtained which again became positive on precipitation of protein. No evidence for a "condensation product" of sugar and protein was found; the rotation observed is merely the sum of the rotations due to dextrose and protein. An increase in the rotation after two days as observed in some cases must be ascribed to changes in the protein.

J. H. BIRKINSHAW.

Determination of hexamethylenetetramine in cerebrospinal fluid. E. BERTEL (Biochem. Z., 1928, 201, 13—14).—The acidified fluid is distilled in steam and the formaldehyde in the distillate is determined by adding standard iodine and sodium hydroxide, acidifying after 30 min., and titrating with standard thiosulphate. P. W. CLUTTERBUCK.

Analysis of colouring matter of urine. VI. M. WEISS (Biochem. Z., 1928, 201, 337—340).—A new spectrometer is described which may also be used as a colorimeter. J. H. BIRKINSHAW.

Renal excretion of chlorides and water. A. R. FEE (J. Pharm. Exp. Ther., 1928, 34, 305—316).—Anaesthetics and narcotics inhibit the water diuresis following the absorption of water from the intestine. The physical theories of renal excretion are not sufficient to explain this effect. A disturbance of a mechanism involving the pituitary body is indicated. B. A. EAGLES.

Study of physiological condition and function by biological analysis of the urine. I. Diagnosis of pregnancy. C. FUNK and H. R. OLIVIER (J. Pharm. Chim., 1928, [viii], 8, 449—453).—A method for the diagnosis of pregnancy, based on the presence of folliculin in the urine, is described. The results confirm those of Aschheim and Zondek (Klin. Woch., 1928, 5, 8). From the sixth week, folliculin is detectable in quantities of 30—50 c.c. of urine, but in normal females it cannot be detected in 1400 c.c. of urine. The method appears to be more specific than that depending on the demonstration in the urine of the hormone of the posterior lobe of the pituitary gland. E. H. SHARPLES.

Fat metabolism of cancer patients. K. KLAUS (Biochem. Z., 1928, 201, 286—291).—The total cholesterol in the blood-serum of 9 women patients was below normal; the fatty acids were normal except in advanced cases. The percentage of cholesterol in the unsaponifiable fraction varied around 56%; the lipaemic coefficient (cholesterol/fatty acids) was about 0.5 J. H. BIRKINSHAW.

Oxidation of fats etc. and metabolism in normal health and diabetes. C. C. PALIT and N. R. DHAR.—See this vol., 48.

Supposed effect of tumour extracts on glycolysis. J. BROOKS and M. JOWETT (*Biochem. J.*, 1928, 22, 1413—1416).—Saline extracts of malignant tumours have no effect on the anaerobic glycolysis of normal rat tissue. Washing tissues with a suitable Ringer's solution does not affect their glycolysis (cf. Waterman, A., 1924, i, 137; *Brit. J. Exp. Path.*, 1925, 6, 300).
S. S. ZILVA.

Ammonium chloride acidosis and diabetic acidosis. F. MAINZER and A. JOFFE (*Z. ges. exp. Med.*, 1928, 59, 492—508; *Chem. Zentr.*, 1928, i, 3085—3086).—Ammonium chloride acidosis is generally followed by alkalosis, conditioned by reduction of the chlorine content and a retarded increase of carbon dioxide. Abolition of diabetic acidosis by insulin treatment is also accompanied by alkalosis and fall in chlorine content.
A. A. ELDRIDGE.

Gastric lipase in various stomach diseases. K. ANDO (*Nagaya J. Med. Sci.*, 1927, 2, 103—108).—The lipase, determined by Ogawa's modification of Michaelis and Rona's tributyrin method, was not decreased in hyperacidity (p_H 1.1—1.5, determined by Michaelis' indicator method) and gastric ulcer (p_H 1.2), whilst in anacidity, gastric cancer, and other diseases with p_H above normal it was considerably lowered.
CHEMICAL ABSTRACTS.

Metabolism in hepatic disease. I. Carbohydrate metabolism. A. OPPENHEIMER (*Z. klin. Med.*, 1928, 107, 467—475; *Chem. Zentr.*, 1928, i, 3087).—The lactic acid value is not higher (13 mg.-%) than normally or in other chronic disease. Administration of sugar does not increase the blood-lactic
A. A. ELDRIDGE.

Cholesterol and its esters in the blood in hepatic disease. A. ADLER and H. LEMMEL (*Deut. Arch. klin. Med.*, 1928, 158, 173—213; *Chem. Zentr.*, 1928, ii, 165).—Normal human blood contains 150—200 mg.-% of total cholesterol (determined by Bloor's method), of which 50—70% is present as ester. When the flow of bile to the intestine is prevented, e.g., by tumour or calculus, the cholesterol value markedly rises, except when an inflammatory process is present. Values in pathological conditions are recorded.
A. A. ELDRIDGE.

Cutaneous and venous blood-sugar curves. I. Normal individuals after insulin, and with liver disease. M. FRIEDENSON, M. K. ROSENBAUM, E. J. THALHEIMER, and J. P. PETERS (*J. Biol. Chem.*, 1928, 80, 269—288).—In the post-absorptive state in normal individuals little difference was found between the cutaneous (arterial) and venous blood-sugar, although the former was usually greater; after ingestion of 50 g. of dextrose the difference became more marked at the time of maximum hyperglycaemia. After a dose of insulin, in a fasting normal individual, the difference generally remained positive, although in one instance it became negative during the period of recovery. In cases of hepatic disease, the pronounced hyperglycaemia resulting from ingestion of 50 g. of dextrose was accompanied by a definitely positive arterio-venous difference in the blood-sugar.
C. R. HARRINGTON.

Human insulin hypoglycaemia. III. Behaviour of the protein fractions of the blood, the bilirubin, blood-concentration, and blood-coagulation, particularly in hepatic disease. O. KLEIN and M. KMENT (*Z. Klin. Med.*, 1928, 107, 476—487; *Chem. Zentr.*, 1928, i, 3085).—The blood coagulation-time and the bilirubin value were reduced, the total protein, the fibrinogen, the serum-protein, and the blood-concentration were increased.
A. A. ELDRIDGE.

Inflammation and condition of irritation and stimulation. I. Gas metabolism. II. Sugar metabolism. F. BRICKER (*Arch. exp. Path. Pharm.*, 1928, 137, 329—338, 339—342).—Determinations have been made of the oxygen, carbon dioxide, and dextrose content of the venous blood in the two ears of a rabbit, one of which had been irritated by the application of xylene or hot water, or by mechanical stimulation.
W. O. KERMACK.

Plasma proteins in leprosy. M. H. NEILL and M. M. DEWAR (*U.S. Pub. Health Service Bull.*, 1927, No. 168, 1—20).—Normal values for plasma are: fibrin, 0.33, albumin 5.23, globulin 2.29%; values obtained in leprosy varied with the condition of the patients, the total protein being about normal, the fibrin increased, and the albumin:globulin ratio lowered.
CHEMICAL ABSTRACTS.

Lipase in the blood-serum of lepers. M. H. NEILL and M. M. DEWAR (*U.S. Pub. Health Service Bull.*, 1927, No. 168, 21—27).—In general, normal values were obtained; low values were associated with acute exacerbation, advanced pulmonary tuberculosis, and liver diseases. Injection of chaulmoogric ester did not increase the blood-lipase.
CHEMICAL ABSTRACTS.

Toxic action of diastase and cell injury. K. BOSHAMER (*Klin. Woch.*, 1928, 7, 978—980; *Chem. Zentr.*, 1928, ii, 169).—Cells of an injured organism are further injured by diastase. Severe injury by diastase in presence of decomposition products of the pancreas indicates that it is a cause of death in pancreatic necrosis.
A. A. ELDRIDGE.

Biochemistry of scurvy. A. ABRAHAM (*Klin. Woch.*, 1928, 7, 353—355; *Chem. Zentr.*, 1928, i, 2960).—Reduced osmotic resistance of the red blood-corpuscles, hypocholesterolaemia, reduction of serum-calcium, increase of serum-potassium, and retarded increase of blood-sugar after administration of dextrose (with protracted course of the blood-sugar curve) were observed.
A. A. ELDRIDGE.

Metabolism in scurvy. II. Nitrogen absorption and retention of guinea-pigs. H. L. SHIFF and S. S. ZILVA (*Biochem. J.*, 1928, 22, 1449—1460).—There are no indications of a disturbed absorption or retention of nitrogen during the early stages of the development of scurvy in growing guinea-pigs. The nitrogen balance becomes negative only when the intake of food is diminished as a consequence of the disease. Although the results obtained were not concordant, it is unlikely that the C/N ratio of the urine of young guinea-pigs is disturbed by the onset of scurvy.
S. S. ZILVA.

Rickets in rats. VIII. Rickets and tetany. A. T. SHOHL and F. C. BING (Amer. J. Physiol., 1928, 86, 633—638).—Rachitic rats cured by irradiation or by the addition of cod-liver oil to the diet show a lessened irritability, whilst those cured by the addition of phosphate show an increased irritability of the neuro-muscular system. The rats cured of rickets by the addition of phosphate exhibited definite symptoms of tetany. B. A. EAGLES.

Irradiated ergosterol in parathyroid tetany. J. C. BROUGHER (Amer. J. Physiol., 1928, 86, 538—541).—Irradiated ergosterol given with milk to parathyroidectomised dogs prevents the development of violent tetany. B. A. EAGLES.

Effect of irradiation on the blood chemistry in tuberculosis. K. C. SPENCE (Brit. J. Actinother., 1928, 3, 148—149).—The effect of irradiation with a mercury-vapour lamp on (1) the clinical condition of the patient and (2) the calcium, phosphate, and cholesterol content of the blood has been studied. In ten out of twelve cases irradiation resulted in an increase in the cholesterol content and an improved clinical condition. F. C. HAPFOLD.

Lipoid phosphorus-cholesterol ratio before and after feeding irradiated eggs to tuberculous patients. D. F. McRAE and T. INGVALDSEN (Amer. Rev. Tuberculosis, 1928, 17, 520—521).—No changes of the ratio in the plasma were observed.

CHEMICAL ABSTRACTS.

Serum-calcium. II. Experimental tuberculosis—intraperitoneal inoculation. III. Experimental tuberculosis—subcutaneous inoculation. J. C. HOYLE (J. Pharm. Exp. Ther., 1928, 34, 259—276, 317—324).—II. Rabbits inoculated intraperitoneally with bovine tuberculosis show changes in their serum-calcium which vary with the course of the disease.

III. In rabbits inoculated subcutaneously with bovine tuberculosis the serum-calcium rises during the formation of the local lesion. On ulceration of the lesion it falls, later returning to normal with improvement in the condition of the ulcer. There is no fall in the serum-calcium in the final weeks of the disease, as is the case following intraperitoneal inoculations. B. A. EAGLES.

Diffusion of oxygen and lactic acid through tissues. A. V. HILL (Proc. Roy. Soc., 1928, B, 104, 39—96).—Particular problems in diffusion are studied mathematically, and the results are applied to diffusion processes in the living organism and in experimental physiology with particular reference to the diffusion of oxygen, lactic acid, and carbon dioxide. W. O. KERMACK.

Iron metabolism. V. HENRIQUES and H. ROLAND (Biochem. Z., 1928, 201, 479—485).—The iron excreted in urine of normal and of diseased men in 24 hrs. amounts to 0.08—0.32 mg.; after daily intravenous injection of iron salts the value may increase to 13.5 mg. in the dog. The iron excretion in bile is inconsiderable, about 0.2 mg. daily in the dog. Daily intravenous injection of ferrous lactate causes no increase. J. H. BIRKINSHAW.

Lactic acid metabolism of the central nervous system. I. H. JUNGMAHN (Biochem. Z., 1928, 201, 259—268).—Lactic acid was determined in the spinal chord of the frog and toad. The average content in the surviving marrow in salt solution was 0.14%; this is gradually given up to the solution. The lactic acid increases to some extent in oxygen and considerably in nitrogen; the lactic acid formed in presence of nitrogen is not removed by oxygen. Stimulation causes a diminution of lactic acid in oxygen, but has no influence in nitrogen.

J. H. BIRKINSHAW.

Artificial elevation of lipin content of central nervous system. I. M. SEREJSKI (Biochem. Z., 1928, 201, 292—297).—Brain-lipins, whether derived from the ox or dog, when administered subcutaneously or orally to dogs, led to an increase in the lipin content of the brain.

J. H. BIRKINSHAW.

Liver-glycogen and muscle training. Y. WAKABAYASHI (Z. physiol. Chem., 1928, 179, 79—82).—The liver-glycogen of untrained rats determined after moderate exercise was practically nil. Trained rats showed only a small decrease.

J. H. BIRKINSHAW.

Inorganic phosphorus of frog muscle in relation to lactacidogen and phosphagen. G. M. BASTEDO and L. IRVING (Amer. J. Physiol., 1928, 86, 505—519).—In the contraction of isolated frog muscles phosphagen is broken down and acid-soluble inorganic phosphorus is liberated. During the period in which a muscle is approaching fatigue there is a decrease in acid-soluble phosphorus. This decrease is due to the production of an acid-stable compound, presumably "lactacidogen," from the liberated inorganic phosphorus. The decomposition of phosphagen and synthesis of lactacidogen in muscle are independent processes. The compounds may be considered to be in indirect relationship, however, since both are in equilibrium with inorganic phosphorus. B. A. EAGLES.

Fission of lactacidogen in muscular contraction. G. EMBDEN and H. JOST (Z. physiol. Chem., 1928, 179, 24—40).—A method of determination of inorganic phosphoric acid, lactacidogen-hexose, and lactacidogen-phosphoric acid is described. A previous series of determinations on the frog's gastrocnemius is repeated, since the earlier figures showing change in inorganic phosphoric acid cannot be used as a measure of lactacidogen hydrolysis in view of Lohmann's discovery of the enzymic conversion of pyro- into ortho-phosphoric acid in striped muscle. The general conclusion that at the moment of contraction a quickly reversible lactacidogen hydrolysis takes place in which the orthophosphoric acid greatly exceeds the lactic acid is confirmed. The quantity of lactacidogen preformed in muscle is much less than was thought previously.

J. H. BIRKINSHAW.

Creatine-phosphoric acid of muscle. A. PAL-LADIN, A. KUDRJAVZEVA, and E. SAVRON (Z. physiol. Chem., 1928, 179, 9—23).—Poisoning of rabbits with phosphorus and tetrahydro- β -naphthylamine produced in general an increase in the creatine, creatine-

phosphoric acid and percentage of creatine bound to phosphoric acid, and a diminution of the lactacidogen of red and white muscle. Although the changes in red and white muscle were mostly in the same direction, the quantitative effects were diverse in the two cases. J. H. BIRKINSHAW.

Influence of sympathetic innervation on the phosphate and creatinine contents of striated mammalian muscle. W. SCHMID (Biochem. Z., 1928, 201, 125—147).—The jaw muscles of white rats on the side from which the sympathetic influence had been removed showed a 10% decrease of organic phosphate compared with the muscle of the normal side, but the creatinine contents of the two sides were identical. P. W. CLUTTERBUCK.

Lactic acid and glycogen content of kidney cortex. J. T. IRVING (Biochem. J., 1928, 22, 1508—1513).—The production of lactic acid in excised kidney cortex is rapid. The glycogen content under the same conditions, on the other hand, changes little. The origin of the bulk of the acid is unknown. It is probable that the glycogen figures obtained are contributed to a larger extent by substances other than glycogen. S. S. ZILVA.

"Acetone body" formation and the chemical affinity of oxygen for carbohydrate and fatty acid. D. M. ERVIN (J. Lab. Clin. Med., 1927, 12, 1059—1065).—An explanation is independent of the theory of dextrose oxidation.

CHEMICAL ABSTRACTS.

Decomposition of acetoacetic and β -hydroxybutyric acids in muscle. I. SNAPPER and A. GRÜNBAUM (Biochem. Z., 1928, 201, 464—472).—When dog's extremities and calf's tongue are perfused with blood to which β -hydroxybutyric acid is added, this shows a decrease of 45—75% and 13—40%, respectively, but no oxidation to acetoacetic acid is observed. About 80% of added acetoacetic acid disappears; part of this, 18—20% in dog's extremities, 29—67.5% in calf's tongue, is recovered from the bone and muscle as β -hydroxybutyric acid.

J. H. BIRKINSHAW.

Decomposition of acetoacetic acid and β -hydroxybutyric acid in the organs of the phloridzin-ised dog. I. SNAPPER, A. GRÜNBAUM, and C. MENDES DE LEON (Biochem. Z., 1928, 201, 473—478).—The kidneys and the extremities of the phloridzin-diabetic dog are able to break down keto-bodies. This activity seems to be unaffected by phloridzin-acidosis, which therefore is characterised by an increased production and not by a diminished breakdown of keto-compounds. J. H. BIRKINSHAW.

Regulation of metabolism. X. Glycogen in adipose tissue and the possibility of conversion of fat into carbohydrate. E. WERTHEIMER (Pflüger's Archiv, 1928, 219, 190—201; Chem. Zentr., 1928, ii, 368).—With dogs, but not with rabbits or guinea-pigs, after hunger followed by feeding with carbohydrate, glycogen is present in the adipose tissue. With rats, after hunger followed by feeding with cooked rice, or white bread, milk, and dextrose, glycogen is present in the subcutaneous and abdominal fat. On administration during feeding of toxic doses of insulin the deposition of glycogen

is small. The fat of frogs in October and November contains glycogen. With dogs deficient in carbohydrate by hunger and treatment with phloridzin, after cessation of acidosis, a conversion of fat into carbohydrate appears to take place in the liver.

A. A. ELDRIDGE.

Lactose metabolism of women. O. WATKINS (J. Biol. Chem., 1928, 80, 33—66).—Lactose was determined in urine by preliminary determination of total sugar by the method of Folin and Berglund (A., 1922, ii, 400), followed by a similar determination on a sample of the urine previously subjected to yeast fermentation. Normal men, and women in the intermenstrual period, tolerate 10 g. of lactose by mouth without excretion of the sugar in the urine. During menstruation the woman's tolerance for lactose may be raised to as much as 20 g.; during pregnancy the tolerance is also raised, whilst in lactation it is normal. In the later stages of pregnancy lactose is excreted in constant small amounts; this excretion rises immediately before delivery and then falls for a few days; at this point it rises again very markedly and then fluctuates until, at the end of a month, it becomes almost constant at a low level.

C. R. HARRINGTON.

Variations in some of the constituents of the blood throughout the menstrual cycle in normal women. H. G. CLOSE and A. A. OSMAN (Biochem. J., 1928, 22, 1544—1547).—In healthy adult females there is a slight decrease in the serum-hydrogen carbonate and corresponding slight increase in the serum-chloride during the menstrual flow. The serum-calcium and serum-urea show no significant change at this time. S. S. ZILVA.

Arginine metabolism. II. K. FELIX, H. MÜLLER, and K. DIRK (Z. physiol. Chem., 1928, 178, 192—201).—Of several arginine compounds substituted in the α -amino-group, d - α -monobenzoyl-arginine was the only one resolved by arginase. Esterification hindered but did not prevent the action. The d - α -monobenzoylarginine was prepared by a Schotten-Baumann reaction; the mixture being maintained at about neutrality, it decomposes at 298° (uncorr.). The hydrochloride has $[\alpha]_D^{20}$ -8.1° . The optimum p_H for arginase action on the benzoyl derivative is 7. J. H. BIRKINSHAW.

Availability of ergothioneine in supplementing diets deficient in histidine. B. A. EAGLES and G. J. COX (J. Biol. Chem., 1928, 80, 249—254).—Ergothioneine is unable to replace histidine in the diet of rats. C. R. HARRINGTON.

Diet deficient in tyrosine. H. D. LIGHTBODY and M. B. KENYON (J. Biol. Chem., 1928, 80, 149—153).—Rats showed normal growth on diets containing as little as 0.0397% of tyrosine. C. R. HARRINGTON.

Animal calorimetry. XXXVII. Specific dynamic action of glycine in normal and adrenalectomised dogs. F. NORD and H. J. DEUEL, jun. (J. Biol. Chem., 1928, 80, 115—124).—After both oral and intravenous administration, glycine exercises a specific dynamic action in adrenalectomised dogs which is only slightly less than that produced in normal animals. C. R. HARRINGTON.

Nutritive properties of gelatin. R. W. JACKSON, B. E. SOMMER, and W. C. ROSE (J. Biol. Chem., 1928, 80, 187—186).—Diets containing gelatin as the sole protein remain unsatisfactory for rats when supplemented with tyrosine, tryptophan, and cystine, or even with the 11 amino-acids in which gelatin is somewhat deficient. The results were not improved by preliminary hydrolysis of the protein, and are therefore not to be ascribed to failure of digestion. When gelatin forms as much as 35% of the diet it seems to produce an unfavourable effect *per se*, since nephritis was observed in many of the animals, and an inhibition of the growth of rats on a caseinogen-carbohydrate diet was produced by substitution of this amount of gelatin for part of the carbohydrate.

C. R. HARRINGTON.

Soya-bean meal in the human dietary. V. DUCCHESCHI (Arch. fisiol., 1928, 25, 428—468; Chem. Zentr., 1928, ii, 115).—Experiments *in vivo* and *in vitro* indicate a high digestive value.

A. A. ELDRIDGE.

Nitrogen, calcium, and phosphorus metabolism in infants fed on soya-bean "milk." E. TSO, M. YEE, and T. CHEN (Chinese J. Physiol., 1928, 2, 409—414).—An infant fed for 4—5 day periods on a daily ration of soya-bean "milk" (720 g.), sucrose (72 g.), and orange juice (4 g.) showed satisfactory nitrogen absorption and retention. The calcium and phosphorus absorption appeared to be inadequate. The addition of cod-liver oil (10—15 g.), calcium lactate (0.6 g.), and cabbage soup (100 g.) greatly increased the calcium and phosphorus retention in a second case.

F. C. HAPFOLD.

Effect of variation of potassium and chlorine in a wheat ration. J. L. ST. JOHN (J. Agric. Res., 1928, 37, 55—64).—Rations containing added potassium do not maintain partly grown rats. There is no evidence that potassium is capable of replacing sodium in the ration. The addition of chlorine did not affect this conclusion. The actual amounts of sodium and potassium present seem to be of more importance than the ratio of the two elements.

H. J. G. HINES.

Interpretation of nutritional experiments. C. NEWCOMB (Indian J. Med. Res., 1928, 16, 537—543).—The variability of the weights of rats under experimental conditions has been examined statistically and coefficients of weight variation have been obtained. Tables are given for finding the minimum significant differences between the mean weight of groups of rats.

W. O. KERMAK.

Formation and fate of urea in the dog, and the relation between urea formation and the retention of amino-acid substances and ammonia in the liver. E. S. LONDON, N. KOTSCHNEV, A. CHOLOPOV, T. S. ABASCHIDZE, and A. K. ALEXANDRY (Pflüger's Archiv, 1928, 219, 238—245; Chem. Zentr., 1928, i, 2962—2963).—The continuous excretion of urea from the liver into the blood-stream takes place 2.5 times as rapidly during digestion as during starvation. Besides the kidneys, the intestinal wall removes urea from the blood. The pancreas produces smaller quantities of urea. Its formation in the liver cannot be ascribed simply to protein

derivatives. The production of urea is increased by alanine, cysteine, and ammonium carbonate, and arrested by arginine and tyrosine.

A. A. ELDRIDGE.

Kidney function. Relationships between action of carbamide, diuresis, and mineral metabolism. R. E. MARK (Arch. exp. Path. Pharm., 1928, 137, 143—167).—Whereas in normal animals, after administration of carbamide, the ratio of carbamide to potassium in the urine is fairly constant, in renal insufficiency (removal of one kidney and partial suppression of the blood supply of the other) an increased excretion of potassium sets in 1—2 hrs. after giving carbamide, decreasing to small values after 8—10 hrs. Carbamide fed to normal animals causes an immediate diuresis, but in animals with defective kidney function diuresis is much delayed.

E. BOYLAND.

Excretion of choline in urine. P. KLEE and S. PETROPULIADES (Arch. exp. Path. Pharm., 1928, 137, 129—142).—Choline is estimated physiologically. After acetylation the acetylcholine is compared with standard solutions in its effect on the isolated frog heart. Normal men excrete 5—50 mg. of choline per day. The amount is increased by exercise, ingestion of lecithin, by subcutaneous or rectal administration of choline chloride, and by tissue-wasting diseases.

E. BOYLAND.

Changes in the nuclear-plasmic ratio of vertebrate poikilotherms during hunger. A. DMOCHOWSKI (Biochem. J., 1928, 22, 1548—1554).—In inanition the nuclear-plasmic ratio is practically constant for frogs (*Rana esculenta*). In the case of axolotls (*Amblystoma*) it rises by 15% after 5 months of hunger and falls to 15% below normal after 11 months of hunger. The ratio of trout after 80 days of hunger rises by 30% for fry and 49% for 2-year-olds. This rise in the nuclear-plasmic ratio is transient, values obtained for the final stages of hunger being subnormal. A short period of restitution does not reduce the nuclear-plasmic ratio of trout to its normal value, but it does so after a prolonged period of restitution. The results obtained with trout support the assumption of the existence of reserve protein.

ZILVA.

Changes in the nuclear-plasmic ratio of mammals during hunger. A. DMOCHOWSKI (Biochem. J. 1928 22, 1555—1561).—The purine-nitrogen content of rabbit skeletal muscle has an average value of 104.6 mg. per 100 g., varying from 85 to 119 mg. The mean value of the nuclear-plasmic ratio is 28.55×10^{-3} . The former and latter values remain constant throughout the duration of inanition. The purine-nitrogen content of rabbit liver varies from 149.5 mg. per 100 g. in fed animals to 162.1 mg. in inanition. The mean nuclear-plasmic ratio is respectively 50.9 and 48.4×10^{-3} before and after starvation. More than 50% of the purines of muscle-tissue can be extracted by water. Results similar to the above were obtained with muscle from which the extranuclear purine substances had been removed by extraction with water.

S. S. ZILVA.

Hunger and the potassium and calcium ion content of blood-serum. B. A. SCHAZILLO and

D. C. KONSTANTINOVSKAYA (Biochem. Z., 1928, 201, 318—322).—Hunger influences the ratio of potassium to calcium ions in the blood-serum of dogs. The potassium varies within normal physiological limits, but the calcium decreases when symptoms of irritability and paralysis appear. J. H. BIRKINSHAW.

Influence of active iron oxide ("siderac") on metabolism. A. A. GOLDBLOOM (Z. ges. exp. Med., 1928, 59, 514—530; Chem. Zentr., 1928, i, 2960).—The urinary C:N quotient was in general increased; the nitrogen balance became more positive.

A. A. ELDRIDGE.

Action of lachrymal fluid on cholesterolæmia and glycæmia. D. MICHAEL and P. VANCEA (Compt. rend. Soc. Biol., 1928, 98, 64—65; Chem. Zentr., 1928, i, 3085).—Injection of lachrymal fluid into dogs causes a continuous, progressive, and long-continued hypercholesterolæmia, as well as a hypoglycæmia.

A. A. ELDRIDGE.

Aminoazotoluene, aminoazotolueneazo- β -naphthol, and tolueneazoacetotoluidide as cicatrising agents. E. JUSTIN-MUELLER (J. Pharm. Chim., 1928, [viii], 8, 441—449).—The behaviour of these compounds in mineral oil suspension or solution when shaken with water and with ovalbumin or blood-albumin solutions has been examined. Emulsions of varying degrees of stability are formed, and from their appearance after filtering through paper and after keeping a method is developed for testing the cicatrising power. The results compare favourably with clinical experience. The action of the substances appears to be one of peptisation.

E. H. SHARPLES.

Relationship between chemical constitution and pharmacological action of local anæsthetics. I. Novocaine, tutocaine, cocaine, and psicaine. K. TOMINAGA and I. HAYASHI (Nagoya J. Med. Sci., 1927, 2, 6—10).—Quantitative differences were observed in the anæsthetic action of six stereoisomerides of cocaine. The four drugs show no remarkable difference in physical properties; pharmacologically, cocaine and psicaine are very similar, whilst tutocaine is weaker. In toxicity, psicaine is intermediate between tutocaine and novocaine.

CHEMICAL ABSTRACTS.

Role of calcium in narcosis and stimulation of decorticated and completely decerebrated animals. H. FISCHER (Arch. exp. Path. Pharm., 1928, 138, 169—189).—During sleep or narcosis in dogs intact or deprived of the cerebral cortex a decrease in the calcium content of the citrated plasma takes place, whilst stimulation of the brain results in an increase. In the case of completely decerebrated animals no alteration in the plasma-calcium occurs as the result of narcosis or stimulation. The potassium content of the blood-plasma varies in an opposite sense to the calcium content. W. O. KERMACK.

Fixation of suspensoids [in the body] by anæsthetics and narcotics. G. SPAGNOL (Arch. exp. Path. Pharm., 1928, 137, 250—256).—Colloidal suspensions of lead and mercury sulphides and many dyes can be fixed in tissues, in which they are not usually precipitated, by the application of anæsthetics,

such as chloroform, or narcotics, such as the urethanes, to the skin. Only electro-negatively charged colloids are precipitated in this way. E. BOYLAND.

Action of colloidal sulphur (sulphosol) on the blood-sugar of experimental animals and of man. G. BUCCIARDI (Arch. Farm. speriment., 1928, 49, 90—96, 97—114).—In the guinea-pig, rabbit, dog, and sheep, small doses of colloidal sulphur produce slight hyperglycæmia, followed by slight hypoglycæmia. The dose necessary to induce these reactions varies slightly in animals of the same, and widely in animals of different, species, the order of diminishing sensitiveness being: sheep, dog, rabbit, guinea-pig. When administered orally to man, sulphosol is uncertain in its effect and may cause slight increases or decreases in the amount of the blood-sugar; hyperglycæmia followed by hypoglycæmia was not observed in man. T. H. PORE.

Effect of alcohol and of anæsthetics on sugar utilisation. W. E. BURGE and D. J. VERDA (J. Pharm. Exp. Ther., 1928, 34, 299—303).—Alcohols were introduced into sugar solutions in which gold fish had been placed and sugar determinations were carried out at intervals on portions of the solutions. Methyl and ethyl alcohol markedly increased the rate of sugar utilisation, whilst chloroform and ether produced a significant decrease. B. A. EAGLES.

Action of alcohol on blood-sugar. J. GAVRILA and T. SPARCHEZ (Compt. rend. Soc. Biol., 1928, 98, 65—66; Chem. Zentr., 1928, i, 3085).—Alcohol slightly reduces the blood-sugar of normal man; the reduction in diabetes is thrice as great.

A. A. ELDRIDGE.

Influence of ethyl alcohol on the excretion of purine substances. L. LA GRUTTA (Riv. Patol. Speriment., 1927, 2, No. 3, 185—196; Chem. Zentr., 1928, ii, 71).—Large doses of ethyl alcohol cause an increase in the destruction of proteins and nucleins, and hence an increase in the amount of their decomposition products in the urine. Moderate and small doses reduce the excretion of total and purine nitrogen and of phosphorus. Immediately after the ingestion of moderate or large doses of alcohol a temporary disturbance of the ratio urea-nitrogen/purine-nitrogen is observed.

A. A. ELDRIDGE.

Blood-sugar after peptone injection in the dog. W. W. BRANDES and J. P. SIMONDS (Amer. J. Physiol., 1928, 86, 618—622).—At the height of peptone shock the sugar content of the blood from the hepatic vein is increased, but there is a hypoglycæmia in the peripheral venous blood. There is an increased glycogenolysis in the liver, but so little blood leaves the liver that a hypoglycæmia of the general circulation results.

B. A. EAGLES.

Hypoglycæmic action of *Phaseolus* preparations. O. GESSNER and K. SIEBERT (Munch. med. Woch., 1928, 75, 853—855; Chem. Zentr., 1928, ii, 169).—The preparations caused a fall in blood-sugar on peroral administration; dextrose- or adrenaline-hyperglycæmia was reduced and abbreviated.

A. A. ELDRIDGE.

Physiological effects of two poisons of the adrenaline series: β -hydroxy- β -(4-hydroxy-

phenyl)-*N*-methylethylamine, and the corresponding ketone. O. EHRLMANN and G. MALOFF (Arch. exp. Path. Pharm., 1928, 136, 172—184).—The former of these two compounds is very similar in its physiological effects to adrenaline. The effects of the ketone depend to some extent on the dosage; some of them are similar to those of adrenaline, others quite the opposite. Both substances are much less powerful than adrenaline. W. MCCARTNEY.

Mechanism of the action of ephedrine and the difference between the activities of its isomerides. O. SCHAUHANN (Arch. exp. Path. Pharm., 1928, 138, 208—218).—Ephedrine acts on the blood-pressure by rendering the vessels more sensitive to adrenaline. *l*-Ephedrine is very much more active than *d*-ephedrine. W. O. KERMAK.

Assays of Chinese ephedrine. C. T. FENG and B. E. READ (Chinese J. Physiol., 1928, 2, 337—344).—The separated male and female flowers of *Ephedra equisetina* and *E. sinica* have been analysed for ephedrine and ψ -ephedrine. The seasonal variation in content has been studied. In the flowering season there is a higher alkaloidal content in the male plants than in the female (13—17% difference), but after the fruiting season the two contents are practically identical. The root, berries, and seeds of *E. equisetina* contain no alkaloid, the nodes contain 32% of the alkaloidal content of the internodes and a greater proportion of ψ -ephedrine. Samples collected in winter gave only 53% of the ephedrine content of mature samples collected in October.

F. C. HAPFOLD.

Comparative study of ephedrine, racemic ephedrine, and ψ -ephedrine. C. PAK and B. E. READ (Chinese J. Physiol., 1928, 2, 435—458).—The approximate ratios of the pressor actions of the three isomerides, in doses of 0.5—1.0 mg. per kg. body-weight, are ephedrine : ephedronine : ψ -ephedrine as 1 : 0.7 : 0.5. A diminished efficiency in the pressor action of the three isomerides was observed with repeated injection, but differences in the maximal rise of blood-pressure, following such repeated injections, were not so great where the dogs were vagotomised and atropinised. Continued perfusion of the peripheral blood vessels of the toad with 0.2% ephedrine-Ringer solution caused an initial vasoconstriction, but vasodilation occurs after prolonged perfusion. The isomerides exerted a mutually immunising effect on the pressor action and lowered one another's activity; e.g., the action of ψ -ephedrine was abolished by previous injection of ephedrine. This immunising effect was more strongly marked in the case of ephedrine after previous injection of ψ -ephedrine or *vice versa*, than in the case of ephedronine after previous injection of ephedrine. F. C. HAPFOLD.

Ephedrine and blood-sugar. I. I. NITZESCU (Compt. rend. Soc. Biol., 1928, 98, 55—57 Chem. Zentr., 1928, i, 3085).—Injection of ephedrine into dogs (not starving) causes slight hyperglycaemia, the duration of which is somewhat extended by simultaneous injection of dextrose. A. A. ELDRIDGE.

Action of ergotamine and adrenaline on the residual nitrogen content of fluid perfusing

isolated organs. G. A. MEDNIKIANZ (Arch. exp. Path. Pharm., 1928, 136, 370—380).—When isolated testicles of cats and rabbits are perfused by Ringer-Locke's solution a gradual decline in the residual nitrogen content occurs. The addition of adrenaline (dilution 1 in 10^6) to the perfusing solution produces a marked increase in the amount of nitrogen. Ergotamine (dilution 1 in 10^5) produces a fall and the previous action of ergotamine destroys the effect of adrenaline. H. R. ING.

Influence of ergotamine on the blood-sugar. Z. CZEZOWSKA and J. GOERTZ (Compt. rend. Soc. Biol., 1928, 98, 148—150; Chem. Zentr., 1928, i, 3085).—In normal and diabetic man ergotamine considerably reduces alimentary hyperglycaemia.

A. A. ELDRIDGE.

Effect of substances of the quinine group on the enzymic functions of the organism. X. Influence of quinine on the dynamics of protein exchange and on oxido-reduction processes. I. A. SMORODINCEV (Biochem. Z., 1928, 201, 66—73).—Quinine restricts the breakdown of protein and the oxidation processes of the organism.

P. W. CLUTTERBUCK.

Influence of arsenic and antimony compounds on enzymic functions of the organism. V. Cause of inhibitory influence of arsenites and arsenates on salivary amylase. I. A. SMORODINCEV and E. A. ILJIN (Biochem. Z., 1928, 201, 34—47).—In well-buffered solutions of p_H 6.8 sodium arsenate has no effect on the action of salivary amylase, the previously observed inhibition being due to change of p_H , but with arsenites, in addition to change of p_H , the arsenic itself appears to take part in the inhibition (cf. A., 1927, 792).

P. W. CLUTTERBUCK.

Action of cyanide on the living cell. M. S. RESNITSCHENKO (Biochem. Z., 1928, 201, 110—124).—With very small concentrations of cyanide in the first stages of poisoning respiration of eggs of *Ascaris megalocephala* is increased due to the alkaline nature of the cyanide, the specific respiratory inhibition, due to the cyanide group itself, being obtained later.

P. W. CLUTTERBUCK.

Effect of magnesium sulphate or lactose on blood volume in normal, beri-beri, and fasting pigeons. O. W. BARLOW and M. S. BISKIND (Amer. J. Physiol., 1928, 86, 594—598).—There is a diminution of the red cell count as well as total blood-volume in fasting or beri-beri pigeons. The anti-anæmic effect of magnesium sulphate or lactose during the course of the inanition is not due to concentration of the blood but to interference with the destruction of blood. B. A. EAGLES.

Pharmacology of lead. III. Distribution of lead between blood and tissue after intravenous injection. B. BEHRENS and G. ANTON (Arch. exp. Path. Pharm., 1928, 137, 305—310).—Lead chloride injected into a jugular vein of a guinea-pig rapidly disappears from the blood until an equilibrium is attained in which most of the lead chloride is taken up by the tissues. W. O. KERMAK.

Pharmacology of lead. IV. Mechanism of lead poisoning of fishes. B. BEHRENS (Arch. exp.

Path. Pharm., 1928, 137, 311—314).—Fish poisoned by lead salts dissolved in the water in which they are immersed show the greatest concentration of lead in the gills, but small quantities are also found in the other organs and in the musculature. The toxic action of the lead appears to be exerted mainly if not entirely through its presence in the gills.

W. O. KERMACK.

Diuretic action of organic mercury compounds. B. VON ISSEKUTZ and F. VON VEGH (Arch. exp. Path. Pharm., 1928, 138, 245—255).—The toxicities and diuretic activities of certain organic mercury compounds have been determined on rats. Diuretic action associated with low toxicity occurs with certain derivatives of camphoric acid.

W. O. KERMACK.

Histochemical detection of mercury in organs. E. CHRISTELLER and R. SAMMARTINO (Z. ges. exp. Med., 1928, 60, 11—33; Chem. Zentr., 1928, i, 2975).—Mercury is deposited chiefly in the kidneys, liver, and lungs. Small quantities are found in the large intestine, spleen, pancreas, heart, and central nervous system. The distribution of mercury shortly after injection is described, and details are given of a modification of Almkvist's method for its detection.

A. A. ELDRIDGE.

Toxicity of thallium sulphate. J. C. MUNCH (J. Amer. Pharm. Assoc., 1928, 17, 1086—1093).—Thallium is a certain, but not a rapid, poison for rats and it is cumulative in action. The minimum lethal dose when fed to rats or intravenously injected into rabbits is 25 mg. of thallium per kg. body-weight. Previous work on the toxicity of thallium is discussed.

E. H. SHARPLES.

Formation from histidine by ultra-violet irradiation of a substance which lowers blood-pressure and stimulates the intestine. F. ELLINGER (Arch. exp. Path. Pharm., 1928, 136, 129—157).—Histidine hydrochloride in 1% solution when irradiated with a quartz mercury-vapour lamp yields small amounts of a decomposition product, which is isolated by the method used for extracting histamine. Within certain limits the formation of this product is unaffected by the p_H of its solutions or by the duration of the irradiation, and photocatalysts do not accelerate the process of its formation. Light of wave-lengths 297 and 302 μ causes irradiated solutions to lose their activity. Unirradiated serum from rabbits, horses, or pigs and also unirradiated skin from guinea-pigs contain considerable amounts of histamine-like substances. Extracts of unirradiated guinea-pig skin are never more active than those from the irradiated skin.

W. MCCARTNEY.

Alterations in the blood determined by X-ray therapy. C. STARNOTTI (Arch. Farm. speriment., 1928, 46, 49—89).—The alterations in the blood produced by X-ray therapy are slight, particularly in relation to those of the secondary irradiation to which X-ray operators are subject, and consist in mild leucocytosis; with excessive treatment, however, the opposite effect may result. The hæmoglobin and red corpuscles remain uninfluenced and the physico-chemical properties are unchanged. The results obtained with 20 patients show that these effects appear immediately

after the application of the rays, but the period after which the maximum effect is reached, and also the duration of the effect, vary in different cases.

T. H. PORE.

Viscosity changes produced in egg-albumin by X-rays. J. A. V. FAIRBROTHER (Brit. J. Radiol., 1928, [ii], 1, 121—125).—The viscosity of egg-albumin suffers a permanent decrease (up to 40%) by a dose of 211,500 e of Mo-K radiation. At the coagulation temperature, 61°, setting is delayed.

CHEMICAL ABSTRACTS.

How many respiratory enzymes are there? O. WARBURG (Biochem. Z., 1928, 201, 486—488).—For oxygen transport nature employs hæmoglobin, but all hæmoglobins are not identical and other means of transport, e.g., hæmocyanin, exist. As for the transport of oxygen, so for respiration, nature makes use for the greater part of one mechanism only. Other enzymes of respiration do exist, however.

J. H. BIRKINSHAW.

Reduction of the disulphide group by enzyme systems. K. A. C. ELLIOTT (Biochem. J., 1928, 22, 1410—1412).—Neither dithiodiglycolic acid nor glutathione is reduced by succinoxidase and succinic acid. Neither leucomethylene-blue nor hypoxanthine with xanthine-oxidase reduces the S-S-group even in the presence of muscle residue.

S. S. ZILVA.

Preparation of succinodehydrogenase free from fumarase. N. ALWALL (Skand. Arch. Physiol., 1928, 54, 1—5; Chem. Abstr., 1928, ii, 60).—The fumarase present in succinodehydrogenase prepared from muscle is decomposed by heating the mixture at 50° for 30 min. The activity of the succinodehydrogenase is thereby only weakened.

A. A. ELDRIDGE.

Enzymic oxidation of oxalic acid by seeds. Constitution of oxalic acid. T. THUNBERG (Skand. Arch. Physiol., 1928, 54, 6—16; Chem. Zentr., 1928, ii, 31—33).—By the use of powder and extracts of seeds of *Malva crispa*, *Citrus aurantium* var. *dulcis*, and *Prunus communis* the action of oxalate in increasing the ability to decolorise methylene-blue in a vacuum was demonstrated. The behaviour of potassium oxalate as a hydrogen donor, forming potassium hydrogen carbonate, is discussed.

A. A. ELDRIDGE.

Function of peroxidase systems and the chemistry of the adrenal cortex. New carbohydrate derivatives. A. SZENT-GYORGYI (Biochem. J., 1928, 22, 1387—1409).—The isolation of a highly reactive *hexuronic anhydride*, isomeric with glycuronic anhydride, m. p. 175—189°, $[\alpha]_D^{25} +24^\circ$, from the adrenal cortex, from oranges, and from cabbages is described. The method is based on the precipitation of the substance with lead acetate and on the purification by reprecipitation with this reagent and with light petroleum from methyl alcohol-ether solution. The hexuronic acid is of biological significance. In its distribution in nature it is closely connected with peroxidase. Its oxidation by hydrogen peroxide in the plant, which is reversible, is catalysed by peroxidase and unless a sufficiency of peroxide is added the peroxidase reaction may be masked by its presence. Molecular oxygen oxidises the acid irreversibly with the formation of a new carboxyl group. This

autoxidation is catalysed by copper but not by iron and manganese. Cyanide inhibits the oxidation. Mild oxidising agents effect a reversible oxidation with loss of two atoms of hydrogen. The oxidation of the hexuronic acid by peroxide and peroxidase is catalysed in plant juices by phenols. In the absence of these substances it is not oxidised by indophenol-oxidase of animal tissue. Pigment formation *in vitro* can be inhibited by concentrations of 1:0.00025 of the acid. It reduces hæmatin compounds slowly. Oxidised hexuronic acid is reduced by animal tissues. The dehydrogenases of the type of the Schardinger enzyme and the succinodehydrase are unable to reduce the oxidised hexuronic acid. The oxidised substance is reduced by the glutathione system. Glutathione and fixed thiol groups strongly reduce the oxidised acid. The author suggests the following scheme of oxidation in the plant: $H_2O_2 + \text{peroxidase} \rightarrow \text{phenol} \rightarrow \text{hexuronic acid} \rightarrow \text{other oxidation systems}$.

S. S. ZILVA.

Enzymic condensation of formaldehyde to sugar. II. J. BODNAR (Biochem. Z., 1928, 201, 281—285).—Both the pulped and the dried leaves of *Tropæolum* are able to convert formaldehyde but not acetaldehyde into sugar. Boiling destroys this power.

J. H. BIRKINSHAW.

Lipases. I. Organ-lipases and the inhibition of lipase action by poisons. K. GYOTOKU (Proc. Imp. Acad. Tokyo, 1928, 4, 503—504).—Serum- and liver-lipases are more sensitive to atoxyl than are other lipases. An atoxyl-sensitive lipase on purification becomes atoxyl-refractory. Sodium fluoride has a poisonous action on lipases. A poisoned lipase cannot be regenerated by dialysis. B. A. EAGLES.

Lipases. II. Determination of lipase in duodenal contents. III. Lipases and proteins. IV. Separation of lipase into two fractions. K. GYOTOKU and S. TERASHIMA (Proc. Imp. Acad. Tokyo, 1928, 4, 505, 506—507, 508—509).—II. The duodenal contents are appropriately diluted with a solution of equal parts of glycerol and 1% ammonium phosphate. The resultant lipase solution is very stable. The tributyrin method of Rona and Michaelis is used.

III. The lipases of blood-serum, pancreatic and gastric juices are always found with the proteins precipitated by 60% saturation with ammonium sulphate.

IV. The addition of quinine to gastric or pancreatic lipases yields two fractions, each of which alone is inactive, but a mixture of the two constituents has a strong lipolytic action. B. A. EAGLES.

Ricinus lipase. I. (A) Hydrolysis of esters and of beeswax. (B) Hydrolysis of carbohydrates. A. PIUTTI and E. DE' CONNO (Annali Chim. appl., 1928, 18, 468—478).—An industrial preparation hydrolyses, not only glycerides, but also, almost quantitatively, other esters, and to some extent sucrose and starch. T. H. POPE.

Biochemical synthesis and hydrolysis of glycerides. L. VELLUZ (Bull. Soc. Chim. biol., 1928, 10, 1213—1226).—The formation of di- and

tri-glycerides by the combination of the fatty acids of olive oil and glycerol in the presence of the enzyme in the cytoplasm of the castor bean (A., 1928, 328) follows the law of mass action. The enzymic hydrolysis of these esters is shown to be a reaction similar to those due to heterogeneous catalysis.

G. A. C. GOUGH.

Influence of double linkings in the biochemical synthesis and hydrolysis of unsaturated glycerides. L. VELLUZ (Bull. Soc. Chim. biol., 1928, 10, 1227—1237).—Reactions analogous to those described in the preceding abstract in which unsaturated acids are substituted for those from olive oil show similar kinetics. The velocities of both synthesis and hydrolysis are inversely proportional to the iodine values of the acids. G. A. C. GOUGH.

Range of action of the phosphatases. C. NEUBERG and K. P. JACOBSON (Biochem. Z., 1928, 199, 498—517).—Derivatives of all the three known forms of phosphoric acid undergo enzymic hydrolysis, the end-product being orthophosphoric acid. To the number of phosphates so far tested with regard to the effect of phosphatases, monomethyl phosphate, trimethyl phosphate, *methylpropylcarbinyl phosphate*, monocetyl phosphate, monocholesteryl phosphate, *di-o-tolyl pyrophosphate*, *di-m-tolyl pyrophosphate*, and *di-α-naphthyl pyrophosphate* are now to be added. With the exception of trimethyl phosphate all these substances are hydrolysed both by takaphosphatase and by animal phosphatases. The extent of the hydrolysis was, in almost all cases, very considerable (up to 90%). The stereochemical specificity of the phosphatases has again been confirmed in the case of the monophosphoric ester of methylpropylcarbinol. Monocholesteryl orthophosphate, m. p. 187° (uncorr.), is prepared from cholesterol and phosphorus pentoxide. It is purified by crystallisation from chloroform or by precipitation from that solvent with acetone. It is insoluble in water (cf. Euler and Bernton, A., 1927, 1066). The tolyl and α-naphthyl pyrophosphates were prepared by the action of phosphorus oxychloride on the phenols in a manner similar to that described for diphenyl pyrophosphate (cf. Neuberg and Wagner, Biochem. Z., 1926, 171, 485). The *dipotassium* salt of *di-o-tolyl pyrophosphate* crystallises in needles. It is very hygroscopic, readily soluble in water, slightly soluble in alcohol, and insoluble in ether, acetone, or chloroform. The *potassium* salt of *di-m-tolyl pyrophosphate*, prepared in the same way, has very similar properties. *Di-α-naphthyl pyrophosphate* is precipitated in the form of rectangular plates, m. p. 78°, when strong acids are added to solutions of its *dipotassium* salt, which has properties resembling those of the salts of the tolyl pyrophosphates and crystallises in rhombohedra. The ester is soluble in ether and in benzene.

W. MCCARTNEY.

Phosphatases of mammalian tissues. II. Pyrophosphatase. H. D. KAY (Biochem. J., 1928, 22, 1446—1448).—Pyrophosphatase is widely distributed in mammalian tissue, the distribution being similar to that of the orthophosphoric esterase. The zone of optimal activity is between p_H 7.2 and 7.8 as against p_H 8.8—9.3 for esterase. S. S. ZILVA.

Metaphosphatase. T. KITASATO (Biochem. Z., 1928, 201, 206—211).—The author's yield (20%) of orthophosphate (cf. A., 1928, 1282) obtained by the action of takaphosphatase on sodium hexameta-phosphate is raised almost to 100% by increasing the enzyme concentration and decreasing the amount of substrate. The conversion is followed colorimetrically and the orthophosphate isolated as the ammonium magnesium salt.

P. W. CLUTTERBUCK.

Isoelectric precipitation of pepsin. II. F. FENGER, R. H. ANDREW, and A. W. RALSTON (J. Biol. Chem., 1928, 80, 187—190; cf. A., 1927, 793).—The previous conclusion is confirmed that the most active preparations of pepsin are obtained by isoelectric precipitation at p_H 2.5; in this way an ash-free product has been prepared containing C 53.15%, H 7.20%, N 14.43%, S 0.88%, P 0.13%; figures are given for the nitrogen distribution.

C. R. HARRINGTON.

Stereochemical specificity of proteolytic enzymes. E. WALDSCHMIDT-LEITZ and H. SCHLATTER (Naturwiss., 1928, 16, 1026).—Trypsin-kinase, which splits off tyrosine, hydrolyses both optical antipodes of *dl*-leucylglycyl-*l*-tyrosine and of *dl*-bromoisohexoylglycyl-*l*-tyrosine; hydrolysis by erepsin, which attacks the free amino-group, takes an asymmetric course. This opens up the possibility of determining where the reaction of the peptide with the specific group of the enzyme molecule occurs by changing the arrangement of the racemic component of the molecule.

J. H. BIRKINSHAW.

Effect of the hydrogen-ion concentration on the rate of hydrolysis of glycylglycine, glycyl-leucine, glycylalanine, glycylasparagine, glycyl-aspartic acid, and biuret base by erepsin. J. H. NORTHROP and H. S. SIMMS (J. Gen. Physiol., 1928, 12, 313—328).—The rates of hydrolysis by erepsin of the above dipeptides have been determined at various hydrogen-ion concentrations and it has been found that the dissociation constants of the substrate exercise a preponderating effect. In order, however, to obtain a complete formulation of these results it must be assumed that erepsin behaves like an acid or base with a dissociation constant of $10^{-7.6}$. This conclusion is confirmed by measurements of the rate of destruction of erepsin by heat.

W. O. KERLACK.

Proteinase and polypeptidase of yeast. W. GRASSMANN and H. DYCKERHOFF (Z. physiol. Chem., 1928, 179, 41—78).—Conditions are described for preparing the polypeptidase and proteinase of yeast by autolysis in presence of chloroform. The almost pure proteinase passes into solution chiefly between the fifteenth and the twenty-fourth hour at p_H 4.8—5.0. It can be purified by adsorption on alumina. The succeeding autolysate contains polypeptidase free from proteolytic action. Yeast polypeptidase is completely inactive towards all proteins, whether of animal or vegetable origin. Hydrocyanic acid and hydrogen sulphide, although inhibitors of poly- and di-peptidase, can activate yeast proteinase. The fresh proteinase preparation is inactive until hydrocyanic acid is added. After several days at neutral reaction the preparation becomes active without hydrocyanic acid. On keeping at p_H 5, the natural

activator is destroyed and the preparation is again inactive without hydrocyanic acid.

The optimum p_H for gelatin hydrolysis by yeast proteinase is 5.0, for fibrin and edestin 7.0, for peptone hydrolysis by polypeptidase, 7.0. Yeast proteinase in its specific action on gelatin can be completely replaced by papain-hydrocyanic acid but not by papain alone or by pepsin.

J. H. BIRKINSHAW.

Coproporphyrin synthesis by dried yeast. H. FINK and K. WEBER (Woch. Brau., 1928, 45, 478—480).—By the addition of dried yeast to highly buffered solutions of sucrose containing carbamide and mineral salts, the optimum reaction for coproporphyrin formation is found to be p_H 4—4.5. The authors express doubt as to whether this is formed by the dried yeast or during development of the living cells contained in the preparation.

F. E. DAY.

Enzymic character of coproporphyrin synthesis in yeast. Cell-free increase of coproporphyrin. R. M. MAYER (Z. physiol. Chem., 1928, 179, 99—116).—The production of coproporphyrin by autolysis of yeast is inhibited by 10% hydrocyanic acid. When the inhibitor is removed after 15 min. by a current of air, coproporphyrin is again formed; after a longer period the result is negative, as the hydrocyanic acid can no longer be completely removed. Chloroform and toluene also have an inhibitory action. Coproporphyrin is formed by cell-free yeast juice; the formation is inhibited by hydrocyanic acid but not by chloroform or toluene. Coproporphyrin is thus a true product of enzyme action. Tap-water produces a rapid disappearance of the coproporphyrin fluorescence of yeast-cells. This is due to calcium or magnesium hydrogen carbonate in solution.

J. H. BIRKINSHAW.

So-called co-enzyme of alcoholic fermentation. A. J. KLUYVER and A. P. STRUYK (Biochem. Z., 1928, 201, 212—258).—Addition of phosphate to ultra-filtered moderately washed zymase is not, but of ultra-filtrate is, able always to bring about fermentation. Addition of acetaldehyde and phosphate to washed zymase is able to bring about fermentation only when sufficient hexosephosphate is retained. By prolonged washing, a filtrate residue is obtained which cannot be reactivated by hexosephosphate, but can by boiled yeast extract. Meyerhoff's co-enzyme is formed by heating a co-enzyme-free zymase solution in presence of phosphate at 100° for a short time and its role is that of inhibiting the endotryptase-zy-mase system, i.e., it is probably identical with Buchner's antiprotease. For cell-free fermentation to take place the following are necessary: zymase and phosphatase, a hydrogen acceptor, hexosephosphate, and antiprotease.

P. W. CLUTTERBUCK.

Purification of co-enzyme from muscle. H. VON EULER and S. GARD (Svensk Kem. Tidskr., 1928, 40, 99—100; Chem. Zentr., 1928, ii, 60).—The co-enzyme in muscle juice was concentrated by lead and mercury precipitation, but appeared to lack an activator of lactic acid formation such as is present in yeast juice.

A. A. ELDRIDGE.

Formation of hexosephosphates; non-fermentable sugars. M. SCHOEN and E. ELION

(Compt. rend. Soc. Biol., 1928, 98, 4—7; Chem. Zentr., 1928, i, 2951).—Zymin does not ferment galactose or arabinose; neither sugar affords hexose-phosphate. The supposed connexion between fermentation and ester-formation is thus supported.

A. A. ELDRIDGE.

Inactivation of invertase and raffinase by heat.

J. M. NELSON and P. PAPADAKIS (J. Biol. Chem., 1928, 80, 163—166).—Autolysed yeast, when heated at 60° for 1 hr., lost 58% of its power to hydrolyse sucrose and 75% of its power to hydrolyse raffinose; this renders the identity of invertase and raffinase doubtful (cf. Willstätter and Kuhn, A., 1923, i, 401; Josephson, A., 1924, i, 919). C. R. HARRINGTON.

Aerobic and anaerobic metabolism of cultivated yeasts. F. WINDISCH (Z. physiol. Chem., 1928, 179, 88—98).—Yeast grown under anaerobic conditions presents a healthier appearance and has a much higher fermenting power than yeast grown under ordinary conditions with access of air.

J. H. BIRKINSHAW.

Decomposition of cellulose by aerobic bacteria.

R. J. DUBOS (J. Bact., 1928, 15, 223—234).—By using strips of filter paper partly immersed in a solution containing sodium nitrate 0.5, dipotassium hydrogen phosphate 1.0, magnesium sulphate heptahydrate 0.5, potassium chloride 0.5, ferrous sulphate heptahydrate 0.01, water 1000 g., kept at 28°, pure cultures of cellulose-decomposing bacteria have been obtained as follows: (a) strict aerobes, unable to utilise any carbon compounds examined except cellulose, (b) strict aerobes which decompose cellulose and grow well on starch agar, but not on nutrient agar, (c) facultative anaerobes, which decompose cellulose, and grow well in ordinary media.

CHEMICAL ABSTRACTS.

Fermentation of maltose by *Bacterium pullorum*. P. R. EDWARDS (J. Bact., 1928, 15, 235—243).—*B. pullorum* does not attack dulcitol or *d*-maltose, but may produce acid from the products of alkaline hydrolysis of maltose.

CHEMICAL ABSTRACTS.

Carbohydrate metabolism of *P. aeruginosa* (*B. pyocyaneus*). H. J. SEARS and M. F. GOURLEY (J. Bact., 1928, 15, 357—366).—Production of acid in presence of a small quantity of dextrose was observed when the nitrogen content of the medium was low. The organism can utilise various sugars.

CHEMICAL ABSTRACTS.

Bacterial metabolism. Influence of phosphate buffer in carbohydrate-free and in dextrose-containing media. C. F. SLANETZ and L. F. RETTGER (J. Bact., 1928, 15, 297—317).—Comparative determinations of total protein-, non-protein-, ammonia-, amino-, and polypeptide-nitrogen, and of biuret were made.

CHEMICAL ABSTRACTS.

Bacterial destruction of acetylmethylcarbinol. O. B. WILLIAMS and M. B. MORROW (J. Bact., 1928, 17, 43—48).—Acetylmethylcarbinol is destroyed by *Aerobacter aerogenes*, the green fluorescent bacterium, and by aerobic spore-formers. It probably serves as a source of carbon.

CHEMICAL ABSTRACTS.

Stability of carbohydrate media. L. D. HENRY and M. S. MARSHALL (J. Lab. Clin. Med., 1927, 12,

474—477).—Unheated (20%) filtered solutions of dextrose, lactose, maltose, sucrose, mannitol, and laevulose stored at 5° retain their specific properties with regard to fermentation for at least 20 months; xylose for at least 12 months. Storage after admixture with culture medium soon renders fermentation reactions non-specific.

CHEMICAL ABSTRACTS.

Bacterial oxidations by molecular oxygen. I. Aerobic oxidation of dextrose and its fermentation products in relation to the viability of the organism. R. P. COOK and M. STEPHENSON (Biochem. J., 1928, 22, 1368—1386).—*B. coli* is capable of oxidising dextrose and its products of fermentation such as lactate, pyruvate, acetate, and formate, by means of molecular oxygen. Ethyl alcohol and acetaldehyde are not oxidised. These compounds do not, however, act as inhibitors in concentrations of 0.01M to the oxidation of other substances. The oxidation of formate proceeds to completion, that of dextrose and lactate to two thirds, and that of acetate to three fourths of completion. When the proportion of the living cells, which varies originally from one third to one tenth of the total number of organisms, is reduced by exposure to ultra-violet light to 0.27% and 0.021% of their original number, the rate of oxidation is only slightly affected. *B. alkaligenes* oxidises the above substrates except dextrose. *B. sporogenes*, on the other hand, does not oxidise any of these substrates.

S. S. ZILVA.

Production of gelatinase by *B. proteus*. A. T. MERRILL and W. M. CLARK (J. Bact., 1928, 15, 267—296).—Synthetic media were employed. In the absence of both calcium and magnesium, no gelatinase was found; in presence of calcium alone the amount was small, and in that of magnesium alone only moderate. Gelatinase was produced anaerobically when dextrose or small quantities of nitrate were added to a synthetic lactate medium.

CHEMICAL ABSTRACTS.

Purification of diphtheria toxin. G. ABT (Ann. Inst. Pasteur, 1928, 42, 1336—1365).—Diphtheria toxin is adsorbed by precipitated di- or tri-calcium phosphate. The precipitate is dissolved by the addition of sodium citrate and citric acid. The calcium is removed and the liquid dialysed against distilled water. Expressed in terms of toxic units per milligram of protein the crude toxin contained only 0.55 unit, whereas the purified toxin contained 22.35 units.

B. A. EAGLES.

Heart hormone. IX. Experiments with a heart extract from warm-blooded animals. L. HABERLANDT (Pflüger's Archiv, 1928, 219, 279—285; Chem. Zentr., 1928, ii, 64).—Experiments with an extract of ox heart are described.

A. A. ELDRIDGE.

Influence of hormones on cell chemistry. J. WOHLGEMUTH [with KLOPSTOCK and HAYASHI] (Deut. med. Woch., 1928, 54, 816—817; Chem. Zentr., 1928, ii, 63).—"Thyreoglandol," "ovoglandol," "testiglandol," and adrenaline cause an increase in the respiration of the skin of the guinea-pig; insulin and hypophysin decrease it. No influence on anaerobic glycolysis was observed. Insulin, thyroxine, folliculin, adrenaline, and "thyreoglandol" stimulate the

production of lactic acid from levulose by the human placenta.

A. A. ELDRIDGE.

Hyphophysin and gluconeogenesis. I. I. NITZESCU and M. BENETATO (Compt. rend. Soc. Biol., 1928, 98, 58—60; Chem. Zentr., 1928, i, 2953).—In starving rabbits an extract of the posterior lobe of the pituitary causes gluconeogenesis in the liver, storage of glycogen up to 2% taking place. Similar results were obtained with adrenaline and insulin. Muscular glycogen is mobilised by pituitary extracts.

A. A. ELDRIDGE.

Extraction of the hormone of the corpora lutea. P. GLEY (Compt. rend. Soc. Biol., 1928, 98, 656—657; Chem. Zentr., 1928, i, 2953).—"Luteocrinin" is obtained from pig's corpora lutea by soaking the minced material in dilute tartaric acid solution, toxic substances being precipitated with lead acetate; the hormone is precipitated with copper hydroxide, the precipitate redissolved in acid, the copper removed with hydrogen sulphide, and the solution neutralised.

A. A. ELDRIDGE.

Testing of commercial ovarian preparations. KOCHMANN (Arch. exp. Path. Pharm., 1928, 137, 187—200).—Tests were made by noting the effect on the growth of the uterus and the production of oestrus, but mainly by observing the effect on metabolism. Several preparations for injection increased metabolism to varying degrees, although some were inactive. Some dry preparations administered by mouth were not tolerated very well and caused reduction in body-weight and in metabolism.

E. BOYLAND.

Testing ovarian preparations. P. TRENDLENBURG and H. GREMELS (Arch. exp. Path. Pharm., 1928, 137, 201—202).—Tests of the preparations for injection, made by examination of the effect on the oestrous cycle, gave results in agreement with those of Kochmann (preceding abstract).

E. BOYLAND.

Oestrus-producing hormone: its preparation and standardisation in a water-soluble form. H. ALLAN, F. DICKENS, E. C. DODDS, and F. O. HOWITT (Biochem. J., 1928, 22, 1526—1543).—The method consists of the saponification of the minced placenta with barium hydroxide and a series of purifications by repeated extraction with butyl alcohol and with ether and by saponification. The active material passes through a porcelain filter and dialyses through parchment. It is stable to prolonged incubation and to short exposures to high temperatures. The preparation is inactive in a single dose, but produces oestrus when given in a series of small injections. A method for the standardisation of the product based on a combination of the multiple dose technique with the statistical method (cf. Coward and Burn, J. Physiol., 1927, 63, 270) is described. By this method the weight of one unit is calculated to be 0.01 mg. The preparation is without effect on blood-pressure or respiration and no ill effects follow when it is injected daily for some months into patients.

S. S. ZILVA.

Heart-lung-adrenal preparation. S. V. ANITSCHKOW and A. I. KUSNETZOW (Arch. exp. Path. Pharm., 1928, 137, 168—179).—The adrenals are included in the circuit of the Starling heart-lung

preparation. Electrical stimulation of the gland causes a marked temporary increase in the secretion of adrenaline; treatment with nicotine produces a permanent increase in the secretion of adrenaline.

E. BOYLAND.

Role of lipins in the vegetative system. I. Antagonistic influence of the physico-chemical state of lipin sols. K. DRESEL and R. STERNHEIMER. IV. Effect of lipins on the blood picture [with R. HIRSCH]. V. Effect of adrenaline on the serum-lecithin and -cholesterol [with F. HIMMELWEIT] (Z. klin. Med., 1928, 107, 739—758, 796—802, 803—809; Chem. Zentr., 1928, ii, 67—68).—V. Injection of adrenaline normally causes an increase of cholesterol and a decrease of lecithin in human blood-serum. In certain pathological conditions the reverse is the case.

A. A. ELDRIDGE.

Absorption of calcium by the musculature of the small intestine during the action of adrenaline. L. JENDRASSIK and S. DONHOFFER (Biochem. Z., 1928, 201, 199—205).—The experiments of Dresel and Wollheim (A., 1925, i, 616) on calcium absorption by the intestine during the action of adrenaline are repeated with a large number of rabbits, but no regularity of results could be obtained.

P. W. CLUTTERBUCK.

Behaviour of the hexosephosphoric acid of the blood towards adrenaline. H. LAWACZECK (Deut. Arch. klin. Med., 1928, 159, 257—266; Chem. Zentr., 1928, ii, 67).—Injection of 1% adrenaline solution (1 c.c.) causes a fall, maximal in 10—15 min., in the blood hexosephosphoric acid; normal values are regained, and a small rise is observed, in 60 min. The blood-sugar value is maximal when the hexosephosphoric acid value has become normal. When defibrinated blood is kept *in vitro*, the hexosephosphoric acid in appreciably increased in 60 min.; the rise is not affected by addition of adrenaline.

A. A. ELDRIDGE.

Behaviour of the hexosephosphoric acid of the blood towards insulin. H. LAWACZECK (Deut. Arch. klin. Med., 1928, 159, 267—274; Chem. Zentr., 1928, ii, 67).—Injection of insulin (30—40 units) causes a rise of blood hexosephosphoric acid (15 min.) followed by a fall (1—1.5 hrs.) to subnormal values. Thus the effect on the acid is most marked when that on the blood-sugar has just begun. Insulin *in vitro* had no effect.

A. A. ELDRIDGE.

Regulation of the production of insulin. III. Action of anhydro-sugars and sugar derivatives. E. GRAFE and F. MEYTHALER (Arch. exp. Path. Pharm., 1928, 136, 360—369; cf. A., 1927, 1115; 1928, 925).—By use of the technique previously described (*loc. cit.*) it is shown that the production of insulin is stimulated by sugar derivatives which contain or can give rise by hydrolysis to a reducing group, such as hexosans, glucosamine, glycuronic acid, dihydroxyacetone, and glyceraldehyde. Non-reducing sugar derivatives such as sorbitol and saccharic acid do not affect the production of insulin.

H. R. INC.

Effect of insulin injected directly into the renal artery on the nitrogen and sugar elimination of the phloridzinised dog. J. GOLDSTEIN

and W. J. STEPHENS (Proc. Amer. Physiol. Soc., Amer. J. Physiol., 1927, **81**, 480).—An immediate decrease in the elimination of sugar and increase in that of nitrogen was observed.

CHEMICAL ABSTRACTS.

Optical activity of insulin-muscle-dextrose-sodium chloride mixtures and hydrogen-ion concentration. C. N. J. GRAM and O. J. NIELSEN (Biochem. Z., 1928, **201**, 369—390).—When fresh muscle was introduced into a mixture of dextrose, salt, and water the dialysate showed in many cases a lower rotatory power than corresponded with the reducing power. In some of these cases insulin was also added to the mixture. Sometimes in presence of insulin the difference disappeared on keeping, the two dextrose figures becoming identical. This subsequent adjustment was observed only in presence of insulin. The p_H of the mixture, originally 7.4, rapidly adjusts itself to 6.0—6.2 when muscle is added. A borate buffer has a disturbing effect on the rotation of dextrose owing to complex formation. The cause of these rotation phenomena is obscure.

J. H. BIRKINSHAW.

Anti-insulin and external secretion of the pancreas. R. MEYER-BISCH, D. BOCK, and W. WOHLBERG (Arch. exp. Path. Pharm., 1928, **136**, 185—202).—Ultra-filtered human pancreatic juice, intravenously administered to rabbits, usually produces a rise in the amount of blood-sugar. The juice contains some substance toxic to these animals. Juice from dogs is less toxic to rabbits and produces smaller increases of blood-sugar. As a rule the amount of blood-sugar increases only when the animals under treatment have previously been receiving acid food. In an alkaline medium the action of anti-insulin is not only suppressed, but may even be reversed as a result of an increased production of insulin. In dogs from which the pancreas has been removed pancreatic juice has a stronger effect than in normal dogs. The external secretion of the pancreas produces in dogs an increase in the protein content of the lymph, a decrease in its alkali reserve, and simultaneous decrease in its sugar content. Anti-insulin is produced in the pancreas and is present in the pancreatic juice.

W. MCCARTNEY.

Iodine content and action of the thyroid gland. Biological method for evaluation of thyroid preparations. H. KREITMAIR (Z. ges. exp. Med., 1928, **61**, 202—209; Chem. Zentr., 1928, ii, 366).—The action of the thyroid hormone can best be followed by observing the loss of weight of guinea-pigs. According to this method the biological action of thyroid preparations is unrelated to the iodine content.

A. A. ELDRIDGE.

Separation of vitamin fraction from cod-liver oil. J. K. MARCUS (J. Biol. Chem., 1928, **80**, 9—14).—The oil is hydrolysed with concentrated aqueous potassium hydroxide together with a trace of alcohol; the resulting soaps are treated with a small amount of water, and the unsaponifiable matter, containing all the vitamins-A and -D of the original oil, is separated by extraction with ethylene dichloride.

C. R. HARINGTON.

Cod-liver oil. E. M. BAILEY, H. C. CANNON, and H. J. FISHER (Conn. Agric. Exp. Sta. Bull., 1928, No. 295, 334—337).—Drummond's colour test for vitamin-A agrees fairly well with standard U.S. Pharmacopœia animal feeding tests. Samples gave the following colour values: six, 5 or less; nine, 5—10; two, 10—20; three, more than 20.

CHEMICAL ABSTRACTS.

Determination of vitamin-A. E. M. NELSON and D. B. JONES (J. Biol. Chem., 1928, **80**, 215—226).—The method laid down in the U.S.P., X, for the determination of vitamin-A is criticised on the ground that account is not taken of the growth-promoting effect of vitamin-D. An improved method is suggested by which the rats are kept on a diet deficient in vitamin-A until the onset of xerophthalmia; the oil to be tested is then added to the diet, and its efficacy determined by the effect on the ophthalmia and on the growth curve.

C. R. HARINGTON.

Distribution of vitamin-A in maize. S. M. HAUGE and J. F. TROST (J. Biol. Chem., 1928, **80**, 107—114).—Inheritance of vitamin-A in a cross of a yellow and white maize followed exclusively that of the yellow colour of the endosperm, and, like the latter, therefore shows Mendelian characteristics.

C. R. HARINGTON.

Relation between antimony trichloride reactions of vitamin-A and of certain carotinoids. B. VON EULER, H. VON EULER, and H. HELLSTROM (Svensk Kem. Tidskr., 1928, **40**, 256—262).—Carotin gives a colour with antimony trichloride similar to that given by materials containing vitamin-A. The colour given by carotin has been examined by means of the photospectrometer and the Lovibond tintometer. The results are similar to but not identical with those given by vitamin-A. The reaction between antimony trichloride and arachis oil has also been examined.

W. O. KERMACK.

Fluorescence of some fats containing vitamin-A. R. S. MORGAN and K. MACLENNAN (Biochem. J., 1928, **22**, 1514—1522).—The unsaponifiable matter from cod-liver oil shows a bright fluorescence when illuminated by ultra-violet light filtered practically free from visible light. The effect of the addition of this fraction on the fluorescence of "jus" (pure rendered beef fat) which is already slightly fluorescent and of hardened coconut oil which is brightly fluorescent has been studied. The fluorescence of butter or butter-fat is yellow, that of margarine blue. The blue fluorescence of margarine can be modified by varying the fat mixture, by addition of unsaponifiable matter from cod-liver oil (small additions of which increase the brightness and diminish the blueness of the fluorescence), and by varying the nature of the pigment present. A sample of "oleo" coloured with sufficient red palm oil to match it with butter-fat and with sufficient unsaponifiable matter from cod-liver oil to bring it up to butter-fat in vitamin-A potency matches butter-fat exactly in fluorescence. A method is described for the determination of the brightness of the fluorescence of a solid fat, the colour being expressed in terms of three additive primaries, red, green, and blue.

S. S. ZILVA.

Synthesis of vitamin-B in the rumen of the cow. S. I. BECHDEL, H. E. HONEYWELL, R. A. DUTCHER, and M. H. KNUTSEN (J. Biol. Chem., 1928, 80, 231—238).—The contents of the rumen of a cow on a diet deficient in vitamin-B were obtained by fistula, allowed to ferment for 5 days at 37°, and extracted with alcohol; the extract was found to be rich in vitamin-B. The predominant organism of the flora of the rumen, *Flavobacterium vitarumen*, was grown on media free from vitamin-B, and the dried bacteria were found to contain the vitamin; the synthesis of vitamin-B by this organism explains why the cow needs minimal amounts only of this vitamin in the diet. C. R. HARRINGTON.

Dietary requirements for fertility and lactation. XIX. Does copper supplement vitamin-B for lactation? XX. Differentiation of vitamin-B complex in rice-polishings. B. SURE [with D. J. WALKER and E. H. STUART] (J. Biol. Chem., 1928, 80, 289—295, 297—307).—XIX. Addition of copper to a vitamin-B concentrate did not reduce the amount of the latter which was required by lactating rats.

XX. The previously observed (A., 1928, 555) inefficiency of the lactating rat in secreting vitamin-B in the milk extends to both vitamin-B₁ and vitamin-B₂; as determined by requirements for lactation, rice-polishings are relatively rich in -B₁ and poor in -B₂. C. R. HARRINGTON.

Antineuritic vitamin. II. Properties of the "curative" substance. J. L. ROSEDALE and C. J. OLIVEIRO (Biochem. J., 1928, 22, 1362—1367).—The antineuritic vitamin of an extract of rice-polishings is destroyed by fermentation and by sterilisation. It contains sacroclastic and lipoclastic but not proteoclastic enzymes. In "dry" beri-beri the pancreas is incapable of lipoclastic and tryptic digestion.

S. S. ZILVA.

Effect of p_H on adsorption of active factors of vitamin-B by fuller's earth. W. D. SALMON, N. B. GUERRANT, and I. M. HAYS (J. Biol. Chem., 1928, 80, 91—101).—Optimal adsorption of vitamin-B₁ by fuller's earth was obtained at p_H 4.0, the efficacy of adsorption decreasing rapidly with increasing alkalinity (which led to simultaneous inactivation) and more slowly with increasing acidity. Adsorption of vitamin-B₂ increases in efficiency up to p_H 0.08, which was the most acid reaction tested. Over the range studied adsorption of vitamin-B₁ was more complete, under the best conditions, than that of vitamin-B₂. C. R. HARRINGTON.

Conversion of vitamin-B into automatin by activation through irradiation. H. ZWAARDEMAKER (Compt. rend. Soc. Biol., 1928, 98, 183—184; Chem. Zentr., 1928, ii, 166).—By irradiation of automatinogen, active automatin could be obtained in heart muscle. Automatin is apparently identical with Deinoor's active substance and Haberlandt's heart hormone; it also has properties similar to those of d'Eykman's irradiated vitamin-B.

A. A. ELDRIDGE.

Antiscorbutic vitamin in cabbage soup, cabbage puree, and turnip juice. E. Tso (Chinese

J. Physiol., 1928, 2, 403—408).—All three preparations protected guinea-pigs from scurvy and also promoted normal growth. F. C. HAPPOLD.

Fluorescence of oils and fats. J. F. CARRIÈRE.—See B., 1929, 26.

Vitamin contents of Japanese foodstuffs. SHIMODA, FUJIMAKI, and SAIKI.—See B., 1928, 942.

Characterisation of the immediate physiological action of water-soluble vitamins. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1928, 10, 1179—1198).—Guinea-pigs fed on a diet deficient in vitamin-C show, on administration of vitamin-C, an increase in the bromine titre of the urine in the case of adult animals, a decrease in the case of young growing animals, and the appearance of a blue reaction of the urine with monomolybdophosphotungstic acid (which is absent during avitaminosis, Bezssonoff, A., 1926, 722). Increase in weight becomes perceptible after 48 hrs. The bromine titre of the urine is proportional to the content of phenol and *p*-cresol and approximately to the density; it has no relation to the degree of pigmentation. The bromine absorbed corresponds approximately with twice the amount of carbon in the urine.

G. A. C. GOUGH.

Immediate physiological effects of avitaminosis-C. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1928, 10, 1199—1212).—Avitaminosis-C causes accumulation of toxic phenolic substances in the blood and consequent inanition. G. A. C. GOUGH.

Antirachitic substances. VIII. Purified ergosterol and its esters. C. E. BILLS and E. M. HONEYWELL (J. Biol. Chem., 1928, 80, 15—23).—The crude sterol from yeast is dissolved in a mixture of 95% alcohol (2 parts) and benzene (1 part), the solution is cooled slowly to commencing turbidity of the mother-liquor, and the crystals of ergosterol are collected; one more recrystallisation from alcohol-benzene gave a product, m. p. 166—183° according to the degree of hydration, $[\alpha]_D^{20}$ -132°, $[\alpha]_D^{20}$ -171°, the rotation of which could not be altered by conversion into an ester and recovery by hydrolysis. Ergosterol purified by the above method yields an *acetate*, m. p. 181°, $[\alpha]_D^{20}$ -90°; *isobutyrate*, m. p. 162° after sintering, $[\alpha]_D^{20}$ -84°; *isovalerate*, m. p. 160° after sintering, $[\alpha]_D^{20}$ -82°; *benzoate*, m. p. 168°, $[\alpha]_D^{20}$ -177°; *cinnamate*, m. p. 179°, $[\alpha]_D^{20}$ -22°, all rotations in chloroform. Careful purification of ergosterol fails to affect its spectrographic properties.

C. R. HARRINGTON.

Vitasterol-D. II. Activation of ergosterol. A. JENDRASSIK and A. G. KEMÉNYFFI (Biochem. Z., 1928, 201, 269—280).—Ergosterol attained its maximum antirachitic activity after 30 min. irradiation; after 10 hrs. the activity was destroyed. No unchanged ergosterol then remained. A material having five times the activity of the irradiated product was obtained by fractionation with ethyl alcohol. The unchanged ergosterol after removal of the active product can be again activated by irradiation. The intensity of the orange colour produced with iodine seems to give an indication of the content of vitasterol-D. J. H. BIRKINSHAW.

Biological inertness of irradiated mycosterols other than ergosterol. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1928, 22, 1426—1428).—A mycosterol "fungisterol" was isolated as the acetate m. p. 117—118°, $[\alpha]_{D}^{20}$ —43°, from the mother-liquor after removal of crystallisable ergosterol from ergot. This sterol, and also two other sterols from the same source were found to be biologically inactive after irradiation.

S. S. ZILVA.

Chronic effects of irradiated saponin and irradiated ergosterol. H. HANDOVSKY (Arch. exp. Path. Pharm., 1928, 137, 264—268).—Administration to rabbits of saponin irradiated by a mercury vapour lamp results in an increase of the carbohydrate of their muscles, whereas administration of non-irradiated saponin causes a decrease. Administration of irradiated ergosterol causes a decrease in the carbohydrate content of the muscles.

W. O. KERMACK.

Duration of effect of ultra-violet irradiation of chickens. W. C. RUSSELL, O. N. MASSENGALE, and C. H. HOWARD (J. Biol. Chem., 1928, 80, 155—162).—The calcium and phosphorus concentrations in the blood of chickens on a diet deficient in vitamin-D was proportional to the time of exposure of the birds to ultra-violet irradiation; a parallelism was observed between the calcium and phosphorus of the blood and the percentage of bone-ash. One exposure of the bird to ultra-violet light of 45 min. duration produced an effect lasting 1 week, whilst longer single exposures up to 270 min. were active for 2 weeks.

C. R. HARRINGTON.

Yeast ergosterol. III. F. REINDEL.—See this vol., 61.

"Hypervitaminosis" and "vitamin balance." L. J. HARRIS and T. MOORE (Biochem. J., 1928, 22, 1461—1477).—Young rats lose weight rapidly and die on a synthetic diet containing 0.1% of irradiated ergosterol. An increase of vitamin-B in the form of marmite to four times the normally adequate level does not appreciably influence this decline. On the other hand further addition of vitamin-B (and -C), through the medium of wheat-germ and orange juice, prevented the loss in weight in two animals. Rats on a diet containing 15% of cod-liver oil and a restricted allowance of the vitamins-B do not thrive as well as animals on a diet containing a similar content of arachis oil. In the former case normal gestation fails (cf. Hartwell, A., 1927, 1107; Sure, *ibid.*, 905). 0.001% of irradiated, non-irradiated, or heated ergosterol in the diet makes no appreciable difference in the condition of rats subsisting on vitamin-B-restricted or vitamin-B-free diet. Massive doses of vitamin-A and -D concentrate from cod-liver oil produce, in conjunction with vitamin-B deficiency, changes such as loss of hair and severe skin lesions. The lethal dose of irradiated ergosterol becomes non-toxic concurrently with the destruction of vitamin-D by over-irradiation.

S. S. ZILVA.

Daily growth and oil content of flax seeds. A. C. DILLMAN (J. Agric. Res., 1928, 37, 357—367).—The most rapid formation of the oil in flax seeds begins about the seventh day after flowering

and continues for a period of 15—18 days. It reaches a maximum 33 days after flowering, coincident with the maximum dry weight of the seed. The bearing of this on the harvesting of flax is discussed.

E. A. LUNT.

Chemical composition of the oil in relation to the morphological and physiological characters of the plant. S. FACHINI and G. DORTA (Giorn. Chim. Ind. Appl., 1928, 10, 460—462).—Olive oils from the northern parts of Italy (Lake Garda, Liguria) contain only small proportions (2—6%) of linoleic acid, whereas certain oils from Southern Italy, Greece, and Northern Africa contain considerable quantities, even as much as 17%, of this acid, together with a high percentage of saturated fatty acids. This result appears to be opposite to that found by Ivanov (A., 1927, 906) for seed oils. The composition of olive oil seems to be influenced by the age and degree of acclimatisation of the plant. The characteristics of an oil depend largely on the biological and morphological factors of the plant furnishing it.

T. H. POPE.

Carbon dioxide assimilation of the sugar beet. H. LUNDEGARDH (Flora, 1928, [ii], 21, 273—300; Chem. Zentr., 1928, ii, 257).—The dependence of the assimilation on temperature follows the same regularities for different plants, but differences exist in the position of the optimum. The results are considered in relation to plant geography.

A. A. ELDRIDGE.

Evolution of carbon dioxide and absorption of oxygen in germinating seeds. G. FRIETINGER (Flora, 1927, [ii], 22, 167—201; Chem. Zentr., 1928, ii, 160).—No parallelism between carbon dioxide evolution and oxygen assimilation was observed, although both are greatly influenced by the medium.

A. A. ELDRIDGE.

Decomposition of hexoses in plants. III. Co-enzyme of plants. W. ZALESKI and E. SCHATALOWA-ZALESKAJA (Biochem. Z., 1928, 201, 190—198).—The power of pea-meal to utilise acet-aldehyde is lost on dialysis but regained on adding boiled extract of dried yeast, a co-enzyme probably identical with co-enzyme. The difference between the aldehydase activity of non-germinating and germinating peas can be compensated for by addition of excess of co-enzyme (cf. A., 1927, 1226).

P. W. CLUTTERBUCK.

Catalase in relation to growth and other changes in plant tissue. J. E. KNOTT (N.Y. Agric. Exp. Sta. Mem., 1927, No. 106, 63 pp.).—The catalase activity of spinach and celery leaves is generally greatest at intermediate ages. Rise (10°) of temperature increased the catalase activity of celery plants; the p_H of the plant juice could not be correlated with catalase activity, which was increased by fertilising with phosphorus and nitrogen.

CHEMICAL ABSTRACTS.

Catalase reaction in pollen. G. LOPRIORE (Ber. deut. bot. Ges., 1928, 46, 413—423).—In general the catalase content of the pollen from various plants increases with the increasing ripeness of the pollen,

E. A. LUNT.

Sodium and potassium content of lentils and peas. W. KÜSTER and J. UMBRECHT (Z. physiol.

Chem., 1928, 179, 139—148).—The sodium and potassium content of the ash of lentils and peas was determined. The average value for small lentils was Na_2O , 0.782%; K_2O , 31.95%, for cultivated lentils, Na_2O , 3.06%; K_2O , 37.4%. Peas had 1.81% Na_2O , 40.35% K_2O in the ash. J. H. BIRKINSHAW.

Physiological function of magnesium in plants. E. CANALS (Bull. Soc. Chim. biol., 1928, 10, 1260—1270).—The magnesium and calcium contents of the ash from various parts of a large number of plants show wide variations (Ca 2.2—35.5, Mg 0.8—5.7%; Ca:Mg 0.81—32.2). Except in herbaceous plants, the leaves contain more magnesium than the stems and the amount of calcium generally increases with the age of the tissue. Dialysis of the juices of fungi and potato shows that a large proportion of the magnesium and calcium exists in an inorganic form, probably as phosphate. G. A. C. GOUGH.

Effect of plasmolysis on carbon dioxide assimilation in plants. H. WALTER (Ber. deut. bot. Ges., 1928, 46, 530—539).—The effect of plasmolysis induced by immersion in sucrose solutions of varying concentrations on the capacity for carbon dioxide assimilation has been investigated in the case of *Elodea canadensis*. E. A. LUNT.

Determination of sulphur and phosphorus in vegetable tissues. R. ECHEVIN and A. CREPIN (Bull. Soc. Chim. biol., 1928, 10, 1248—1259).—After oxidation by means of nitric acid, the sulphur is determined as barium sulphate and the phosphorus titrated with uranium acetate solution.

G. A. C. GOUGH.

Valerian root and the formation of sucrose. H. KUNZ-KRAUSE (Apoth.-Ztg., 1928, 43, 484—485; Chem. Zentr., 1928, i, 2733).—Sucrose was deposited from ethereal tincture of valerian. The occurrence of sucrose with certain monocarboxy-acids suggests a relationship between the genesis of sucrose and the appearance of fatty acids, particularly butyric and valeric.

A. A. ELDRIDGE.

Glucosides of digitalis leaves. A. WINDAUS (Arch. exp. Path. Pharm., 1928, 135, 253—258).—A comparative review of the work of Cloetta (A., 1926, 755) and of the author (A., 1923, i, 1107; 1924, i, 1215; 1925, i, 1295; 1926, 153; Nachr. Ges. Wiss. Göttingen, 1926, 170; 1927, 422) on the chemistry of digitoxin, gitoxin (bigitalin), and gitalin.

W. O. KERMACK.

Glucosides of *Adonis vernalis*. K. FROMHERZ (Münch. Med. Woch., 1928, 75, 818—820; Chem. Zentr., 1928, ii, 75).—Two highly active digitalis-like glucosides differing in degree of activity can be isolated from *Adonis vernalis*.

A. A. ELDRIDGE.

***Oenanthe sarmentosa*.** F. J. GOODRICH and E. V. LYNN (J. Amer. Pharm. Assoc., 1928, 17, 1096—1104).—The dried leaves and stems of *O. sarmentosa* grown on the American Pacific coast contain 0.038% of oil having $d^{15.5}$ 0.9188, $[\alpha]_D^{20} +7.78^\circ$, n_D^{20} 1.4918, and congealing at -12° . It is principally composed of terpenes and contains sulphur (1.28%) and furfuraldehyde. The dried fruit gives 0.35% of oil ($d^{15.5}$ 0.9032, $[\alpha]_D^{20} +7.52^\circ$, n_D^{20} 1.4942, congealing pt. -10.5°) also containing sulphur (0.91%) but no furfuraldehyde.

It consists mainly of terpenes and contains phellandrene, probably α -phellandrene. The rhizomes and roots yield 0.1% of oil (on dried material) having $d^{15.5}$ 0.9304, $[\alpha]_D^{20} +7.52^\circ$, 1.4898, and containing furfuraldehyde and a small amount of sulphur. Pectin is present in the rhizome in an amount equivalent to 2.36% of pectic acid (on dry material). The dry material also contains 3.14% of reducing sugars, starch, sucrose, gums, and resins. Alkaloids were not present in any part of the plant, but small amounts of glucosides may be present. The plant is not toxic to guinea-pigs or rats.

E. H. SHARPLES.

Principle extracted from *Sphacele parviflora*. Linn. V. HASENFRATZ (Compt. rend., 1928, 187, 903—904).—The white solid, m. p. 105° , isolated from the dried leaves of *S. parviflora*, Benth (yield 3 g./kg.), by steam-distillation and crystallisation of the product from alcohol, is proved to be identical with the sesquiterpene alcohol ledol, $\text{C}_{15}\text{H}_{26}\text{O}$ (Hjelt, A., 1896, i, 248), isolated from *Ledum palustre*, Linn.

J. W. BAKER.

Isolation of mesaconic acid from cabbage leaves. H. W. BUSTON (Biochem. J., 1928, 22, 1523—1525).—Mesaconic acid is present in the fraction of the ether-water extract of leaves which is precipitated by alcohol and in the "dicarboxylate" fraction left after precipitation of bases with phosphotungstic acid. In the former it is liberated from its calcium salt by dilute sulphuric acid and extracted with alcohol. From the latter fraction after decomposing the barium dicarboxylates it is extracted with alcohol and purified partly by extraction with ether and partly by precipitation as the calcium salt from this alcoholic extract.

S. S. ZILVA.

Amaryllyis. NARITA (Imp. Japanese Inst. Nutrition; Bull. soc. hyg. aliment., 1927, 15, 481—504, 524—551).—The air-dried plants contained: water 80.53, crude protein 1.19, crude fat 0.23, crude fibre 0.72, carbohydrates (as dextrose) 17.32, ash, 0.01%. "Sekisanine," $\text{C}_{24}\text{H}_{36}\text{N}_2\text{O}_6$, m. p. 200° (0.05%), and "lycorine," $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_2$, m. p. 248° (0.13%), were present.

CHEMICAL ABSTRACTS.

Nutritional chemistry of raw food substances. I. The banana. K. KONDO, M. NAKAJIMA, and T. SUZUKI. II. The water-melon. K. KONDO and T. HAYASHI (Mem. Coll. Agric. Kyoto, 1928, 6, 23—53, 55—72).—I. The following percentage composition is given for the edible portion of the banana fruit: water 70%, total nitrogen 0.29%, protein 1.83%, starch 4.69%, reducing sugars 12.23%, non-reducing sugar 1.94%, pectins 0.38%, fibre 0.34%, ash 1.04%.

II. Analyses of the juice of different varieties of ripe water-melons give the following average results: water 92%, sugars 6—8%, chiefly laevulose, ash 0.3%, nitrogen 0.08%.

E. A. LUNT.

Comparative plant chemistry. XXI. Chemistry of latex-bearing plants. IV. J. ZELLNER (Monatsh., 1928, 50, 211—215).—The dried latex of *Campanula trachelium*, L., yielded a small ether-soluble fraction containing resin acids, but no sensible quantity of fatty acids. A wax alcohol, m. p. 87° , was isolated. Euphorbone or sterols were absent. The alcoholic extract, evaporated to dryness and

crystallised from water, yielded a glucoside, *campanulin*, (?) $C_{12}H_{18}O_6$, m. p. 210° (decomp.), from which dextrose and a phenolic substance were obtained. Acetylation of the glucoside yielded an *acetyl* compound, $C_{24}H_{38}O_{14}$, m. p. 202° , with simultaneous loss of water. The mother-liquors of the campanulin contained "tannoid" substances, but no sugars or alkaloids. The aqueous extract of the dried latex contained chiefly inorganic salts. The extract with dilute alkali contained proteins.

The dried latex of *Lactarius rufus*, Scop., yielded, on extraction with light petroleum, a considerable amount of lactic acid. Only resinous substances could be isolated from the mother-liquors. The small alcohol-soluble fraction contained mannitol and dextrose. The aqueous extract appeared to contain a weakly acidic carbohydrate as a potassium compound. The extract of the residue with alkali yielded proteins on acidification. The composition is similar to that of the latex of *L. vellereus* (A., 1921, i, 212).

R. K. CALLOW.

Plugging substance in the vessels of hops. T. C. THURPP (Ann. Bot., 1928, 42, 1027—1028).—A plugging substance, insoluble in concentrated acids and incapable of ordinary staining, has been found in the vessels of hops.

E. A. LUNT.

Water-soluble protein in wheat seed. R. HERZNER (Biochem. Z., 1928, 202, 320—328).—The properties of the carefully purified water-soluble protein of wheat seeds (leucosin) show that it belongs to a group of substances analogous to the animal pseudoglobulins.

W. MCCARTNEY.

Proteins of buckwheat flour. M. HARA (Imp. Japanese Inst. Nutrition; Bull. soc. hyg. aliment., 1927, 15, 481—504, 524—551).—The following values are recorded (percentages of total nitrogen within parentheses): amino-nitrogen 0.0525 (8.19), humin-0.0487 (7.60), cystine-0.0117 (1.82), arginine-0.1527 (23.82), histidine-0.0158 (2.43), lysine-0.0204 (3.19), monoamino-0.2599 (40.53), non-amino-0.0874 (13.63), total 0.6590 g.

CHEMICAL ABSTRACTS.

Protein content of Italian millet. KONDO (Imp. Japanese Inst. Nutrition; Bull. soc. hyg. aliment., 1927, 15, 481—504, 524—551).—The following values are recorded: water 13.57, crude protein 11.12, albuminoids 10.36, fat 5.32, nitrogen-free extract 63.68, fibre 1.71, ash 0.87%. The protein (30 g.) contained: total nitrogen 0.6009, humin-0.0155 (2.54% of total), amide-0.0734 (12.03), arginine-0.0592 (9.71), cystine-0.0135 (2.21), histidine-0.0720 (11.81), lysine-0.0369 (6.05), monoamino-0.3015 (49.43), non-amino-0.0290 g. (4.76).

CHEMICAL ABSTRACTS.

Prearginine in edestin and its resistance to hydrolysis. H. S. SIMMS (J. Gen. Physiol., 1928, 12, 231—239).—Titration data indicate that edestin contains no free arginine but that this amino-acid is present in the form of prearginine (cf. A., 1928, 837). Partial hydrolysis of edestin (up to 18% of the total hydrolysis) by pepsin does not convert prearginine into arginine. The second carboxyl groups of glutamic and aspartic acids are in part present as amides and 50% are otherwise combined, possibly as anhydrides, whilst 6% are free to ionise. Samples of edestin

hydrolysed to the extent of 5, 14, or 18% were equally effective in promoting growth of sarcomatous fibroblasts.

W. O. KERNACK.

Basic nitrogen of plant extracts. H. B. VICKERY (Plant Physiol., 1927, 2, 303—311).—Phosphotungstic acid is an uncertain precipitating agent for the true basic nitrogen of plants, since it may precipitate non-basic nitrogenous substances as well as compounds of polypeptide nature which yield simple monoamino-acids on hydrolysis. The method is satisfactory with simple mixtures.

CHEMICAL ABSTRACTS.

Purine bases of the seed and meal of the soya bean. V. DUCCESCHI (Arch. Sci. Biol., 1928, 12, 181—184; Chem. Zentr., 1928, i, 3082—3083).—The dry seed contains 0.191% and the dry meal 0.233% of purine bases.

A. A. ELDRIDGE.

Location and disappearance of alkaloids in the epidermis of the tobacco leaf. J. CHAZE (Compt. rend., 1928, 187, 837—839).—The epidermal cells of the tobacco leaf present several types in regard to their nicotine content; in one type, a brown liquid containing alkaloids is observed to exude. When the hairs of the leaf exude this liquid the nicotine content of the cell at the base of the hair diminishes.

G. A. C. GOUGH.

Origin of ethereal oils in plants. L. FRANCESCONI (Riv. Ital. Ess. Profumi, 1928, 10, 2—6, 33—36; Chem. Zentr., 1928, i, 2414).—It is supposed that isoamyl alcohol, from the decomposition of protein, yields isovaleraldehyde, whence isocitronellal, rhodinal, and citronellal are produced. Citronellal gives rise to geraniol and hence linalool; ring-closure affords limonene or terpineol. Ring-closure of rhodinal gives rise to menthone, and of citronellal to isopulegol. Geraniol by ring-closure and hydration gives α -pinene; linalool by ring-closure and wandering of a hydroxyl group gives terpineol.

A. A. ELDRIDGE.

Potentiometric determinations in the protoplasm and cell sap of *Nitella*. C. V. TAYLOR and D. M. WHITAKER (Protoplasma, 1927, 3, 1—6).—A non-polarisable micro-electrode is described and figured. The protoplasm produced a potential of +0.093 to +0.030 volt; the values are considered to indicate the oxidation-reduction potential. The p_H of the cell sap was 5.47—6.16.

CHEMICAL ABSTRACTS.

Composition of the cellular fluid of *Valonia macrophysa*. R. HOBBER and J. HOBBER (Pflüger's Archiv, 1928, 219, 260—272; Chem. Zentr., 1928, i, 2945—2946).—The cellular fluid of *Valonia macrophysa* contains more potassium, but less sodium, calcium, magnesium, and sulphate than the sea-water; the concentrations of chloride are equal.

A. A. ELDRIDGE.

Influence of oxygen and carbon dioxide on the growth of *Ophiobolus graminis*. H. FELLOWS (J. Agric. Res., 1928, 37, 349—355).—The variation in the amount of growth obtained both on solid and on liquid media of the wheat fungus, *O. graminis*, with variation in oxygen and carbon dioxide concentrations has been observed. It is unlikely that the variations in these two gases as found in arable soils are great enough to affect materially the growth of this organism.

E. A. LUNT.

Importance of oxygen in the formation of carbamide by fungi. N. N. IVANOV and M. I. SMIRNOVA (Biochem. Z., 1928, 201, 1—12).—Mushrooms accumulate carbamide only when in an atmosphere containing oxygen. The role of oxygen in the synthesis of carbamide is discussed and is regarded as analogous to its role in the synthesis of asparagine (cf. A., 1927, 383). P. W. CLUTTERBUCK.

Colour variation in the moulds. A. BLOCH-WITZ (Ber. deut. bot. Ges., 1928, 46, 516—524).—A review is given of the literature dealing with the colour variations in the vegetative filaments and conidia of the moulds, and of individual experiments on *Aspergillus flavus* relating the colour variation with the p_H of the medium. E. A. LUNT.

Chemistry of the higher fungi. XIX. *Polyporus pinicola*, Fr. E. HARTMANN and J. ZELLNER. **XX. *Omphalia Campanella*, Batsch, *Marasmius Scorodonius*, Fr., *Boletus cavipes*, Opat., and *Calocera viscosa*, Pers.** N. FROSCHL and J. ZELLNER (Monatsh., 1928, 50, 193—200, 201—210).—XIX. Fractionation of the alcoholic extract of *Polyporus pinicola* yielded a substance, m. p. 140—141° (acetyl compound, m. p. 67—68°), identical with the cerebrin from *Amanita muscaria* (Zellner, A., 1911, ii, 425), trehalose, and a final fraction. Extraction of the final fraction with light petroleum yielded, after saponification, sterols (0.3—0.4% of the dry fungus), separated into ergosterol and fungisterol, resin, acetic and butyric acids, glycerol, choline, and an acid fraction insoluble in water, from which was separated a neutral, crystalline substance, m. p. 195—196° (possibly identical with a product obtained from *Scleroderma aurantium*, Vaill., by Bamberger and Landsiedl; A., 1907, ii, 45), an amorphous neutral substance, m. p. 87—88°, a substance giving a cholesterol reaction, $(C_{10}H_{18}O)_n$, m. p. 142—144°, and amorphous resin acids. Extraction of the final alcohol fraction with ether yielded similar fractions, substances, m. p. 221—222° and 215°, and a substance of sterol character, $(C_4H_8O)_n$, m. p. 188°. Tannins were obtained by extraction of the final alcoholic fraction with water, leaving a residue containing phlobaphens. The results are contrasted with those of the investigation of *Polyporus officinalis* by Schmieder (Diss., Erlangen, 1886).

XX. *Omphalia Campanella*, examined by similar methods, yielded sterols, liquid and solid fatty acids, resin, mannitol, dextrose, choline, phlobaphen, and amorphous carbohydrates.

Marasmius Scorodonius was subjected to steam-distillation. The ethereal extract of the distillate yielded a paraffin, m. p. 55°, and an oil with a garlic-like odour, (?) $(C_2H_5S)_n$, 0.2% of the dry fungus. The aqueous extract of the fungus yielded *marasmin*, $C_7H_{15}O_3N$, m. p. 242° after darkening at 195°, a neutral substance with reducing properties, and from the mother-liquors were obtained choline and dextrose, but neither mannitol nor trehalose. The portion of the aqueous extract insoluble in alcohol yielded a glucosan. From the portion insoluble in water was obtained a substance of cerebrin character, m. p. 133°, a mixture of sterols, and liquid and solid fatty acids, the last containing palmitic and stearic acids and a higher fatty acid.

From *Boletus cavipes*, well-defined products were isolated with difficulty. The ethereal extract yielded sterols, resin, and liquid fatty acids, identified with oleic acid and linoleic acid by oxidation to dihydroxy- and tetrahydroxy-stearic acids, respectively. The alcoholic extract yielded mannitol and a syrupy glucosan. The aqueous extract contained polysaccharides of the type of viscosin.

The alcoholic extract of *Calocera viscosa* yielded trehalose. The light petroleum extract of the final fraction from alcohol yielded, after saponification, a mixture of sterols of the usual type, in the mother-liquors of which the amorphous, reddish-yellow colouring-matter collected, and a mixture of fatty acids in which isovaleric, oleic, palmitic, and stearic acids were recognised. The ethereal extract of the final alcohol fraction yielded, after separation of resin acids and resin, *caloceryl*, m. p. 255° (decomp.), a neutral, stable substance for which the formula $C_{22}H_{38}O_8$ is proposed. With acetyl or benzoyl chlorides, two substances of similar character, m. p. 128°, were formed. Dextrose and choline were separated from the residue of the alcoholic extract. The aqueous extract of the fungus yielded slimy polysaccharides, probably present in the fungus as potassium or magnesium compounds, yielding mannose on hydrolysis. R. K. CALLOW.

Alcoholic fermentation by *Aspergillus flavus*, Brefeld. J. L. YUILL (Biochem. J., 1928, 22, 1504—1507).—*A. flavus* does not produce kojic acid under conditions in which *A. oryzae* produces it. In presence of chalk the former organism, unlike the latter, produces considerable quantities of ethyl alcohol (equivalent to 15—25% of the sugar consumed) in the presence of air. During the fermentation with *A. flavus* some calcium citrate is formed and some soluble calcium salts precipitable by alcohol. When the mould forms spores the yield of alcohol is much reduced and the quantity of citrate increased.

S. S. ZILVA.

Conditions of the action of asparaginase from *Aspergillus niger*. D. BACH (Compt. rend., 1928, 187, 955—956).—The action of asparaginase from *A. niger* in the conversion of asparagine into ammonium aspartate occurs only on the alkaline side of the isoelectric point of the acid (p_H 4.5—10) and is greatest at 42° and p_H 8.6. At p_H 7.6 the optimum temperature is 31° and in both cases the action extends from 7° to 70°. The reaction is never more complete than 80%, and the destruction of the enzyme, which occurs in the extract of the mould, is inhibited by asparagine. G. A. C. GOUGH.

Formation of calcium oxalate crystals in vegetable cells in ultra-violet light. G. NADSON and E. ROCHLINE-GLEICHGERWICHT (Compt. rend. Soc. Biol., 1928, 98, 363—365; Chem. Zentr., 1928, i, 2949).—Exposure to ultra-violet light causes the appearance of calcium oxalate in *Elodea densa*, *E. canadensis*, and *Pterygophyllum hepaticifolium*.

A. A. ELDRIDGE.

Diurnal variation of the gaseous constituents of river waters. IV. R. W. BUTCHER, F. T. K. PENTELow, and J. W. A. WOODLEY (Biochem. J., 1928, 22, 1478—1489; cf. A., 1927, 899; 1928, 1163).

—The effect of the pollution by effluents on the dissolved oxygen of the river Lark was less marked on Jan. 25–27th, 1928, than in November, 1927. The diurnal variation was still evident. During February 16–17th, when the effects of the winter pollution were disappearing, the range of variation of oxygen content was smaller than at any other time of the year, *i.e.*, 66–77% saturation. The figures obtained in March 1928 indicate the commencement of that rapid increase of diatoms which occurs every spring. In the case of the river Itchen the oxygen curves of January, February, March, and May show an increasing range of variation with the increase in the hours of daylight and with increase in the number of diatoms. The river Lark results are summarised for the period March 1927–March 1928. The factors affecting the dissolved oxygen content of river water are discussed.

S. S. ZILVA.

Sunlight and chemical nitrification. J. ZÓŁCINSKI (Pedologie, 1928, 19, No. 1–2; Chem. Zentr., 1928, i, 2443).—Nitrification takes place in sunlight in aqueous ammonium salt solutions of humus substances; the nitrate disappears again in the dark. The effect is more pronounced in silica vessels than in glass. Nitrification does not take place in colloidal solutions. Natural humus undergoes nitrification more slowly than artificial; the presence of ignited alumina promotes the change. A. A. ELDRIDGE.

Laboratory apparatus. II. H. J. FUCHS (Biochem. Z., 1928, 201, 332–337).—1. An apparatus is described for low-temperature evaporation in a vacuum. Only ground-glass joints are used. The liquid is allowed to drop into the distillation flask, where it is sprayed over the walls. The receiver contains concentrated sulphuric acid and is cooled in a water-bath.

2. A fractional distillation apparatus for the purification of liquids of low b. p. consists of a double rectifier so arranged that the heat for the second stage of evaporation is supplied by the vapour of the first stage. J. H. BIRKINSHAW.

New micro-burette. E. M. P. WIDMARK and S. L. ORSKOV (Biochem. Z., 1928, 201, 15–21).—The principle of the instrument is based on the displacement of a volume of the titration fluid by mercury which in turn is displaced as the result of the movement of a steel cylinder operated by means of a micrometer screw, the reading on the screw (calibrated against the amount delivered) thus giving the volume of fluid used. The instrument has a capacity up to 200 mm.³, it can be connected directly with the titration flask, air thus being excluded, and provision is made for easy washing (cf. A., 1926, 211).

P. W. CLUTTERBUCK.

Haldane apparatus for small volumes of gas. H. C. BAZETT (Amer. J. Physiol., 1928, 86, 556–564).—A modified gas analyser is described capable of analysing mixtures of carbon dioxide and oxygen with a neutral gas in any proportion in volumes up to 2.0 c.c. The error varies from ± 0.04 to $\pm 0.2\%$, according to the volume available. B. A. EAGLES.

Improvements in Carpenter's apparatus for gas analysis. F. STRIECK (Biochem. Z., 1928, 202, 1–4).—Two changes are made which enable a double

analysis to be carried out in 12–14 min. (see Z. ges. exp. Med., 1920, 54, 613). R. W. CLUTTERBUCK.

Manometric measurement of small partial pressures of oxygen. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1928, 202, 387–389).—A description of an apparatus for determining the partial pressure of oxygen is given. The oxygen is absorbed by a solution of ferrous pyrophosphate. Partial pressures of a few ten thousandths of an atmosphere may be measured. W. McCARTNEY.

Micro-determination of hydrogen peroxide, nitrogenous compounds, and fermentation carbon dioxide. Paechtner's ponderovolumeter. P. LUY (Biochem. Z., 1928, 201, 165–184).—Paechtner's ponderovolumeter for the determination of small amounts of gas in terms of pressure changes in a closed space within which the gas is formed is successfully used to follow the decomposition of hydrogen peroxide by permanganate, the formation of nitrogen by treatment of carbamide or ammonium sulphate with hypobromite, and the production of carbon dioxide during the fermentation of dextrose by yeast.

P. W. CLUTTERBUCK.

Determination of p_H in cells and tissues. T. PETERFI (Z. wiss. Micros., 1928, 45, 56–59; Chem. Zentr., 1928, i, 2737).—A technique employing gelatin coloured with Clark's indicators is described.

A. A. ELDRIDGE.

Use of the quinhydrone electrode. R. R. McKIBBIN and L. I. PUGSLEY (Canadian Chem. Met., 1928, 12, 283–286).—Comparative p_H determinations were made on a number of biological solutions with the hydrogen gas electrode, the quinhydrone electrode, and where possible colorimetrically. With fruit juices the quinhydrone electrode consistently gave rather higher results than the other and equilibrium was reached at once. With milk, urine, and soil extracts agreement was close. With human saliva the results appear uncertain. The use of the quinhydrone electrode with gold wire, which is described in detail, is very convenient with such solutions and quite accurate below p_H 8.0. C. IRWIN.

Wash-bottle for the gas cell. H. SCHREUS (Biochem. Z., 1928, 200, 339).—A wash-bottle is described which permits rapid change of the washing fluid without loss and without entrance of air into the flask.

P. W. CLUTTERBUCK.

Apparatus for the micro-determination of carbon by the method of Nicloux. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1928, 10, 1273–1276).—Another method of avoiding the use of a stopcock in the apparatus of Nicloux is described. This consists of a bulb pipette filled with sulphuric acid and bent in such a way that the hydrostatic pressure at the capillary tip is small. The flow of acid is regulated by means of a rubber tube and clip. G. A. C. GOUGH.

Micro-determination of potassium in biological media. A. LEULIER, L. VELLUZ, and H. GRIFFON (Bull. Soc. Chim. biol., 1928, 10, 1238–1247).—Directions are given for the adaptation of the method already described (A., 1928, 1205) to biological substances. Deproteinisation is effected by means of trichloroacetic acid in the cases of milk and blood and the resultant filtrates are neutralised with lithium

carbonate. Tissue is oxidised either by treatment with nitric acid and hydrogen peroxide or by sulphuric and perchloric acids. Ammonia is eliminated in all instances with sodium nitrite and acetic acid.

G. A. C. GOUGH.

Determination of small amounts of iodine in organic products. II. G. PFEIFFER (Biochem. Z., 1928, 201, 298—304; cf. A., 1928, 928).—Fatty acids which would otherwise distil into the receiver are intercepted by a special condenser from which the condensate can be run off. They are received in dilute potassium hydroxide solution and removed as calcium salts.

J. H. BIRKINSHAW.

Determination of small amounts of iodide in presence of much chloride. F. KIEFERLE and E. ERBACHER (Biochem. Z., 1928, 201, 305—317).—Potentiometric titration with mercuric perchlorate gave exact results and was superior to titrations with silver nitrate and with palladium chloride. The method could not be applied to milk, for which it was originally intended.

J. H. BIRKINSHAW.

Micro-titration of iodine. A. STURM (Biochem. Z., 1928, 200, 273—279).—Comparative determinations of iodine by the colorimetric micro-method of Fellenburg (A., 1925, i, 329) and by the titrimetric method of Winkler (A., 1916, ii, 109) showed that the former gives low results in presence of moderate concentrations of salts. On the other hand, when the iodine content of the investigated solution is less than 3 γ , the change of colour of the starch iodide in the titration is delayed. A curve is given showing the variation of this delay with the iodine content of the solution (from 1 to 3 γ) and from this the error due to the delay may be corrected. Very small amounts of iodine cannot be determined by either method in presence of high concentrations of salts.

P. W. CLUTTERBUCK.

Methods for the determination of fat. G. ROSENFELD (Biochem. Z., 1928, 200, 280—288).—A large number of determinations of fat in a variety of dried tissues are carried out by the author's method, boiling with alcohol and extracting for 6 hrs. with chloroform (Centr. inn. Med., 1905, No. 14), and by other methods, special attention being directed to the effect on the result of choice of extraction solvent, the manner of its use, and the method of decomposition of the tissue. The author's method gives results 30% higher than that of Kumagawa and Suto and higher results also than those of Dormeyer, Liebermann, and Nerking. Soxhlet extraction of the dried ground tissue with chloroform removes more fat than extraction with either ether or light petroleum. Carbon tetrachloride extracts much less fat than chloroform and the extract is also very nitrogenous. Acetone gives good extraction.

P. W. CLUTTERBUCK.

Quantitative extraction of cholesterol and its esters from tissues and body fluids. E. MULLER (Z. Biol., 1928, 88, 132—138).—Of many methods only a modification of that of Fex (cf. A., 1920, i, 697) is found to be quantitative. Tissue in the moist state gives better extraction than that dried either in air or by treatment with plaster of Paris or anhydrous sodium sulphate. Serum or liver is treated with 2% sodium hydroxide solution and the solution

is extracted with ether in a continuous extractor. The extracted cholesterol is precipitated from alcoholic solution with digitonin.

E. BOYLAND.

Micro-determination of cholesterol. Y. HORIYE (Biochem. Z., 1928, 202, 403—408).—The titrimetric method of Szent-Gyorgyi (A., 1923, ii, 344) gives unsatisfactory results. His gravimetric method is much better, especially when the wash-liquor of Caminade (A., 1923, ii, 264) is used.

W. MCCARTNEY.

Colorimetric determination of lactic acid. B. MENDEL (Biochem. Z., 1928, 202, 390; cf. A., 1926, 212).—The concentration of the sulphuric acid should be kept constant and the colour allowed to develop at 25°. As little as 1 g. of lactic acid can then be determined.

W. MCCARTNEY.

Chlorophyll from tropical plants and its determination by means of the spectrograph. R. H. DASTUR and N. A. BUHARIWALLA (Ann. Bot., 1928, 42, 949—964).—A spectrographic method is described by means of which the chlorophyll content of single leaves can be compared. This method has been applied to a study of the correlation between the chlorophyll content and the water content of the leaves of a number of plants.

E. A. LUNT.

Membranes for ultra-filtration, of graduated fineness down to molecular sieves. J. W. MCBAIN and S. S. KISTLER (J. Gen. Physiol., 1928, 12, 187—200).—Cellophane has many advantages as a membrane for use in ultra-filtration. Its permeability may be increased by allowing it to swell in water, when it becomes permeable to most substances soluble in water but impermeable to all but the finest colloidal particles. Cellophane may be made permeable to solvents not completely miscible with water by allowing it to swell in water, and then replacing water by other solvents, if necessary through one or more intermediate solvents, e.g., by replacing the water first with ethyl alcohol and then with amyl alcohol. Cellophane membranes may be made impermeable to simple solute molecules by filtering through them a suitable colloidal material, e.g., cellulose dissolved in Schweitzer's reagent. A method is also given for the preparation of collodion membranes of graded permeability, and the properties of certain membranes of animal origin are discussed.

W. O. KERMACK.

Technique of electrodialysis. G. ETTISCH and W. EWIG (Biochem. Z., 1928, 200, 250—257).—A cell is described for electrodialysis, usable with any membrane, the middle chamber of which can be varied in size from 50 to 1 c.c., the being controlled by an indicator paper method.

P. W. CLUTTERBUCK.

Electrolysis in biochemistry. A. W. KEIL and H. G. SCHIECK (Z. Biol., 1928, 88, 153—156).—Electrolysis was efficacious in preparing hexone bases from protein hydrolysates, as found by Foster and Schmidt (cf. A., 1923, i, 963), in separating glycocholic acid from bile, and creatinine from meat extract. Up to 80 volts and 120 amp. are used, sometimes with water-cooling. Lead electrodes in place of carbon, and porcelain diaphragms, with or without celluloid, in place of gelatin treated with formaldehyde, give better results.

E. BOYLAND.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1929.

General, Physical, and Inorganic Chemistry.

Standard solar wave-lengths (3592—7148 Å.). R. BURNS, W. F. MEGGERS, and C. C. KIESS (U.S. Bur. Stand. J. Res., 1928, 1, 297—317).—The Bureau of Standards and the Allegheny Observatory have co-operated in measuring the wave-lengths in the international system of selected dark lines in the solar spectrum. In the octave 3592.027—7148.159 Å. 729 lines have been measured, the majority having a probable error less than 1 part in 4,500,000 parts. The corrections to be applied to Rowland's table are given.

C. J. SMITHIELLS.

Spectral intensities of radiation from non-harmonic and aperiodic systems. B. CASSEN (Proc. Nat. Acad. Sci., 1928, 14, 880—882).—Mathematical. The matrix components of the components of acceleration of a general quantum dynamic system are derived, from which expressions for the spectral intensities and spatial distribution of radiation can be obtained.

A. J. MEE.

Spectrographic investigation of spark discharge. U. NAKAYA and Y. FUJIOKA (Proc. Imp. Acad. Tokyo, 1928, 4, 464—466).—Four types of spark discharge are distinguished and respectively named three-part spark, short-spark, broken line spark, and flame-like spark.

W. E. DOWNEY.

Relationships of the hydrogen spectra under various conditions of excitation. I. The spectra in the oscillatory discharge and in the Paschen hollow cathode. Z. BAY and W. STEINER (Z. physikal. Chem., 1928, B, 1, 239—252).—At 0.05 mm. pressure the Balmer series, as far as the H_α line, and the complex line spectrum are strongly developed, but the continuous spectrum is relatively weak; as the pressure increases up to 3—7 mm. the continuous spectrum increases in intensity at the expense of the other types. The influence of current density is less characteristic, an increase from 50 to 500 milliamp. resulting in only a strengthening of the α lines of the red Fulcher bands and a simultaneous intensity change in the blue. In the hollow cathode the red Fulcher bands and the region 5700—6000 Å. are considerably weaker than in the Geissler tube, whereas the region 5600—5700 Å. and a region in the neighbourhood of the green Fulcher bands between 5303 and 5434 Å. are somewhat stronger. The distribution of intensities differs throughout the spectrum; the Balmer series are of similar intensities in the two tubes, but the continuous spectrum is appreciably weaker in the hollow cathode. In the oscillatory discharge the whole green region is weakened and the

red Fulcher bands, especially 6224 and 6327 Å., are considerably weakened; the α lines in the red are of increased intensity relative to the principal lines, an effect which is noticeable, although to a smaller extent, on increase of pressure in the ordinary tube. Characteristic of the oscillatory discharge spectrum is the strength of a group of lines between 5761 and 5836 Å., and also the relatively slight influence exerted by the walls of the discharge tube on the Balmer series, which are prominently displayed; the continuous spectrum is somewhat weakened. There is but little difference between the oscillatory discharge spectrum in the ordinary tube and in the hollow cathode. The significance of the results is discussed.

H. F. GILLBE.

"Forbidden" hydrogen lines. A. RUBINOWICZ (Physikal. Z., 1928, 29, 817—823).—A theoretical investigation of forbidden transitions in the simplest case, namely, the Lyman series of hydrogen, using the Schrödinger methods.

R. A. MORTON.

Study of the energy relations in the helium spectrum. I. C. CORNOG (Physical Rev., 1928, [ii], 32, 746—752).—The relations between the lines of the helium spectrum as functions of the accelerating $P.D.$ were investigated, in particular near the critical points of the gas. Photographs of the spectrum produced in an equipotential space using an equipotential cathode were studied photometrically to determine the variation of line intensities on passing the various critical potentials. The 54.2 volt point, at which double ionisation is first possible, is dealt with. Spectra were taken at intervals between 50 and 60 volts, and the plates showed a marked intensity maximum near 54.2 volts for all lines measured.

N. M. BLIGH.

Helium lines in stellar spectra. O. STRUVE (Nature, 1928, 122, 995).—Estimates of the intensities of the absorption lines 4472 and 4388 Å. for various stars are recorded. Mean values are 5.2 and 3.2, respectively. It is concluded that whilst the relative abundance of atoms in the mp^3 and mP levels is subject to considerable variations in different stars, the average ratio triplet/singlet in stellar spectra is not very different from that observed in the laboratory under normal pressures.

A. A. ELDRIDGE.

Striations in high-frequency discharges [in argon etc.]. S. P. MCCALLUM and W. T. PERRY (Nature, 1929, 123, 48—49).

Structure of the spectrum of ionised argon (A II). T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 771—779).—See this vol., 3.

Zeeman effect of the spectrum of ionised argon (A II). C. J. BAKKER, T. L. DE BRUIN, and P. ZEE-MAN (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 780—799).—See this vol., 3.

New type of low-frequency low-voltage discharge in a neon lamp. G. R. PARANJPE and K. SHESHADRIENGAR (Nature, 1928, 122, 959—960).

Auroral red line. J. KAPLAN (Proc. Nat. Acad. Sci., 1928, 14, 882—884).—The red "line" in the spectrum of the aurora borealis, previously supposed to be an unclassified oxygen line, has been re-examined and found to be a band belonging to the first positive group of nitrogen. The green line is probably the only oxygen line in the auroral spectrum. A. J. MEE.

Quantum explanation of the auroral green line based on measurements of the Zeeman effect. L. A. SOMMER (Z. Physik, 1928, 51, 451—470).—The magnetic resolution of the auroral green line $5577.350 \pm 0.005 \text{ \AA.}$, due to a field of 6080 gauss produced by a solenoid wound round the discharge tube, has been measured by means of a Fabry-Perot interferometer. The resolution corresponds, within the limits of experimental accuracy, with the normal Zeeman effect. From this it is deduced that the line belongs to the arc spectrum of oxygen, being given by the combination $2^1D_2 - 2^1S_0$, where 1D_2 and 1S_0 are deep-lying metastable terms. The line is thus explained on the quantum theory as due to a transition of small excitation potential and generally small probability. Analysis of the terms 1D_2 and 1S_0 indicates the existence of a singlet system in oxygen. This explanation of the green line also accounts for the existence of red and violet oxygen lines in the spectra of the aurora and of the night-sky radiation, these lines being of the same origin as the green line (viz., transition between deep-lying metastable terms).

E. B. ROBERTSON.

Spark spectrum of sulphur, S II, in the Schumann region. P. LACROUTE (Compt. rend., 1928, 187, 975—976; cf. A., 1928, 1065).—The new lines 1813.86, 1815.75, 1820.37 (?), 1820.81, and 1834.76 \AA. , forming part of the multiplet $b^4P - a^2P$, are recorded. Combinations between the terms b^4P and $4p^4D$ or a^2D were not detected, and the line 1993.37 \AA. corresponding exactly with the notation $4p^4P_3$ is an example of an exception to the rules of selection. J. GRANT.

Spectra of doubly-ionised arsenic, antimony, and bismuth. R. J. LANG (Physical Rev., 1928, [ii], 32, 737—745).—These spectra were partly analysed by the use of the irregular doublet law and the Moseley law and the published data for the two preceding elements of each isoelectronic sequence. In As III and Bi III the important terms from the configurations ns^2np , ns^2nd , $ns^2(n+1)s$ were located and, except the quadruplet P terms, those from the $nsnp^2$ configuration. ($n=4$ for As III, 5 for Sb III, and 6 for Bi III). In As III alone the $-P$ term of the np^3 configuration was found. The terms of Sb III located consist of some of those for the first three configurations only. N. M. BLYTH.

Fine structure of the sharp series triplet, $2^3P_{0,1,2} - 2^3S_1$, of optically-excited mercury radi-

ation. E. H. COLLINS (Physical Rev., 1928, [ii], 32, 753—760).—The possibility of varying fine-structure patterns by changing the method of excitation was investigated. Measurements were made with two Lummer-Gehrcke plates, first with mercury vapour only in the resonance tube, giving excitation by absorption of 4358, and, secondly, with mercury vapour and nitrogen present at 2—4 mm. pressure, giving excitation by absorption of both 4358 and 4047 \AA. For the first condition of excitation the wave-length differences are for 5461, 0; for 4358, —157, —107, —20, 0, +30, +46, +183; for 4047, —116, —62, —52, 0. For the second condition, for 5461 they are —235, 0; for 4358, —107, —20, 0, +30, +183; for 4047, —110, —62, —53, 0. Comparisons under the two conditions and also with the fine structure of the arc show differences making it evident that differences in fine structure exist depending on the method of excitation. N. M. BLYTH.

Spectra of mercury above the ionisation potential. L. R. MAXWELL (Physical Rev., 1928, [ii], 32, 715—720).—Experiments were made to separate the effects due to direct impacts and to recombination, and to determine which of these processes contributes the more to the production of the arc lines. Positive ions were withdrawn before they recombined by an electric field perpendicular to the beam of electrons having velocities greater than the ionisation potential. Contrary to the previous explanation of the complete arc spectrum above the ionisation potential, the intensity of the arc lines was found to be independent of the electric field, indicating that recombination contributes very little to the formation of these lines. Hence in addition to simple excitation the arc spectrum can be explained either as due to the return to the 1^1S_0 state by an electron displaced from an inner energy level to a virtual orbit while one of the electrons of the valency group falls in to fill the vacated level, or as due to a special type of recombination called initial recombination. Spark lines due to singly- and doubly-charged ions show a variation of intensity along their length such that it is possible to distinguish them from the arc lines. It is also possible to differentiate between the lines of the first and second spark spectra.

N. M. BLYTH.

Determination of the mean life for the 4797 \AA. spark line of doubly-ionised mercury. L. R. MAXWELL (Physical Rev., 1928, [ii], 32, 721—726; cf. preceding abstract).—The spark line 4797 \AA. due to ions moving in a particular direction through a beam of electrons was obtained showing a peculiar variation of intensity. Calculations were made to determine how the intensity of the line should vary with respect to its position across the beam and for different uniform and non-uniform electron current densities of the beam. Comparison with experiment showed that the line is produced at a single electron impact, the average life of the excited state being 4×10^{-7} sec. The mean life for the first order spark lines could not be measured, but was estimated to be less than 1×10^{-7} sec. N. M. BLYTH.

Wave-length measurements in the arc and spark spectra of hafnium. W. F. MEGGERS (U.S.

Bur. Stand. J. Res., 1928, **1**, 151—187).—Using hafnium salts of the highest available purity, the arc and spark spectra of hafnium were photographed with concave grating and prism spectrographs. The chief impurities encountered were niobium, zirconium, and titanium. Some 1500 lines between 2155.72 and 9250.27 Å. have been measured and ascribed to hafnium. Comparison of these results with the earlier measurements of zirconium spectra proves that hafnium was invariably present as an unrecognised impurity. It is suggested that 4093.17 Å. is the "raie ultime" for neutral hafnium atoms and 2773.37 Å. the one for ionised atoms. The stronger Hf II lines are identified with faint Fraunhofer lines in the sun's spectrum. W. E. DOWNEY.

Some multiplets of doubly-ionised lead. S. SMITH (Proc. Nat. Acad. Sci., 1928, **14**, 878—879).—The spectrum of doubly-ionised lead (Pb III) is investigated, and the lines arising from combinations between triplet terms are identified. A. J. MEE.

Broadening of spectral lines by self-absorption. H. C. BURGER and P. H. VAN CITTERT (Z. Physik, **51**, 1928, 638—651).—A relationship is deduced between the broadening of a line due to self-absorption and the absorption coefficient for the line. Measurements of the widths of some of the strong helium lines have been made with a Fabry-Perot interferometer for various values of the discharge current, and the widths of the lines without absorption found by extrapolation. The broadening of the line for each value of the discharge current is calculated, and hence the absorption coefficient. Helium is particularly suitable for the work on account of the large "Doppler-width" of its lines due to its small atomic weight. For the red line 2^1P-3^1D (6678 Å.) the absorption coefficient is very large, as is indicated by theory, only about 0.2% of the light emitted inside a discharge tube 2 mm. wide with a current of 20 milliamp. emerging. Measurements on the triplet lines are rendered difficult by multiplet structure, but resolution can be effected by cooling the discharge tube in liquid air. Most of the work was, however, carried out at the ordinary temperature, and no great accuracy is claimed. For the triplet line 5876 Å. the ratio of the absorption coefficients of the components P_2-D and P_1-D has been found to be about 100:50. E. B. ROBERTSON.

Extinction law for various atoms. H. SEYFARTH (Z. Krist., 1928, **67**, 422—429; Chem. Zentr., 1928, ii, 424).—Mathematical. A. A. ELDRIDGE.

Spectrum of aluminium in the extreme ultra-violet. E. EKEFORS (Z. Physik, 1928, **51**, 471—480).—The spectrum of aluminium in the extreme ultra-violet has been examined by means of a 1-metre vacuum spectrograph. Lines due to Al II and Al III have been identified between 480 and 1300 Å. These have been identified with the lines predicted by Paschen, and from them the values of the terms $6s$, $7s$, $6p$, and $7p$ for Al III have been calculated. In the Al II spectrum the triplet $3p_{1,2,3}-5s$, predicted by Paschen, has also been observed. Observations have been extended as far as 320 Å., but in this region the lines are too weak and diffuse to be measured accurately. E. B. ROBERTSON.

Interferometer measurements of wave-lengths in the vacuum arc spectra of titanium and other elements. C. C. KIESS (U.S. Bur. Stand. J. Res., 1928, **1**, 75—90).—More than 300 lines have been measured between 6743 and 2941 Å. for the vacuum arc spectrum of titanium by means of a Fabry-Perot interferometer. W. E. DOWNEY.

Quantitative spectroscopic analysis of alloys. Sensitivity of spectral lines. T. NEGRESCO.—See this vol., 161.

Efficiency of ionisation in hydrogen by positive-ion impact at 7000 volts. R. W. GURNEY (Physical Rev., 1928, [ii], **32**, 795—798).—If ionisation is not accompanied by transfer of kinetic energy, the method used, in which hydrogen at low pressure is bombarded with positive potassium ions, permits a comparison of the ionising efficiency with that of electron impact. It is concluded that either the efficiency is less than 1/150 of that of 50-volt electrons, or that ionisation is accompanied by transfer of kinetic energy. N. M. BLIGH.

Ionisation by collisions of the second kind in mixtures of oxygen with the rare gases. H. D. SMYTH and E. C. G. STUECKELBERG (Physical Rev., 1928, [ii], **32**, 779—783).—An extension of the work of Harnwell (cf. A., 1927, 604, 709). Mixtures of oxygen with argon, neon, and helium and incidental effects of water vapour were studied, and evidence of the following collisions of the second kind was obtained: (1) $A^+ + O_2 \rightarrow O_2^+ + A$. (2) $A^+ + H_2O \rightarrow H_3O^+ + A$ (very strong). (3) $H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$. (4) $Ne^+ + O_2 \rightarrow O^+ + O + Ne$. (5) $He^+ + O_2 \rightarrow O^+ + O + He$. The view is confirmed that the ratio O_2^+/O^+ is independent of the pressure, suggesting that the O^+ is formed directly by electron impact without the need of additional collisions, in contrast to the cases of hydrogen and nitrogen, but the exact value of the first ionising potential is uncertain. N. M. BLIGH.

Ionisation potentials and grating energies of atoms in the solid state. S. C. BISWAS (J. Indian Chem. Soc., 1928, **5**, 561—568).—Following on the assumption of the existence in an atom of a repulsive force varying inversely as some power of the distance, it is deduced that the product of the lattice energy and the fourth root of the compressibility of the elements will be a constant quantity dependent on the lattice type and on the unknown exponent of the repulsive force. The computed values of this product are approximately constant for elements in groups IA, IB, IIA, and IIB, with mean values 10, 7.3, 10, and 10.5, respectively. A method, based on thermochemical data, is given for the calculation of the heat of hydration of gaseous ions, which is independent of the concept of lattice energy.

F. G. TRYHORN.

Ionising potentials and far ultra-violet lines of light atoms. L. A. TURNER (Physical Rev., [ii], **32**, 727—736).—Theoretical. An extension and discussion of the work of Millikan and Bowen (cf. A., 1927, 912, 998). By interpolation, the ionising potentials of F and F⁺ are found to be 17.4 and 34.5 volts. These values improve the regularity of the values of $(\nu/R)^{1/2}$ corresponding with the ionising

potentials of atoms of the first short period. The energy for removal of a $2s$ electron from each of many of the atoms and ions of these elements (L_{11} levels for an atom) is calculated by use of the $s^2p^{n-1}-sp^n$ lines. The effect of removal of a $2s$ electron on the subsequent removal of a $2p$ electron is found for the boron, fluorine, and neon atoms to be an increase of $(v/R)^{1/2}$ by about 0.45. This is used to predict the wave-lengths of missing $s^2p^{n-1}-sp^n$ lines of C, N, N^+ , and O. New identifications of the far ultra-violet lines of magnesium are proposed and the third ionising potential is found to be 80.4 ± 1 volts. A pair of fluorine lines are tentatively identified as the $2s^22p^{5/2}P-2s2p^{6/2}S$ lines. N. M. BLIGH.

Critical potentials of light elements for simultaneous transitions. B. B. RAY and R. C. MAJUMDER (Nature, 1929, 123, 49).—The hypothesis of simultaneous transitions (Ray, A., 1928, 1296) is supported by Moseley curves for elements from iron to copper for such transitions as $2M_1, 2M_2, M_2+M_3, M_1-M_2, (M_2-M_1-M_3), \dots$, etc. A. A. ELDRIDGE.

Ionisation processes of iodine interpreted by the mass-spectrograph. T. R. HOGNESS and R. W. HARKNESS (Physical Rev., 1928, [ii], 32, 784—790).—The relative numbers of the ions I^+ , I_2^+ , and I_3^+ were measured as a function of pressure from 2×10^{-5} to 4×10^{-3} mm. In the primary process of electron collision I^+ and I_2^+ were both formed. I_2^+ was also formed in secondary collision from I^+ by the process $I^+ + I_2 \rightarrow I_2^+ + I$ and I_3^+ was formed from I_2^+ by the process $I_2^+ + I_2 \rightarrow I_3^+ + I$. Evidence and argument against other possibilities are given. The disappearing potentials of I^+ and I_2^+ were both 9.3 volts. Pressure-intensity relationships were determined for the ions I^- , I_2^- , and I_3^- which were found to exist in quantities comparable with those of positive ions. I^- is formed according to $I_2 + E^- \rightarrow I^- + I$. I_2^- and I_3^- are not formed by collision with free electrons, but as a result of secondary collisions of I^- and I_2^- , respectively, with I_2 molecules: $I^- + I_2 \rightarrow I_2^- + I$; $I_2^- + I_2 \rightarrow I_3^- + I$. N. M. BLIGH.

Hydrogen ions as the cause of the occurrence of spectral selectivity in the photo-electric effect for potassium. R. SUHRMANN (Physikal. Z., 1928, 29, 811—815).—Thoroughly purified and dried hydrogen brings about no increase in photo-electric sensitivity when introduced into a potassium cell. Using a specially designed cell, the introduction of H^+ ions is shown to effect an increase in sensitivity from 3.6×10^{-4} to about 2×10^{-2} Coul./g.-cal. The maximum photo-electric effect at $440 \mu\mu$ is regarded as due to a very loose union between potassium and ionised hydrogen at the metal surface only. R. A. MORTON.

New photo-electric effect. F. M. PENNING (Physica, 1928, 8, 137—140; Chem. Zentr., 1928, ii, 317).—A lecture experiment. The arc potential of a discharge tube containing neon (20 mm.) and argon (0.001%) increases by 50 volts when the gas is exposed to irradiation from another neon tube, thus confirming the theory of ionisation by metastable atoms. A. A. ELDRIDGE.

Surface layers on tungsten and the activation of nitrogen by electron impact. C. KENTY and L. A. TURNER (Physical Rev., 1928, [ii], 32, 799—811; cf. A., 1927, 913).—Traces of oxygen cause the formation of a layer which renders the tungsten filament insensitive to active nitrogen, whilst traces of hydrogen prevent formation of the nitrogen layer and remove it if already present. The amount of nitrogen adsorbed was shown to be of the order of magnitude necessary to produce a layer of single atoms. Activation of a stream of nitrogen reduces the thermionic emission from a tungsten filament in the stream, similarly to the effect of the active form of nitrogen produced in an arc struck in nitrogen. It seems probable that the activated form is atomic nitrogen. N. M. BLIGH.

Effect of water vapour on the mobility of gaseous ions in air. H. A. ERIKSON (Physical Rev., 1928, [ii], 32, 791—794).—Results additional to previous work (cf. A., 1927, 1002) indicate that an H_2O molecule gives up an electron to the final positive air ion and thus forms an H_2O^+ ion of a greater mobility. It is also shown that the reciprocal of the mobility bears a linear relationship to the humidity. N. M. BLIGH.

Directions of emission of photoelectrons. P. AUGER (Compt. rend., 1928, 187, 1141—1142).—The author's experiments (A., 1928, 453) are extended to the $K\alpha$ radiation of molybdenum (0.71 \AA.) in hydrogen containing a trace of argon, and the following values (*loc. cit.*) found: 77° , $\cos \omega$ 0.169, ρ 1.9, σ 1.32 (or 1.41 using the value of the K -level of argon). J. GRANT.

Liberation of electrons by means of X-rays. H. BEHNKEN (Physikal. Z., 1928, 29, 836—837).—The number of electrons liberated from an element under the action of homogeneous X-rays increases in general with increasing atomic number. R. A. MORTON.

Electron counting tube. H. GEIGER and W. MÜLLER (Physikal. Z., 1928, 29, 839—841).—A thin wire evenly covered with a semi-insulating layer is placed axially in a metal tube. At a suitable pressure of gas (e.g., air at 5 cm. of mercury) the electric field between wire and tube can be so regulated that each electron entering the tube at any place can be registered by means of a thread electrometer. The arrangement has the advantage of exposing an area up to 100 cm.^2 As examples of the use of the apparatus the measurement of potassium β -radiation and of cosmic rays are quoted. R. A. MORTON.

Dosage of cathode-particles from Lenard high-power tubes. R. THALLER (Physikal. Z., 1928, 29, 841—846).—A convenient condenser method is described for measuring the output from high-power tubes. R. A. MORTON.

Measurements on the ionisation of air by means of electron streams. W. SCHMITZ (Physikal. Z., 1928, 29, 847—848).—A new apparatus is described. R. A. MORTON.

Mean life-period of ions in the air above the sea. V. F. HESS (Physikal. Z., 1928, 29, 849—851).—A preliminary account of recent measurements at Heligoland on the origin of the ionisation of the air above the sea. R. A. MORTON.

Motions of electrons in ethylene. J. BANNON and H. L. BROSE (Phil. Mag., 1928, [vii], 6, 817—824).—The velocity in the direction of the electric force and the velocity of agitation of electrons in ethylene are both dependent only on the ratio of the electric force to the gas pressure. The result is thus similar to those obtained by Townsend and Bailey (A., 1922, ii, 43) in nitrogen and hydrogen, and Brose (Phil. Mag., 1925, [vi], 50, 543) in oxygen. Ethylene undergoes a change, demonstrated only by an increase in the velocities of the electrons, after exposure in the apparatus. It is suggested that this change is due to the action of ultra-violet radiation.

A. E. MITCHELL.

Energy losses of electrons in hydrogen. H. JONES and R. WHIDDINGTON (Phil. Mag., 1928, [vii], 6, 889—910).—Measurements of the energy losses of electrons in hydrogen are described. The most probable effect of a collision between a hydrogen molecule and an electron of velocity 50 volts or greater is the excitation of the C state. The probability of effective collision with 150-volt electrons is 1—2%. At low velocities energy losses of 8—9 volts are observed and it is suggested that these are associated with the dissociation of the molecule and the excitation of the continuous spectrum. The direct stimulation of the B_0 and other low-vibrational B states is considered to be impossible, since no loss of 11.1 volts was found. There is no definite indication that any energy losses are due to direct dissociation.

A. E. MITCHELL.

Spatial distribution of photoelectrons produced by X-rays. E. J. WILLIAMS, J. M. NUTTALL, and H. S. BARLOW (Proc. Roy. Soc., 1928, A, 121, 611—625).—Previous work on the longitudinal asymmetry and dispersion of the photoelectron distribution produced by X-rays is reviewed, with special reference to the demands of modern theory. The possible sources of error in the observation and measurement of photoelectron tracks are discussed: the wave-length of the radiation producing the photoelectrons, the method of examining the photographs, the effect of "choosing" tracks on which measurement is made, and the statistical errors arising from the inaccurate measurement of the directions of individual photoelectrons. The photo-electric emission from oxygen and nitrogen due to the absorption of X-rays of wave-lengths 0.54, 0.61, and 0.71 Å. has been studied experimentally. It is shown that the observed dispersion is adequately expressed by the $\cos^2 \theta$ law, and that the distribution observed indicates a "distortion" of the symmetrical $\cos^2 \theta$ curve corresponding with a value of the asymmetry factor σ of about 1.4.

L. L. BIRCUMSHAW.

Effect of the image force on the emission and reflexion of electrons by metals. L. W. NORDHEIM (Proc. Roy. Soc., 1928, A, 121, 626—639).—It has been shown (A., 1928, 452, 681) that the phenomena of electron emission or reflexion by metals can be dealt with by calculating the emission or reflexion coefficient for the electrons at the surface of the metal and integrating over all incident electrons according to Sommerfeld's conductivity theory; the cold emission in intense electric fields has been treated in

the same way. The surface of the metal is considered as a region of sudden variation of potential, which, according to the wave mechanics, produces a reflexion. In the previous papers, R , the reflexion coefficient, and D , the emission coefficient, have been calculated for certain idealised linear forms of the potential steps. In reality the form of the potential is a smooth curve, and in the present paper D and R are calculated for a field which more nearly approaches actual conditions.

L. L. BIRCUMSHAW.

Diffusion of electrons. E. RUPP (Physikal. Z., 1928, 29, 837—839).—See A., 1928, 1068.

Polarisation of light from hydrogen canal rays in an electric field. A. WEIGL (Naturwiss., 1928, 16, 1042).—The polarisation of the light from hydrogen canal rays in an electric field of which the lines of force are perpendicular to the direction of the rays falls to zero as the field strength is increased. For an angle of 45° between field and rays, and for a $P.D.$ of 600 volts, the originally elliptically polarised light becomes almost completely circularly polarised. The observations were made under a pressure of 0.1 mm. of mercury. For the higher pressures and voltages there is linear polarisation in the direction of the lines of force. These results are those which would be expected by Hanle's theory, but Rupp's experiments on this theory, which can explain only the elliptical polarisation of light in oblique fields, are not in agreement.

A. J. MEE.

Attempt to separate the isotopes of cadmium. A. A. SUNTER (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926, 4, 173—177).—After 13 evaporations of cadmium in a vacuum, in each of which half was removed, no difference in at. wt. (densimetric) was observed.

CHEMICAL ABSTRACTS.

Separation of the isotopes of chlorine. F. A. JENKINS (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926, 4, 93—98).—Fractionation of hydrogen chloride by diffusion against air at atmospheric pressure through porous pipe stems afforded a fraction in which the chlorine had at. wt. 35.418. By determination of at. wts. from the densities of hydrogen chloride solutions the efficiencies of diffusion apparatus can be compared.

CHEMICAL ABSTRACTS.

Isotope effect in the spectrum of chlorine. A. ELLIOTT (Nature, 1928, 122, 997).—Three strong bands and a fourth weaker band in the absorption spectrum of chlorine have been analysed, and the rotation constants for the normal and excited states of the chlorine molecule determined. The first three are due to absorption by $\text{Cl}^{35}\text{Cl}^{35}$ molecules, and the fourth by $\text{Cl}^{35}\text{Cl}^{37}$ molecules. The isotopic band due to $\text{Cl}^{37}\text{Cl}^{37}$ has not been observed. Absolute values of the upper vibration quantum numbers have been calculated.

A. A. ELDRIDGE.

Atomic weight of antimony from different sources. K. R. KRISHNASWAMI (J. Indian Inst. Sci., 1928, 11A, 161—172).—An amplification of a previous paper (A., 1927, 1120).

Ionisation measurements of γ -rays. J. A. CHALMERS (Phil. Mag., 1928, [vii], 6, 745—762).—It is pointed out that the ionisation produced in a

chamber is dependent only on primary γ -rays through the intermediary of the secondary β -rays and may not necessarily indicate a definite property of the γ -rays. The relative ionisations of the Ra-B and Ra-C γ -rays showed marked alterations when the electroscope lining was altered and the γ -ray beam kept the same. The results are in fair agreement with the accepted ideas on the absorption and scattering of β - and γ -rays and demonstrate the importance of an "ionisation function" in γ -ray measurements. It is concluded that ionisation measurements with γ -rays can give only approximate results in the determination of energy quantities. A. E. MITCHELL.

Heat of β - and γ -radiation of radium. A. DORABIALSKA (Rocz. Chem., 1928, 8, 475—485).—The heats of β - and of γ -radiation of radium in equilibrium with its degradation products are respectively 9.1 and 12.4% of the total heat of radiation.

R. TRUSZKOWSKI.

γ -Rays and the evolution of heat from radium and mesothorium. D. K. YOVANOVITCH (J. Phys. Radium, 1928, [vi], 9, 297—306).—The determination of the amount of mesothorium in a mixture containing it and its disintegration products by comparison with a radium standard involves a number of errors. A new calorimetric method is described for the determination which is not accompanied by these difficulties. The heat evolved by a preparation containing mesothorium in disintegrating into radiothorium is measured. The micro-calorimeter used is described. Mme. Curie's relationship for preparations containing radium and mesothorium in unknown proportions, viz., $R = \Delta/I$, where Δ is the ratio of heat evolved by the radium and mesothorium preparation to that evolved by a radium standard, and I is the intensity of the preparation measured in γ -rays in proportion to a radium standard, is verified experimentally. The ratio of mesothorium to radium is deduced for one particular preparation. A. J. MEE.

Determination of the direction of γ -rays. W. KOLHORSTER (Naturwiss., 1928, 16, 1044—1045).—The method makes use of two Geiger counters one behind the other, which will indicate when one and the same secondary electron traverses both counters. When this coincidence is obtained, the axis of the pair of counters gives the direction of the electrons concerned. A. J. MEE.

Absorption measurements with secondary β -rays. W. BOTHE and W. KOLHORSTER (Naturwiss., 1928, 16, 1045).—The arrangement of two Geiger counters used for the determination of the direction of γ -rays (cf. preceding abstract) may also be used for measuring the absorption of β -rays by placing a layer of absorbing material between the counters. A. J. MEE.

Radioactivity of the lighter elements. W. G. GUY (Abstr. Theses Univ. Chicago Sci. Ser., 1925—1926, 4, 87—91).—By a method sensitive to 0.003 of the β -radiation from potassium, the elements tantalum, tungsten, lanthanum, selenium, arsenic, tin, antimony, aluminium, and mercury, and compounds of sodium, calcium, barium, strontium, carbon, chlorine, bromine, copper, iron, lead, magnesium, manganese, nickel,

silver, and zinc were found to be non-radioactive. The activities of rubidium and potassium are in the ratio 1:39:1. The absorption coefficient in aluminium of the β -rays from potassium chloride under saturation conditions varies from 39.6 to 55.4 with aluminium thicknesses of 0.0135—0.0405 cm.; for rubidium salts it decreases from 593 to 522 with thicknesses of 0.0017—0.0051 cm. Certain organic compounds of potassium are anomalous.

CHEMICAL ABSTRACTS.

Thorium emanation. J. SEBOR (Chem. Listy, 1928, 22, 521—526).—The value of the disintegration constant for thorium emanation obtained from freshly prepared solutions differs from that for solutions which have been kept for some time, whence it is concluded that the discrepancies between the values obtained by different authors are not due to experimental errors. The constant increases slightly with the period of accumulation of the emanation.

R. TRUSZKOWSKI.

Variation with state of the optical properties of potassium and caesium. J. B. NATHANSON (J. Opt. Soc. Amer., 1928, 17, 343—349).—A glass cell containing the alkali mirror was heated by means of a small electric oven enclosing the mirror of metal, and observations were made at temperatures above and below the m. p. of the metals. When the metal changed from the solid to the liquid state, it was found that the angle of azimuth of restored plane polarisation, as well as the phase difference of the components of the light vector parallel and perpendicular to the plane of incidence, changed by only a small amount. After due allowance for the effects of strains in the glass cells, it was concluded that the optical properties of the liquid alkali surface are closely identical with those of the solid alkali surface.

W. E. DOWNEY.

Cosmic radiation and radioactive disintegration. L. R. MAXWELL (Nature, 1928, 122, 997).—Perrin's view that the disintegration of radioactive elements may be due to their absorption of cosmic radiations is probably incorrect, since the activity of a source of polonium was unchanged when shielded by being placed 1150 ft. below the surface of the earth. A. A. ELDRIDGE.

Assignment of quantum numbers for electrons in molecules. II. Correlation of molecular and atomic electron states. R. S. MULLIKEN (Physical Rev., 1928, [ii], 32, 761—772).—Revisions and amplifications are given of various results in a previous paper (cf. A., 1928, 1067). An attempt is made to determine the electronic states of the atomic products which would result by dissociation from each of a number of molecular states previously dealt with. Some suggested new values of the heats of dissociation for the normal states of certain molecules are: N_2 , 9.5; N_2^+ , 7.1; NO, 7.3; CO^+ , 8.3; NO^+ , 11.2 volts. The alkali and hydrogen halides are briefly discussed with reference to their electronic states and dissociation products. N. M. BLIGH.

Proportion of energy radiated by incandescent solids in various spectral regions. L. L. HOLLADAY (J. Opt. Soc. Amer., 1928, 17, 329—342).—Theoretical. It is shown that from a table of the

proportion of spectral energy omitted from a black-body radiator at a given temperature between wavelengths zero and λ , the proportion of energy ϕ , emitted in a given spectral region may be computed for a black-body radiator of any other temperature. Similarly, the energy emitted from the same spectral region by a non-black-body radiator having colour temperature T_c may be computed by multiplying the value of ϕ for a black-body radiator at temperature T_c by a simple factor G . W. E. DOWNEY.

Hydrogen chromosphere. W. H. MCCREA (Proc. Camb. Phil. Soc., 1928, 24, 506—515).—Stratton has found that the intensities of the lines of the Balmer series cannot be accounted for on the assumption of thermodynamic equilibrium for the hydrogen in the chromosphere. The extent of departure from thermodynamic equilibrium is calculated, the gas being supposed to be in radiative equilibrium with black-body radiation incident on it from one side only, mechanical equilibrium being assumed possible. It is found that this state could scarcely be distinguished from thermodynamic equilibrium, although it would be characteristic of a temperature slightly lower than that of the incident radiation. A. J. MEE.

Group-theory of the reciprocal action of atoms. W. HEITLER (Z. Physik, 1928, 51, 805—816).—Theoretical aspects of the chemical linking in polyatomic molecules are considered. R. A. MORTON.

Vector-framework of the atom according to quantum mechanics. E. FUES (Z. Physik, 1928, 51, 817—827).—Mathematical. R. A. MORTON.

Explanation of some properties of spectra in terms of the quantum mechanics of the spinning electron. J. VON NEUMANN and E. WIGNER (Z. Physik, 1928, 51, 844—858).—A first approximation has been made to a solution of the Schrodinger differential equation, taking into account the electron spin. Connexions with Landé's g -formula and the Burger-Dorgelo summation rules have been established. R. A. MORTON.

Scattering power of a bare nucleus according to wave mechanics. G. TEMPLE (Proc. Roy. Soc., 1928, A, 121, 673—675).—The scattering power of a nucleus is defined as the volume density of electricity in the scattered wave when the volume density of the incident wave is unity around the nucleus. The investigation of the scattering of an infinite plane wave by a bare nucleus (Mott, *ibid.*, A, 118, 542) involves the behaviour of a power series near its circle of convergence, and Mott's result is now obtained by a simpler and more direct method. L. L. BIRCUMSHAW.

Wiedemann-Franz law. E. GRUNEISEN (Z. physikal. Chem., 1928, B, 1, 379—383).—Polemical against Eucken (A., 1928, 825). M. S. BURR.

Evolution of the odd-numbered elements. W. V. HOWARD (J. Physical Chem., 1928, 32, 1725—1742).—Theoretical. Certain peculiarities in the mass numbers of the elements are pointed out and rules similar to those of Russell (A., 1923, ii, 748) are given for relations between the elements (cf. also Harkins, A., 1923, ii, 479). The first elements to form were those of even number between carbon and

nickel together with hydrogen and helium, after which evolution continued in three ways by the formation of (i) the higher even-numbered elements, (ii) those of odd numbers, and (iii) the elements between nitrogen and lithium. The lower isotopes of any element are shown to be less stable than the higher, which fact determines their abundance. The odd-numbered elements formed by a disintegration process of those of even number whereby one or both of the lowest (less stable) isotopes lost a positive charge from the nucleus and one electron. The formation of gold from mercury, the disintegration experiments of Rutherford and Chadwick, the composition of meteorites, and the formation of magmas are discussed in relation to this hypothesis. L. S. THEOBALD.

Transmutation of elements. L. THOMASSEN (Metall.-Wirts., 1928, 7, 703—708; Chem. Zentr., 1928, ii, 520).—Negative and inconclusive experiments designed to detect transmutation in an X-ray tube are described. A. A. ELDRIDGE.

Average life period of an atom. J. H. J. POOLE (Nature, 1928, 122, 960—961).—The life of a terrestrial atom is at least 10^{21} years. A. A. ELDRIDGE.

Average life period of an atom. H. JEFFREYS (Nature, 1929, 123, 87).—A polemical note. (cf. Poole, preceding). A. A. ELDRIDGE.

Sub-atomic energy. A. S. EDDINGTON (Mem. Manchester Phil. Soc., 1927—1928, 72, 101—117).—A lecture.

Electrical conductivity of stellar matter. S. CHAPMAN (Month. Not. Roy. Astron. Soc., 1928, 89, 54—57).

Viscosity in the stars. S. ROSSELAND (Month. Not. Roy. Astron. Soc., 1928, 89, 49—53).

Some difficulties in the spontaneous emission of radiation. L. GOLDSTEIN (Compt. rend., 1928, 187, 1285—1286).—The incompatibility which appears to exist between the two fundamental notions of the stationary state (Bohr-Sommerfeld) and the spontaneous change of configuration of the atom is discussed in the light of the Broglie-Schrodinger and Dirac analyses of undulatory mechanics. It is concluded that existing atomic structures provide no real physical reason for the possibility of the spontaneous emission of radiation. J. GRANT.

Structure of diatomic molecule spectra according to the quantum mechanics. E. WIGNER and E. E. WITMER (Z. Physik, 1928, 51, 859—888).—The method of the theory of groups has been applied to the deduction of the characteristics of a rotation band, and to electron terms in molecules. R. A. MORTON.

Interpretation of spectra of molecules. IV. F. HUND (Z. Physik, 1928, 51, 759—795).—An attempt is made to systematise molecular spectra on the basis of electron terms for molecules, analogous to those in use for atomic spectra (cf. A., 1927, 183, 495, 809). R. A. MORTON.

Visible radiation characteristics of incandescent oxides. (Miss) M. L. PHILLIPS (Physical Rev., 1928, [ii], 32, 832—839).—Energy radiated in the visible spectrum of various rare-earth and other oxides

and their mixtures when heated to bright redness between 1400° and 2000° Abs. by cathode-ray bombardment and by gas-air and oxygen-gas flames was measured by an optical pyrometric method. In general, linear relations were found between the logarithm of the reddish-blue intensity ratio and the reciprocal of the brightness temperature, and between the logarithm of the candle power emitted per unit surface area and the logarithm of the brightness temperature. Different modes of heating gave different radiation curves for the same oxide.

N. M. BLIGH.

Origin of the continuous spectrum of the hydrogen molecule. J. G. WINANS and E. C. G. STUECKELBERG (Proc. Nat. Acad. Sci., 1928, 14, 867—871).—The Rydberg denominators and their differences for the singlet and triplet *S*-terms of hydrogen and helium are calculated. It is shown that the continuous spectrum of hydrogen extending from the ultra-violet into the visible originates in the transition from any one of the excited triplet levels to the ground state of the system (1^3S).

A. J. MEE.

Continuous spectrum of hydrogen. F. H. NEWMAN (Phil. Mag., 1928, [vii], 6, 807—811).—The continuous spectrum of hydrogen has been excited in the gas at 10^{-3} mm. pressure by passing an intermittent discharge between two iron electrodes, one of which is maintained at a potential of 200 volts different from a third electrode. The spectrum varies according to the water vapour content of the gas, but in all cases only very few of the lines of the Balmer series appear, all of which have wave-lengths above 4102 Å. In the presence of water vapour the continuous spectrum is absent, being replaced by the water bands and some lines of the Balmer series. The limit of the continuous spectrum on the red side is approximately 4690 Å. The results indicate that the continuous spectrum arises from atomic excitation and not from the aggregation of molecules. By analogy with Franck's explanation (Ann. Physik, 1921, [iv], 44, 693) of the continuous spectrum of iodine, it is suggested that the continuous character of the spectrum corresponds with the continuous distribution of the initial kinetic energy of the assimilated electrons.

A. E. MITCHELL.

Molecular spectrum of hydrogen with wave-length determinations of 3667 lines between 24861 and 3314 Å. W. FINKELNBURG (Z. Physik, 1928, 52, 27—118).—An extensive research into the molecular spectrum of hydrogen between the line (4861 Å.) and the ultra-violet end of the spectrum (3314 Å.). The spectrum was obtained by means of a large Rowland's concave grating, giving on the photographs a dispersion of 1.98 Å. per mm. 3667 lines were investigated in the above range, the wave-lengths and intensities being recorded in a table. The calculated probable error in the wave-lengths is 0.0035 Å. for the stronger lines, and almost double this value for the weaker ones. More than 2000 lines have been investigated for the first time; 1052 of the lines were classified into three classes on the basis of the intensity differences of the lines with different conditions of excitation.

A. J. MEE.

Band spectrum of chlorine or hydrogen chloride. E. B. LUDLAM (Nature, 1929, 123, 86—87).—The band spectrum of chlorine burning at a silica jet in hydrogen has been observed. Hydrogen chloride is believed to be the emitter of the bands.

A. A. ELDRIDGE.

Emission band spectrum of chlorine. Y. OTA and Y. UCHIDA (Japan J. Phys., 1928, 5, 53—58).—The emission spectrum of rarefied chlorine excited by uncondensed discharges was studied with the object of measuring more exactly the wave-lengths of band heads and arranging them in new series schemes. The wave-lengths of 58 band heads between 487 and 392 μ were measured, and the bands classified into three systems, arranging each in a two-dimensional scheme of vibration quantum numbers. The spectrum radiated by electrically excited chlorine is quite different from the ordinary absorption spectrum.

N. M. BLIGH.

Emission band spectrum of bromine. Y. UCHIDA and Y. OTA (Japan J. Phys., 1928, 5, 59—66).—Wave-lengths of 80 band heads were measured; the band heads were analysed into two systems of two-dimensional schemes having common final states. The relation between the emission and absorption bands is discussed.

N. M. BLIGH.

New band system of carbon monoxide. R. K. ASUNDI (Nature, 1929, 123, 47—48).—Bands were observed at 3893.2, 3681.1, 4125.0, and 4380.3 Å.; with the exception of the band at 3681.1 Å., the bands have been analysed. The final state is identical with that of the Ångström bands. The bands are probably due to the transition $3^1S \rightarrow 2^1P$. The new system has only one n'' progression. Three of the bands are identified with those recorded by Duffenlack and Fox (A., 1928, 6).

A. A. ELDRIDGE.

New band system in carbon monoxide. G. HERZBERG (Naturwiss., 1928, 16, 1027—1028).—Using the electrodeless ring discharge with feeble excitation at 1 mm. pressure of carbon monoxide, the spectrum obtained shows the Ångström *a* bands very intensely, and also a second group of bands resembling, but not identical with, the Ångström *b* bands obtained with an ordinary discharge tube. The new system exhibits a constant frequency difference $\Delta\nu = 5004 \text{ cm}^{-1}$, but the data cannot be harmonised with Birge's classification (A., 1927, 184) of the Ångström bands. The final state in the new bands is the same as the initial state in the fourth positive group of carbon monoxide. A new electron state of the molecule is postulated.

R. A. MORTON.

Band spectrum of lithium. K. WURM (Naturwiss., 1928, 16, 1028).—Lithium vapour shows two absorption band systems in the visible, one in the red and the other in the blue-green. The fluorescence spectrum obtained by illuminating the vapour at 600—700° by means of white light is identical with the blue-green absorption system, but is better defined. The data are expressed by means of a formula from which the convergence of the levels for the unexcited molecule leads to the value 1.69 volts for the work of dissociation.

R. A. MORTON.

Infra-red spectra of ammonium salts in the transition region. G. HETTNER and F. SIMON (Z. physikal. Chem., 1928, B, 1, 293—300).—An apparatus for the measurement of optical absorption at low temperatures is described. It has been used for the examination of the infra-red absorption spectrum of ammonium chloride at wave-lengths 2—8 μ and at temperatures between -160° and 20° . The variation, with temperature, of percentage of light transmitted, or the isochromate, for particular wave-lengths, and also the transmission of different wave-lengths for the same temperature, have been determined. The absorption band at 7.1 μ becomes sharper as the temperature falls and moves a little towards regions of longer wave-length. The band at 5.6 μ also becomes sharper but moves towards regions of shorter wave-length. The band at 3.1 μ does not appear to undergo any change. Sharp breaks are found in the isochromate at about -30° . This corresponds with a similar break in the temperature-molecular heat curve of the salt and is to be ascribed to a change in the nuclear vibration bands due to a rearrangement of the ammonium radical at this temperature. The isochromate of ammonium sulphate for 7.15 μ has a break between -40° and -50° . The specific heat in this region has not been determined. M. S. BURR.

Near infra-red vibration spectrum of the carbonates. H. H. NIELSEN (Physical Rev., 1928, [ii], 32, 773—778).—Mathematical. The frequencies and intensities of the near infra-red absorption regions of the carbonate group are investigated theoretically, and the results are found to be in satisfactory agreement with experimental values.

N. M. BLIGH.

Infra-red absorption spectra of organic carbonates. F. K. BELL (J. Amer. Chem. Soc., 1928, 50, 2940—2950).—The absorption spectra of methyl, ethyl, propyl, butyl, isobutyl, isoamyl, and phenyl carbonates were investigated, the last-named being in the molten state. The absorption curves show the same general shape, particularly between 1 and 3 μ , and between 3.6 and 5 μ . Between 8.0 μ and 12.0 μ characteristic differences occur. A band characteristic of the carbonyl linking occurs at 5.75 μ , although intensity observations indicate that this band may really be two superposed bands. A broad band at 7.8 μ may result from a combination of frequencies characteristic of the carbon-hydrogen and carbonyl linkings. The intensity of the band at 3.4 μ increases with increasing mol. wt., but Bonino's empirical formula does not hold (cf. A., 1926, 775). It is suggested that the normal and *iso*-esters are to be regarded as two distinct types of carbonates.

S. K. TWEEDY.

Characteristic differentiation in the spectra of saturated hydrocarbons. F. S. BRACKETT (Proc. Nat. Acad. Sci., 1928, 14, 857—864).—The near infra-red spectra of saturated hydrocarbons have been investigated and some differentiation has been observed. The results can be used for the determination of the relative binding forces exerted on the hydrogen atoms when attached to the primary, secondary, and tertiary carbon atoms in a hydro-

carbon. There is probably complete identity in the binding forces between the hydrogen atoms and the carbon atoms in benzene, a conclusion which is in accord with the prevailing ideas of organic chemistry. The binding force in benzene is considerably greater than that in saturated hydrocarbons. A. J. MEE.

Diffuse molecular spectra. B. ROSEN (Z. Physik, 1928, 52, 16—20).—The spectrum of the sulphur molecule, S_2 , has been investigated between the wave-lengths 3000 and 5000 Å. The fading of the bands cannot always be explained on the assumption of inner collisions. Sometimes it is due to the increase in effective cross-section at higher amplitudes of nuclear oscillation. The dissociation energy of the sulphur molecule agrees with that obtained from the convergence limit of the band series. In the work of Henri on the subject both causes of fading of bands were present, viz., external collisions due to higher nuclear amplitude and inner collisions.

A. J. MEE.

Band spectra of aluminium hydride. E. BENGTSSON (Z. Physik, 1928, 51, 889—894).—The aluminium arc in hydrogen at atmospheric pressure emits a band system in the visible (4067—4568 Å.), but at low pressures new ultra-violet bands make their appearance. Two bands at 2229 and 2254 Å have been studied closely. Combination relations and a scheme of levels are applied to the entire band system. Electron terms, the moment of inertia, and the nuclear separation have been calculated.

R. A. MORTON.

Ultra-violet spectra emitted by a mixture of hydrogen and mercury vapour. H. JEZEWSKI (J. Phys. Radium, 1928, [vi], 9, 278—296).—Evidence has been obtained for a new system of ultra-violet bands in mercury hydride. These bands were analysed and tabulated, and equations have been calculated giving the line frequencies as a function of the quantum numbers. Changes in the distribution of intensity of the continuous spectrum of hydrogen, caused by the presence of metallic vapours, were attributed to the superposition of the continuous spectrum of hydrogen and the continuous spectra due to the dissociation of metallic hydrides. The high-order lines of the mercury series were investigated.

N. M. BLIGH.

Measurement of absorption spectra in the visible and ultra-violet regions. H. FROMHERZ (Z. physikal. Chem., 1928, B, 1, 301—323).—Calculations have been made of the optical requirements of an apparatus for the photographic measurement of absorption spectra with a rotating sector (cf. Scheibe and others, A., 1924, ii, 712) and a reciprocal light track to obtain a maximum light strength. The apparatus has been tested by measurements of the absorption spectrum of potassium chromate solution. The results are in good agreement with those of other investigators.

M. S. BURR.

Rare earths. XXX. Absorption spectra studies. L. L. QUILL and P. W. SELWOOD [with B. S. HOPKINS] (J. Amer. Chem. Soc., 1928, 50, 2929—2937).—The absorption spectra of the nitrates of praseodymium, neodymium, samarium, and erbium are specifically influenced by the presence of nitric

acid. The influence exerted on the absorption bands of neodymium nitrate by magnesium nitrate or rare-earth nitrates is similar to the influence exerted by nitric acid itself; hydrochloric acid produces quite a different effect on neodymium chloride. The deviations from Beer's law of neodymium nitrate solutions somewhat resemble the effect of the addition of nitric acid. Delauney's work (A., 1927, 847) cannot be confirmed. Absorption spectra are unsuitable for the qualitative analysis of mixed rare-earth salts, owing to the changes exerted by one salt on the absorption spectra of another. These changes, however, are quite distinct from those recorded by Harris and Hopkins during the concentration of illinium residues (A., 1926, 780, 810). S. K. TWEEDY.

Variation of extinction coefficient with temperature. B. K. MUKERJI, A. K. BHATTACHARJI, and N. R. DHAR (J. Physical Chem., 1928, 32, 1834—1840).—Measurements of the extinction coefficients for the absorption of light in the visible region of the spectrum have been made for the following solutions: chromic acid; chromic acid and oxalic acid or quinine sulphate in excess of sulphuric acid; eosin; potassium permanganate; copper sulphate; cuprous chloride (in hydrochloric acid); iodine in potassium iodide or alcohol; iodine and potassium or ammonium oxalate or ferrous sulphate; iodine and sodium nitrite or formate both in the presence of sodium acetate; and Rochelle salt and bromine in the presence of sodium acetate. The extinction coefficient increases linearly with a rise in temperature. This is explained by a diminution in the complexity of the solvates with a rise in temperature. It accounts for the increase in quantum yield with temperature frequently observed in photochemical reactions. L. S. THEOBALD.

Fluorescence of benzene and its infra-red absorption. V. POSEJPAL (Compt. rend., 1928, 187, 1046—1048).—Analogies of the Raman effect exist for fluorescence and phosphorescence spectra. The fluorescence spectra of benzene in the liquid or vapour state lead to the same infra-red absorption bands as those of the Raman spectra, and the calculated and experimental values are in good agreement. J. GRANT.

Polarisation of light emitted by fluorescence. P. SOLEILLET (Compt. rend., 1928, 187, 976—978).—An attempt is made to express as a function of a number of finite measurable quantities the change in polarisation of fluorescent light following a change in direction of the exciting radiation or of the ray studied. J. GRANT.

Permanent luminescence of certain uranium salts. R. COUSTAL (Compt. rend., 1928, 187, 1139—1140).—The permanent luminescence of uranium compounds is independent of time, temperature, and the previous insolation. Infra-red radiation is without effect. These results are shown only by crystalline salts in the solid state. The luminescence is most intense when the ultra-violet fluorescence is greatest, and if it is assumed to be a result of the radioactive properties of the salt, then the luminous yield may be shown by calculation to be of the order of 1%. J. GRANT.

Raman effect in aqueous solutions and the polarisation of the Raman lines. A. CARRELLI, P. PRINGSHEIM, and B. ROSEN (Z. Physik, 1928, 51, 511—519).—The Raman spectra of pure water and of aqueous solutions of nitric acid, sodium nitrate, sodium nitrite, ammonium nitrate, and ammonia on irradiation with a mercury arc have been photographed. The connexion between the frequency differences occurring in these spectra is discussed, and it appears that even apparently optically inactive nuclear vibrations come into action in the Raman effect. Photographs taken with solutions of sodium chloride and hydrochloric acid show, as is to be expected, no displaced lines; probably such lines are produced, even in crystals, only by the nuclear oscillation of the molecule groups and not by the oscillations of the complete ionic lattice which are detected by measurements on residual rays. The polarisation of single lines in the Raman spectra of toluene, benzene, and carbon tetrachloride is not uniform, but appears to possess widely differing values according to the part of the molecular mechanism concerned in the scattering.

E. B. ROBERTSON.

Ultra-violet Raman spectrum of water. I. R. RAO (Nature, 1929, 123, 87).—For every bright line in the mercury arc spectrum there is a Raman band in the spectrum of the light scattered by water.

A. A. ELDRIDGE.

Raman effect in X-ray scattering. K. S. KRISHNAN (Nature, 1928, 122, 961—962).

Critical potentials of molecular hydrogen. E. U. CONDON and H. D. SMYTH (Proc. Nat. Acad. Sci., 1928, 14, 871—875).—The main experimental observations concerned with the radiation from hydrogen when bombarded by electrons of different speeds are collected and explained theoretically. Curves showing the potential energy as a function of nuclear separation are drawn for five different electronic states of the hydrogen molecule. Below 11 volts the only possible transition which can occur is to the 1^3S state, but the probability of this is small. Hence only a little atomic hydrogen will be produced by electrons of this speed. A little above 11 volts, excitation to the 2^1S state is possible. Return from this state would give radiation which is photoelectrically active. Electrons of greater speeds can (1) excite directly to the 1^3S state, hydrogen atoms of large kinetic energy being formed, (2) excite to the 2^1S state, producing radiation, or (3) excite to the 2^3S state, which would revert to the 1^3S state, giving off a continuous spectrum and forming atomic hydrogen. Some or all of these probably occur in experiments in which a critical potential of 11.5 volts has been noted. For higher speeds the mechanism is uncertain. A. J. MEE.

Magnetic susceptibility of ozone. V. I. VAIDYANATHAN (Indian J. Physics, 1928, 3, 151—163).—Investigation was made using a retorsional method, with special attention to the elimination of errors due to temperature changes and current fluctuations. It is concluded from the results of a large number of experiments that ozone is diamagnetic.

N. M. BLYTH.

Absence of effect of an electric field on the magnetic susceptibilities of hydrogen chloride and nitric oxide. L. M. MOTT-SMITH (Physical Rev., 1928, [ii], 32, 817—823).—A repetition and extension of the work of Huber (cf. A., 1926, 1189). The susceptibilities investigated both parallel and perpendicular to an electric field of about 8000 volts/cm. were unchanged in every case. Classical theory indicates a 13% change in the susceptibility of nitric oxide measured along the electric field and due to the magneto-electric directive effect. The negative result perpendicular to the field is in agreement with quantum mechanics and favours the new quantum theory. N. M. BLIGH.

Diamagnetism and structure of ethylene. V. I. VAIDYANATHAN (Indian J. Physics, 1928, 3, 165—174).—Using a torsional method, the magnetic susceptibility of ethylene was investigated, and the gas was found to be diamagnetic with a molecular susceptibility of 15.3×10^6 , in fair agreement with Pascal's additive law. A regularity in the susceptibility of molecular and atomic configurations is observed, and it is found that for nitrogen, sulphur, ethylene, and argon the susceptibility is a linear function of the number of electrons. The structure of the ethylene molecule is discussed from the magnetic and chemical points of view. N. M. BLIGH.

Dielectric cohesion of the rare gases. M. CURIE and A. LEPAPE (Compt. rend., 1928, 187, 1283—1285).—The dielectric cohesions (α) of the rare gases prepared by Lepape's method (A., 1928, 970) and purified by fractionation over cooled coconut charcoal have been determined at 17° by a modification of the method of Bouty for various pressures and electric fields. In the series neon to xenon α increases, whilst the resonance and ionisation potentials decrease with the atomic number. Helium is an exception to the rule, and the experimental values for argon are considered untrustworthy. J. GRANT.

Refractive indices of a mesomorphic substance in the solid state. (MLLE.) J. ZADOC-KAHN (Compt. rend., 1928, 187, 1138—1139).—Measurements of the three principal refractive indices of solid *p*-azoxyanisole, crystallised from light petroleum, for λ 0.5893, 0.5780, and 0.5460, have shown that the birefringence is one of the highest known, ($n_p - n_r$) being 0.634, 0.649, and 0.696, respectively. The prism method was used, three prisms being cut with a microtome and arranged so that in the position of minimum deviation each prism furnished two out of the three indices. J. GRANT.

Refraction of helium and argon and its dependence on pressures lower than atmospheric. F. SCHACHERL (Publ. Fac. Sci. Univ. Masaryk, 1928, No. 98, 1—15).—From measurements of the refraction of helium and argon at pressures between 91 and 760 mm., and at 16°, it was found that, for argon, the influence of pressure on refraction was greater than its influence on the density of the gas, with the consequence that the specific refraction of argon, like that of polyatomic gases, increases with pressure. No conclusions could be reached from the results for helium. The refraction of argon, at normal temper-

ature and pressure, and for wave-length 5462.3 Å., is $(n-1) = 282.7 \times 10^{-6}$. The rate of increase with pressure of the specific refraction of oxygen is exactly twice that obtaining in the case of argon.

F. G. TRYHORN.

Refractivities of carbon monoxide, nitrogen, and nitrous oxide, and their dependence on pressures lower than atmospheric. F. SCHACHERL (Publ. Fac. Sci. Univ. Masaryk, 1928, No. 99, 1—29).—The refractivity of carbon monoxide, nitrogen, and nitrous oxide has been measured at 16°, and at pressures between 91 and 760 mm. For carbon monoxide and nitrogen the relationship between the displacement of the interference fringes and the pressure is given by $ds/dp = \alpha_1 + \beta_1 p$, whilst for nitrous oxide the same relationship is expressed by $ds/dp = Bp^2$. For light of wave-length 5462.3 Å., the refractivities, expressed as $(n-1) \times 10^6$, are for carbon monoxide, nitrogen, and nitrous oxide, respectively, 336.89, 302.83, and 507.79. For nitrogen, as for all other gases previously measured, the value of $p\beta$, where $\beta = \beta_1/2\alpha_1$, in the equation $n-1 = Kp(1 + \beta p)$ is constant for pressures up to 1500 mm. For all gases so far investigated the values of β are greater than those of the coefficient β_p in the equation $\rho = Kp(1 + \beta_p p)$ representing the relationship between pressure and density. The specific refraction of these gases therefore increases with pressure, and with the exception of that of carbon dioxide and of nitrous oxide is proportional to $\log_e p$. The relationship between specific refraction and pressure cannot be expressed as an additive function of the atomic composition of the gas, although an additive relationship holds for gas mixtures. The pairs of isosteres CO₂, N₂O and N, CO show analogous relationships between pressure and their specific refraction.

F. G. TRYHORN.

Dipole moments of some methane and ethane derivatives. J. W. WILLIAMS (Z. physikal. Chem., 1928, 138, 75—84).—The dielectric constants and densities at 25° have been measured of ethylene chloride, bromide, iodide, and cyanide, methyl and ethyl iodide, ethylene glycol, acetonitrile, propionitrile, and benzonitrile in benzene solution. The effect on the dipole moment of a molecule of the introduction of a substituent group is deduced by regarding the dipole moments of the above compounds as due to the substituent groups alone and considering the rest of the molecule as non-polar. Calculations have been made of the angular distortion produced in the tetrahedral symmetry of the carbon atoms by the introduction into the molecule of a given substituent.

F. G. TRYHORN.

Optical properties of some artificial minerals. P. GAUBERT (Bull. Soc. Franç. Min., 1927, 50, 504—515; Chem. Zentr., 1928, ii, 334—335).—Values of n_D for various artificial minerals are: MgAl₂O₄ (coloured red by chromium or blue by cobalt) 1.721; gahnite, ZnAl₂O₄ (coloured red by chromium), 1.80; corundum, Al₂O₃, w 1.7689, ϵ 1.7609, d 3.988; 3Ca₃(PO₄)₂.CaCl₂, w 1.642, ϵ 1.637; 3Sr₃(PO₄)₂.SrCl₂, w 1.658, ϵ 1.664; 3Ba₃(AsO₄)₂.BaCl₂, w 2.14, ϵ 2.13; monetite, CaHPO₄, n_a 1.623, n_r 1.604, d 2.928 (trigonal); rhombic SrHPO₄, n_a 1.625, n_r 1.608; BaHPO₄, n_a 1.635, n_r 1.617; iron-leucite 1.619, d 2.59; potass-

ium silicoberyllate 1-523, d 2-531; sodium silicoberyllate, $\text{Na}_5\text{Be}_6\text{Si}_{14}\text{O}_{37}$, 1-545—1-532, d 2-552; sodium silicotitanate, $\text{Na}_4\text{Si}_4\text{Ti}_5\text{O}_{20}$, n_a 1-655, n_γ 1-623, d 2-88. A. A. ELDRIDGE.

Chemical constitution and rotatory power. M. BETTI and G. B. BONINO (Atti II. Cong. Naz. Chim. pura Appl., 1926, 1244—1247; Chem. Zentr., 1928, ii, 523).—When the fourth root of the optical rotatory power of the condensation products of 1-aminobenzyl- β -naphthol with benzaldehyde and its substitution products is plotted against the negative logarithm of the dissociation constant of the acid corresponding with the aldehyde, analogous structures (e.g., m -derivatives) give values falling on the same curve. The results can be used for determination of dissociation constants of acids.

A. A. ELDRIDGE.

Action of heat and loss of water on the optical properties of heulandite. P. GAUBERT (Compt. rend., 1928, 187, 1057—1059; cf. this vol., 16).—If, as the author's experiments indicate, the rise of temperature of heulandite heated in an inert liquid produces a rotation of the plane of the optical axes and increases their divergence, then the gradual loss of a half-molecule of water brings the axes together again until the crystal is uniaxial, and then causes them to open out perpendicular to the original plane. Consequently, below the temperature (109°) at which water is first evolved, the optical properties depend on the water content. Optical anomalies indicate the presence of sectors or banded structures without changing the sense of the phenomena. J. GRANT.

Influence of solvents on rotation of optically active compounds. XXVI. Optical activity of malic acid in presence of sodium molybdate. T. S. PATTERSON and C. BUCHANAN (J.C.S., 1928, 3006—3019).—The rotation of malic acid in the presence of sodium molybdate has been examined. Solutions were made up containing a fixed amount of the acid with varying amounts of the salt and the rotation was determined for several colours. With increase in the concentration of the salt the rotation thrice becomes zero and shows two minima and a maximum. The rotation of several solutions was examined at different temperatures. It was found that, in general, the temperature-rotation curves are of the same nature as those obtained with other optically active substances in various solvents. The change in rotation with rise of temperature is, as a rule, similar to that obtained by decreased concentration of sodium molybdate. Similar experiments were made with two other concentrations of malic acid; with dilute solutions the rotation at the second minimum has a positive value, whilst with the more concentrated solutions the minimum rotation has a negative value. The rotation of the solid derivative obtained from two molecules of malic acid and one molecule of sodium molybdate was also examined for six colours of light at different temperatures.

H. INGLESON.

Rotation dispersion and circular dichroism of caryophyllene nitrosite. S. MITCHELL (J.C.S., 1928, 3258—3260).—The rotatory dispersion of caryophyllene nitrosite in benzene has been examined and

found to show the Cotton effect. From measurements of the absorption spectra, using both right- and left-handed circularly polarised light, it has been shown that this substance exhibits circular dichroism.

J. L. BUCHAN.

Quantum theory of molecule formation. H. LESSHEM (Z. Physik, 1928, 51, 828—841).—A revised theory is submitted showing closer agreement with chemical notions, in particular with the position of the rare gases in the periodic table.

R. A. MORTON.

Molecular structure and chemical linking. F. HUND (Physikal. Z., 1928, 29, 851—852).—Preliminary. Two-centre systems are considered using as examples CN, LiH, and He_2 term schemes.

R. A. MORTON.

Structure of water. S. PENNYCUICK (J. Physical Chem., 1928, 32, 1681—1696).—Theoretical. The marked activity of the auxiliary valency fields of both hydrogen and oxygen in water provides a simple explanation of many of the unique properties of this substance. The structure of the water molecule is best represented by the tetrahedron with the electrons in pairs at the tetrahedral corners (cf. Huggins, A., 1926, 458). The resulting polarity enables the water molecules to unite with other molecules solely by means of its own negative electron pairs and its positive hydrogen nuclei.

The difference between true association and the quasi-association (van der Waals, Proc. K. Akad. Wetensch. Amsterdam, 1910, 13, 107) of normal liquids is discussed, and in conformity with the X-ray structure of ice, it is concluded that the associated molecule in liquid water is the molecule $(\text{H}_2\text{O})_6$ and that water is a mixture of relatively stable compound molecules of a benzene-ring structure in a normal solvent. The view that water is a mixture of $(\text{H}_2\text{O})_3$, $(\text{H}_2\text{O})_2$, and H_2O molecules is untenable.

Evidence derived from the effect of pressure on aqueous systems, the maximum density, the latent heat, the dielectric constant, and other properties of water is discussed and is shown to favour ring association, and the abnormal activity of the auxiliary fields of the oxygen and hydrogen atoms.

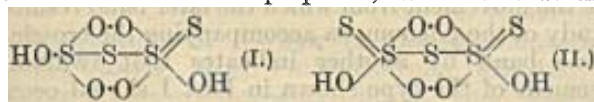
L. S. THEOBALD.

Size of ions and its influence on the properties of salt-like compounds. L. PAULING (Z. Krist., 1928, 67, 377—404; Chem. Zentr., 1928, ii, 318).—The forces operating between ions are discussed from the point of view of quantum mechanics and a simple approximate expression is given for these forces as a function of the size of ions. The derivation of interionic distances to a first approximation by neglect of deviations from additivity is discussed. The influence of radius relationships on physical properties of the alkali halides, and on the axial ratios of crystals of the rutile type and of anatase, is discussed, together with the question of the relative stabilities of the various crystal structures.

A. A. ELDRIDGE.

Constitution of the polythionic acids. J. A. CHRISTIANSEN (Forh. III nord. Kemistmotet, 1928, 177—179).—The existing formulæ for tetra- and penta-thionic acids are criticised. The reactions of these acids are best explained by the assumption

that they contain a six-membered ring, and the formulæ I and II are proposed; The fact that the



vapour of sulphur trioxide is bimolecular lends support to these views.

H. F. HARWOOD.

Constitution of the boron hydrides. F. EPHRAIM (Helv. Chim. Acta, 1928, 11, 1094—1097).—It is shown that the formation of the boron hydrides may be explained satisfactorily on the octet theory of distribution of the outer electrons.

R. N. KERR.

Effective cross-section of neutral molecules of gases with respect to slow electrons. C. RAMSAUER (Physikal. Z., 1928, 29, 823—830).—A summary of recent work.

R. A. MORTON.

Effective cross-section and molecular structure. E. BRÜCHE (Physikal. Z., 1928, 29, 831—834).—A review (cf. A., 1927, 4, 181, 492, 1011, 1119; 1928, 453).

R. A. MORTON.

Share of "reflexion" in the total effect of the action of slow electrons on gas molecules. R. KOLLATH (Physikal. Z., 1928, 29, 834—836).—The effective cross-sectional area arises from three factors: (a) reflexion without loss of velocity, (b) absorption, temporary or permanent, (c) velocity loss, with or without deflexion. In an attempt to ascertain the relative importance of these factors it is shown that the first rising portion of the cross-section curves (starting from low velocities) in the argon group and the first maxima in the nitrogen and carbon dioxide groups arise from factor (a). With higher velocities factor (b) appears. In some cases the curve connecting cross-sectional area with electron velocity in volt^{1/2} shows two maxima; the first is always due to "vertical" reflexion without velocity loss, but no clear evidence is available as to the origin of the second, or as to the role of factor (c).

R. A. MORTON.

Determination of the wave-length of the $K\alpha$ line of carbon. B. B. WEATHERBY (Physical Rev., 1928, [ii], 32, 707—711).—A simplified form of vacuum spectrometer with line grating was used, connected directly with the X-ray tube, and based on Compton's theory of a line grating used at grazing incidence with the X-rays striking within the angle of total reflexion. The region investigated lay between the soft X-rays and the extreme ultra-violet. Measurements made for varied angles of incidence and distances from grating to plate gave a mean value of 45.4 Å. for the $K\alpha$ carbon line.

N. M. BLIGH.

Total reflexion of X-rays from nickel films of various thicknesses. H. W. EDWARDS (Physical Rev., 1928, [ii], 32, 712—714).—Measurements were made of the critical angles for nickel sputtered films of various thicknesses. The maximum value agrees with that calculated from the Lorentz dispersion formula. It is concluded that the values decreasing to a minimum found for thinner films are not due to abnormal values of the density of nickel in these films, but that the phenomenon of total X-ray

reflexion requires an electron layer of definite thickness and is not a superficial effect. Evidence was found that the density of silver films is independent of the method of deposition.

N. M. BLIGH.

Study of physical purity by X-ray powder spectrograms. II. N. H. KOLKMEIJER (Z. physikal. Chem., 1928, 138, 311—312; cf. A., 1928, 1078).—Polemical against Levi (A., 1928, 1079). The fact that yellow and red mercuric oxide give the same X-ray spectrogram does not prove that there is only one form. There may be red and yellow oxide in each in different proportions.

M. S. BURR.

Are characteristic X-rays polarised? E. O. WOLLAN (Proc. Nat. Acad. Sci., 1928, 14, 864—867).—The polarisation of characteristic X-rays has been determined by a method using integrated intensity measurements. It is found that the $K\alpha$ lines of molybdenum are not polarised to a greater extent than 1%.

A. J. MEE.

Polarisation of characteristic X-rays. H. MARK and K. WOLF (Z. Physik, 1928, 52, 1—7).—By means of a new photographic method it has been shown that there is no polarisation of the characteristic K-radiation from copper, within an experimental error of about 1%.

A. J. MEE.

Coloration of kunzite and hiddenite by X-rays. P. L. BAYLEY (J. Opt. Soc. Amer., 1928, 17, 350—355).—Kunzite, a pale pink variety of spodumene (lithium aluminium silicate), turns bluish-green under the action of X-rays and resembles hiddenite, another variety of spodumene. Spectrophotometric examination of irradiated kunzite and hiddenite from 3000 Å. to 4.5 μ shows that these two green varieties have not the same absorption curve and are not identical.

W. E. DOWNEY.

Structure of the Compton shifted line. J. W. M. DUMOND (Proc. Nat. Acad. Sci., 1928, 14, 875—878).—Special apparatus is described for investigating the structure of the Compton shifted line. The experimental curves are compared with those calculated from Jauncey's theory. The agreement for scattering by aluminium is good, but the experimental distribution for beryllium is wider than the theoretical. Two faint lines also appear at wave-lengths 768 and 777 X., the shift of which is too great for them to be regarded as Smekal transitions, and the lines do not correspond with the characteristic fluorescent radiation of any known element. The possibility of accounting for the extra breadth of the shifted line by considerations of double scattering is being investigated.

A. J. MEE.

K X-Ray absorption edge of iron. G. A. LINDSAY and H. R. VOORHEES (Phil. Mag., 1928, [vii], 6, 910—920).—The multiple structure of the X-ray absorption edge of iron has been examined both for the metal and for compounds. The principal edge moves to shorter wave-lengths with increase of valency. With mechanical mixtures of bi- and trivalent iron the absorption patterns of the two ions are superimposed. In the case of the compound lepidomelane in which both ions occur no such superposition occurs, suggesting that in such compounds the iron ions are all alike. The multiple structure

extends over a wide range, the magnitude of which is explained by the ejection of electrons from the outer orbits together with the *K*-electron.

A. E. MITCHELL.

Quantum efficiency for the action of X-rays on silver bromide. II. J. EGGERT and W. NODDACK. (*Z. Physik*, 1928, 51, 796—804; cf. A., 1927, 841, 1154).—It is shown for two additional types of emulsion that each quantum of absorbed X-radiation sets free about 1000 atoms of silver, all within a single grain. The quantum efficiency in terms of grains rendered developable is about 1, and for the wavelength 0.5 Å. this result is independent of the type of emulsion. With smaller quanta, the number of liberated silver atoms in each grain becomes less, so that with ultra-violet and visible light more quanta will be needed to make the grain developable. With harder X-rays, the primary photoelectron may reach a neighbouring grain and two or more may be rendered developable by each absorbed quantum. The discrepancy between the data of March (A., 1928, 492) and the authors is discussed. R. A. MORTON.

Mode of formation of Neumann bands. I. Mechanism of twinning in the body-centred cubic lattice. II. Evidence that the bands are twins. III. Movement from which the twinning results. S. W. J. SMITH, A. A. DEE, and J. YOUNG (*Proc. Roy. Soc.*, 1928, A, 121, 477—486, 486—500, 501—514).—I. Artificial or mechanical twinning may be regarded as the result of a movement within a crystal by which the orientation of the atoms, in a band bounded by parallel planes, becomes a mirror image with respect to these planes of that in the unchanged matrix on either side. An examination has been made of the atomic movements which can occur under the influence of a transient shearing stress in a single crystal possessing a body-centred cubic lattice. It is shown that the mirror image relation can result from each of several different atomic movements with respect to the same twin plane.

II. The simplest way of testing whether the twin relationship exists between the orientation in a band and that in the neighbouring matrix is to make a section of the material perpendicular to the {112} plane to which the band is parallel and to compare the pits produced simultaneously on band and matrix by suitable etching. In such case, the etch-pits in the band and those in the matrix, if similarly developed, should be mirror images of one another in planes represented by the traces of the bands. For the meteorites examined, the most suitable etching agent was found to be a dilute solution of copper ammonium chloride. A number of photomicrographs, illustrating the results obtained, are reproduced.

III. Examination of the etching pits alone is not sufficient to fix the precise character of the movement from which the twinning results. For this purpose, the extent and the direction of the movement of the matrix on one side, with respect to that on the other, when a band of measurable width is formed must be determined. Since all the bands are not formed simultaneously, the tracks of some must pass through the matrix across the tracks of others formed earlier. The displacement of the parts of an earlier track

with respect to one another, produced during the formation of a later band, can then be used to determine the movement from which the later band results. A study of the phenomena accompanying the crossing of one band by another indicates that twinning movement of the type shown in Part I should occur most easily. L. L. BIRUMSHAW.

Diffraction of cathode rays by calcite. S. NISHIKAWA and S. KIKUCHI (*Proc. Imp. Acad. Tokyo*, 1928, 4, 475—477).—An extended account of work already published (A., 1928, 1312).

W. E. DOWNEY.

Diffraction of cathode rays by mica. IV. S. KIKUCHI (*Proc. Imp. Acad. Tokyo*, 1928, 4, 471—474; cf. A., 1928, 1174).—Using monochromatic radiation, it is found that the net-like pattern produced by thin mica is due to the diffraction by a two-dimensional lattice, of which the scattering centres are arranged in an equilateral triangle network.

W. E. DOWNEY.

Measurement of absolute intensity of X-rays. M. STEENBECK (*Ann. Physik*, 1928, [iv], 87, 811—849).—A method is described for the determination of the absolute number of quanta which pass in unit time through the area of cross-section of a beam of X-rays. The number of quanta absorbed over a given track are counted as ions, the rays being made to pass perpendicular to the lines of force of a homogeneous electric field, and the resulting ions counted by means of a Geiger counter. It is necessary to ascertain the fraction of ions registered by the counter. The ionising power of a monochromatic ray was measured and its intensity obtained in this way. For the formation of ionic doublets the necessary energies for Cu-*K*α and Cr-*K*α are practically the same, and are in agreement with other determinations. The possible errors in the method are discussed.

A. J. MEE.

X-Ray studies in the system lead-thallium. F. HALLA and R. STAUFER (*Z. Krist.*, 1928, 67, 440—454; *Chem. Zentr.*, 1928, ii, 319).—The lattice parameter of pure lead (using sodium chloride for comparison) is 4.924 ± 0.010 Å. The constant for mixed crystals containing 35 at.-% Pb (i.e., at maximum m. p.) is 4.871 ± 0.007 Å. The cubic face-centred unit cell contains four molecules. The m. p. maximum is therefore not due to compound formation.

A. A. ELDRIDGE.

X-Ray studies of the univalent metal perchlorates. W. BÜSSEM and K. HERRMANN (*Z. Krist.*, 1928, 67, 405—408; *Chem. Zentr.*, 1928, ii, 318).—The lattice constants of rhombic bipyramidal perchlorates are: ammonium: *a* 9.22, *b* 5.80, *c* 7.42 Å.; potassium: *a* 8.85, *b* 5.66, *c* 7.24 Å.; rubidium: *a* 9.27, *b* 5.81, *c* 7.53 Å.; caesium *a* 9.82, *b* 6.00, *c* 7.79 Å.; tellurium: *a* 9.42, *b* 5.88, *c* 7.50 Å. The unit cell contains four molecules; space-group *V*_h¹⁶.

A. A. ELDRIDGE.

X-Ray studies on the nitrides of iron. G. HAGG (*Nature*, 1928, 122, 962; cf. A., 1928, 605, 1081).—All preparations with maximum nitrogen content give the same photograms which are ascribed to a new phase, ζ, in which the iron atoms form an orthorhombic lattice having *a* 2.758, *b* 4.819, *c* 4.419 Å.

Close relations exist between the ϵ and ξ phases. The latter is probably the nitride Fe_2N .

A. A. ELDRIDGE.

Diffraction of X-rays in liquids containing heavy atoms. J. A. PRINS (*Nature*, 1929, 123, 84). Heavy atoms are introduced into a liquid, and their mutual arrangement is determined by an X-ray spectrographic method. Application to solutions of iodine ions in water, and of carbon tetrachloride and methylene iodide in benzene supported the author's theoretical views, the amount of scattering at small angles being considerable. At higher concentrations of iodine ions, however, the effect was reversed; in explanation, electrostatic repulsion of the iodine ions is suggested. The method has also been applied to the study of long-chain organic acids.

A. A. ELDRIDGE.

Energy levels of the elements chromium to lanthanum in the X-ray region. F. P. MULDER (*Arch. Néerland.*, 1928, 11, 167—205; cf. Coster and Mulder, A., 1926, 987).—A spectrograph of the Siegbahn type was used, having an analysing crystal of gypsum which oscillated automatically through an angle of $1-2^\circ$, this being necessary to eliminate the defects of the crystal. The source of the X-rays was a modified Siegbahn tube with a tungsten anticathode. The substance to be examined was placed in the path of the rays in the form of a screen. The absorption of a few of the substances was measured by special methods which are given. In the L_I , L_{II} , and L_{III} series the wave-lengths of the discontinuities for a number of elements have been measured to within about 2X. From these values, and those found by other workers, the energy levels L_I , L_{II} , L_{III} , M_I , M_{II} , M_{IV} , N_I , N_{II} , N_{III} , N_{IV} , N_V , O_I , and $O_{II, III}$ have been calculated for the elements from chromium to lanthanum. The probable sources of error are discussed and their magnitudes indicated. Curves are given showing the relation of $\sqrt{\nu}/R$ to the atomic number for the various Röntgen terms and explanations are given for the breaks in these curves. It is found that the X-ray method gives lower values for the energy levels than does the optical method, for in the latter case the atoms are free, whilst in the former they are combined in a crystal.

J. L. BUCHAN.

Lattice dimensions of spinel (MgAl_2O_4). E. POSNJAK (*Amer. J. Sci.*, 1928, [v], 16, 528—530).—Examination of a sample of artificially prepared spinel by the powder method showed the length of the edge of the unit cube containing eight MgAl_2O_4 molecules to be 8.03 ± 0.01 Å., whence $d_{\text{calc.}} = 3.628$.

R. CUTHILL.

Crystal structure of phosphides of bivalent and trivalent metals. L. PASSERINI (*Gazzetta*, 1928, 58, 655—664).—X-Ray examination of the phosphides of zinc, cadmium, and magnesium shows that these compounds crystallise in the cubic system with a non-ionic structure of the zinc arsenide type (cf. A., 1928, 1313), the elementary cell containing two molecules of M_3P_2 . For the three phosphides in the above order the values of a are 5.68, 6.06, and 5.92 Å., and of d 4.678, 5.956, and 2.162, respectively. The distances between the metal and phosphorus atoms are Zn—P 2.46, Cd—P 2.62, and Mg—P 2.56 Å.,

from which the values 1.13, 1.13, and 0.94 Å., respectively, are calculated for the radius of the neutral phosphorus atom. Aluminium phosphide has a cubic structure of the zinc-blende type with a unit cell containing four molecules of AlP ; $a = 5.42$ Å. and $d_{\text{calc.}} = 2.424$. The distance Al—P is 2.34 Å., which gives a value of 0.91 Å. for the radius of the phosphorus atom.

O. J. WALKER.

Alums of organic bases. I. Alums of methylamine. A. QUILICO (*Gazzetta*, 1928, 58, 682—690).—By means of the Laue and powder methods it is shown that the structure of methylammonium alum, $\text{NH}_3\text{MeAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, is similar to that of the unsubstituted ammonium alum. The replacement of the hydrogen atom by a methyl group merely causes a slight increase in the length of the unit cell, which in both cases contains four molecules of $\text{M}'\text{M}''(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, from 12.16 to 12.44 Å. The corresponding values of $d_{\text{calc.}}$ are 1.674 and 1.614. From the increase in the lattice constant the molecular volume of the methyl radical is calculated to be 18.67 cm^3 .

O. J. WALKER.

Crystal structure of praseodymium dioxide. P. SCHERRER and J. PALACIOS (*Anal. Fis. Quim.*, 1928, 26, 309—314).—An X-ray examination has been made, by the Debye-Scherrer method, of grey and black specimens of praseodymium dioxide. The photographs in each case were identical. The structure is of the fluorite type, the side of the unit cube being 5.39 Å. The unit cell contains 4 molecules, and $d_{\text{calc.}} = 7.32$ (cf. Goldschmidt, *Z. Krist.*, 1928, 67, *Strukturber.*, 1928).

R. K. CALLOW.

Crystal structure of Cu_5Al_4 . A. J. BRADLEY (*Phil. Mag.*, 1928, [vii], 6, 878—888).— δ -Copper-aluminium containing 16—19% Al has a cubic structure with 52 atoms per unit cell comprising 36 copper atoms and 16 aluminium atoms, corresponding with the formula Cu_5Al_4 . The space-group is T_d^2 with eight sets of structurally equivalent atoms. The structure is essentially of the caesium chloride type, each lattice point being replaced by a cluster of 26 atoms with tetrahedral symmetry. The atomic co-ordinates are almost the same as those in Cu_5Zn_8 (Bradley and Thewlis, A., 1926, 1087).

A. E. MITCHELL.

Crystal structure of zircon. L. VEGARD (*Z. Krist.*, 1928, 67, 482—484; *Chem. Zentr.*, 1928, ii, 318).—Polemic (cf. Wyckoff and Hendricks, A., 1928, 821).

A. A. ELDRIDGE.

Isomorphism between hexachloro-salts of pyridine and cerium, thorium, tin, lead, and quadrivalent titanium. V. CAGLIOTI (*Atti II Cong. Naz. Chim. pura Appl.*, 1926, 1182—1193; *Chem. Zentr.*, 1928, ii, 519—520).

Crystallographic investigation of some rare-earth nitrates. E. E. FLINT (*Trans. Inst. Econ. Min. Met. Moscow*, 1928, No. 34, 59—72).—A study of the salts $3\text{Mg}(\text{NO}_3)_2 \cdot 2\text{X}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$, where X = Ce, Nd, Pr, or La.

CHEMICAL ABSTRACTS.

Crystal structure of *n*-monopropylammonium halides. S. B. HENDRICKS (*Z. Krist.*, 1928, 67, 465—471; *Chem. Zentr.*, 1928, ii, 321).—The lengths of the edges of the tetragonal unit cell (containing

one molecule) are: *n*-propylammonium chloride *a* 4.48, *c* 7.40; bromide *a* 4.57, *c* 7.36; iodide *a* 4.85, *c* 7.33 Å.

A. A. ELDRIDGE.

Crystal structure of triethylammonium halides. S. B. HENDRICKS (Z. Krist., 1928, 67, 472—481; Chem. Zentr., 1928, ii, 320).—The dimensions of the unit cell of the dihexagonal-pyramidal crystals are: triethylammonium chloride *a* 8.38, *c* 7.08; bromide *a* 8.56, *c* 7.49; iodide *a* 8.78, *c* 7.74 Å. The cell contains two molecules. The space-group is C_{2h}^2 .

A. A. ELDRIDGE.

Crystallographic data for "cardiazol," pentamethylenaminotetrazole, and "dilaudid." H. STEINMETZ (Z. Krist., 1928, 67, 434—439; Chem. Zentr., 1928, ii, 321).—"Cardiazol" (pentamethylenaminotetrazole), monoclinic prismatic, has *a*:*b*:*c*=1.8171:1:1.5690, β 120° 15'; *n* 1.617, from toluene, benzene, or ether. Pentamethylenaminotetrazole, monoclinic prismatic, has *a*:*b*:*c*=1.6455:1:2.4725, β 95° 23'; *n* 1.592; hydrate (from water) monoclinic prismatic, *a*:*b*:*c*=0.5368:1:0.5943, β 95° 52'. "Dilaudid" (Knoll A.-G.), $C_{17}H_{19}O_3$, rhombic, has *a*:*b*:*c*=0.75(16):1:0.49(12).

A. A. ELDRIDGE.

Crystal structure of bixbyite and artificial manganese sesquioxide. W. ZACHARIASEN (Z. Krist., 1928, 67, 455—464; Chem. Zentr., 1928, ii, 318—319).—Bixbyite, hitherto supposed to be $Fe^{II}Mn^{IV}O_3$, and to be isomorphous with perowskite, has a regular hemihedral symmetry; the body-centred unit cube has *a* 9.35±0.02 Å. and contains sixteen molecules of $FeMnO_3$. It cannot be isomorphous with perowskite, and no space-group corresponding with the above formula is possible; the difficulty vanishes if the formula $(Fe,Mn)_2O_3$, space-group T^+ , is assumed; moreover, relationship to sesquioxides is apparent from the Laue diagram. Artificial manganese sesquioxide has the same structure; *a* 9.41±0.01 Å. Metal-oxygen distances are 2.08 and 2.10 Å., respectively. The dependence of the structure type (corundum-, C_2 -, A_2 -, and As_2O_3 -types) in which sesquioxides crystallise to the ion radii ratio R_M/R_O-r is indicated by: corundum- 0.43<*r*<0.53, C_2 - 0.53<*r*<0.80, A_2 - 0.80<*r*<1.

A. A. ELDRIDGE.

Structural relation between beryl and cordierite. B. GOSSNER (Zentr. Min. Geol., 1928, A, 204—207; Chem. Zentr., 1928, ii, 531).—Cordierite has *a* 9.78, *b* 17.1, *c* 9.33 Å., with 4 mols. of $Mg_2Si_5O_{12} \cdot 2Al_2O_3$ in the unit cell. The structure is compared with that of beryl.

A. A. ELDRIDGE.

Constitution of nitrated cellulose. F. D. MILES and J. CRAIK (Nature, 1929, 123, 82).—X-Ray studies on nitrated ramie afford little support for Herzog and Náray-Szabó's view (A., 1928, 48; Náray-Szabó and Susich, *ibid.*, 818) that "nitrocelluloses" are mixtures of cellulose trinitrate and cellulose. The diagram of nitrated ramie containing less than 7.5% N shows the same spacings as that of its denitrated product, but different relative intensities, and is much weaker. The spacings remain constant with increasing degree of nitration. Diffractions characteristic of the trinitrate do not appear. With 7.5—10.5% N the nitrated material partly loses its fibre structure, but the denitrated product is of the same type as

previously. The structure of the denitration product from more highly nitrated ramie is indistinguishable from that of pure cellulose, and different from that of the other denitration products.

A. A. ELDRIDGE.

Crystallography of aliphatic dicarboxylic acids. W. A. CASPARI (J.C.S., 1928, 3235—3141).—The crystal structures of adipic, pimelic, suberic, azelaic, sebacic, brassylic, and hexadecanedicarboxylic acids have been determined, the lengths of the axes *a*, *b*, and *c* of the unit cell and the angle β being recorded. In each case *a* and *b* are approximately the same, whilst *c* is proportional to the number of carbon atoms, there being two series, one for those acids with an odd number of carbon atoms and the other for those with an even number. It is concluded that all these long-chain aliphatic compounds are built up of two parallel chains of carbon atoms. Suggested models for these molecules are given.

J. L. BUCHAN.

Hall effect and magnetic induction in a bar of electrolytic iron. E. M. PUGH (Physical Rev., 1928, [ii], 32, 824—828).—The Hall effect was measured in a bar of electrolytic iron in contrast to the usual method of measuring it in thin sheets, and the magnetic induction was also measured simultaneously. Plotting the Hall $E.M.F.$ and the permeability against the magnetic induction, the linear relation is found in each case to break down at maximum permeability, whence it is concluded that the condition of the iron which causes the break from a linear relation in the Hall effect is the same as that which causes maximum permeability. The Hall coefficient is of the same order of magnitude in the bar as in a thin sheet if the value of *B* instead of *H* is used in the calculation.

N. M. BLOKH.

Magnetic properties of complex compounds and their electronic constitution. P. RAY and H. BHAR (J. Indian Chem. Soc., 1928, 5, 497—511).—The magnetic susceptibilities of 47 complex compounds, mostly containing iron, nickel, or cobalt, have been measured. The magneton values deduced from these measurements are discussed from the points of view of Cabrera, Welo and Baudisch, and of Bose. No one of the theories of these workers appears to be uniformly applicable.

F. G. TRYHORN.

Monel metal. I. Electrical and thermal properties and magnetostriction. A. SCHULZE (Z. Metallk. 1928, 20, 403—406).—The electrical resistance, thermoelectric power against copper, coefficient of thermal expansion, and magnetostriction of several samples of monel metal after different mechanical treatments have been determined. Above the Curie point (100°) the temperature coefficient of electrical resistance falls to about one fifth its value at 0—100°. Like nickel, monel metal undergoes contraction in a magnetic field, but the magnetostriction effect is much less marked, maximum contraction occurring in a field of 20—30 gauss. Work-hardened monel metal, however, does not undergo magnetostriction.

A. R. POWELL.

Monel metal. II. Magnetisation curves of monel metal. A. KUSSMANN (Z. Metallk., 1928, 20,

406—407).—The intensity of magnetisation of monel metal in a constant magnetic field is about twice as great for the alloy slowly cooled from 600° as it is for the alloy quenched from 600°. For pure nickel-copper alloys of the same composition, however, the same results are obtained in both cases. It appears, therefore, that some of the minor constituents of monel metal have a greater solid solubility at 600° than at the ordinary temperature. A. R. POWELL.

Role of conductivity electrons in ferromagnetism. J. DOREMAN and R. JAANUS (*Naturwiss.*, 1928, 16, 1026).—The question whether the elementary magnet consists of the electron bound to the positive metallic ion, or the "free" conductivity electron, has been investigated. The specific heat of the latter in metallic nickel undergoes a sudden change at the Curie point, identical in sign and magnitude (per electron) with the change in specific heat of metallic nickel (per atom) measured calorimetrically. The conducting electron in metallic nickel therefore acts as the elementary magnet. R. A. MORTON.

Electromotive behaviour of single metal crystals. P. A. ANDERSON (*Nature*, 1929, 123, 49).—The primary cleavage face (basal pinacoid) of a zinc crystal yields potentials constant to 0.0001 volt, and reproducible to less than 0.001 volt. The potential is identical with that of the electrolytically deposited crystal conglomerate within the range of variation of duplicate conglomerate electrodes. Measurements on artificially prepared surfaces indicate a qualitatively regular decrease of potential with increase of inclination to the primary cleavage plane. A. A. ELDRIDGE.

Magnetic properties in relation to chemical constitution. T. M. LOWRY and F. L. GILBERT (*Nature*, 1929, 123, 85).—A magnetic study of pervalent salts (PCl_5 , SbCl_5 , SbMe_3Cl_2 , SbMe_3Br_2 , SbMe_3I_2 , α - and β - TeMe_3Cl_2 , TeMe_3Br_2 , and TeEt_2I_2 , α - TeMe_3I_2 , and α - TeMe_3I_4) and analogous compounds (PCl_3 , POCl_3 , AlCl_3 , TeI_3 , BiI_3 , CsI_3) and co-ordination compounds, including the lithium, beryllium, aluminium, cobalt, nickel, and ferric derivatives of benzoylcampor shows that all except those containing a metal of the transition series are diamagnetic. Hence all the electrons in these compounds to which single-electron linkings have been assigned are magnetically paired. Mercurous chloride, mercuric chloride, and cuprous iodide are diamagnetic, whilst cupric chloride is paramagnetic. The mercurous salts contain bivalent mercury, whilst the copper in cuprous salts is univalent; cupric sulphide may, in reality, be cuprous disulphide. A. A. ELDRIDGE.

Crystal structure and ferromagnetism. O. VON AUWERS (*Physikal. Z.*, 1928, 29, 921—927).

Electrical conductivity [of metals]. W. J. DE HAAS (*J. Phys. Radium*, 1928, [vi], 9, 265—277).—A short critical discussion is given of conductivity theories, with evidence against the theory of free electrons. Experiments are described for the two last-named of the super-conductors thallium, indium, lead, mercury, and tin recognised by Onnes, showing that the electrical resistances exhibit a hysteresis effect in a magnetic field. The effect was investigated

for various temperatures. Sharp changes in the resistances of these metals were observed, and are explained as being connected with the formation of metallic crystals. For intense magnetic fields the resistance curve is found to be that of normal metals. The super-conductivity state may be stable or unstable. N. M. BLAGH.

Thermal and electrical conductivity of a copper crystal at various temperatures. W. G. KANNA-LUIK and T. H. LABY (*Proc. Roy. Soc.*, 1928, A, 121, 640—653).—Whilst the thermal method for the determination of the thermal conductivity of metals is the simplest, the electrical method is considered to be better adapted for very low temperatures, i.e., near 20° Abs. The thermal conductivity of a copper crystal has been determined by the thermal method over the temperature range 19° to -183°. The heat losses have been considerably diminished by the use of a high vacuum, and eliminated at the ordinary temperature by a special method. The thermal conductivity λ is found to be 0.989 g.-cal. cm. sec. deg. at 19.4°, 1.054 at -73.7°, and 1.131 at -174.8°. The value of λ at 19.4° is about 4% higher than that of polycrystal copper (in agreement with Schott, *Ber. Deut. physikal. Ges.*, 1916, 18, 27), whilst the values obtained at lower temperatures are considerably less than Schott's values. The electrical conductivity, κ , of the single crystal is found to be the same as that of ordinary polycrystal copper. The values obtained for the Wiedemann-Franz constant, $\lambda/(\kappa T)$, at 90.2° and 273.2° Abs. are 1.69 and 2.42×10^{-8} watt ohm deg.⁻², respectively. L. L. BIRUMSHAW.

Resistance of alloys. L. NORDHEIM (*Naturwiss.*, 1928, 16, 1042—1043).—Matthiessen's rule regarding the resistance of alloys is considered from the point of view of the modern theory of metallic conduction. Resistance is due to the distortion of the exact periodicity of the metal lattice. In alloys, even in the absence of irregularity due to heat, there are irregularities due to the different powers of single lattice points for scattering the electrons. For very low temperatures the resistance plotted against the concentration gives a hyperbolic curve. For small concentrations the relationship is linear. The results obtained by calculation were tested practically with silver-gold alloys and the agreement is good.

A. J. MEE.

Allotropic modifications of phosphorus. A. SMITS (*Compt. rend.*, 1928, 187, 980—982).—The results of Nicolaïev (*A.*, 1928, 827) are brought into line with the author's theory of allotropy and confirm his conclusion that phosphorus consists of three types of molecules, α_1 , α_2 , and β , white phosphorus being a mixture of the two α types, the transition point of which is at the ordinary temperature, whilst the $\alpha \rightarrow \beta$ transformation occurs appreciably only at high temperatures. J. GRANT.

Heat of fusion of s-phenylallylthiocarbamide. V. P. SCHISCHOKIN (*Ann. Inst. Anal. Phys. Chem.*, 1928, 4, 183—194).—The specific heat of phenylallylthiocarbamide increases with rise of temperature from 0.307 at 50° to 0.423 at 99.8°, and the heat of fusion is 6600 ± 100 g.-cal./mol. R. TRUSZKOWSKI.

Relationship between surface tension and heat of vaporisation. H. SIRK (Z. Physik, 1928, 52, 21—26).—The relationship existing between surface tension and heat of vaporisation is calculated on the basis of Debye's dipole theory. The constant obtained by dividing the molecular heat of vaporisation by the product of the total surface energy per sq. cm. and the molecular surface is 2.71×10^8 , a value in approximate agreement with the experimental number obtained by Walden. The deviation of the experimental from the calculated figure arises in the fact that approximations are made in the theory, and that the surface layer is not necessarily unimolecular.

A. J. MEE.

Determination of isotherms at high pressures. A. MICHELS and R. O. GIBSON (Ann. Physik, 1928, [iv], 87, 850—876).—A new apparatus for determining isotherms at high pressures is fully described. In particular, the isotherms of neon between 0° and 100° at 20—500 atm. are determined. The accuracy is estimated to be not greater than 1 in 2000.

A. J. MEE.

Application of the rule of Dulong and Petit to molecules. D. H. ANDREWS and E. HAWORTH (J. Amer. Chem. Soc., 1928, 50, 2998—3002).—The heat capacities between 100° and 336° Abs. are recorded for mono-, di-, tetra-, and hexa-chlorobenzene and for mono- and di-bromobenzene. The heat capacity per halogen atom in the compounds is relatively independent of the number of halogen atoms attached to the ring and approaches the value of 6 g.-cal./1° at the ordinary temperature, suggesting the applicability of Dulong and Petit's rule. Theoretical considerations based on the observed frequencies of the compounds in the infra-red lend support to this suggestion. The carbon-halogen linking seems to have the same mechanical strength in the above compounds.

S. K. TWEEDY.

The Majorana thermal effect. A. L. T. MOESVELD (Chem. Weckblad, 1928, 25, 702—703).—The fact that certain metals which have been fused or strongly heated, and then quenched, may remain for long periods at temperatures slightly higher than those of the surroundings is attributed to the liberation of energy accompanying slow transition from a metastable to a stable state.

S. I. LEVY.

Determination of the pressure and density of moist, saturated ammonium bromide vapour. A. SMITS and R. PURCELL (J.C.S., 1928, 2936—2944).—Using the densi-tensimeter (cf. A., 1928, 1209) the vapour pressures and vapour densities of moist ammonium bromide were determined. $\log p$ was found to be a linear function of $1/T$, hence the latent heat of evaporation between 300° and 400° is independent of temperature. Total dissociation of the salt was observed in this range of temperature. This heat calculated from the experimental data is 44,000 g.-cal. The vapour-pressure equation is $\log_e p = -10980/T + 20.8$. The densi-tensimeter measurements were checked by finding the pressure of the saturated and unsaturated vapour of a weighed quantity of salt in a known volume. The straight lines formed by plotting $\log p$ against $1/T$ did not intersect but merged into one another, indicating

perceptible adsorption of ammonium bromide on the walls of the vessel. The work of Smith and his co-workers (A., 1914, ii, 628; 1915, ii, 86) is critically examined and possible sources of inaccuracy are pointed out.

H. INGLESON.

Determination of the pressure and density of moist, saturated ammonium chloride vapour. A. SMITS and W. DE LANGE (J.C.S., 1928, 2944—2952; cf. preceding abstract).—The heat of vaporisation of ammonium chloride within the range 254—353° is not a temperature function and the density determinations showed that dissociation of the saturated vapour is practically complete over the same range. The results of Smith and his collaborators indicating some 60% dissociation are incorrect. The results of Braune and Knoke (A., 1928, 829) agree with those of the authors. The vapour-pressure equation is $2.303 \log_{10} p = -9903/T + 20.5$ and the heat of vaporisation is 39,600 g.-cal., giving a sublimation temperature of 339.3°.

Unlike the bromide, ammonium chloride is not appreciably adsorbed on the quartz and on the glass walls of the apparatus.

H. INGLESON.

Velocity of sound in air, nitrogen, and oxygen, with special reference to the temperature coefficients of the molecular heats. W. G. SHILLING and J. R. PARTINGTON (Phil. Mag., 1928, [vii], 6, 920—939).—The velocity of sound in air, nitrogen, and oxygen has been determined by the method previously described (*ibid.*, 1927, [vii], 3, 273) up to 1000°. In the case of air the temperature range has been extended to 1300°. The molecular heats of the gases over the temperature range have been calculated and are tabulated. A criticism by Cornish and Eastman (A., 1928, 468) of the method of determination of the tube correction is answered satisfactorily.

A. E. MITCHELL.

Vapour pressures in small capillaries. I. Water vapour. II. [Toluene.] J. L. SHERESHEFSKY (J. Amer. Chem. Soc., 1928, 50, 2966—2980, 2980—2985).—I. The vapour pressure of water in glass or quartz capillaries was measured by exposing capillaries containing water to the vapour of dilute solutions of known vapour pressure and measuring the rate of condensation or evaporation of water in the capillary. The pressure at which the rate of evaporation or condensation is zero, and is equal to the vapour pressure of the water in the capillary, is then obtained graphically. The lowering of vapour pressure of water is much larger than that calculated by Kelvin's equation; the large value is probably to be attributed to an increase in the surface tension of the liquid in the capillary. The abnormally great lowering observed in glass capillaries is due to the solubility of the glass.

II. In similar experiments with toluene, results are obtained which are not in agreement with the classical theory; this theory is believed to be incorrect.

S. K. TWEEDY.

Vapour density of formic acid. H. C. RAMSPERGER and C. W. PORTER (J. Amer. Chem. Soc., 1928, 50, 3036—3038).—The recent measurements of Coolidge (A., 1928, 1084) are in agreement with the

authors' results (A., 1926, 659), but not with the figures of earlier investigators, whose measurements may have been vitiated by traces of impurities.

S. K. TWEEDY.

Properties of substances and mixtures at 0° Abs. connected with change of state. R. D. KLEEMAN (J. Physical Chem., 1928, 32, 1841—1855; cf. A., 1927, 1142).—Mathematical. At 0° Abs., the internal heat of evaporation is zero, and the three possible physical interpretations of this result are discussed. The form of the equation of state of the vapour of a substance at or near 0° Abs. is investigated and it is deduced that the change in molecular motion of a gas with rise in temperature is zero at this point. The bearing of this result on specific heat is then considered. The properties of the heat and work of mixing substances in the gaseous state, of the change in free energy, and the heat of formation of gaseous substances at 0° Abs. are developed together with those of the internal specific heat of a vapour in contact with the condensed state. Other theorems are developed. L. S. THEOBALD.

Determination of reaction affinity in systems of solid salts. J. N. BRONSTED and W. T. RICHARDS (J. Amer. Chem. Soc., 1928, 50, 3028—3035).—A thermodynamic method is described for calculating the free energy change of reactions between solid salts, from vapour-pressure measurements on solutions of individual components of the system saturated with respect to one or more of the other components, or to allied substances. From such measurements, carried out in a special tensimeter, the vapour pressure of the reaction $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}(s) + 2\text{NH}_4\text{Cl}(s) = \text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}(s)$ is found to be 3560 g.-cal.

S. K. TWEEDY.

Viscosity constants and surface layers. J. TRAUBE and S. H. WHANG (Z. physikal. Chem., 1928, 138, 102—122).—The effect of numerous substances of varying chemical character on the viscosity of water has been determined by measuring the rate of flow of water through a capillary tube (inclined at differing angles to the horizontal) of which the walls were coated with a film of the substance under investigation. Oleic acid and, in general, polar substances, as well as capillary-active water-soluble compounds, such as amyl alcohol, octyl alcohol, and amyl acetate, increase greatly the rate of flow of water. The viscosity constant is uninfluenced by films of non-polar substances such as paraffin, benzene, and carbon tetrachloride. Films of solid polar substances such as stearic acid, lac, rubber, and benzene derivatives act similarly to those of liquid polar compounds in lowering the viscosity constant of water. The theoretical, biological, and technical aspects of the phenomenon are discussed.

F. G. TRYHORN.

Fluidity of mercury. E. C. BINGHAM and T. R. THOMPSON (J. Amer. Chem. Soc., 1928, 50, 2878—2883).—The viscosity of mercury measured in a copper capillary is abnormally high (Tammann and Himmüher, A., 1927, 304), particularly when the copper tube is amalgamated, and decreases with increasing time. This is due, not to a "slipping" effect, but to dissolution of copper in the mercury

and subsequent recrystallisation on the walls of the capillary, the effective diameter, and therefore the "constant," of the capillary being progressively changed as a consequence. Values are recorded for the viscosity of mercury over the temperature range 0—100°, measured in glass tubes.

S. K. TWEEDY.

Calculation of intermolecular forces of organic compounds. M. DUNKEL (Z. physikal. Chem., 1928, 138, 42—54).—Reasons are advanced for considering the heat of sublimation of a compound at 0° Abs. to be an additive function of its constitution, and to be a measure of the molecular cohesive forces. As an approximation, an examination has been made of the values of the molar heats of evaporation (λ) of numerous substances between 0° and 100°, and it has been shown that these exhibit additive relationships within fairly narrow limits of accuracy. The average increment in the normal paraffin and normal monohydric alcohol series is 980 g.-cal. per CH_2 group. The introduction of an *iso*-group in these compounds reduces λ by 460 g.-cal. The numerical alteration in λ has been calculated for a number of atomic groupings and substituent groups; values of λ calculated from these factors are in satisfactory agreement with experimental data.

F. G. TRYHORN.

Diffusion of aspherical particles. R. GANS (Ann. Physik, 1928, [iv], 87, 935—947).—Mathematical. Equations for the diffusion of oblate and prolate particles are worked out.

A. J. MEE.

Metallic diffusion. A. E. VAN ARKEL (Metall. Wirt., 1928, 7, 656—657; Chem. Zentr., 1928, ii, 334).—Determinations of the change in electrical conductivity of a copper wire coated with nickel, and of a nickel wire coated with copper, kept at 800°, gave a diffusion constant of 5×10^{-11} .

A. A. ELDRIDGE.

Determination of concentration gradients by means of curved light rays. A new method of observation. O. LAMM (Z. physikal. Chem., 1928, 138, 313—331).—The curvature of the path of a beam of light as it passes through a medium of continuously changing refractive index can be made the basis of a photographic method of determining concentration gradients. The deformation of the image of a scale as seen through the medium of varying concentration can be determined by measurements on the photograph. The theory of the method is discussed and the method has been tested experimentally by a determination of the diffusion coefficient of sucrose in water at 20°. The value found, 0.399, is in good agreement with the results of other investigators.

M. S. BURR.

Suitable vapour-gas mixtures for experiments with Wilson's cloud method. L. MEITNER (Z. physikal. Chem., 1928, 139, 717—721).—An equation is deduced showing that the factor which determines the expansion necessary for cloud formation is γ , the ratio of the specific heats of the vapour-gas mixture. This ratio is determined by γ_1 and γ_2 , the respective ratios for the gas and the vapour. If γ_1 and γ_2 be equal, the expansion ratio is independent of pressure; this condition is nearly realised in a water

vapour-carbon dioxide mixture. With water vapour, gases with high values of γ_1 such as the inert gases require the lowest expansion ratios. Where water vapour is not suitable, the use of alcohol vapour is suggested. R. N. KERR.

Viscosity of binary liquid systems. N. N. EFREMOV (Ann. Inst. Anal. Phys. Chem., 1928, 4, 118—159).—For mixtures of allyl alcohol and chloral the viscosity curves exhibit a maximum when equimolecular quantities of the constituents are present; this is attributed to the formation of a compound. A corresponding maximum is also shown by the temperature coefficient of the viscosity. The density increases continuously with the chloral content. The vapour pressure passes through a maximum at 85–95 mol.-% of chloral. The viscosity isotherms for the system nitrobenzene-*isobutyl* alcohol are smooth curves with a minimum which is progressively displaced with rise in temperature towards the axis of the more viscous constituent, *isobutyl* alcohol. The density curves are very nearly straight lines. The curves representing the influence of temperature on the viscosity are also continuous curves, the shape of which, however, depends on the temperature and on the content of *isobutyl* alcohol, which has a much higher coefficient than nitrobenzene.

R. TRUSZKOWSKI.

Molecular association. I. Connexion between the vapour pressures of binary liquid mixtures and the polarity of the molecules forming them. J. ERRERA (Z. physikal. Chem., 1928, 138, 332—344).—An extended account of work already published (A., 1928, 1316).

Molecular association. Relations between the viscosity of binary liquid mixtures and the polarity of the molecules of the constituents. J. ERRERA (Compt. rend., 1928, 187, 1278—1280; cf. A., 1928, 1316).—When the molecules of the two components of a binary liquid mixture are non-polar or are of opposite polarity, the viscosity-concentration curves for a particular temperature are always concave if they are not straight lines. When the curve is convex the two components are both dipolar. Evidence for the validity of these rules is quoted and certain anomalies are discussed. J. GRANT.

Constant-boiling mixture of hydrogen fluoride and water. C. W. MUEHLBERGER (J. Physical Chem., 1928, 32, 1888—1889).—The constant-boiling mixture, d_{20}^{20} 1.138, b. p. 110.8°/732 mm., contains $38.18 \pm 0.10\%$ of hydrogen fluoride at 735 mm. pressure. Deussen's value for the concentration of hydrogen fluoride in the constant-boiling mixture (A., 1906, ii, 531) is too high. L. S. THEOBALD.

Equilibria of certain binary systems containing 2 : 4 : 6-trinitro-*m*-xylene. N. N. EFREMOV and A. M. TICHOMIROVA (Ann. Inst. Anal. Phys. Chem., 1928, 4, 65—91).—Fusion diagrams are given for the systems: 2 : 4 : 6-trinitro-*m*-xylene-naphthalene, -acenaphthene, -anthracene, -phenanthrene, -fluorene, -2 : 4 : 6-trinitrocresol, -*m*-dinitrobenzene, -2 : 4 : 6-trinitrotoluene, -2 : 4 : 6-trinitroresorcinol, -picric acid, -picryl chloride, -tetryl, -1 : 3 : 5-trinitrobenzene. 2 : 4 : 6-Trinitro-*m*-xylene differs from

other trinitro-compounds in not forming definite compounds with hydrocarbons. None of the substances studied depresses the m. p. of trinitro-*m*-xylene to any great extent unless added in comparatively large amount. Solid solutions are formed only in the cases of trinitrobenzene and trinitrotoluene. The properties of the above mixtures are advantageous for the filling of moulds with the fused mixtures, in spite of the high viscosity and lack of mobility of the latter. R. TRUSZKOWSKI.

One of Kurnakov's problems. N. V. LIPIN (Ann. Inst. Anal. Phys. Chem., 1928, 4, 39—47).—Mathematical. A general expression is derived for the fusion curves of binary mixtures, in the presence or absence of dissociation. R. TRUSZKOWSKI.

Representation of binary fusion curves by a general expression. N. V. LIPIN (Ann. Inst. Anal. Phys. Chem., 1928, 4, 48—58; cf. preceding abstract).—The expression derived in the preceding paper is given in a simplified form. R. TRUSZKOWSKI.

Fusion curves in a special co-ordinate system. N. V. LIPIN (Ann. Inst. Anal. Phys. Chem., 1928, 4, 59—64; cf. preceding abstracts).—By using a modified system of co-ordinates the expressions derived in the preceding papers are obtained in a simpler form. R. TRUSZKOWSKI.

Electrical conductivity of binary liquid systems containing amines [or pyridine] and allylthiocarbimide. N. VOSKRESENSKAJA (Ann. Inst. Anal. Phys. Chem., 1928, 4, 160—182).—The electrical conductivity of the systems allylthiocarbimide-dimethylaniline, -diethylaniline, -pyridine, -methylaniline, and -ethylamine changes for some time after a given mixture is prepared, but finally attains a constant value. The first three systems, in which compound formation does not occur, show a maximum conductivity at a particular concentration. In the case of the secondary amines, which combine with allylthiocarbimide, two maxima are to be found on the conductivity curves, and a minimum which corresponds with equimolecular proportions of the components. R. TRUSZKOWSKI.

Thermodynamic potential curves of fused mixtures in which compound formation occurs. A. B. MŁODZIEJOWSKI (Ann. Inst. Anal. Phys. Chem., 1928, 4, 247—281; cf. A., 1926, 25).—Theoretical. A number of types of curves of the ξ function are discussed, the geometrical consideration of which leads to the conclusion that if a binary compound does not dissociate into its components in the liquid phase, it must be considered as an independent component of the system. R. TRUSZKOWSKI.

Solubility of carbon dioxide in water. K. BUCH (Forh. III nord. Kemistmötet, 1928, 184—192).—The absorption coefficient of carbon dioxide has been determined by two methods. In the first series of experiments carbon dioxide and air were shaken for 15 min. with water containing a few drops of hydrochloric acid, and the resulting aqueous solution and residual gas analysed. The quantities of carbon dioxide used were chosen so that its partial pressure ranged from 8×10^{-4} to 0.67×10^{-4} atm., and the corrected mean value of the coefficient from a

number of experiments at 20.8° is 0.83, or 0.85 if the three determinations where the concentration was lowest be omitted. In the second series, carbon dioxide at atmospheric pressure was passed through distilled water for $\frac{1}{2}$ hr. at 19.8°, followed by shaking of the water with the gas for 15 min., and analysis of residual gas and solution as in the previous method. The mean value thus obtained for the absorption coefficient is 0.856. The results agree fairly well with those previously obtained by Bohr, and the higher figures obtained by Hantzsch and Vagt are regarded as incorrect. H. F. HARWOOD.

Solubility of sodium benzenesulphonate in water and in solutions of sodium sulphate. F. H. RHODES and A. W. LEWIS (Ind. Eng. Chem., 1928, 20, 1366—1367).—Measurements of the solubility in water and in solutions of sodium sulphate containing 5, 10, and 15% Na_2SO_4 were made between 0° and 105°. At 0° the solubility of the sulphonate in water is 26.8 g./100 g. of solution, rising to 58.5 g. at 105°. The solubilities at 50° in pure water, and in 5, 10, and 15% Na_2SO_4 solutions are, respectively, 41.9, 38.6, 34.4, and 25.8 g. At temperatures below 66.8° the stable solid phase in contact with aqueous solutions is the dihydrate $\text{C}_6\text{H}_5\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$, whilst above this temperature the anhydrous salt is the stable form. H. INGLESOR.

Solubility of mercuric bromide in ethyl and methyl alcohols. K. L. MALHOTRA (J. Indian Chem. Soc., 1928, 5, 545—547).—The solubility of mercuric bromide has been measured in 99.73% and 87.73% ethyl alcohol, and in 99.78% methyl alcohol at temperatures between 0° and 80°. Needle-shaped crystals of an additive compound, $\text{HgBr}_2\cdot\text{MeOH}$, are slowly deposited from a saturated solution of mercuric bromide in methyl alcohol.

F. G. TRYHORN.

Solubility. XI. Solubilities of liquid stannic iodide in several liquid paraffins. (Miss) M. E. DICE and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1928, 50, 3023—3027).—The critical solution temperatures of stannic iodide, and the solubility of this substance in the neighbourhood of these temperatures, were measured in *n*-octane, *n*-heptane, *n*-hexane, and *isooctane*. The order of the critical temperatures is in accord with the internal pressures of the solvents, which increase for the normal hydrocarbons in the order of increasing mol. wt. *n*-Octane has a higher internal pressure than *isooctane*; this difference between a normal and an *isoparaffin* is probably general. For symmetrical binary systems of non-polar liquids (*i.e.*, systems in which the mol. fraction of each constituent is 0.5 at the critical solution temperature), the mutual solubility curves may be represented by $\log [(1-N_1)/N_1] = k(1-2N_1)/T$ as a first approximation, where N_1 is the mol. fraction of component 1 in one phase, and k is a constant depending, in part, on the difference in internal pressure of the two components. S. K. TWEEDY.

Solubility relations for lactose-sucrose solutions. I. Lactose-sucrose solubilities at low temperatures. P. N. PETER (J. Physical Chem., 1928, 32, 1856—1864).—The solubility of lactose in aqueous sucrose solutions and of sucrose in solutions

of lactose has been determined at 0° and at -3°. In the former case, the changes in solubility are inversely proportional, approximately, to the concentration of the sucrose. In saturated solutions of sucrose, the solubility is reduced to about one half that in water. Owing to the limited solubility of lactose at 0° and -3°, the solubility of sucrose at these temperatures is practically unaltered by the presence of the former sugar. Concentrated solutions of sucrose readily yield strongly supersaturated solutions of lactose, but on account of the high viscosity of the solution the latter may crystallise but slowly. Viscosity and not solubility appears to be the prime factor controlling crystallisation. The crystallisation of lactose in dairy products is discussed in the light of the above conclusions. L. S. THEOBALD.

Phenylallylthiocarbamide as a solvent. V. P. SCHISCHOKIN (Ann. Inst. Anal. Phys. Chem., 1928, 4, 195—224).—The heat of fusion of phenylallylthiocarbamide is derived on the basis of the Hildebrand-Mortimer theory of concentrated solutions (A., 1921, ii, 23; 1922, ii, 621) from measurements of the temperatures at which crystallisation takes place from various mixtures containing different proportions of this substance. Where no chemical interaction takes place, as with aniline, *o*-nitroaniline, and diphenylamine, the curves connecting the reciprocal of the saturation temperature with the logarithm of the molecular concentration of the substance which first crystallises out are rectilinear; in the case of chloroform, paraldehyde, trichloroacetic acid, acetic anhydride, acetic acid, benzene, toluene, naphthalene, *p*-dibromobenzene, allylthiocarbamide, nitrobenzene, and ethyl and methyl alcohols the curves deviate more or less from the rectilinear, indicating chemical reaction between the components, such as combination, solid solution, or solvation. The value calculated for the latent heat of fusion is in good agreement with that obtained experimentally (see this vol., 127). R. TRUSZKOWSKI.

Solubility in mixed solvents. II. Solubility of a substance which is miscible in all proportions with one of the solvents. E. ANGELESCU (Z. physikal. Chem., 1928, 138, 300—310).—The solubility of phenol in mixtures of water with the different dihydroxybenzenes in various proportions has been determined. The values obtained are in good agreement with those calculated from the formula previously deduced (A., 1928, 579), $S_c - S_0 = KC^p$, where S_c is the solubility in 100 g. of one solvent mixed with C g. of the other, S_0 the solubility in 100 g. of pure solvent, and K and p are constants. This is the limiting case of a sagged curve when the difference in solubility in the two solvents is very large. M. S. BURR.

Selective solvent action. VII. Solubilities in mixed solvents. (Miss) N. GREGG-WILSON and R. WRIGHT (J.C.S., 1928, 3111—3115).—The solubility of acetonitrile in mixed solvents has been measured at 20°. The solvents used were water or benzene with various alcohols and also mixtures of different alcohols. In each case measurements were carried out with mixtures containing various proportions of the constituents. The solubility of phenanthrene

in aqueous ethyl alcohol has also been determined. It is suggested that the increased solubility usually noted with mixed solvents is due to the effect of the different solvents on the different radicals of the solute molecule.

J. L. BUCHAN.

Solubility and dissolution velocity of solid substances. E. N. GAPON (*Z. Elektrochem.*, 1928, 34, 803—805; cf. Noyes and Whitney, A., 1897, ii, 479; Nernst, A., 1904, ii, 315).—Mainly theoretical. It is deduced thermodynamically (i) that the critical increment in the velocity of dissolution is equal to the heat of dissolution of the dissolving substance in nearly saturated solution plus $0.5RT$, and consequently is dependent only on the nature of the solute, and (ii) that the velocity coefficient is, at all temperatures, proportional to the solubility and $T^{\frac{1}{2}}$. On the other hand, it can be shown from the Noyes-Nernst diffusion theory (*loc. cit.*) that the critical increment depends entirely on the nature of the solvent and is equal to $W + RT$, where W is the value obtained for the solvent by Drucker, and that the velocity coefficient changes with the fluidity of the medium. Solubility measurements for benzoic acid at 20°, 30°, and 40° support the first set of conclusions.

L. S. THEOBALD.

Significance of lower and higher critical solution temperatures. Ternary system water-nicotine-acetone. P. LEONE (*Atti II Cong. Naz. Chim. pura Appl.*, 1926, 1209—1220; *Chem. Zentr.*, 1928, ii, 525—526).—Acetone increases the mutual solubility of water and nicotine; the two-phase system disappears at acetone concentrations >35—44%. The molecular variations (Timmermans) in the critical solution temperature are for a given ratio water/nicotine not constant, but increase somewhat with the acetone concentration. The molecular variations for the lower critical solution temperature are between 100 and 150, and for the upper usually below 100.

A. A. ELDRIDGE.

Partition coefficient in the fractional crystallisation of radium barium bromide solutions. Z. T. WALTER with H. SCHLUNDT (*J. Amer. Chem. Soc.*, 1928, 50, 3266—3270).—The partition of radium between crystals and mother-liquor is characterised by a constant ratio. The fractionation process is represented with equal approximation by the equations of Doerner and Hoskins and of Schlundt, but not by the equation of Chlopin and Nikitin (A., 1927, 1133). The results show that radium is more efficiently concentrated by using the bromide than by using the chloride or sulphate.

S. K. TWEEDY.

Distribution coefficients of ions. N. BJERRUM (*Forh. III nord. Kemistmotet*, 1928, 92—105).—The sum of the ionic distribution coefficients for various salts dissolved in alcohol and water respectively can be calculated from the solubilities of the salts in these liquids. The distribution exponent, P , may be used instead of the distribution coefficient, V , in expressing the results, the relationship being $P = \log V$. In the case of weak acids the sum of the ionic distribution exponents can be calculated by employing Larsson's formula $P_{\text{anion}} + P_{\text{H}} \log K_{\text{H}_2\text{O}} \log K_{\text{ak}} - P_{\text{undiss. acid}}$; the last term can be calculated from solubility determinations of the acid in the two media. The values of the

distribution exponents of the individual ions have been calculated from electropotential measurements: the figures obtained range from 4.1 for potassium ion to -3.9 for the stearate ion. The results always show a tendency for the ions to be concentrated in the aqueous rather than in the alcoholic solution, and this is ascribed to the high dielectric constant of water. The theoretical importance of these ionic distribution coefficients in the study of the properties of solutions of electrolytes, and the need for further experimental data, are emphasised.

H. F. HARWOOD.

Adsorption [of gases at low pressures]. W. KALBERER and H. MARK (*Z. physikal. Chem.*, 1928, 139, 151—162).—The adsorption of carbon dioxide and argon by silicic acid and of carbon dioxide by aluminium foil at various temperatures between -22° and 225° and mainly at very low pressures has been investigated. When no special outgassing is carried out, the adsorbing surface behaves uniformly and yields linear adsorption isotherms at low pressures; these isotherms pass through the origin of the co-ordinate system. In the case of carbon dioxide at 0°, the isotherm at pressures less than 0.2 mm. shows a rise from linearity which is accentuated by heating the adsorbent between 200° and 300° in a high vacuum and avoiding contact with air before adsorption takes place. This treatment reveals in the surface active centres which have taken up gases by contact with air in the usual conditions. Aluminium foil is similarly activated and the processes of activation by outgassing and of de-activation by contact with air are reversible. The heats of adsorption of argon and of carbon dioxide by silicic acid in the linear range of the isotherm are 2500 and 6200 g.-cal./mol. respectively, whilst in the steeper range the mean value for carbon dioxide is 7500 g.-cal./mol. The thickness of the adsorption layer of carbon dioxide on aluminium is of the order 1.5×10^{-8} cm. Equations representing adsorption are discussed.

L. S. THEOBALD.

Influence of temperature on gas adsorption. H. ZEISE (*Z. physikal. Chem.*, 1928, 138, 289—299).—Theoretical. On the basis of previous experimental data for the adsorption of different gases by charcoal, the author discusses the variation with temperature of the coefficients c_1 and c_2 in Langmuir's adsorption isotherm for gases, $x = c_1 c_2 p / (1 + c_2 p)$, where x is the weight of gas adsorbed per g. of charcoal and p the pressure. It is shown that $c_1 = a_1 - b_1 T$ and $c_2 = 10^{a_2} / T^{b_2}$, where a_1 , b_1 , a_2 , and b_2 are constants for any particular gas. There must therefore be a critical adsorption temperature $T' = a_1 / b_1$ above which no pressure, however great, will bring about adsorption. Expressions are also obtained for the dependence on temperature of the maximum number of adsorbed molecules, and of σ , the relative time of attachment of adsorbed molecules.

M. S. BURR.

Adsorption of gaseous mixtures of alcohol and ether from air by different silica gels. L. VON PUTNOKY and G. VON SZELENY (*Z. Elektrochem.*, 1928, 34, 805—812).—The simultaneous adsorption of alcohol and ether from mixtures of their vapours

with air at 20° by various brands of commercial silica gel and by one prepared by hydrolysis of silicon tetrachloride has been studied by a new dynamic method in which analysis of the gas mixtures has been effected by means of a three-chambered gas interferometer. The six gels were heated immediately before use to constant weight at 200° under a pressure of 15–20 mm. The total weight of alcohol and ether adsorbed increases with an increase in the proportion of these substances in the air used, and the ratio weight of alcohol adsorbed/weight of ether adsorbed varies with, but is always greater than, the ratio weight of alcohol/weight of ether in the mixture before adsorption. When the latter is 1:2, the former varies from 0.56 to 0.66, according to the nature of the gel; with an initial ratio 7:8, it varies from 0.94 to 1.1; and with ratios 1:1 and 4:3, more alcohol than ether is adsorbed. At the ratio 7:8, the ratio of the amounts of alcohol to ether adsorbed for a given gel is practically unchanged by doubling or trebling the absolute amounts of these substances in the gas mixture. Adsorption data for the six gels are given. L. S. THEOBALD.

Sorption of carbon tetrachloride at low pressures by activated charcoals. I. R. CHAPLIN (Proc. Roy. Soc., 1928, A, 121, 344–358).—The sorption of carbon tetrachloride vapour by charcoal has been investigated in the absence of other gases between 0° and 70° and at pressures of 1×10^{-4} to 2.3×10^{-1} mm. The pressure was measured by means of a Pirani gauge calibrated by a method which is given. The apparatus and method are described in detail; the experimental results will be given in a later paper. J. L. BUCHAN.

Adsorption of gases at heteropolar crystal faces. J. H. DE BOER (Metall.-Wirt., 1928, 7, 657; Chem. Zentr., 1928, ii, 334).—The author's mathematical conceptions are supported by experiments on the adsorption of iodine vapour by calcium fluoride. A. A. ELDRIDGE.

Adsorbing power and vapour pressure of adsorbed water by acidic, neutral, and alkaline earths. H. ISOBE (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 1133–1159).—The adsorbing power for water vapour of earths from various localities in Japan has been measured. For the earth from a particular locality, the adsorbing power is maximal when the earth is neutral, and decreases if it becomes either acid or alkaline. Vapour-pressure measurements have also been made at a series of temperatures on earths containing varying amounts of moisture. The form of the vapour-pressure isotherms for water contents of 2–4% and 4–8% is different according as the earth is acid, alkaline, or neutral. R. CUTRILL.

Adsorption of quinine, oxalate, and dextrose by fuller's earth and charcoal (norit). N. R. GUERRANT and W. D. SALMON (J. Biol. Chem., 1928, 80, 67–89).—Different samples of fuller's earth vary both qualitatively and quantitatively in their adsorptive capacities. For a given sample the most important determining factor is p_H in the case of electrolytes (quinine hydrogen sulphate and oxalic acid) and effective surface in the case of non-

electrolytes (dextrose). Treatment of the earth with acid diminishes its power of adsorbing oxalate and, to a smaller extent, of quinine, whilst its adsorptive capacity for dextrose is not affected; subsequent electro-dialysis restores the adsorptive power for quinine only. Ignition of the earth has little effect on its adsorptive capacity for oxalate and for dextrose, and electro-dialysis of otherwise untreated earth slightly reduces its power of adsorbing quinine. Adsorption of quinine and of dextrose by "norit" is affected by the p_H in a similar way; oxalic acid is adsorbed by norit only in acid solution, in which, however, the degree of adsorption is higher than that obtained with fuller's earth at any p_H .

C. R. HARRINGTON.

Absorption of ions by solutions of aluminium hydroxide and vanadium pentoxide. D. N. CHAKRAVARTY and N. R. DHAR (J. Indian Chem. Soc., 1928, 5, 539–543).—The adsorption of bromate, chloride, iodate, chromate, ferrocyanide, and oxalate ions by an aluminium hydroxide sol, prepared in the cold, has been found to decrease in magnitude in the above order. The order of decreasing adsorption of positive ions by a dialysed vanadium pentoxide solution was found to be: K, Al, Th, Ba. The experimental results show that with both these sols a univalent ion is adsorbed in greater quantity than a bivalent or tervalent ion. F. G. TRYHORN.

Kinetic theory of absorption. T. PECZALSKI (Compt. rend., 1928, 187, 1035–1037).—The phenomena associated with the absorption of a gas by a porous substance and with the action of salts on metals (A., 1927, 634) may be expressed in terms of the diminution in the mean path of the molecules of the adsorbed substance when it enters the pores, the linear dimensions of the latter being smaller than the mean path of the molecules of the surrounding gas. Expressions are obtained for the pressure inside the pores, and for the rise in temperature due to the adiabatic compression it produces, and it is shown that those molecules which have the greatest mean free path are, as a rule, most readily absorbed. J. GRANT.

Lyosorption in organic liquids. W. HALLER (Kolloid-Z., 1928, 46, 366–367).—When a fine suspension is allowed to settle, the volume of the sediment attains a definite value in time, but this value varies by more than 50% according to the liquid employed. Experiments with nine different powders in a number of liquids showed that the liquid is a more important factor than the solid phase. In all cases the volume of the sediment was greatest in carbon tetrachloride and least in alcohol or acetone. The phenomenon bears no relation to the density or viscosity of the liquid and is not due to an electric $P.D.$ between the solid and liquid phases, but appears to be due to retention of the liquid by the solid particles, each of which acquires a sheath of molecules of the dispersion medium. The phenomenon has been named "lyosorption." The process can be reversed by tightly packing the powder in a tube and measuring the rate of flow of various liquids through the tube. In those liquids showing lyosorption it is evident that the pores of the powdered mass

gradually increase in size. Such a process is analogous to swelling and it is suggested that many cases of swelling of gels can be explained in terms of lyosorption. E. S. HEDGES.

Area of internal surface of charcoal as determined by the adsorption of normal aliphatic alcohols from aqueous solution. W. E. GARNER and F. E. T. KINGMAN (Trans. Faraday Soc., 1929, 25, 24—29).—The adsorption isotherms of *n*-butyl alcohol in aqueous solution have been measured for "norit" (ash content 0.2% after purification), using a Zeiss interferometer to determine the concentrations of the alcohol solutions (cf. Adams, A., 1915, ii, 478). The effect of cleaning the charcoal by evacuation and admitting air at high temperatures is to increase the adsorption. In all cases there are no obvious breaks in the adsorption isotherms, which are not of the same type as those previously obtained by the surface-tension method (A., 1927, 617). Some abnormality occurs in one or other of the methods at low concentrations. A photomicrographic investigation of the surface of the charcoal gave a value of 0.18 m.² per g., which is obviously a very small proportion of the total area of the charcoal. O. J. WALKER.

Thickness of adsorbed vapour films. II. G. H. LATHAM (J. Amer. Chem. Soc., 1928, 50, 2987—2997).—The adsorption experiments of Frazer, Patrick, and Smith (A., 1927, 722) are continued with acetonitrile, nitromethane, and toluene. These substances are strongly adsorbed on glass surfaces which have been treated with acid, the layers being 30—60 mols. thick; they are not adsorbed at all, or only in unimolecular layers, on fire-polished glass surfaces, and such surfaces may be regarded as plane from the point of view of adsorption. Adsorption experiments in presence of silica gel indicate that treatment of glass surfaces with acid may produce a thin layer of silica. Amalgamated platinum surfaces absorb water strongly, a layer about 30 mols. thick being formed, whereas on amalgamated silver surfaces the layer never exceeds the thickness of one molecule.

S. K. TWEEDY.

Oxide films responsible for the tints on heated copper. U. R. EVANS (Nature, 1929, 123, 16).—Removal of metal by anodic treatment in potassium sulphate solution has permitted isolation of oxide films from copper; the colours are due to cuprous oxide. Cupric oxide, which is formed under strongly oxidising conditions, obscures the colours. Within the interference-colour range, the cuprous oxide films are transparent. Opaque areas, due to metallic copper, are observed in films isolated from copper showing the first-order tinting colours.

A. A. ELDRIDGE.

Theoretical aspects of the Traube-Whang phenomenon. L. J. WEBER and H. NEUGEBAUER (Z. physikal. Chem., 1928, 138, 161—168; cf. Traube and Whang, this vol., 129).—When a liquid is flowing through a capillary tube on the wall of which is a layer of a second substance, the boundary conditions will be largely dependent on the polarity of the wall substance. If this is sufficiently strongly polar, the tangential field within the layer of liquid adsorbed on it will be more or less homogeneous, so

that movement of the liquid molecules in this layer will be possible in a direction parallel to the wall, their mobility being dependent on the degree of homogeneity of the field. Under these conditions, the amount of liquid *Q* flowing out per second is given by the extended form of Helmholtz's equation $Q = -(p - p_0) \{ R^4 + 8B\eta R^2(v/\phi + R/2) \} 8\eta l$, where *p* and *p*₀ are the pressures at the two ends of a capillary of length *l* and radius *R*. — is the surface tension and *η* the viscosity, *φ* is the molecular surface of the adsorbed layer and *v* the molecular volume of the liquid, and *B* is a constant given by the equation $u_0 = KB$, where *u*₀ is the boundary velocity, and *K* the average force exerted on the molecules in the adsorbed layer. By means of this expression, the mobility of the molecules in the adsorbed layer in the experiments of Traube and Whang (*loc. cit.*) may be calculated. From similar considerations, Stokes' formula for the velocity *v* of a sphere of radius *R* falling under the influence of a force *F* becomes $F = 6\pi\eta v R (1 + 2B\eta/R + 8B\eta v/R^2\phi) / (1 + 3B\eta/R + 8B\eta v/R^2\phi)$. R. CUTHILL.

Diffusion rings. G. LINCK (Chem. Erde, 1928, 4, 88—94).—Observation on the diffusion of silver nitrate and potassium chromate solutions in gelatin have been made under the microscope.

L. J. SPENCER.

Electro-osmosis of mixtures of electrolytes. A. BOUTARIC and M. DOLADILHE (Compt. rend., 1928, 187, 1142—1144).—The rate of transport (*v*) of solutions of copper sulphate and nitrate, which are electro-osmotically opposite, follows the same laws for the mixed as for the pure solutions, i.e., *v* varies directly with the current and inversely as the concentration. No simple relation exists between *v* and the ratio (*s*) of the normalities of the solutions constituting the mixture, but the composition corresponding with zero transport is related to *s* by a hyperbolic expression of the form $x \times s^{8.7} = 72.5$, and if *s* = 1, *v* varies linearly as a function of *x*. J. GRANT.

Diffusion and membrane potentials. IV. Comparison of anion and cation effects. E. B. R. PRIDEAUX (Trans. Faraday Soc., 1929, 25, 20—23; cf. A., 1927, 1033).—Previous measurements of the potentials which are set up at a parchment paper membrane between solutions of the alkali salts of organic acids of different concentrations have been extended to different types of electrolytes over one concentration range, viz., 0.1*N* and 0.01*N*. Diffusion and membrane potentials for solutions of acetic acid and of piperidine are given. In the case of acetic acid the membrane causes only a very slight increase in the diffusion potential, whilst with piperidine instead of the expected diminution a slight increase was observed. The nature of the membrane potential is discussed.

O. J. WALKER.

Measurement of osmotic pressure. R. V. TOWNEND (J. Amer. Chem. Soc., 1928, 50, 2958—2966).—An apparatus for measuring osmotic pressure is described, based on the following principle. The solution is placed in contact with its vapour, and pure solvent at the surface of a thin porous plate is also placed in contact with the vapour. The rate of evaporation of pure solvent into the vapour is

measured for varying downward tensions applied to the porous plate. These rates are plotted as a function of the applied tension and the curve is extrapolated to zero rate, which corresponds with a tension equal to the required osmotic pressure. The measurements are made under air-free conditions.

S. K. TWEEDY.

Condition of iodic, hydrofluoric, and chromic acids and their salts in aqueous solutions. N. R. DHAR (J. Indian Chem. Soc., 1928, 5, 558—592).—Comparison of the data for the electrical conductance, lowering of f. p., and elevation of b. p. of solutions of iodic acid indicates that this substance is partly polymerised in solution. The precipitation concentrations of solutions of the acid and of its salts for ferric hydroxide solutions show that the iodate ion exists in the bivalent form $I_2O_6^{2-}$. Similar experiments with hydrofluoric acid and with fluorides show that these also are associated in aqueous solutions. The second dissociation constant of chromic acid has been determined from measurements of the increase in solubility of carbon dioxide in solutions of potassium chromate. The constant is of the order of 5×10^{-8} . The data for electrical conductance and coagulating power of potassium dichromate solutions are in agreement with the view that this substance in solution exists partly as $KHCrO_4$ molecules.

F. G. TRYHORN.

Extinction coefficients of mixtures of mercuric chloride and organic acids in the ultra-violet as experimental evidence of the formation of unstable intermediate compounds. III. J. C. GHOSH and T. L. K. RANGACHARYA (J. Indian Chem. Soc., 1928, 5, 569—578; cf. Ghosh and Mitra, A., 1928, 687).—To verify the assumptions (a) that an equilibrium exists in solution between mercuric chloride and an organic acid and an intermediate complex formed by the loose combination of one molecule of each reactant, and (b) that a definite value of molecular extinction coefficient for each wave-length characterises the intermediate complex, measurements have been made of the molecular extinction coefficients of solutions of mercuric chloride (0.001M) containing, respectively, varying concentrations of formic, acetic, propionic, oxalic, malonic, succinic, glycollic, lactic, tartaric, and mandelic acids. It was found that the value of the equilibrium constant which characterises the intermediate compound (a) decreases for each successive addition of a CH_2 group in a homologous series, (b) increases roughly fifteen-fold on passing from a monobasic to a dibasic acid, and (c) increases in the case of a monobasic acid on the introduction of a terminal hydroxyl group.

F. G. TRYHORN.

Colour of iodine solutions. F. H. GETMAN (J. Amer. Chem. Soc., 1928, 50, 2883—2890).—Iodine solutions were investigated spectrophotometrically between 680 and 430 m μ . Violet solutions exhibit an almost constant absorption maximum between 520 and 540 m μ , whilst brown solutions show a smaller, less constant, intensity maximum between 460 and 480 m μ . Lachman's conclusion, that saturated solvents (hydrocarbons and their halogen derivatives) produce violet solutions, and unsaturated solvents (ethyl alcohol, acetone, pyridine, etc.) brown

solutions, is confirmed (A., 1903, ii, 283). Iodine solutions tend to change on keeping; their colour and stability on exposure to ultra-violet radiation seem to depend somewhat on the degree of saturation of the solvent.

S. K. TWEEDY.

Preparation of colloidal gold solution. R. A. KILDUFFE and W. W. HERSON (J. Lab. Clin. Med., 1927, 12, 810—813).—The method permits the preparation of solutions requiring minimal adjustment of reaction, and invariably giving normal or paretic curves with normal or paretic fluids, respectively.

CHEMICAL ABSTRACTS.

Preparation of highly sensitive negative emulsions in the laboratory. K. KIESER (Z. angew. Chem., 1928, 41, 1292—1295).—A bromide solution is prepared of 100 g. of ammonium bromide and 2.5 g. of potassium iodide in 1 litre of water; 245 g. of silver nitrate are dissolved in 500 c.c. of water and the solution is treated with ammonia (d 0.91) until the brown precipitate of silver oxide just redissolves (about 250 c.c. of ammonia are required). In a large flask are placed 20 g. of gelatin, 80 c.c. of water, and 100 c.c. of the above bromide solution and, after 1 hr., the mixture is digested on the water-bath at 45° until a homogeneous liquid is obtained. The whole is transferred to a dark room lit by a ruby lamp and 30 c.c. of the silver solution are quickly added with vigorous agitation. After 45 min. on the water-bath at 45° a further 30 c.c. of the silver solution are added as before and heating is continued for 15 min. with frequent agitation. The flask is then cooled by rotation in ice water so that a thin layer of emulsion is formed over the inside surface; this is then cooled for several hours in an ice-chamber, and washed for 10 hrs. in a slow current of ice-cold water passed through the flask. The washed emulsion is melted at 45°, treated with 2 c.c. of 10% potassium bromide solution and 2 c.c. of 10% chrome alum solution, filtered, and kept at 45° for 1—3 hrs. to ripen; it is then ready for coating the plates or films in the usual way.

A. R. POWELL.

Electric moment of colloidal particles of vanadic anhydride. J. ERRERA (J. Phys. Radium, 1928, [vi], 9, 307—309).—The electric moment of colloidal particles of vanadic anhydride has been calculated by a method due to Debye from a knowledge of the dielectric constants of the colloidal solution at low concentrations. The value found is 415×10^{-18} , which is considerably greater than that for molecules of substances such as ether and water. It appears that with age not only are long chains of colloidal particles formed in the solution, but that there is also a rearrangement of atoms and molecules within the colloidal particles themselves.

A. J. MEE.

Effect of non-electrolytes on the stability of colloids. II. Ferric hydroxide sol. S. G. CHAUDHURY and A. GANGULI (J. Physical Chem., 1928, 32, 1872—1874; cf. A., 1928, 1187).—The effect of methyl and ethyl alcohol, carbamide, sucrose, glycerol, and pyridine on the coagulation of a ferric hydroxide sol by potassium chloride, sulphate, and ferricyanide [?] has been studied. Methyl and ethyl alcohol and pyridine sensitise the sol irrespective of

the valency of the precipitating ions. Carbamide sensitises the sol towards the chloride and ferricyanide, whilst sucrose and glycerol show the same effect towards the sulphate and ferricyanide.

L. S. THEOBALD.

Figures produced by the desiccation of colloidal solutions. P. BARY (Rev. gén. Colloid., 1928, 6, 209—221).—The deposit produced by evaporating a colloidal solution of ferric hydroxide at 50—60° in a porcelain basin consists of numerous filaments arranged either concentrically or radially, the latter form tending to appear when the chloride content of the solution is high. Examination under the microscope has shown the concentric filaments to be composed of a number of fibrils, having a diameter of about 3 μ with their centres about 9 μ apart, arranged parallel to each other with their long axes in the direction of the filament. The radial filaments consist of fibrils oriented transversely to the filament and thus apparently identical with the former case. In either instance, the fibrils are yellow and have a composition represented by $20\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{Cl}_6 + \text{aq.}$ and are separated by a gelatinous reddish-brown material containing a higher percentage of chlorine. The proportion of fibrillar matter to the interfibrillar cement is greater during the initial stages of evaporation. It is believed that the yellow matter composing the fibrils is pre-existent in the solution and is not produced at the moment of deposition, for solutions of colloidal ferric hydroxide were observed to deposit a similar substance when kept for 12 or 15 months. Similar structures produced by other colloids can be examined by evaporating the sol at 50—60° in a small beaker in which is inclined a small microscope slide. Under these conditions, a periodic structure of regularly-spaced lines of deposit is formed and to these preparations the term "pectograph" has been given. The pectographs of colloidal solutions of antimony sulphide, arsenious sulphide, gold, tannin, sulphur, molybdenum sulphide, Congo-red, diamond-green P extra, and fuchsin are described and it is suggested that the method may be utilised in the determination of the structure of different colloidal solutions.

E. S. HEDGES.

Electrical double layer of colloids. Silver iodide sol. H. R. KRUYT and P. C. VAN DER WILLIGEN (Z. physikal. Chem., 1928, 139, 53—63).—The peptisation of silver iodide, prepared from silver nitrate and potassium iodide, by various potassium salts has been investigated in connexion with the formation of the electrical double layer. Stable sols are obtained by the peptising action of the chloride, bromide, iodide, cyanide, and thiocyanate of potassium, all of which possess anions which, apparently, are able to fit into the space lattice of silver iodide. Such electrolytes can produce an electrical double layer. On the other hand, the nitrate, sulphate, carbonate, monohydrogen phosphate, and dichromate of potassium bring about flocculation, whilst the ferricyanide occupies an intermediate position. Cataphoretic measurements of the positively-charged silver iodide sol show that with dilution the positive charge decreases to zero and then changes in sign, whilst the stability of the sol corresponds with this behaviour.

Dialysis brings about coagulation of the positive but not of the negative sol. The conductivities of these sols were also measured. The connexion between isomorphism and peptising power supports the conception put forward that the electrical double layer is brought about by lattice forces. The formation of the negative charge of silver iodide in contact with pure water is still an open question. The hydroxyl ion, although not fitting into the space lattice of the iodide, appears to possess a special facility for forming the double layer. The charge in pure water remains below the critical value and a small concentration of potassium iodide (0.005—0.01 mol./litre) suffices to cause peptisation, whereas with silver nitrate a much higher concentration (0.1—0.5 mol./litre) is required to reach the positive critical value for peptisation.

L. S. THEOBALD.

Critical potential in the coagulation of colloids by electrolytes. J. N. MUKHERJEE and S. P. RAICHOUDHURI (Nature, 1928, 122, 960—961).—The nature and mode of preparation of the colloid have considerable influence on the cataphoretic speed at the coagulating concentration of the electrolyte. Curves correlating the concentration of electrolyte with the cataphoretic speed contradict the assumption that coagulation takes place at a critical potential. A fall in the cataphoretic speed during the course of the coagulation indicates some irreversible change during aggregation.

A. A. ELDRIDGE.

Lyophilic colloids. I. Agar. H. R. KRUYT and H. G. B. DE JONG (Kolloidchem. Beih., 1928, 28, 1—54).—Methods of purification of agar are detailed. For dilute agar sols, the relative increase in viscosity has a definite value at each temperature and decreases with rising temperature. The connexion between the relative increase in the viscosity and the concentration of the sol is somewhat complicated, the curve being at first slightly convex to the concentration axis, and later slightly concave. The viscosity of agar sols is lowered by all electrolytes at small concentrations. Equivalent concentrations of the chlorides of potassium, sodium, lithium, ammonium, and of potassium sulphate, thiocyanate, and ferrocyanide produce a practically constant lowering of viscosity. A similar relation is found in the series barium chloride, strontium chloride, magnesium sulphate, and cadmium sulphate, the decrease in viscosity being greater than in the former case. The magnitude of the effect depends on the valency of the cation. Cataphoretic experiments show that the agar sol is negatively charged; the charge is capillary-electric in nature. The decrease in viscosity caused by hydrochloric acid on potassium hydroxide is greater than that caused by barium chloride. In accordance with the strong adsorption of organic ions, fuchsin produces a much stronger decrease in viscosity than potassium chloride. With high concentrations of electrolytes, where the electro-viscous effect is absent, the relative decrease in viscosity is a measure of the degree of hydration; this increases in the series potassium sulphate < chloride < nitrate < thiocyanate. Experiments have been conducted on the salting out of agar solutions by various electrolytes at high concentrations and also on the effect of adding alcohol or acetone in

presence and in absence of electrolytes. When the charge on the agar particles is removed by electrolytes in water as the dispersion medium, the sol still remains stable, but when the dispersion medium is alcohol-water or acetone-water the sol is flocculated under these conditions. Alcohol or acetone has the greatest influence at medium concentrations, for which the viscosity of their mixtures with water is greatest. It would therefore seem that the stability of agar sols is due not only to the charge on the particles, but also to hydration of the particles. This factor is considered to constitute the chief difference between the suspensoid and emulsoid types of colloids. In the suspensoid type, removal of the charge on the particles causes immediate coagulation because the particles are feebly hydrated, if at all, whilst in the emulsoid type the sol preserves its stability unless a dehydrating agent such as alcohol is present simultaneously. The relations found with agar are thus generalised to a theory of stability of hydrosols and are applied in particular to sols of proteins. E. S. HEDGES.

Jellies and gels. W. OSTWALD (Kolloid-Z., 1928, 46, 248—267).—Previous schemes for the classification of gels are reviewed and a new scheme is proposed, which is based on the mode of production of the gel. Different types thus arise according to whether the gel is formed by falling of temperature, by chemical reaction, by coagulation, swelling, fermentation, or by geological influences. Allied systems include undercooled melts and solutions, slimes, and foams. A distinction is also made between lyogels, which are rich in liquid, and xerogels, which are in a relatively dry state. The process of gelatinisation is discussed together with the existing experimental data in regard to the changes taking place within the gel. As a result, gels are defined as systems rich in liquid, of varying composition (liquid-liquid, liquid-solid, solid-liquid, etc.) and of varying degree of dispersion, although mainly colloidal, the particles of which either by mechanical growth or through other causes are in such proximity to each other that the liquid exists mainly in the form of lyspheres. Theories of swelling are critically examined, and since so many factors have to be considered in special cases the author concludes that no general theory of swelling can be given. E. S. HEDGES.

Free and bound liquid in gels. W. B. HARDY (Kolloid-Z., 1928, 46, 268—277).—Published work on the ratio of free to bound liquid in gels is discussed and the problem is treated from the point of view of adhesion forces. The range of attraction of the particles is considered to be of the utmost importance in colloid-chemical problems. As an analogy to a gel system, a system consisting of a layer of lubricating material between two metal plates is described. E. S. HEDGES.

Concentration differences of dissolved substances in opposition to osmotic pressure in gels. R. AUERBACH (Kolloid-Z., 1928, 46, 321—323).—It is shown that differences of concentration of dissolved substances can be set up at the boundary of a gel and water or at the boundary of two gels of different concentration. The phenomenon is of importance in biological systems, where differences of

concentration are encountered which are far removed from those required by osmotic equilibrium.

E. S. HEDGES.

Jellies and gelatinous precipitates. P. P. VON WEIMARN (Kolloid-Z., 1928, 46, 356—358).—A summary of the author's views and previously published experiments on the classification of gels, the conditions of formation, the form of the disperse particles, the effect of mechanical agitation, and the relation of gelatinous precipitates to flocculent precipitates and to gels. E. S. HEDGES.

Cooling curves of gelatinising systems. H. H. FISCHER (Kolloid-Z., 1928, 46, 359—366).—Cooling curves for various soap solutions have been constructed and in each case at the point of setting a break occurs in the curve, indicating evolution of heat. In a note added to the paper, A. LOTTERMOSER states that he has obtained similar results with soap solutions and has observed the same phenomenon in the cooling of gelatin sols. E. S. HEDGES.

Dependence of swelling on the amount of solid phase. P. P. KESTENBAUM (Kolloid-Z., 1928, 46, 367—368).—Observations on the swelling of different quantities of gelatin in a constant volume of water show that small amounts of gelatin undergo the most swelling. At higher temperatures this effect is enhanced. Similar experiments in solutions of electrolytes show that these have a great influence on the results and in some cases a large amount of gelatin may swell the most, whilst in others a maximal or minimal amount of gelatin may be observed. E. S. HEDGES.

Thermal, mechanical, and X-ray analysis of swelling. R. O. HERZOG and K. WEISSENBERG (Kolloid-Z., 1928, 46, 277—289).—A theoretical paper, which considers the analysis of gels from both the energetic and material points of view. The energetic analysis is treated from the point of view of thermodynamics, mechanics, and molecular kinetics, and the material analysis includes the degree of dispersion, distribution of phases, volume, texture, and fine structure of the particles. The processes of gelatinisation and swelling are discussed in the light of the views expressed. E. S. HEDGES.

Thixotropy. H. FREUNDLICH (Kolloid-Z., 1928, 46, 289—299).—A summary of the author's and other work on thixotropy. It is pointed out that alteration of temperature is not the only factor controlling the sol-gel transformation and that many gels, if not all, can be converted into the sol state by sufficient mechanical agitation, the sol setting to a gel once more when left at rest. This is important in considering the structure of gels. Gels are considered to have a liquid dispersion medium. E. S. HEDGES.

Syneresis. A. KUHN (Kolloid-Z., 1928, 46, 299—314).—A critical examination is made of a considerable amount of published work on syneresis, and the following general conclusions are reached. Certain gels (silicic acid, caoutchouc, etc.) show increased syneresis with rising concentration, whilst others (dyes, starch, agar, cellulose acetate, etc.) behave in the reverse way. There appears to be no general rule for the influence of temperature. The

degree of syneresis varies with the dispersion medium and is sensitive to small amounts of additive agents: in general, the syneresis is greatest when the gel is in the least stable state. The influence of pressure and of surface and the composition of the exuded liquid are also discussed. Syneresis is discussed as a combined process of structural alterations and desolvation.

E. S. HEDGES.

Syneresis and swelling of gelatin. M. KUNITZ (J. Gen. Physiol., 1928, 12, 289—312).—When solid blocks of isoelectric gelatin gel containing less than 10% of the protein are immersed in distilled water or buffer solution at p_H 4.7 they contract and lose water, whilst if the concentration of protein is more than 10% they tend to imbibe water and swell. The loss of water which is finally suffered by a block containing less than 10% of gelatin immersed in water is the same as that which a similar block loses by syneresis when this process is induced by mechanical means, and it is concluded that the shrinkage in water is similar in nature to syneresis and that this term may be conveniently used for the former phenomena. Gelatin gels containing acid, alkali, or salt suffer a greater loss of water than isoelectric gelatin of the same concentration after the acid, alkali, or salt has been removed by dialysis. Quantitative measurements of the loss of water by dilute gels of various gelatin content satisfy an expression similar to that deduced by Northrop (cf. A., 1927, 825) for the swelling of more concentrated gels. The theory of the swelling and contraction of gelatin gels is discussed.

W. O. KERMACK.

Birefractometry of plastic masses. W. STAUF (Kolloid-Z., 1928, 46, 345—350).—A lecture on the characterisation of plastic materials by optical methods.

E. S. HEDGES.

The bioelectric model. R. BEUTNER and T. KANDA (Z. physikal. Chem., 1928, 139, 107—116).—A survey of previous work shows that the maximum variation of $P.D.$ obtained when various parts of plants are placed in contact with salt solutions of varying concentration can be reproduced only by a few substances such as salicylaldehyde or solutions of fatty acids in cresol or similar substances. These substances, however, give an $E.M.F.$ in the opposite direction to the parts of the plants which have been investigated. On the other hand, substances which give an $E.M.F.$ in the required direction do not give the necessary variation with concentration. It has now been found that collodion furnishes a suitable model. A collodion membrane gives an $E.M.F.$ of the same order and in the same direction as an apple when both are in contact with a potassium chloride solution of the same concentration.

R. N. KERR.

$E.M.F.$ in acid and alkaline plant-tissue. K. STERN (Z. physikal. Chem., 1928, 139, 224—234).—The $E.M.F.$ developed in plant-tissue under different conditions have been investigated. Mechanical irritation by brushing, or the action of chemical substances such as concentrated sulphuric acid, citric acid (0.1*N*), and concentrated ammonia solution gives rise to an $E.M.F.$ of about 0.01 volt, and in all cases the side irritated is negative with respect to that not

irritated. Potassium chloride solutions give rise to similar $E.M.F.$ and in arrangements of the type dilute electrolyte|plant-tissue|concentrated electrolyte, the side of the tissue in contact with the dilute electrolyte is positive with respect to the other side. The effect is practically reversible and is greater with 0.01*N*/0.001*N* solutions than with 0.1*N*/0.01*N* solutions. The results are discussed in relation to the conclusions of Haber and Klemensiewicz (A., 1909, ii, 785) on the electrical effects observed in muscle-tissue.

L. S. THEOBALD.

Van der Waals' equation and the principles of thermodynamics: the Maxwell-Clausius relation and Clapeyron's formula deduced from this equation. V. KARPEN (Compt. rend., 1928, 187, 1039—1042).—If van der Waals' equation holds for the liquid and vapour phase of a fluid, it may be used for the direct calculation, independently of Carnot's principle, of the Clapeyron and Maxwell-Clausius relationships.

J. GRANT.

Rapid calculation of the degree of dissociation. Application to carbon dioxide. P. JOLIBOIS and P. MONTAGNE (Compt. rend., 1928, 187, 1145—1147).—A graphic method is described.

J. GRANT.

Symmetrical and asymmetrical hydrogen and the third law of thermodynamics. Thermal equilibrium and the triple point pressure. W. F. GIAUQUE and H. L. JOHNSTON (J. Amer. Chem. Soc., 1928, 50, 3221—3228).—The vapour pressure of hydrogen at the triple point falls from 5.38 to 5.34 cm. when the hydrogen has been kept at the temperature of liquid air for 197 days. This may be due to a change of the hydrogen molecules from the asymmetric to the symmetric form (Heisenberg, A., 1927, 290; Dennison, *ibid.*, 291, 817). Fowler's statistical calculation of the entropy of hydrogen containing the two forms of molecules (A., 1928, 469) is inaccurate; 4.39 g.-cal./1° must be added to the molar entropy calculated by the usual methods.

S. K. TWEEDY.

Electrolytic dissociation. M. A. RABINOVITSCH (Ukraine Chem. J., 1928, 3, 237—434).—A theory of solution and electrolytic dissociation is proposed. It is shown that there is no abrupt transition from electrolytes to non-electrolytes, the difference between which is due to the degree of intramolecular ionisation. The electrolytic properties of solutions are due to the peculiar molecular structure of the solvates formed, these complex molecules having their chemical affinities satisfied to a greater extent than are those of the molecules of the solvent alone. Strong electrolytes are considered to be those the molecules of which exhibit high polarity, and dissociation is greatest in a highly polar solvent. Dissociation is thus considered as a phenomenon having its origin in the interaction of molecules. The consequences of this point of view are that it becomes unnecessary to assume complete dissociation of strong electrolytes, or to consider the solvent merely as a dielectric medium. Ostwald's equation is not applicable to strong electrolytes, the solvated molecules and ions of which have a marked tendency towards association, as a result of their high polarity. Anomalous dissociation curves, where the degree of dissociation first falls to a minimum with

rising concentration, and then rises to a maximum, are the result of the simultaneous action of two opposing influences, solvation, favoured at low concentrations, and polymerisation, favoured at high concentrations. At the minimum, both influences affect conductivity to an equal extent, whilst at the maximum dissociation of the polymerised solvate complex is practically complete.

R. TRUSZKOWSKI.

Ethyl acetate equilibrium. R. C. CANTELO and R. D. BILLINGER (J. Amer. Chem. Soc., 1928, 50, 3212—3215).—The esterification of acetic acid by ethyl alcohol was investigated at 78° in presence of the chloride, thiocyanate, and iodide of sodium, which salts form a Hofmeister series. The equilibrium constant, $K = [\text{ester}][\text{water}]/[\text{acid}][\text{alcohol}]$ increases with rising salt concentrations, the relation being linear in the case of sodium chloride. The order of the effects of the anions is not that of a Hofmeister series (cf. Schlesinger, A., 1926, 1109). S. K. TWEEDY.

Ebullioscopic determination of complexes formed by mercuric chloride and alkali chlorides. Association of mercuric chloride. F. BOURION and E. ROUYER (Ann. Chim., 1928, [x], 10, 263—355; cf. A., 1928, 1185).—The association of mercuric chloride in aqueous solution has been studied ebullioscopically for C 0.175—1.75 mol./litre. Whilst the authors agree with Linhart (A., 1915, ii, 99) that at 25° and 40° the equilibrium is $2\text{HgCl}_2 \rightleftharpoons \text{Hg}_2\text{Cl}_4$ for $c < 0.37$ they consider that at 100° between 0.5 and 1.75 mols./litre it is exclusively $3\text{HgCl}_2 \rightleftharpoons \text{Hg}_3\text{Cl}_6$, although double molecules possibly exist when c is less than 0.2. The density of mercuric chloride in aqueous solution at 15° is 5. In the application of the ebullioscopic method to the determination of complexes formed with alkali chlorides it is necessary to consider the concentration of both the single and the associated molecules of mercuric chloride. The maximum deviation of the rise in b. p. for corresponding solutions containing mercuric chloride and potassium, ammonium, or sodium chloride from the additive value for the separate salt solutions corresponds with 0.4 of mercuric chloride and 0.6 of the alkali chloride, which suggests the existence of a mixture of the complexes M_2HgCl_4 and MHgCl_3 ($\text{M} = \text{K}, \text{NH}_4$, or Na), a view which is confirmed by other evidence. The values of $k = C_{\text{H-Cl}} \times C_{\text{MCl}}^2 / C_{\text{M}_2\text{HgCl}_4}$ are 0.0545 for potassium and 0.131 for sodium chlorides (concentrations calculated at 15°). A study of the reduction of mercuric chloride with sodium formate, a stoichiometrically termolecular reaction, confirms Linhart's result (A., 1915, ii, 91) that the bimolecular velocity coefficient is constant when a large excess of sodium formate is used. A similar result is obtained in presence of an excess of sodium acetate, the value of the termolecular coefficient decreasing as the reaction proceeds. An explanation is suggested in terms of the complexes formed by mercuric chloride and sodium acetate (and hence, presumably, with sodium formate) at 100°, the most probable composition being $4\text{HgCl}_2 \cdot 5\text{Me} \cdot \text{CO}_2\text{Na}$. The reduction is thus formulated by the bimolecular reaction $[4\text{HgCl}_2 \cdot 5\text{H}(\text{Me}) \cdot \text{CO}_2\text{Na}] + \text{H} \cdot \text{CO}_2\text{Na} = 2\text{HgCl} + \text{HCl} + \text{NaCl} + \text{CO}_2 + 5\text{H}(\text{Me}) \cdot \text{CO}_2\text{Na} + 2\text{HgCl}_2$, a constant bimolecular coefficient being obtained

with a sufficient excess of sodium formate or acetate, but with insufficient excess the sodium chloride produced forms a stable, more difficultly reducible complex with the mercuric chloride, thus causing the bimolecular coefficient to diminish as the reaction proceeds. Mercuric cyanide raises the b. p. normally at all concentrations up to 1.75 mols./litre (except for evidence of slight association at the highest concentrations) and the absence of hydrolysis is shown to be due to its very small ionisation constant (10^{-15}). By methods similar to those employed above, the formation of complexes between mercuric cyanide and alkali or alkaline-earth halides has been studied. With potassium, sodium, and ammonium chlorides and potassium iodide these are of the type $\text{M}'[\text{HgCNX}]$ ($\text{M}' = \text{metal}$, $\text{X} = \text{halogen}$), and with magnesium, calcium, and strontium chlorides of the similar type $\text{M}''[\text{Hg}(\text{CN})_2\text{X}_2]$, and, with the exception of the last two, all these complexes have been isolated. No evidence of any complex formation with the double molecule $\text{Hg}_2(\text{CN})_4$ was obtained. Unlike the other alkaline-earth metals, barium chloride forms the complex $\text{Ba}[\text{Hg}_2(\text{CN})_4\text{Cl}_2]$. The value of $k = c_{\text{Hg}(\text{CN})_2} \times c_{\text{MX}} / c_{\text{M}[\text{Hg}(\text{CN})_2\text{X}]}$ is 1.3 for potassium chloride and 0.87 for the bromide (concentrations calculated at 15°). The density of mercuric cyanide in aqueous solution at 15° is 4.

J. W. BAKER.

Buffer studies. X. Buffering of faeces. II. M. KARTAGENER (Helv. Chim. Acta, 1928, 11, 1084—1094; cf. *ibid.*, 548).—The hydrogen-ion concentrations of sodium hydroxide solutions of progressively decreasing concentrations have been measured alone and after shaking with secondary and tertiary calcium orthophosphates. On addition of these salts the p_{H} is always displaced towards the acid side. The amount of displacement depends on the p_{H} of the original solution, being smaller for the more alkaline solutions. The amount also differs for the two salts; above an initial alkali concentration of 0.0025*N* the displacement is greater with the secondary salt, but below that concentration the tertiary salt has the greater effect. The amounts of calcium and phosphate ions in the supernatant liquid have been determined analytically for one series. The ratio $\text{Ca} : \text{PO}_4$ increases with diminishing alkalinity and is lower for liquids shaken with tertiary salt than for those with secondary salt. These results are explained on the hypothesis that calcium hydroxide is formed from the phosphate in solution by hydrolysis and is adsorbed on the surface of the solid phosphate.

The effect of adding solid calcium phosphate to a buffer solution was also investigated. An acetic acid-acetate buffer was titrated electrometrically with acid and alkali. Quantities of this solution were then shaken with tertiary calcium phosphate and again titrated (a) with solid phase present and (b) after filtering. The degree of buffering, measured by the slope of the titration curve, of the heterogeneous buffer system does not differ greatly from that of the original solution, but the buffer capacity, measured by the amount of acid required before a turning point is reached on the curve, is increased to an extent depending on the concentration of the solid phase. The increase in the buffering capacity is much less marked

if the solid phase be removed by filtration. The composition of the acetate buffer was so chosen that addition of the phosphate caused a lowering of p_H , but it is emphasised that, despite this, the acid capacity of the heterogeneous system is raised.

R. N. KERR.

Chemical antagonism of ions. I. Effect of sodium-magnesium and potassium-magnesium mixtures on the activity of the oxalic ion, C_2O_4 . II. Antagonism between anions and also between cations and anions in their effect on oxalate activity. H. S. STARRS (J. Gen. Physiol., 1928, 12, 241–258, 259–267).—I. The activity of the oxalic ion has been derived from conductivity measurements of magnesium chloride and sodium chloride (or potassium chloride). The activity is depressed by sodium chloride but more so by magnesium chloride. When, however, sodium chloride is present as well as magnesium chloride the depression of the activity is less than when magnesium chloride alone is present. The following equation, which is partly empirical, has been found to fit the experimental observation: $k = [(inactivated\ C_2O_4'') / (active\ C_2O_4'')] \times [(Na^+ + K^+ + 2Mg^{++} + A) / (\gamma Mg(C_2O_4')^{1.5})]$, where A is an empirical constant depending on the concentration of oxalate ion and γMg is the activity of the magnesium ion.

II. The anomalous effect of the sulphate ion on the activity of the oxalate ion which is exerted in a direction opposite to that of magnesium ion is antagonised by sodium chloride and an equation similar in form to that given above is also satisfied in this case. In solutions of magnesium sulphate more dilute than 0.03*M*, the effect of magnesium predominates over that of sulphate, whilst in more concentrated solutions the effect of the sulphate ion predominates. In solutions containing both sodium sulphate and magnesium chloride marked antagonism between the magnesium and sulphate ions is observed. As the activity of proteins is presumably influenced in a similar way by inorganic ions, biological antagonism of ions may be related to these phenomena. W. O. KERMAK.

Ionic concentrations and activity coefficients of weak electrolytes in certain salt solutions. H. S. HARNED and R. A. ROBINSON (J. Amer. Chem. Soc., 1928, 50, 3157–3178).—A general method is described for measuring the activity coefficients and the hydrogen- or hydroxyl-ion concentrations of weak acids and hydroxides in salt solutions of varying concentrations by *E.M.F.* measurements on cells with no liquid junction potentials and also on cells with negligibly small such potentials. The method was applied to acetic acid by using cells of the type $H_2|HCl, MCl|AgCl|Ag$ and $H_2|HOAc, MCl|AgCl|Ag$, where $M = K, Na, Li$, or 0.5*Ba*. With the progressive addition of salt, the dissociation of the acid passes through a maximum, whilst the ionic activity coefficients pass through a minimum (cf. Harned, A., 1927, 206). A method of correcting the calculated results for the influence of the undissociated acetic acid molecules in the solution is given. The above general method is also applied to weak bases, BOH , viz., ammonia and its methyl derivatives, by measuring the *E.M.F.* of cells of the type: $H_2|MOH, MCl(c)|$

$MCl(c)|AgCl|Ag$ and $H_2|BOH, MCl(c)|MCl(c)|AgCl|Ag$, M being K, Na , or Li , which, when combined, represent a cell with a negligible junction potential. The activity coefficients of ammonia in sodium chloride solutions are progressively diminished as methyl groups are introduced into the molecule or as the salt concentration is increased. The order of the salt effects is the same as in the case of acetic acid. The results show that the ionic activity coefficients of acetic, mono- and di-chloroacetic acids (cf. A., 1928, 251) are smaller in the solution of a given concentration of that salt which possesses the higher activity coefficient in pure water. The same is true for ammonia and monomethylamine, and probably also for di- and tri-methylamines. In the presence of more than 0.1*M*-sodium chloride, 0.01*M*-tetramethylammonium hydroxide seems to be more highly dissociated than sodium hydroxide. S. K. TWEEDY.

Transformation of chromates into dichromates. E. CARRIERE and P. CASTEL (Compt. rend., 1928, 187, 1292–1294).—The ionic equilibrium $2CrO_4'' + 2H^+ \rightleftharpoons Cr_2O_7'' + H_2O$ has been studied at 20° by the conversion of barium chromate into barium dichromate by the addition of a measured amount of hydrochloric acid, the end-point being reached when the solution becomes clear. The hydrogen-ion concentration of the equilibrium mixture was calculated from the law of mass action applied to the ions concerned assuming complete dissociation, and good agreement was found between the observed and calculated values for low concentrations. The concentration of acid required decreases with temperature, and the equilibrium constant at 18° is 3×10^{-15} .

J. GRANT.

Transformations of rubidium halides by pressure. P. W. BRIDGMAN (Z. Krist., 1928, 67, 363–376; Chem. Zentr., 1928, ii, 317).—The conversion of rubidium chloride, bromide, and iodide at high pressure into a second modification has been studied by a differential volumetric method. Thermodynamic data are tabulated. A. A. ELDRIDGE.

Vapour pressures of aqueous solutions of potassium iodide and sodium bromide at 25°. J. N. PEARCE, M. D. TAYLOR, and R. M. BARTLETT (J. Amer. Chem. Soc., 1928, 50, 2951–2958).—The above vapour pressures were measured up to saturation by the method previously described (Pearce and Snow, A., 1927, 302). The osmotic pressures of the solutions calculated by Fraser's formula deviate from those obtained by Lewis' expression above 0.8*M*. Other thermodynamic properties of the solutions are calculated also. S. K. TWEEDY.

Volatility with steam of water-soluble organic substances. A. I. VIRTANEN and L. PULKKI (J. Amer. Chem. Soc., 1928, 50, 3138–3151).—If a solution containing y_1 parts of volatile substance in x_1 parts of water is distilled and a solution of y_2 parts of substance in x_2 parts of water is left, then, according to Wiegner $(\log y_1 - \log y_2) - k(\log x_1 - \log x_2)$, where k is the distillation constant of the substance and indicates its volatility in steam, supposing condensation of the steam to be eliminated. Values of k are recorded for some organic substances in water; in a homologous series k increases 0.6 for each CH_2 group

in acids and 10 for each such group in amines, due to the degree of hydration regularly decreasing as the carbon chain is lengthened. A method is given whereby an aqueous solution of two volatile substances may be analysed by a single distillation provided the values of k are less than 5. The method may be extended to mixtures of three volatile substances, two distillations then being necessary. The presence of neutral salts in the solution of the volatile substance generally augments the value of k , the anion having a much greater influence in this respect than the cation. The effect is due to a diminution in the hydration of the substance.

S. K. TWEEDY.

Iron-zinc system. Y. OGAWA and T. MURAKAMI (Tech. Rep. Tôhoku, 1928, 8, 53—69).—The compounds FeZn_7 and FeZn , are formed.

C. W. GIBBY.

System tungsten-carbon. K. BECKER (Z. Metallk., 1928, 20, 437—441).—Röntgenographic and micrographic examination of the system tungsten-carbon shows the presence of only two carbides at the ordinary temperature, namely W_2C and WC . At 2600° , however, the latter dissociates, leaving a residue of the composition W_3C_2 which on cooling decomposes into a eutectoidal equimolecular mixture of W_2C and WC . The lower carbide melts undecomposed in an atmosphere with a sufficiently high partial pressure of carbon, but it is decarburised by melting in hydrogen or in a vacuum; at 2400° it undergoes a transformation into $\beta\text{-W}_2\text{C}$. On heating tungsten wire in methane-hydrogen mixtures carburisation ensues, the minimum concentration of methane to produce carburisation increasing with rise of temperature; at this minimum concentration WC is the first product formed up to 1900° , $\alpha\text{-W}_2\text{C}$ from 1900° to 2400° , and $\beta\text{-W}_2\text{C}$ above 2400° .

A. R. POWELL.

Cryoscopic studies of the transition points of compounds of organic solvents with salts. I. H. ÔSAKA (Bull. Chem. Soc. Japan, 1928, 3, 289—297; cf. A., 1928, 1095).—The lowering of the transition point (25.5°) at which the compound $\text{NaI}\cdot 3\text{COMe}_2$ loses acetone by the dissolution of foreign substances has been studied and the molecular depression, referred to 100 g. of acetone, has been determined as 24.0, using as solutes naphthalene, camphor, benzoic acid, acetanilide, *p*-nitroaniline, phthalic anhydride, benzil, and coumarin. The maximum variation in the constant so obtained was less than 5%. For the compound $\text{HgCl}_2\cdot\text{COMe}_2$, transition point 20.7° , the same mean value was obtained for the molecular depression of the transition point, but the results were less concordant than with the former substance.

F. G. TRYHORN.

Ammonium sulphite and hydrogen sulphite. I. Solubility and transition point of ammonium sulphite. F. ISHIKAWA and H. MUROOKA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 1160—1176).—The solubility of ammonium sulphite in water has been determined from the cryohydric point up to 100° , and some f.-p. measurements have been made. The transition point of the monohydrate to the anhydrous salt is $80.8^\circ \pm 0.2^\circ$.

R. CUTHILL.

Solution of the ternary equilibrium diagram and a contribution to the Al-Cu-Zn system.

M. HAMASUMI and S. MATOBA (Tech. Rep. Tôhoku, 1928, 8, 71—98).—A general method for the interpretation of ternary equilibrium diagrams based on its resolution into solubility surfaces is described. By this method the results of Hanson and Gayler (A., 1925, ii, 974) and of Nishimura (Mem. Coll. Eng. Kyoto, 1927) for the system Al-Cu-Zn are compared with one another and with experiments by the authors. Hanson and Gayler's diagram is considered to be the more acceptable.

C. W. GIBBY.

System lead nitrate-ammonium nitrate-water. G. MALQUORI (Atti II Cong. Naz. Chim. pura appl., 1926, 1135—1140; Chem. Zentr., 1928, ii, 517).—Only lead nitrate and ammonium nitrate exist as solid phases. The lead nitrate content of solutions (at 0° , 10° , and 20°) is but little affected by large amounts of ammonium nitrate; that of the latter is greatly influenced by the former.

A. A. ELDRIDGE.

Physico-chemical investigation of amino-acids. G. TAKAHASHI and T. YAGINUMA (Proc. Imp. Acad. Tokyo, 1928, 4, 561—564).—Equilibrium data are recorded for the system *l*-leucine-HCl- H_2O , at 15° and 30° ; specific rotation and rotatory dispersion have been determined at different concentrations. A metastable form of *l*-leucine is obtained by crystallisation from hot alcoholic hydrogen chloride.

S. J. GREGG.

Equilibrium of silver oxide and silver chloride with aqueous potassium chloride and potassium hydroxide. R. F. NEWTON (J. Amer. Chem. Soc., 1928, 50, 3258—3261).—The ratio of the chloride- and hydroxide-ion concentrations at equilibrium at 25° is independent of the method of preparation of the silver oxide and is substantially the same as that found by Noyes and Kohr (A., 1903, ii, 201). It has the same value in 0.05*M*-solution of hydroxide ions as in 0.1*M*-solution.

S. K. TWEEDY.

Synthesis of carbamide from ammonia, carbon dioxide, and water from a physico-chemical point of view. E. TERRES and H. BEHRENS (Z. physikal. Chem., 1928, 139, 695—716).—The study of the ternary system ammonia-carbon dioxide-water (A., 1921, ii, 448) has been extended to temperatures above 60° . As considerable pressure was developed at these higher temperatures the use of steel bombs for reaction vessels was found necessary. The equilibrium conditions were determined at 80° , 100° , and 120° with both ammonium hydrogen carbonate and carbamate as solid phase and ammonia solutions of gradually increasing concentrations as liquid phase. The amounts of ammonia and carbon dioxide in the liquid phase were determined and the relation between them is shown graphically. The isothermals at 80° and 100° so obtained afford evidence of a double salt, hydrogen carbonate-carbamate. The formation of this solid phase is also proved by microscopical examination. No similar formation of double salt is obtained at 120° . The temperature at which it is no longer formed is 106° , which is also the m. p. of ammonium hydrogen carbonate. Above this temperature the solid phase consists only of hydrogen carbonate or carbamate. Experiments were also made at 135° and, in spite of experimental difficulties, it is

shown that at this temperature both hydrogen carbonate and carbamate are converted into carbamide and can no longer exist as the solid phase. A space diagram of the ternary system is given. From the experimental data the solubility of ammonium hydrogen carbamate in water over the range of temperature investigated can be deduced. The solubility curve is a straight line. R. N. KERR.

Equilibrium between aluminium carbide and nitrogen at high temperatures. C. H. PRESCOTT, jun., and W. B. HINCKE (J. Amer. Chem. Soc., 1928, 50, 3228—3237).—The reaction $4\text{AlN} + 3\text{C} = \text{Al}_4\text{C}_3 + 2\text{N}_2$ was studied between 1774° and 1909° Abs. The equilibrium pressures are represented by the equation $\log p \text{ (mm.)} = 12.772 - 27697/T$, whence the free energy change at 1 atm. is $253,630 - 90.58T$ g.-cal. and the heat of reaction $-253,630$ g.-cal. For the reaction $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ the free energy change is $127,065 - 67.57T$ g.-cal. at 1 atm. and the heat of reaction $-127,065$ g.-cal., in agreement with the observations of Fraenkel (A., 1913, ii, 509).

S. K. TWEEDY.

- **System $\text{Al}(\text{NO}_3)_3\text{--KNO}_3\text{--HNO}_3\text{--H}_2\text{O}$ between 0° and 60°.** G. MALQUORI (Gazzetta, 1928, 58, 781—791; cf. A., 1928, 1328).—The solubility data for the ternary systems which are possible with the above components are completed by determining the isotherms for the system $\text{Al}(\text{NO}_3)_3\text{--HNO}_3\text{--H}_2\text{O}$ at 0°, 40°, and 60°. These results are combined to give a model which shows the equilibrium relationships for the quaternary system and defines the conditions in the Blanc process for the fractional crystallisation of potassium and aluminium nitrates from solutions of leucite in nitric acid. O. J. WALKER.

Eutectic surfaces. W. WAHL (Forh. III nord. Kemistmotet, 1928, 180—183).—In four-component systems a eutectic surface results when three of the components form mixed crystals in which the fourth is insoluble, the surface being defined by the three binary eutectic points and the eutectic lines of the three ternary systems. A eutectic surface likewise results if the four components form mixed crystals in pairs, the pairs being mutually insoluble in one another. Systems of the latter type are of theoretical importance in dealing with the crystallisation of the igneous rocks, and have been hitherto little investigated. The author has studied the system naphthalene- β -naphthol-azobenzene-stilbene, in which the two binary systems naphthalene- β -naphthol and stilbene-azobenzene form mixed crystals which are insoluble in one another. The six binary and four ternary systems have been studied in detail, and the form of the eutectic surface has been determined. This latter cuts one side of the concentration tetrahedron close to the azobenzene corner, and consequently lies very obliquely in the tetrahedron. Eutectic surfaces of this type are to be expected in the systems involved in the crystallisation of the igneous rocks. One of the simplest cases is afforded by the meteoric stones consisting of anorthite and a pyroxene of the enstatite-augite series, containing three isomorphous components. The remaining igneous rocks contain as a rule several series of isomorphous components. In general, if the rocks crystallise so rapidly that equi-

librium is not attained, then crystallisation takes place mainly along the paths leading to the eutectic surface (volcanic rocks), but when equilibrium can be established the final crystallisation takes place along eutectic surfaces (plutonic rocks).

H. F. HARWOOD.

Heat capacity and entropy of barium bromate from 16° to 300° Abs. Entropy of bromate ion. B. S. GREENSFELDER and W. M. LATIMER (J. Amer. Chem. Soc., 1928, 50, 3286—3290).—The heat capacities of barium bromate monohydrate were measured between 16.36° and 295.88° Abs. by the method previously described (A., 1928, 1096). The absolute molal entropy of this salt at 298.1° Abs. was calculated as 80.72 g.-cal./1°. The molal heat and free energy of solution are 15064 and 17171 g.-cal. at 25°, whence the entropy of solution is 26.48 g.-cal./1°, and the entropy of the bromate ion 43.6 g.-cal./1°.

S. K. TWEEDY.

Calorimetric investigations. II.b. Benzoic acid as a standard for the calibration of bomb calorimeters. P. E. VERKADE (Chem. Weekblad, 1928, 25, 666—667; cf. *ibid.*, 1923, 20, 513; A., 1922, ii, 740).—A critical account of the recent determinations of the heat of combustion of benzoic acid by Roth, Doepke, and Banse (A., 1928, 712) and by Jaeger and von Steinwehr (*ibid.*, 1096).

S. I. LEVY.

Calorimetric researches. XV. Thermochemical study of cycloparaffins and their derivatives. I. Experimental data for five- and six-membered cyclic diols. P. E. VERKADE, J. COOPS, jun., C. J. MAAN, and (FRAU) A. VERKADE-SANBERGEN (Annalen, 1928, 467, 217—239).—The heats of combustion of several pairs of *cis*- and *trans*-1:2-diols have been determined by methods previously described (A., 1925, ii, 490; 1926, 893), the values being based on that of benzoic acid, 6324 g.-cal. 15/g. (air) (A., 1925, ii, 871). The following numbers give the molecular heats of combustion (kg.-cal. 15°) at constant volume, Q_v , the figures in parentheses being the values at constant pressure, Q_p : *cis*-cyclopentane-1:2-diol, b. p. 79°/1.5 mm., 695.2 (696.0); *trans*-cyclopentane-1:2-diol, setting pt. 53.7°, 693.3 (694.1); *cis*-1-methylcyclopentane-1:2-diol, b. p. 95°/7 mm., 846.5 (847.6); *trans*-1-methylcyclopentane-1:2-diol, m. p. 64.8—65.6°, 844.2 (845.3); *cis*-1-phenylcyclopentane-1:2-diol, m. p. 64.6—65.4°, 1412.6 (1414.1); *cis*-hydrindene-1:2-diol, m. p. 107.6—107.8°, 1097.5 (1098.4); labile *cis*-hydrindene-1:2-diol, m. p. 100.5—101.5°, obtained by hydrolysis of the *cis*-1:2-diacetate, 1098.6 (1099.5); *trans*-hydrindene-1:2-diol, m. p. 158.6—159.6°, 1095.8 (1096.7); *cis*-1:2:3:4-tetrahydronaphthalene-1:2-diol, m. p. 102.5—103.5°, 1249.6 (1250.8); *trans*-1:2:3:4-tetrahydronaphthalene-1:2-diol, 1248.3 (1249.5); *cis*-1:2:3:4-tetrahydronaphthalene-2:3-diol, m. p. 124.2—125°, 1249.7 (1250.8); *trans*-1:2:3:4-tetrahydronaphthalene-2:3-diol, m. p. 135.5—136°, 1248.4 (1249.5); *cis*- + *trans*-1:2:3:4-tetrahydronaphthalene-2:3-diol, m. p. 141—142.4°, 1247.7 (1248.9); *cis*-cyclohexane-1:2-diol, m. p. 98.4—99.2°, 840.4 (841.6); *trans*-cyclohexane-1:2-diol, m. p. 103.6—104.4°, 841.4 (842.6); *cis*-1-methylcyclohexane-1:2-diol, m. p.

67.5—68.5°, 991.1 (992.6); *trans*-1-methylcyclohexane-1:2-diol, m. p. 84—85°, 993.6 (995.1); *cis*-1-phenylcyclohexane-1:2-diol, m. p. 95.5—96°, 1561.4 (1563.1); *trans*-1-phenylcyclohexane-1:2-diol, m. p. 99—99.5°, 1562.3 (1564.0).

The *cis*-diols in the cyclopentane and cyclohexane series have lower m. p. than the corresponding *trans*-diols. Permanganate oxidation of cyclopentenes and cyclohexenes yields the *cis*-compounds, whilst the *trans*-forms are obtained by acid hydrolysis of the corresponding oxides. The *cis*-derivatives form acetone compounds and with boric acid in presence of potassium hydroxide give crystalline complexes. The *trans*-forms do not form such derivatives. A critical discussion on the structure of cycloparaffins is to be published.

H. BURTON.

Constitution and thermochemistry. A. GOSSELIN and M. GOSSELIN (Compt. rend., 1928, 187, 1050—1052).—The formulae derived from Werner's theory and the theory of partial valency are shown to be in accord with the additivity of the heats of linking of the atomic groups. These thermal data may be obtained from the heats of separation of simple binary or ternary compounds, and the heat of formation of the complex compound then derived from its formula. The heats of formation of 38 organic and inorganic compounds have been calculated from the values of the heats of atomic dissociation of the 17 elements concerned, and the values obtained are shown to be in agreement with experimental results. J. GRANT.

Moving boundary method applied to the measurement of the absolute velocity and the transport number of ions and of the rate of migration of colloidal particles. J. N. MUKHERJEE (J. Indian Chem. Soc., 1928, 5, 593—607).—When a homogeneous solution AR has two indicator solutions BR and AR', of lower density, on its surfaces the ions A and R will be moving at the two boundaries $\leftarrow \text{AR}|\text{BR}$ and $\text{AR}'|\text{AR} \rightarrow$, through a uniform ionic environment, and if the potential gradient, or the current density and the concentration, in the solution AR of constant concentration be known their transport numbers can be determined, because although the drag at the boundary may have a disturbing effect its magnitude will be very small inside the electrolyte AR. The conditions at the boundary will not be governed by Kohlrausch's equations. In this respect the current density and the transport numbers of the anion in the two layers are important factors. It is shown that even in those cases in which it is possible to determine the transport numbers by the boundary method the movement of the boundary does not necessarily give the correct mobilities of both ions unless the transport number of the common ions has the same value in both electrolytes. In extending these considerations to the determination of cataphoretic velocities it would appear that the theoretical basis of such measurements must rest on securing a uniform ionic environment during the movement of the colloidal particles.

F. G. TRYHORN.

Theory of the mobilities of the hydrogen and hydroxyl ions in aqueous solution. E. HÜCKEL (Z. Elektrochem., 1928, 34, 546—562).—It is assumed that the reaction $\text{H}_3\text{O}^+ + \text{H}_2\text{O} = \text{H}_2\text{O} + \text{H}_3\text{O}^+$ pro-

ceeds, without heat exchange, with a frequency which increases as the temperature is raised. A model is adopted for the H_3O^+ ion which leads to a deduction of the proportionality between mobility and field strength (Ohm's law), and an expression is deduced for the velocity of the H_3O^+ ions in unit field. The two terms of the expression relate to the motion of the ions as a whole and to the transference of protons according to the above equation, respectively. Expressions are also deduced for the mean life of the H_3O^+ ion, which is of the order of 3×10^{-11} sec. at the ordinary temperature. The theory applies equally well to hydroxyl ions, the assumed reaction being $\text{OH}' + \text{H}_2\text{O} = \text{H}_2\text{O} + \text{OH}'$. Suggestions are offered for testing the theory experimentally. In certain non-aqueous solutions the usual transport process may be accompanied by another, anomalous transport process.

S. K. TWEEDY.

Incompatibility between theories of complete dissociation and migration data for bivalent ions. J. W. MCBAIN and P. J. VAN RYSELBERGE (J. Amer. Chem. Soc., 1928, 50, 3009—3017).—Migration experiments with salts of cadmium, magnesium, lithium, potassium, and calcium in 0.05M. solution in presence of a large excess of anion indicate that the excess of anion combines with undissociated salt molecules to form complex ions. Salts containing multivalent ions, therefore, cannot be completely dissociated in solution except at extreme dilution (MacInnes and Cowperthwaite, A., 1927, 1031).

S. K. TWEEDY.

Electrical conductivities of uni-univalent salts in benzonitrile. A. R. MARTIN (J.C.S., 1928, 3270—3293).—The conductivity of solutions of certain uni-univalent inorganic salts in benzonitrile has been determined using a pure sine wave alternating current of 1000 cycles per sec. Tables are given showing the conductivities of potassium, sodium, and lithium iodides, lithium bromide, and silver nitrate at various concentrations and temperatures. The viscosity of benzonitrile over the same temperature range has also been measured and it is found that Λ_0 is directly proportional to the fluidity of the solvent. The results are discussed from the point of view of the Debye-Hückel-Onsager theory, postulating incomplete dissociation which conforms to the mass action law, and it is shown that the variation of conductivity with concentration can be satisfactorily explained on this basis. In very dilute solutions dissociation is complete and it is only the coulomb forces between the ions which determine their mobilities.

J. L. BUCHAN.

Electrical conductivity as a criterion of type of combination. G. VON HEVESY (Z. Elektrochem., 1928, 34, 463—472).—The question is discussed, in the light of previous work by the author (cf. A., 1926, 667; 1927, 815; 1928, 112), from the point of view of solid diffusion and conductivity in the molten state.

S. K. TWEEDY.

Dispersion of the conductivity of strong electrolytes. P. DEBYE and H. FALKENHAGEN (Z. Elektrochem., 1928, 34, 562—565).—A short account of the above phenomenon together with the authors' theory is given (cf. A., 1928, 596, 957).

S. K. TWEEDY.

System aluminium bromide-potassium bromide in benzene. W. A. PLOTNIKOV and S. JAKUBSON (Z. physikal. Chem., 1928, **138**, 251—259).—Solutions of aluminium bromide in benzene possess only very slight electrical conductivity, but the conductivity of mixed solutions of aluminium bromide and potassium bromide is considerable. If the amount of potassium bromide in these latter solutions is kept constant, and the amount either of benzene or of aluminium bromide increased, the conductivity falls, whilst if the amount of potassium bromide is increased and the amounts of benzene and aluminium bromide remain the same, the conductivity rises. Benzene solutions of aluminium bromide contain principally Al_2Br_6 molecules; addition of potassium bromide to such solutions causes a rise in the f. p., from which it is concluded that further polymerisation accompanied by complex formation occurs. When the mixed solution is electrolysed, metallic aluminium separates at the cathode, the decomposition tension being 1.9 volts. R. CUTHILL.

Electrochemistry of solutions of phosphorus pentachloride in bromine. W. A. PLOTNIKOV and S. JAKUBSON (Z. physikal. Chem., 1928, **138**, 235—242).—The specific conductance of solutions of phosphorus pentachloride in bromine first increases with increase in the chloride concentration, then passes through a maximum, and falls until the point of saturation of the solution is reached. A maximum is present also on the concentration-molecular conductivity curve, but is preceded by a minimum. This anomalous behaviour may be explained by supposing that with increasing dilution ionisable complexes of the type $n\text{PCl}_5 \cdot m\text{Br}_2$, which are present in concentrated solutions, break down into the non-ionised components, and finally with further dilution the chloride ionises. When the solution is electrolysed chlorine is liberated at the anode approximately in accordance with Faraday's laws, and the current passing is directly proportional to the voltage applied. R. CUTHILL.

Electrode potential of nickel. III. Mechanism of the re-activation of the passive state of nickel. K. MURATA (Bull. Soc. Chem. Japan, 1928, **3**, 267—276; cf. A., 1928, 846).—In a discussion of previous experimental results the reactivating action of hydrogen on a nickel electrode which has been affected by oxygen is attributed to the catalysing action of the nickel on the union of hydrogen and oxygen. In this process the superficially oxidised nickel is reduced. Thermodynamically it is deduced that the equilibrium conditions in the nickel half-cells are expressed by $\times a_{\text{Ni}^{2+}} \times a_{\text{OH}^-} = 10^{-19.56}$, whence it is calculated that when the activity product ($a_{\text{Ni}^{2+}} \times a_{\text{OH}^-}$) is equal to the solubility product of the nickelous hydroxide the corresponding partial pressure of hydrogen is 0.22 atm. This is the critical pressure above which equilibrium can alone be established and below which nickel will tend to go into solution with the precipitation of nickelous hydroxide until p_{H_2} rises to the critical value. The changes with time of the *E.M.F.* of cells prepared in an atmosphere of hydrogen or nitrogen are explained by the above behaviour.

The abnormally low potentials obtained by some previous workers are attributed to the reduction by hydrogen of superficially oxidised nickel with the production of a layer of extremely finely-divided nickel. Calculations have been made of the free energy changes occurring at nickel electrodes with the following results: $\text{Ni(s)} + \text{O}_2 + \text{H}_2 = \text{Ni(OH)}_2(\text{s})$, $\Delta F_{298} = -11228$ g.-cal.; $\text{Ni} + 2\text{OH}' = \text{H}_2 + \text{Ni(s)} + 2\text{H}_2\text{O}$, $\Delta F_{298} = -26695$ g.-cal.; $\text{NiO(s)} + \text{H}_2 = \text{Ni(s)} + \text{H}_2\text{O(l)}$, $\Delta F_{298} = -6752$ g.-cal.; $\text{Ni(OH)}_2(\text{s}) + \text{H}_2 = \text{Ni(s)} + 2\text{H}_2\text{O(l)}$, $\Delta F_{298} = -892$ g.-cal.; $\text{Ni}^{2+} + 2\text{OH}' = \text{Ni(OH)}_2(\text{s})$, $\Delta F_{298} = -25800$ g.-cal.; $\text{Ni}^{2+} + 2\text{OH}' = \text{NiO(s)} + \text{H}_2\text{O(l)}$, $\Delta F_{298} = -19940$ g.-cal.; $\text{NiO(s)} + \text{H}_2\text{O(l)} = \text{Ni(OH)}_2(\text{s})$, $\Delta F_{298} = -5860$ g.-cal.

F. G. TRYHORN.

P.D. at the surface of separation between metal and air. (FRL.) M. ANDAUER (Z. physikal. Chem., 1928, **138**, 357—368).—By the method previously employed (A., 1927, 316) a large number of metals have been examined. Contrary to the earlier observations, the metal-air *P.D.* is not the same for all metals and cannot therefore be neglected. It also varies with the amount of ionisation of the air. Attempts have been made to determine the absolute *P.D.* by heating the metal above 180° to remove any film of water at the surface. For the same piece of metal the value obtained is reproducible, but it varies with different samples of the same metal and with the treatment. Attempts to determine the absolute potential of the decinormal calomel electrode gave the value -0.26 volt, which differs by 0.83 volt from the value previously found (*loc. cit.*). M. S. BURR.

Effect of gases on the electrical double layer of aqueous solutions. A. BÜHL (Ann. Physik, 1928, [iv], **87**, 877—908).—A new method for investigating the double layer is described which makes use of the measurement of the *P.D.* of the layer. It is thus possible to find the effect of gases on the layer by a static method, the surface being undisturbed. It is first shown that when gaseous nitrogen, hydrogen, or oxygen is dissolved in pure water or in dilute solutions of alkali chlorides there is no change in the conductivity. The gases form no ions, and they do not affect the degree of dissociation of the water or salt solutions. Hence the diffusion potential at the boundary between a solution containing, and one not containing, dissolved gas is zero. This fact renders the method possible. The apparatus used is described. It was found that the gas in the space above the liquid had no effect on the *P.D.* of the double layer at the surface of aqueous solutions. The *P.D.* of the double layer is, however, increased by dissolved gases, the increase being dependent on the concentration of the electrolyte. The *P.D.* varies with the time of absorption, finally reaching a steady value. An attempt is made to use these facts to explain the nature of the double layer. Gas absorbed from the space above the solution forms at first only an electrically neutral "capillary layer." Gas dissolved in the liquid is positively adsorbed on the surface. A. J. MEE.

Metallic-non-metallic electrode pairs. B. KAMIENSKI (Z. physikal. Chem., 1928, **138**, 345—348).—Carborundum forms an ideal inert electrode the potential of which is almost independent of the

concentration of electrolytes in the solution in which it is placed. Such an electrode, combined with a metallic electrode, should form a suitable electrode pair for electrometric titration. The method of construction of a suitable form of carborundum electrode is described.

M. S. BURR.

Electrocapillary curve of mercury. A. FRUMKIN and A. OBRUTSCHEVA (*Z. physikal. Chem.*, 1928, **138**, 246—250).—The method used by Bennewitz and Deljannis to determine the electrocapillary curve of mercury (A., 1927, 316) is defective, for there is probably no simple relation between the potential of dropping mercury and that of stationary mercury under the conditions of their experiments. If the two are placed in conducting communication and their common potential is measured with an electrometer, the maximum on the electrocapillary curve observed by Bennewitz and Deljannis is absent.

R. CUTHILL.

Explanation of the "electro-capillary" Becquerel phenomenon. H. FREUNDLICH and K. SOLLNER (*Z. physikal. Chem.*, 1928, **138**, 349—356).—If a solution of a metallic salt is separated by a porous wall from a solution which gives an insoluble precipitate with the metal ion, it is found that separation of metal takes place if (a) the precipitate behaves partly or wholly as a metallic conductor, or (b) the *E.M.F.* of the concentration chain between the higher concentration of the metal ions in the metal salt solution, and the very low concentration in the other solution, is greater than the decomposition potential leading to the separation of the metal. If, in place of the sodium sulphide solution combined with a metal salt solution which was studied by Becquerel, a sodium selenide solution is employed, separation of metal takes place very readily because the copper selenide is a metallic conductor. The porous wall is not necessary, except as a support to the precipitate. The necessity for the presence of an anodic depolariser in the case of pairs such as silver nitrate-potassium hydroxide, and copper sulphate-potassium hydroxide, studied by Becquerel, is to be explained by a reduction of the decomposition potential until requirement (b) is fulfilled. No copper separates from the pair copper sulphate-potassium ferrocyanide because there is no metallic conduction.

M. S. BURR.

Preparation of photo-electric cells of thallium. Q. MAJORANA and G. TODESCO (*Atti R. Accad. Lincei*, 1928, [vi], **8**, 9—14).—Photo-electric cells have been constructed with thallium sulphides prepared by heating mixtures of thallium and sulphur under varying conditions and in different atmospheres. Various media for the support of the sulphide were investigated, the best being, respectively, Wood's metal, and an amalgam of equal parts of cadmium, zinc, tin, and mercury, which hardens after some hours. Details are given of the preparation and performance of photo-electric cells made from these materials.

F. G. TRYHORN.

Properties of Fournier's photo-electric cells.

DUBOIS (*J. Phys. Radium*, 1928, [vi], **9**, 310—336).—These cells make use of a fine crystalline deposit of metallic sulphides, the resistance of which falls immediately it is illuminated. The cells differ in

properties from selenium cells. They can be used with light fluctuating at high frequencies (above audible frequency). The properties of these cells are complex, and a number of experiments are described to investigate their mechanism. A theory giving a simple explanation of dissymmetric photoconductivity is propounded and discussed. Some applications of the cells are given.

A. J. MEE.

Electrochemical polarisation of platinum. E. I. SPITALSKI and V. V. PITSCHEVA (*J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1351—1381).—Rotation has no influence on the velocity of depolarisation of platinum anodes. The depolarisation potential P_1 obtaining while the current is passing is distinguished from that found after the current has ceased (P_2); the latter potential is inversely proportional to the density of current previously used. The value of P_1 varies with the area of the anode. The processes taking place in the anode are characterised by P_2 rather than by P_1 . The addition of chemical depolarisers, such as salts of iron, makes little difference to the value of P_1 at currents stronger than 0.033 amp./sq. cm.; at 0.005 amp./sq. cm. P_1 is, however, considerably smaller than in the absence of iron. The previous history of the anodes affects the magnitudes of P_1 and P_2 obtained. The above phenomena are explained on the basis of dissolution in platinum of atomic and molecular oxygen.

R. TRUSZKOWSKI.

Corrosion and residual current. I. Significance of the residual current in the dissolution of metals. II. Significance of the residual current in the deposition of metals. F. TODT (*Z. Elektrochem.*, 1928, **34**, 586—591, 591—595).—I. The current densities for pairs of metals in 0.1*N*-hydrochloric acid or in standard acetate solution (p_H 4.62) have been measured (cf. Centnerszwer and Straumanis, A., 1926, 131). In general the current strength is proportional to the area of the nobler metal and approximately independent of that of the other metal. It is independent of the overvoltage and, unless the internal resistance of the cell is sufficiently large, is increased by agitation of the electrolyte. The diminished current density observed when the electrolyte is heated and then covered with a layer of paraffin regains its original value when the oil layer is broken. The current density observed when air is bubbled through the solution is increased if the air is replaced by oxygen, and decreased if it is replaced by hydrogen. Addition of hydrogen peroxide also produces a large increase in current strength. The electrochemical process involves excess dissolution at the surface of the less noble metal; the process is maintained at the other electrode by the oxygen which diffuses to the surface of the latter. The results indicate that the process of corrosion involves a residual current of an intensity which depends on the quantity of oxygen which diffuses to the metal surface. The results of several previous investigations (e.g., those of Liebreich, A., 1928, 483) are explained on the basis of this theory.

II. The limited time during which a platinum electrode immersed in *N*-cadmium sulphate (with or without acid) assumes the cadmium potential is investigated. The higher the current density the smaller is

the amount of cadmium necessary to produce the cadmium potential for a given duration (cf. Oberbeck, *Ann. Physik*, 1887, **31**, 337). The phenomenon is adequately explained by means of the above residual current theory. The *P.D.* between platinum and a latinum sheet to which a small piece of cadmium has been fused is measured for three different electrolytes by means of an improved valve method in which the variations of the valves are automatically compensated, and the range of measurement is widened without increasing the grid potential. S. K. TWEEDY.

Passivity of metals. W. J. MULLER (*Z. Elektrochem.*, 1928, **34**, 858).—A correction (cf. A., 1928, 1319). L. S. THEOBALD.

Passivity [of chromium]. (FRL.) A. M. HASEBRINK (*Z. Elektrochem.*, 1928, **34**, 819–829; cf. Schmidt, A., 1923, ii, 732).—Chromium which has been previously rendered passive by treatment with nitric acid becomes active when heated in dry nitrogen at 500° for 30 min., and retains this activity for a definite time when preserved in the gas, but eventually becomes passive again. Chromium which has been treated with hydrochloric acid and allowed to become passive by exposure to air is also activated by treatment with nitrogen at 500°, but remains passive for an indefinite time in this gas at the ordinary temperature. Similar behaviour is shown by chromium which has been heated and kept in hydrogen, the formation of an oxygen layer in the last case being impossible. Nitrogen, hydrogen, and carbon dioxide in the molecular state do not activate chromium which has been passivated, and long contact with these gases in the cold does not passivate chromium which has been activated by scratching with a diamond. The passive state is brought about only by oxygen, and the readiness with which different specimens of chromium are activated or passivated depends on the nature and content of the occluded gases. These are not the cause of passivity or activity, but only modify the rate at which the oxygen layer, the true passivating agency, is formed. Iodine can also activate chromium, but, contrary to Hittorf, it can never render this metal passive.

Rubbing of the chromium with emery in an indifferent atmosphere is accompanied by a fall and then a rise in potential of the metal. Finally, after frequent rubbing a lower end-value is reached and this is independent of the nature of the atmosphere in which the rubbing takes place. Introduction of oxygen into the electrolyte raises the potential, which falls on rubbing the surface, and then quickly reaches its higher value. Prolonged and frequent rubbing is required to reduce the potential to its original value. Electrolytic hydrogen and oxygen change the potential markedly. The low potential arises from the hydrogen-free layer of the metal exposed by rubbing, and the large increase in potential produced by the passage of oxygen over the chromium supports the oxygen-layer theory of passivity.

Sheets of iron behave differently, according to their composition and treatment, in the electrolysis of potassium nitrate solutions; some are active and some are passive at low current densities. Generation of hydrogen or oxygen at one side of the sheet is accom-

panied by an apparent increase in electrolysis, but it is shown that this is a mechanical effect of the evolved gas which removes splinters of iron from the surface.

The results disprove the surface tension theory of Hittorf and Schmidt (*loc. cit.*) and the hydrogen theory of passivity, but support the oxygen-layer theory.

L. S. THEOBALD.

Theory of passivity. III. Current density-time curves in cases of coating passivity. W. J. MULLER and K. KONOPICKY (*Monatsh.*, 1928, **50**, 385–391).—Further investigation of the current density-time curves (A., 1928, 1319) shows that the coating of such an electrode proceeds only to about 99% according to the law of surface deposition (*ibid.*, 247). From this point further growth of the layer is in thickness and not in area. The values of *A* in the formula $t = C + A[-1/(i_0 - i) + 2.3/i_0 \cdot \log(i_0 - i)/i]$ do not remain constant but show a steady increase, indicating that with considerable deposition another form of coating process is obtained. For the relation between current density and time in cases of growth of thickness the authors derive the formula $t - t_0 = B(1/i^2 - 1/i_0^2)$, where $B = \chi EF_0 s/k(1-u)$ (all the terms of which with the exception of F_0 are measurable electrochemical data). The validity of this was demonstrated for copper (*ibid.*, 247), and for lead in sulphuric acid at an *E.M.F.* below that necessary for the formation of lead peroxide, and in part also for aluminium. The values of the active free surface (F') for copper and lead are found to be 0.8×10^{-3} cm.² and 0.93×10^{-3} cm.², respectively, agreeing within the limits of experimental error with those deduced theoretically.

H. BURTON.

Calculation of velocity coefficients. II. A. L. T. MOESVELD and W. A. T. DE MEESTER (*Z. physikal. Chem.*, 1928, **138**, 226–234).—The objections raised by Wagner (A., 1925, ii, 406) and Schmid (A., 1926, 480) to the method of determining velocity coefficients described previously (A., 1923, ii, 141) are without foundation. The modified method proposed by Schmid is of inferior accuracy. R. CUTHILL.

Ignition of gas by spark and its dependence on the nature of the spark. T. TERADA and K. YUMOTO (*Proc. Imp. Acad. Tokyo*, 1928, **4**, 467–470).—A gaseous mixture containing 16% of carbon monoxide and 84% of air is more easily ignited by means of an inductive spark than by a capacity spark of the same energy.

W. E. DOWNEY.

Thermal decomposition of ozone at low pressures. E. H. RIESENFELD and H. J. SCHUMACHER (*Z. physikal. Chem.*, 1928, **138**, 268–285).—The thermal decomposition of ozone mixed with oxygen has been studied at 85° and 95° for partial pressures of ozone varying from about 60 to 6 mm. At these pressures, the unimolecular reaction predominates, the bimolecular reaction which occurs simultaneously at higher pressures (A., 1928, 24) being of little account, and the velocity coefficients of both reactions are not appreciably influenced by variations in the partial pressure of oxygen or by the presence of argon. Nitrogen, however, and still more carbon dioxide accelerate the bimolecular reaction. Alteration in the ratio of the surface to the volume of the reaction vessel affects the reaction velocity much less than it

would if the unimolecular reaction were purely a wall reaction, so that it seems that the main reaction is homogeneous, although under ordinary conditions there appears to be some slight wall effect in addition. From the facts that in the experiments of Perman and Greaves (A., 1908, ii, 480) and of Griffith and McKeown (A., 1925, ii, 1168) variation of the surface of the vessel affected the velocity considerably, and also that the observed velocities were exceptionally high, it appears probable that these authors' results were vitiated by the presence of catalysts in the gas or in the apparatus. The results of the present experiments for the unimolecular reaction may be considered to supersede those of Riesenfeld and Bohnholtzer (A., 1928, 24) on account of their greater accuracy. R. CUTHILL.

Explosion temperature of gas mixtures at various pressures. A. B. SAGULIN [with G. RIABININ, PROSKURNIN, and A. KOWALSKI] (Z. physikal. Chem., 1928, B, 1, 275—291).—The relationship between temperature and minimum pressure p_m at which explosion occurs has been determined for a number of gaseous mixtures, and in all cases the relationships $(p_m/T) - A/T + B$ is valid, where A is a characteristic of the reaction and independent of the conditions thereof, and B a constant which usually has a minimum value when about 66% of one compound is present, increasing as the diameter of the vessel decreases. The following values of A have been determined: $H_2 + Cl_2$, 2500, $H_2 + Br_2$, 4000, $CS_2 + O_2$, 4000, $CH_4 + O_2$, 7000, $C_2H_6 + O_2$, 4200, $C_3H_8 + O_2$, 3800, $C_5H_{12} + O_2$, 2200; for the last three reactions A changes abruptly at 680° to a uniform value of 7000, i.e., that for methane and oxygen. The significance of the results is discussed. H. F. GILLBE.

Gaseous explosive reaction at constant pressure. Effect of inert gases. F. W. STEVENS (J. Amer. Chem. Soc., 1928, 50, 3244—3258).—A more detailed account of an investigation of the kinetic effect of indifferent gases (nitrogen, helium, argon, carbon dioxide) on the reaction $2CO + O_2 = 2CO_2$ (cf. A., 1928, 1331). The velocity of propagation of the reaction zone is given roughly by $k'p_{CO}(p - p_{CO})^\alpha + \beta p_g$, where α is the fraction of oxygen in the initial components of partial pressure $p - p_{CO}$, p being the total pressure, β is a constant for a given indifferent gas, and p_g is the initial partial pressure of that gas. S. K. TWEEDY.

Striations in explosive flames. G. B. MAXWELL and R. V. WHEELER (Nature, 1928, 122, 995).—The frequency of striations in a photograph of the flame of a 3.35% pentane-air mixture at 4 atm. initial pressure ignited at one end of a horizontal cylinder was 1200 per sec., the value being independent of the composition and initial pressure of the explosive mixture, but varying inversely as the length of the vessel. Egerton and Gates' view that the striations are due to a stationary wave compounded of sound-waves reflected from the opposite end-plates of the cylinder is supported. The striated appearance of the flame during an explosion always preceded a 'knock.' A. A. ELDRIDGE.

Highly attenuated flames. III. M. PÓLANYI and G. SCHAY (Z. physikal. Chem., 1928, B, 1, 384).—A correction (cf. A., 1928, 1339). The nitrogen pressure

at which the sodium fluorescence is reduced to half is given as 20 mm. instead of 1.5 mm. This does not affect the conclusions. An error in calculation is also noted. M. S. BURR.

Explosions in closed cylinders. I. Methane-air explosions in a long cylinder. II. Effect of length of the cylinders. W. A. KIRKBY and R. V. WHEELER (J.C.S., 1928, 3203—3214; cf. Woodbury and others, J. Soc. Automotive Eng., 1921, 8, 209; Morgan, A., 1927, 630).—Methane-air mixtures were exploded in a cylinder 200 cm. long and 10 cm. in diameter and records obtained of the movement of flame and the development of pressure. A close correlation was found between pressure development and flame movement, increase of pressure being always accompanied by increase in the velocity of propagation of the flame and *vice versa*. When the position of the point of ignition was varied, the maximum pressure was recorded with ignition at the middle point of the cylinder. No higher pressure was obtained with dual ignition, although a sustained period of maximum pressure occurred with the two ignition points a considerable distance apart.

When methane-air mixtures containing 8—11% of methane were ignited at one end of the cylinder the flames became strongly vibratory towards the end of their travel. Experiments on the ignition of 9.5% methane-air mixtures in a cylinder the length of which could be varied showed that the explosion ceased to become vibratory when the length was less than 140 cm. F. J. WILKINS.

Explosions in closed cylinders. III. Movement of flame. O. C. DE C. ELLIS and R. V. WHEELER (J.C.S., 1928, 3215—3218; cf. preceding abstract).—In order to study further the manner of movement of flame in methane-air mixtures, "snapshot" photographs of the similar flames obtained by the ignition of carbon monoxide-oxygen mixtures were taken. The results permit of an explanation of the close correlation found in the earlier work between pressure development and flame movement. F. J. WILKINS.

Effect of anti-knock materials on the speed of initial uniform movement of the flame in hydrocarbon-air mixtures. Y. NAGAI (Proc. Imp. Acad. Tokyo, 1928, 4, 525—528).—The speed of the initial uniform movement of the flame was determined photographically, using tubes 26 cm. in diameter and 108 cm. long, the hydrocarbon being obtained from redistilled petrol and its proportion in the mixture varying between 1.0 and 4.0 mol.-%. Diethyl selenide, lead tetramethyl, and tin tetramethyl were used as anti-knock materials, in proportions varying from 0.2 to 1.5 mol.-%.

In each case the speed of the initial uniform movement decreased to a minimum value and then remained constant as the concentration of anti-knock material increased. The addition of the anti-knock material is believed to raise the calculated minimum temperature at which the flame can be propagated until that of the anti-knock material is reached, when the latter itself burns and can therefore raise the flame propagation temperature of the hydrocarbon no further. S. J. GREGG.

Decomposition of persulphates in aqueous solution. A. KAILAN and E. LEISEK (*Monatsh.*, 1928, 50, 403—428; cf. Kailan and Olbrich, A., 1927, 213).—The velocity of decomposition of sodium persulphate, alone and with the addition of sodium hydrogen sulphate, sodium sulphate, nitrate, or hydroxide, phosphoric acid, disodium hydrogen and trisodium phosphates, or potassium hydroxide, and of potassium persulphate, alone and with the addition of potassium nitrate, potassium and sodium hydroxides, has been studied at 99.4° by the method previously described (*loc. cit.*). For numerical data the original must be consulted, but the results show that in the autodecomposition of sodium persulphate the value of the unimolecular coefficient decreases with increasing original concentration; the values found are 2—8% higher than those for potassium persulphate (cf. *loc. cit.*). Addition of neutral sulphate causes a larger decrease in the coefficient than admixture of hydrogen sulphate (cf. Green and Masson, J.C.S., 1910, 97, 2083). Comparison of the rates of decomposition of sodium and potassium persulphates with added sodium or potassium sulphate indicates that sodium ions retard the decomposition of the persulphate ions to a smaller extent than potassium ions. This is verified by the fact that increasing concentration of added sodium hydroxide to sodium persulphate causes an increase in the velocity of decomposition (cf. Levi and Migliorini, A., 1907, ii, 81) to a greater extent than potassium hydroxide. Nitrate and phosphates accelerate decomposition. In the series of sodium persulphate decompositions the agreement between the observed unimolecular coefficients and those calculated from an interpolation formula expressed as a function of the concentrations of sodium, nitrate, hydroxide, and phosphate (HPO_4'') ions, and the difference between the hydrogen- and sulphate-ion concentrations, is fairly good.

The decomposition of approximately 0.1*N*-potassium persulphate solution in 0.6—14*N*-sulphuric acid at 25° was also examined, using the method described by Palme (A., 1920, ii, 685). The qualitative detection of Caro's acid is possible with 0.35*N*-acid. In 2.7 or 14*N*-sulphuric acid the amount of hydrogen peroxide present is 1—2 or 6—12% of the then existing Caro's acid. The unimolecular velocity coefficient for the decomposition of persulphuric acid, with or without formation of Caro's acid, is shown to be a function of the sulphuric acid concentration.

H. BURTON.

Influence of concentrated electrolytes on the course of chemical processes. Potassium permanganate. M. BOBTELSKI and D. KAPLAN (*Z. anorg. Chem.*, 1928, 177, 323—336).—The velocity of decolorisation of a solution of potassium permanganate containing sulphuric acid and oxalic acid in presence of various chlorides, nitrates, and sulphates has been determined. Chlorides, especially of the alkali metals, have a much greater catalytic influence than have nitrates or sulphates. For the sulphates, the effect decreases in the order lithium, magnesium, ammonium, sodium, potassium, the last three functioning anticatalytically. Ammonium nitrate is a powerful catalyst, sodium nitrate has zero influence,

and potassium nitrate retards the reaction. The chlorides are moderately sensitive to temperature, the sensitiveness increasing in the order ammonium, potassium, magnesium, aluminium, whereas the influence of the nitrates varies but little with temperature, and that of the sulphates to a slightly greater degree than is the case with the nitrates. The temperature effect is maximal over the range 5—25°. The salts exhibiting the greatest temperature effect also show the greatest variation in their influence with concentration; ammonium nitrate is in this respect exceptional. The concentration effect decreases in the order aluminium chloride, cadmium sulphate, magnesium chloride, zinc chloride, zinc sulphate, potassium chloride, ammonium chloride, ammonium nitrate, sodium chloride, ammonium phosphate; lithium sulphate, magnesium sulphate, potassium sulphate, ammonium sulphate, sodium sulphate, potassium nitrate, sodium nitrate; and, in hydrochloric acid, calcium chloride, strontium chloride, barium chloride; the alkaline-earth chlorides come between magnesium chloride and potassium chloride in the first series.

H. F. GILLBE.

Molecular formula and constitution of hypophosphoric acid. A. ROSENHEIM and H. ZILG (*Z. physikal. Chem.*, 1928, 139, 12—20).—Measurements of the velocity of decomposition of sodium hydrogen hypophosphate by 0.5*N*- and *N*-sulphuric acid at 60°, and by 0.5*N*- and 0.25*N*-sulphuric acid at 100° show the reaction to be unimolecular and dependent on the concentration of hydrogen ions. The decomposition of hypophosphoric acid should therefore be represented by the equation $\text{H}_4\text{P}_2\text{O}_6 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{PO}_3 + \text{H}_3\text{PO}_4$, and not by the equation $2\text{H}_2\text{P}_2\text{O}_6 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{PO}_3 + \text{H}_3\text{PO}_4$. The formula, $\text{H}_4\text{P}_2\text{O}_6$, thus obtained for the acid disagrees with that from the alkyl hypophosphates, R_2PO_3 (Rosenheim, A., 1910, ii, 708). The structural formula of hypophosphoric acid is discussed and a co-ordination formula $[\text{O}_3\text{P} \dots \text{PO}_3]\text{H}_4$ assigned to it. In a comparison of the pyrophosphates and the hypophosphates the new compounds, $\text{Na}_4\text{P}_2\text{O}_6 \cdot 1.5\text{H}_2\text{O}$, $\text{Na}_3(\text{NH}_4)_2\text{P}_2\text{O}_6 \cdot 7\text{H}_2\text{O}$, $\text{NH}_4[\text{CrP}_2\text{O}_6] \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)_2[\text{CuP}_2\text{O}_6] \cdot 4\text{H}_2\text{O}$, and $\text{Na}_2[\text{NiP}_2\text{O}_6] \cdot 12\text{H}_2\text{O}$, are described. The analogy between the composition and properties of these two classes of salt is complete only in a few cases. A transition temperature at 74.6° has been observed between the new hydrate and sodium hypophosphate decahydrate.

L. S. THEOBALD.

Rate of oxidation of quinol by oxygen. H. VON EULER and E. BRUNIS (*Z. physikal. Chem.*, 1928, 139, 615—630).—A kinetic study of the rate of oxidation of quinol in a solution saturated with oxygen. The rate was measured by passing oxygen through a 0.1*M*-solution to which a phosphate buffer solution had been added. The benzoquinone formed was determined by titration with titanous chloride. At constant pressure of oxygen the rate of reaction over the range of p_{H} investigated (7.08—8.16) is proportional to the square of the concentration of hydroxyl ions and also to the concentration of the doubly-charged quinol ions. For a given acidity the rate of oxidation is proportional to the concentration of oxygen; reaction takes place in a solution saturated

with oxygen five times as quickly as in one saturated with air.

The values of $k[\text{quinol}]/[\text{quinol}^-]$ have been calculated from the experimental results for k and previously known figures for the dissociation constant. A good constant was obtained of which the average value was 5900. This gives a value of reactivity independent of oxygen pressure for $-\text{OC}_6\text{H}_4\text{O}^-$ of $rq_{\text{O}_2} : [\text{O}_2] = 4.2 \times 10^7$.

The rate of oxidation of quinol in alkali solution is not checked by addition of potassium cyanide solution, showing that no iron ions or complexes function as catalysts. No evidence of the formation of hydrogen peroxide during the reaction was obtained.

It is shown that for quinhydrone electrodes in which there is large excess of either benzoquinone or quinol there are slight deviations from the usual formula for the electrode potential. R. N. KERR.

Velocity of hydrolysis of methyl mono- and dichloroacetates. A. SKRABAL and M. RUCKERT (Monatsh., 1928, 50, 369—384).—The velocity of hydrolysis of methyl chloroacetate by acid and alkali in aqueous solution and by water has been studied at 25°. The velocity coefficient for hydrolysis with hydrochloric acid (k_a) with the minute as the unit of time is 0.00507; for ammonia in presence of ammonium chloride (k_a) 8170, whilst for water (k_w) two values, 1.23×10^{-5} and 1.5×10^{-5} , are deduced, the former being considered the more probable. For methyl dichloroacetate the corresponding values are 14.03×10^{-3} , 1.7×10^5 (with disodium hydrogen phosphate), and 9.2×10^{-4} . In all the cases studied hydrolysis is much more rapid than with methyl, ethyl, or vinyl acetates. H. BURTON.

Piezochemical studies. XXIX. Effect of pressure on reaction velocity. Part played by the medium in homogeneous liquid systems. A. L. T. MOESVELD and W. A. T. DE MEESTER (Z. physikal. Chem., 1928, 138, 169—225; cf. A., 1925, ii, 283).—In the case of homogeneous reactions occurring in solutions, the reaction velocity may be profoundly influenced by the attractions and repulsions existing between solvent molecules on the one hand and solute molecules on the other, for such forces, by bringing about deformation of the solute molecules, will, in general, affect their reactivity. It may be that one part of the solute molecule exerts an attraction on the solvent molecules greater than that exerted by the other part, so that with a mixed solvent partial local separation of the components is brought about, and as a result the deformation of the solute molecule is greater than is possible with a simple solvent. When a substance which is insoluble in a particular pure solvent is brought into solution by addition of a second solvent, the deformation will be maximal when the amount of the latter is only just sufficient to keep the solute in solution. If the external pressure is increased, effects due to intermolecular forces will be enhanced, owing to the molecules being brought into closer proximity to each other. It therefore seems probable that if in a mixed solvent medium in which a reaction is taking place the tendency for local differences in concentration to be set up can be opposed, e.g., by increasing the velocity of the molecules by raising the

temperature, the effect of variations in pressure on the reaction velocity will be diminished. On the other hand, increase in the concentration of a solute will cause the system to approach more closely to heterogeneity, and the pressure coefficient of the reaction velocity ought therefore to rise. Such changes in concentration will also occur in the course of the reaction, so that even when the pressure remains constant the deformation, and consequently the velocity coefficient, will vary. Addition to the system of a foreign substance which causes partial separation of the solvent mixture will also cause the solute system to approach the point of separation, i.e., the deformation will increase. In order to test the truth of these conclusions, experiments have been made on the hydrolysis by sodium hydroxide of *l*-bornyl acetate dissolved in a 31.5% aqueous solution of ethyl alcohol, which contains just sufficient alcohol to keep the system homogeneous. The measurements were made at 17—32°, and under pressures of 1, 500, 1000, and 1500 atm., the progress of the reaction being followed by conductivity determinations. The pressure coefficient of the velocity coefficient is positive, and, as expected, decreases with rise in temperature. Addition of borneol or excess of the ester brings the system nearer to being heterogeneous, and the pressure coefficient consequently increases. Measurements of the rotatory power of the ester in aqueous-alcoholic solutions indicate that the optical activity is probably to some extent dependent on the composition of the solvent. R. CUTHILL.

Decomposition of formic acid by sulphuric acid. II. E. R. SCHIERZ and H. T. WARD (J. Amer. Chem. Soc., 1928, 50, 3240—3243; cf. A., 1923, ii, 230).—The velocity of decomposition of formic acid by concentrated sulphuric acid (85—97%) over the temperature range 15—45° was investigated. The critical increment is practically constant over successive 10° intervals for all acid concentrations, in agreement with the conclusion that the critical increment is independent of temperature in isolated reactions. The temperature coefficient diminishes as the velocity coefficient increases. The sulphuric acid acts primarily as a dehydrating agent; the velocity coefficient is a continuous function of the percentage composition of the acid (Lichty, A., 1907, ii, 445). For equal acid concentrations, small quantities of water have a greater effect the higher is the temperature of decomposition. S. K. TWEEDY.

Polymerisation. I. Polymerisation of styrene. N. A. MILAS (Proc. Nat. Acad. Sci., 1928, 14, 844—849).—The rates of absorption of oxygen by styrene, styrene and perbenzoic acid, styrene and anthracene, and benzaldehyde were measured at 110°. The oxidation of styrene alone showed an induction period of 10 min. The rate of oxygen absorption is increased by the addition of perbenzoic acid, but there is a corresponding increase in the rate of polymerisation. Anthracene, which is known to be an excellent absorber of light energy, when added to the styrene caused the oxidation to proceed at a relatively high rate, but completely inhibited the polymerisation. The anthracene alone, under the experimental conditions, was not oxidised. Anthracene will also

strongly inhibit the oxidation of the benzaldehyde formed by the oxidation of styrene. The reaction which takes place when styrene is oxidised in presence of anthracene shows selective inhibition. The polymerisation of styrene seems to be effected by energy which is liberated during the formation and subsequent reaction of the initial products of the oxidation with unoxidised styrene molecules.

A. J. MEE.

Absorption velocity of gases by liquids. S. HATTA (Tech. Rep. Tohoku, 1928, 8, 1—25).—The rate of absorption of carbon dioxide by potassium hydroxide solution, when mixed with air, has been investigated. By using two independent stirrers the thicknesses of the gas and liquid films at the interface could be varied independently. The effects of changes of temperature, alkali concentration, and partial pressure of carbon dioxide were also studied. By considering the diffusion velocity through the double film, and the velocity of the chemical reaction, equations are obtained which are in good agreement with the experimental results. C. W. GIBBY.

Velocity coefficient of kinetic processes in heterogeneous systems as a function of temperature and intensity of agitation. W. HELLER (Rocz. Chem., 1928, 8, 445—474).—Measurements of the velocity of dissolution of plates of tin or cadmium in aqueous ferric chloride, or of magnesium in aqueous ammonium chloride, calculated according to the equation $K = (2.303v/s \cdot \Delta t) \log(a - x_1)/(a - x_2)$, where v is the volume of solution, s the surface of the plate, a the initial concentration of the reaction solution, and x_1 and x_2 are its concentrations at the beginning and end of an interval of time Δt , show that K is a linear function at constant temperature of the velocity of revolution n of the stirrer and, at constant n , of the temperature. It hence follows that the temperature coefficient of these reactions is independent of n . This dependence of K on temperature follows from Nernst's diffusion theory, assuming that the thickness of the adhesion layer is independent of temperature at constant value of n . K is given as a simultaneous function of n and t by the expression $K = (An + C_0)(t - J)$, where C and J are parameters characteristic of the given process without regard to the apparatus used, whilst A depends on both the process and the apparatus. It is possible by introducing the conception of a "normal" stirrer to eliminate the dependence on the given apparatus. Any value of K is taken as normal at any given temperature for any given apparatus, and the number of revolutions of another stirrer in another apparatus necessary to obtain the same value of K is determined. The A parameter can thus be made independent of the given apparatus, thereby rendering comparable results obtained on different apparatus. R. TRUSZKOWSKI.

Rate of dissolution of zinc in sulphuric acid under pressure. T. C. POULTER and G. E. FRAZER (Proc. Iowa Acad. Sci., 1927, 34, 215, 216).—Whilst surface condition, size, and shape of the pieces of zinc and local concentration of the acid are important, increase of pressure up to 6000 atm. has little effect.

CHEMICAL ABSTRACTS.

Catalytic decomposition of hydrogen peroxide in an acid chlorine-chloride solution. II. Interpretation of the rate measurements in concentrated solution. R. LIVINGSTON (J. Amer. Chem. Soc., 1928, 50, 3204—3211).—The equation for the velocity of the above decomposition, $v = \chi[H_2O_2][H][Cl]f_{HCl}$, where f is the activity coefficient and χ is a constant, is more accurately written $v = K[H_2O_2][H][Cl]f_{HCl}^u \times 10^{uk}$, where u is the ionic strength and K , k are constants. This equation is supported by the experimental results previously obtained (A., 1926, 364). Further confirmation is obtained from determinations of the activity coefficients of hydrogen peroxide in solutions of sodium chloride and sulphate by means of partition experiments with isoamyl alcohol. The activity-rate theory does not appear to represent the facts. The results obtained in this and the analogous bromine reaction (A., 1926, 251) lend considerable support to the validity of Bronsted's reaction velocity theory.

S. K. TWEEDY.

Catalysis and processes of transformation of colloids. I. Catalysis of [decomposition of] hydrogen peroxide by ferric salts. II. Mechanism of hydrolysis of iron salts and the properties of colloidal hydrosols. III. Colloidal hydrogels of iron and their transformation. E. I. SPITALSKI, N. N. PETIN, and E. I. BUROVA (J. Russ. Phys. Chem. Soc., 1928, 60, 1271—1289, 1291—1316, 1317—1332; cf. A., 1925, ii, 53).—I. The catalytic action of ferric chloride on the decomposition of hydrogen peroxide is studied in slightly acid, neutral, and slightly alkaline solutions. In acid solutions a stable hydrosol of basic salt forms, in contrast to the precipitate which forms when ferrous sulphate is used. In spite of this difference, the reaction follows the same course in both cases, viz., in acid solution the velocity coefficient increases hyperbolically with increasing p_H , reaches a maximum at neutrality, and again falls as the reaction of the solution increases in alkalinity, attains a minimum value at a relative alkalinity expressed by $C_{NaOH}/3C_{Fe} = 0.8$, again rises to a second maximum at $C_{NaOH}/3C_{Fe} = 1.0$, at which p_H an iron hydrogel separates. This hydrogel is the actual catalyst in alkaline solution. It is concluded that in solution the ferric ion is the only catalyst able to decompose hydrogen peroxide present, but that the intermediate stages of the reaction are not sufficiently known to allow of the formation of any theories as to its mechanism.

II. The specific catalytic action of ferric ions on the decomposition of hydrogen peroxide affords the basis of a method for the examination of the mechanism of hydrolysis of iron salts and of the properties of colloidal hydrosols. The catalytic activity of ferric chloride hydrosols diminishes rapidly with time, whilst the conductivity of such solutions remains approximately constant, and this effect is the more marked the greater is the alkalinity of the medium. The gel precipitated from concentrated ferric chloride solutions by the addition of alkali acts as a powerful anticatalyst if added to hydrogen peroxide solutions containing active ferric chloride hydrosol, although these gels have a chlorine content and a specific electroconductivity little different from those of the

hydrosol. The above results show that the effect of hydrolysis is to lead to the adsorption of ferric ions on the colloid formed, the velocity of this process increasing with the active surface of the adsorbent.

III. The catalytic action of ferric salts on hydrogen peroxide in alkaline solutions is due to the formation of ferric hydroxide, which separates as a precipitate. These catalytically active hydrogels are irreversibly inactivated with time, this inactivation being initiated by alkali. The mechanism of the catalysis of hydrogen peroxide in alkaline solution consists in the dissolution of the iron hydrogels formed, to give rise to homogeneously soluble iron compounds, which are intermediate stages in the reaction. The ageing of the hydrogel appears to be due to the depressive influence of alkalis on its dissolution in alkaline solutions of hydrogen peroxide, and this again leads to the dehydration of the hydrogel particles to form larger aggregates at the expense of the smaller ones. As a result, the active surface is diminished, and possibly also the microcrystalline structure of the precipitate is changed.

R. TRUSZKOWSKI.

Velocity of oxidation of hydrogen bromide by chromic acid in presence of acids. M. BOBTELSKI and A. ROSENBERG (Z. anorg. Chem., 1928, 177, 137—144).—The influence of a large number of metallic sulphates on the velocity of liberation of bromine from hydrogen bromide by chromic acid in presence of sulphuric acid has been studied. With the exception of the sulphates of the alkali metals and of cadmium, which retard the reaction, all the salts investigated have a marked accelerative effect which increases as the salt concentration increases; with increase of concentration of the salts which retard the reaction the retardation increases. The catalytic influence of chromic sulphate is much greater than that of ferric and aluminium sulphates at the same concentration. Manganous sulphate also exerts an abnormally large influence, the reaction velocity in presence of 2*N*-manganous sulphate being about double that in 4*N*-chromic sulphate solution. The catalytic influence of bivalent cations is in general much less than that of trivalent cations. 1.25*N*-Cadmium sulphate reduces the oxidation velocity to less than one tenth of its normal value.

H. F. GILLBE.

Catalytic effects in concentrated salt mixtures. M. BOBTELSKI and D. KAPLAN (Z. anorg. Chem., 1928, 177, 119—123; cf. A., 1928, 715).—The influence of salts at high concentrations (2.5*N*) on the velocity of decolorisation of potassium permanganate solution by oxalic acid in presence of various inductors has been studied. The greater influence is exerted by the anion, and in general the sulphate ion produces acceleration and the chloride ion retardation, whilst the nitrate ion occupies an intermediate position. Specific effects, however, are found for certain combinations of inductor and neutral salt; e.g., ammonium nitrate enormously increases the inductive action of potassium thiocyanate, but reduces that of the arsenite ion. It is observed that the effect of strong reducing agents at low concentrations is not destroyed by the presence of oxidising agents at high concentrations.

H. F. GILLBE.

Inhibition of chemical reactions. II. Mechanism of the inhibition of esterification by alkaline substances. K. C. BAILEY (J.C.S., 1928, 3256—3258; cf. A., 1928, 718).—The reaction between ethyl alcohol and acetic acid is inhibited not only by pyridine but also by other alkaline substances such as quinoline, piperidine, ammonia, and sodium hydroxide. It is suggested that these act by withdrawing acetic acid from an alcohol-acid complex formed preparatory to reaction on the surface of the containing vessel. In conformity with this theory the inhibiting action of the organic bases was found to be the greater the stronger was their basicity. Benzyl chloride acts as a weak positive catalyst; *m*-cresol, benzene, and chloroform have little effect.

F. J. WILKINS.

Acid and salt effects in catalysed reactions. XVIII. Dynamics of autocatalysed ester hydrolysis. H. M. DAWSON and W. LOWSON (J.C.S., 1928, 3218—3227; cf. A., 1928, 1101).—Since the autocatalysed hydrolysis of ethyl acetate, when carried out in glass vessels, is subject to considerable retardation owing to the dissolution of traces of alkali from the glass walls, the reaction has been studied in fused silica flasks. Up to the point at which the reverse action can no longer be neglected, the reaction may be divided into two stages. In the first, the velocity is determined by the joint catalytic action of the hydrogen and hydroxyl ions, and in the second by the catalytic action of the hydrogen ion only. The equations derived on this basis describe accurately the autocatalytic phenomena observed as well as the retarding influence of small quantities of alkali. The speed of the uncatalysed reaction and the catalytic activity of the water molecules are too small to have any measurable influence on the course of the reaction.

F. J. WILKINS.

Reversible addition of ethyl alcohol to *p*-bromobenzonitrile catalysed by sodium, potassium, and lithium ethoxides. C. N. MEYERS and S. F. ACREE (J. Amer. Chem. Soc., 1928, 50, 2916—2922).—The catalytic activities of the above ethoxides at *N*/32 to *N*/2048 on the above reaction were investigated. If both the ethoxide ions and non-ionised ethoxide molecules are catalytically active, the equation $vK = K_i\alpha + K_m(1-\alpha)$ should hold for any ethoxide, where *K* is the velocity coefficient of the reaction when the ethoxide is ionised to the extent α at the concentration *N*/*v*, *v* is the dilution, *K_i* is the sum of the velocity coefficients for unit concentration of ethoxide ions in the two opposing reactions, and *K_m* is the sum of the corresponding coefficients for un-ionised ethoxides. *K_i* is the same for the three ethoxides; *K_m* decreases in the order sodium, potassium, lithium. The theory outlined enables a satisfactory explanation to be given for the fact that *vK* is independent of α for sodium ethoxide, changes slowly for potassium ethoxide, increases greatly for lithium ethoxide, and becomes the same in all cases at high dilution. Any possible activity of the metal cations may be disregarded in dilute solution, but in concentrated solution a salt effect is apparent.

S. K. TWEEDY.

Catalysis in the hydration of acetic anhydride. M. KILPATRICK, jun. (J. Amer. Chem. Soc., 1928, 50,

2891—2902).—The rate of hydration of acetic anhydride in 0.07M solution was measured dilatometrically at 0°. In pure water the effects of the H_3O^+ , OH^- , and acetate ions are negligible over a wide range. The neutral salt effect is negative and specific. The formate ion, used as a sodium formate-formic acid buffer, is a remarkably good catalyst; experiments with butyrate and propionate buffers indicate that in these cases, and perhaps also in the case of formate, an intermediate compound is formed, which may be a mixed anhydride. S. K. TWEEDY.

Mechanism of the formation of 2:4-dinitrophenol from benzene and nitric acid in presence of mercury salts as catalysts. A. I. ZAKHAROV (J. Chem. Ind. Moscow, 1927, 4, 960—964).—When the mercuric nitrate catalyst has already been used in the oxidation of benzene, the reaction is of the second order; otherwise its course is complicated, since a certain amount of acid is withdrawn from the main reaction for the activation of the catalyst. When dilute acid is used its activity is directed towards oxidation and nitrophenols are formed; with acid of comparatively high concentration, nitrobenzene results. The role of the catalyst consists in the nitration of the original benzene. The fact that the nitrophenols are accompanied by some nitrobenzene is ascribed to the intermediate formation of mercury-nitrobenzene compounds. This explains the enhanced activity of used solutions. From solutions of 59—60% acidity containing 30% of catalyst, at 35—40°, the original yield of 40% of dinitrophenol is successively increased to 50—55, 65, 75, and 80%.

CHEMICAL ABSTRACTS.

Autoxidation of benzaldehyde. R. KUHN and K. MEYER (Naturwiss., 1928, 16, 1028—1029).—By repeated vacuum distillation in an atmosphere of carbon dioxide, followed by fractional crystallisation under aseptic conditions at the temperature of liquid air, it has been possible to obtain benzaldehyde so pure that it no longer undergoes autoxidation. Small additions of salts of heavy metals such as iron, copper, nickel, and manganese greatly accelerate oxidation. Ferrous salts are fifteen times as effective as ferric salts. The catalysis by ferric salts shows an induction period followed by rapid oxidation, and concomitant with the increase in oxygen uptake an orange-brown colour appears in the aldehyde. The colour appears at once with ferrous salts, and the coloured product appears to be the intermediate catalytic compound. The iron in the hæmin complex is fifty times as active as ferrous iron, whilst phosphate hæmin is quite ineffective.

R. A. MORTON.

Catalytic decomposition of sodium hypochlorite solutions. II. Iron oxide as promoter in the copper oxide catalysis of sodium hypochlorite. J. R. LEWIS (J. Physical Chem., 1928, 32, 1808—1819; cf. A., 1928, 376).—Data for the promoter action of iron oxide on the catalytic decomposition of sodium hypochlorite solution at 35° by copper oxide have been obtained by the method previously described (*loc. cit.*). The reaction is proportional to the concentration of the catalyst. With the unpromoted catalyst, the values of k =volume of oxygen evolved/time in min. and of k_1 , the usual

unimolecular coefficient, decrease rapidly after 4—5% of the reaction has been completed. This decrease is modified by an increase in the amount of the promoter until constant values for k_1 are obtained. When small quantities of catalyst are added to an excess of the promoter, the values of k remain constant whilst those of k_1 increase. An equiatomic mixture of copper and iron is the most effective. The temperature coefficient for the unpromoted reaction lies between 2.1 and 1.2 over the range 25—45° and for the promoted reaction it is normal (2.3) between 25° and 35° but diminishes (1.7) between 35° and 45°. The function of the promoter is to preserve the active points on the catalyst and the results agree with the view that a catalyst-hypochlorite complex is formed. Reproducible results were obtained only when the hypochlorite solution was added to a solution of a mixture of ferric and copper chlorides and not when the mixed oxides were prepared by precipitation with sodium hydroxide. In this case, the treatment of the catalyst before use determined its activity.

L. S. THEOBALD.

Autoxidation and antioxygenic action. XXXIII. Catalytic properties of antimony, bismuth, and their derivatives, and of some derivatives of vanadium. C. MOUREU, C. DUFRAISSE, and M. BADOCHÉ (Compt. rend., 1928, 187, 1092—1096).—In general, metallic antimony and its oxygenated compounds (1%) have only a slight catalytic activity, whilst the halogen compounds, bismuth and its compounds, with the exception of the trichloride and tribromide, and vanadium compounds (1%) are usually highly active. In most cases very small changes suffice to invert the sign of catalysis; e.g., bismuth triphenyl is antioxygenic to acetaldehyde and pro-oxygenic to *l*-pinene, whilst two catalysts of similar structure may act in opposite senses towards the same autoxidisable substance.

J. GRANT.

Autoxidation and antioxygenic action. Catalytic properties of silicon, boron, and their derivatives. C. MOUREU, C. DUFRAISSE, and P. LAPLAGNE (Compt. rend., 1928, 187, 1266—1269; cf. this vol., 36).—Both boron and silicon and their derivatives show positive and negative catalytic effects in concentrations of 1%, and a close resemblance exists between the curves representing the opposite effects for a particular substance. The catalytic properties of silica depend on its purity and on the method of preparation employed.

J. GRANT.

Heterogeneous catalysis of hydrogen peroxide by copper compounds. E. I. SPITALSKI, N. N. PETIN, and B. A. KONOVALOVA (J. Russ. Phys. Chem. Soc., 1928, 60, 1237—1270).—Copper ions have no catalytic action on the decomposition of hydrogen peroxide; the catalyst is cupric hydroxide contained in the precipitate forming in the reaction mixture together with cupric peroxide, which is an intermediate product. In slightly acid solution the velocity coefficient of the reaction at first falls to a minimum and then rises to the end of the reaction, whilst in neutral or feebly alkaline solution this coefficient rises to a maximum value at completion of the reaction. The absolute velocity also depends on the reaction of the medium and is much smaller in

more concentrated solutions of substrate. When very concentrated solutions of peroxide are used (15*N*), the precipitate obtained consists chiefly of cupric peroxide, the velocity of decomposition of which is comparatively small; it has no catalytic action. In dilute peroxide solutions, however, the precipitate contains at first only active cupric hydroxide, which then becomes partly converted into peroxide; this process explains the initial fall in absolute velocity observed. Cupric peroxide, being unstable, breaks up into oxygen and cupric hydroxide, which again acts catalytically; this process corresponds with the increase in velocity which supervenes later. Active precipitates of cupric hydroxide become progressively inactivated by the introduction of fresh quantities of peroxide, whereby they are converted to an increasingly great extent into peroxide. The copper catalyst ages on keeping, but if a reaction mixture to which an aged catalyst has been added be constantly agitated, the velocity coefficient is then of the same order as that obtained by using freshly-precipitated catalyst.

R. TRUSZKOWSKI.

Catalytic processes in the solid phase. I. Decomposition of potassium permanganate. S. ROGINSKY and E. SCHULZ (*Z. physikal. Chem.*, 1928, 138, 21—41).—A study has been made of the velocity of decomposition at various temperatures of solid potassium permanganate and ammonium dichromate, and of the effect on these decompositions of traces of oxides. The decomposition of the pure substances is autocatalytic, the maximum velocity being attained after 0.75—2 hrs. from the beginning of the reaction. The velocity of decomposition increases with decrease in size of the particles of the material and in the presence of traces of the end-products of the reaction. The decomposition is greatly accelerated by the presence of the oxides of nickel, cobalt, manganese, iron, and copper. Oxides of tungsten, magnesium, titanium, mercury, calcium, uranium, and silicon appear to be without effect. Moderate catalytic activity is shown by the oxides of silver, tin, lead, antimony, chromium, zinc, aluminium, and cadmium. Of the oxides which are catalytically active in the decomposition of potassium permanganate the majority are of deep colour, electrically conducting, paramagnetic, and show similar activity in catalysing the decomposition of potassium chlorate, silver oxide, and mercuric oxide. No relationship is apparent between the crystal structure of these oxides and their catalytic powers. The kinetics of the above decomposition are considered from the point of view of the formation of centres of decomposition in the surface of individual crystals, and an equation is developed which applies satisfactorily to the case of potassium permanganate.

F. G. TRYHORN.

Oxidation of mercury in presence of glowing platinum. A. J. LEIPUNSKY (*Z. physikal. Chem.*, 1928, B, 1, 369—374).—In presence of glowing platinum oxygen reacts with mercury vapour to form mercuric oxide. The reaction velocity increases with rise of temperature of the platinum. It is independent of the pressure of oxygen, but decreases with increasing pressure of mercury vapour. Glowing

nickel has no action. The results may be explained by the assumption that the reaction is catalytic and that oxygen is activated by adsorption on the platinum surface. No evidence of the excitation of mercury atoms has been obtained. M. S. BURR.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. II. Synthesis of methyl alcohol with catalysts composed of copper and zinc. P. K. FROLICH, M. R. FENSKE, P. S. TAYLOR, and C. A. SOUTHWICH, jun. (*Ind. Eng. Chem.*, 1928, 20, 1327—1330; cf. A., 1928, 1112).—The synthesis of methyl alcohol was carried out using a gaseous mixture composed of 70.8% of hydrogen, 26.5% of carbon monoxide, 2.1% of nitrogen, and 0.6% of oxygen, from which water vapour, carbon dioxide, and iron carbonyl had been removed. Small amounts of finely-powdered catalysts were placed, after reduction with methyl alcohol vapour at 220°, in a pressure-resisting converter. This vessel was externally heated in a lead bath and designed so that the gas mixture which passed through it was heated by counter-current. At 204 atm. the rate of the exit gases corresponded with 28 litres/hr./3 c.c. of catalyst. As no pyrometer was placed in contact with the catalyst the latter was placed in a roll of copper gauze to dissipate the heat of reaction. The assumption is made that the temperature of the bath is not more than 10° below that of the catalyst. A comparison of the efficiencies of the various oxide mixtures indicates that the activity slowly increases with rise in percentage of zinc oxide and, in the neighbourhood of 50 mol.-%, very rapidly, reaching a maximum at about 65 mol.-%. This conclusion is in good agreement with that arrived at previously (*loc. cit.*), thus emphasising the suitability of the decomposition method in catalyst testing. All the catalysts employed showed a slight but measurable decrease in activity after 8 hrs. use. Although methyl formate was produced in the decomposition of methyl alcohol by the catalysts, no methyl formate was detected in the synthetic experiments.

H. INGLESON.

Catalytic activity of metallised silica gels. V. Oxidation of ethylene. L. H. REYERSON and L. E. SWEARINGEN (*J. Amer. Chem. Soc.*, 1928, 50, 2872—2878; cf. A., 1928, 252, 376).—Silica gel metallised with copper, platinum, or palladium is very active in promoting the oxidation of ethylene. It begins to be effective at 100°. Silica gel metallised with silver is not so effective, but in all cases no intermediate compounds can be detected. The reaction rate is proportional to the oxygen concentration and inversely proportional to the ethylene concentration. A mechanism is suggested for the reaction which accounts for this. S. K. TWEEDY.

Efficiency of different contact substances for the sulphuric acid contact process. II. B. NEUMANN and E. GOEBEL.—See B., 1929, 51.

Theory of processes at unpolarisable electrodes. M. VALMER (*Z. physikal. Chem.*, 1928, 139, 597—604).—Electrolytic precipitation and dissolution of metals in the solid and liquid state are compared on the assumption that in the solid state an adsorption layer is formed round the crystals in which the

adsorbed atoms are in a state between the atomic and ionic. Polarisation, attributed to this adsorption layer, has been obtained in certain cases with zinc electrodes and zinc sulphate as electrolyte. No polarisation is obtained with liquid zinc amalgam electrodes or with two others in which the zinc is present as small crystals. Using two other electrodes with larger crystals considerable polarisation, both anodic and cathodic, is obtained with current densities of 0.25 milliamp. per cm.² R. N. KERR.

Electrolysis through a crystalline diaphragm. W. A. PLOTNIKOV, M. RABINOVITSCH, and P. B. ZYVOTINSKI (Z. physikal. Chem., 1928, 138, 260—267).—If in the electrolysis of an aqueous solution of silver nitrate the electrodes are contained in separate vessels connected by a "bridge" which is composed of a mixture of solid silver iodide with 10% of silver chloride and is heated at 150—160°, the current passes through this diaphragm by means of the silver ions only, but the amount of decomposition at the electrodes is in accordance with Faraday's laws, whilst diffusion between the anode and cathode vessels is completely prevented. If, owing to photochemical action, or for other reasons, the bridge contains colloidal silver, the silver particles migrate towards the anode. R. CUTHILL.

Electrolysis of sodium sulphide solutions. W. R. FETZER (J. Physical Chem., 1928, 32, 1787—1807).—The electrolysis of solutions of sodium sulphide (4.5*N*) at 20° yields, with low current densities, sodium polysulphide as the only product; with higher current densities, sodium sulphate and dithionate, but no thiosulphate, are formed. With sodium sulphide or polysulphide as electrolyte and low current densities, the electrochemical equivalent of sulphur is 16/*F*, and the electrolysis of a solution of sodium hydrogen sulphide yields polysulphide and hydrogen sulphide in the ratio Na₂S₂:2H₂S. The current required to liberate sulphur from solutions of mono- or poly-sulphide increases to a maximum with an increase in concentration of polysulphide and then falls towards zero. With the monosulphide, it increases with an increase in the rate of rotation of the anode, but with the polysulphide it remains unchanged over the range 220—700 r.p.m. An increase in current required accompanies a rise in temperature. An electrolytic method for the preparation of sodium hydroxide free from carbonate is described. L. S. THEOBALD.

Rate of photochemical combination of chlorine and hydrogen in glass capillary tubes. D. L. CHAPMAN and P. P. GRIGG (J.C.S., 1928, 3233—3235; cf. A., 1928, 970).—Under the same conditions of illumination the rate of photochemical union of hydrogen and chlorine in capillary tubes is considerably less than in wider tubes. This result is explained by the hypothesis that the union of the gases is due to an unstable catalyst which is formed by light and is destroyed when it comes into contact with glass. F. J. WILKINS.

Yield in photochemical reactions in [rapidly] intermittent light. M. PADOA and N. VITA (Atti

II Cong. Naz. Chim. pura appl., 1926, 1256—1258; Chem. Zentr., 1928, ii, 524).—Experiments on the autoxidation of hydrogen iodide in light which had passed through a rotating sector screen showed that the photochemical yield at first increased with the number of alternations (transparent and dark) of the sectors, and then decreased to a constant value. Alternations, without dark sectors, of two or more colours caused greater dependence of yield on the velocity. Maxima were observed.

A. A. ELDRIDGE.

Influence of photographic reactions on the Weigert effect in photochloride. H. ZOCHER and K. COPER (Z. physikal. Chem., 1928, 139, 263—272; cf. A., 1928, 593).—The anisotropy of silver induced in the photochloride by the Weigert effect is shown to persist throughout many photographic reactions. Changes in concentration of the silver are accompanied by characteristic variations in the anisotropy, which is also strongly modified by photographic processes such as washing, drying, fixing, etc. Anisotropic gold, platinum, and copper are formed by replacement of the silver when the plate coated with the anisotropic silver chloride is submitted to the action of toning baths of suitable salts of these metals. The results are discussed. L. S. THEOBALD.

Photochemical action of bromine on methyl maleate and fumarate. R. SCHMIDT (Z. physikal. Chem., 1928, B, 1, 205—238).—It is assumed that the photosensitive reaction between bromine and methyl maleate depends on the formation of bromine atoms by the action of light. The quantum yield of methyl fumarate varies with the initial concentrations of ester and bromine, the intensity and wave-length of the incident light, and the temperature. The experimental results are in accordance with the equation $\Delta\phi/\phi_{\infty} = k_1[\text{Br}]^2/k_0I$, where ϕ is the quantum yield when a negligible number of bromine atoms are withdrawn by recombination or addition to the ester, $\Delta\phi$ is the difference between ϕ and a function of the ester concentration, I is the intensity of the incident light, and k_0 and k_1 are constants. The significance of the variations of the quantum yield with the wave-length of the light and the temperature is discussed. Study of the addition of bromine to methyl fumarate affords values for the quantum yield which are in agreement with those to be expected from Wachholtz's investigation of the ethyl esters. The theoretical conception of the identity of the intermediate stages of the tautomeric change of the maleic ester and of the addition of bromine to the fumaric ester is supported by the relationship between the quantum yield $\phi_{0.1N}$ and the bromine concentration. In aqueous solution the quantum yield is approximately the same as in carbon tetrachloride solution. H. F. GILLBE.

Changes in cellulose nitrate when exposed to light. V. COFMAN and H. B. DEVORE (Nature, 1929, 123, 87).—The production of a red colour when celluloid containing malachite-green is exposed to sunlight (Rayleigh, A., 1928, 1341) is apparently due to the liberation of oxides of nitrogen. The wave-length most effective in the acid decomposition of cellulose nitrate is 3100 Å. A. A. ELDRIDGE.

Reaction of ketones with alcohols under the influence of light. IV. Photo-electric effect of benzophenone. G. H. VISSER (Rec. trav. chim., 1928, 47, 1037—1041).—In order to determine the primary reaction in the photochemical oxidation of alcohols in presence of aromatic ketones, the photo-electric emission of electrons from benzophenone has been investigated by means of a Geiger ionisation chamber. The "threshold" wave-length necessary for the emission of electrons is between 302.5 and 253.7 $m\mu$, which agrees well with the pronounced band at 260 $m\mu$ in the absorption spectrum of benzophenone and probably corresponds with an ionisation of the molecule. This is not the spectral region, however, which is active in the photochemical oxidation of alcohols.

O. J. WALKER.

Photochemical yield in the chlorophyll assimilation [of carbon dioxide] with complex and intermittent lights. M. PADOA and N. VITA (Gazzetta, 1928, 58, 647—654).—From a study of the photochemical action of light on green plants, as measured by the amount of oxygen evolved, it is shown that the sum of the separate actions of red, yellow, and green light is greater than the action of the corresponding amount of white light. Intermittent white light (cf. A., 1927, 528) also has a different effect from continuous light on the photochemical yield. At certain interruption frequencies maximum yields are obtained, which in some cases are three times as great as the yield obtained by using continuous illumination. These results are compared with those previously obtained (A., 1928, 1102) with other photochemical reactions.

O. J. WALKER.

Action of ultra-violet rays on the formation of sugars and complex aldehydes from solutions of alkali and alkaline-earth metals hydrogen carbonates and of carbon dioxide in presence of reducing and colloidal catalysts. G. MEZZADROLI and E. VARETON (Zymologica, 1928, 3, 165—171; cf. A., 1928, 255).—Exposure of these hydrogen carbonate solutions to ultra-violet rays results in increase of the reducing power (determined iodimetrically) of the solutions to a maximum, followed by rapid decrease. Under similar conditions, solutions of carbon dioxide prepared by continuous passage of the gas through water show progressive increase in reducing properties. The presence of colloidal or reducing catalysts increases, in some cases three- or four-fold, the maximum reducing powers. The greatest yield of reducing substances, referred to the carbon dioxide reacting, is obtained with calcium hydrogen carbonate in presence of finely powdered magnesium.

T. H. POPE.

Effect of ultra-violet light on the dielectric properties of crystals. A. A. AARDAL (Proc. Iowa Acad. Sci., 1927, 34, 276).—Variation of the dielectric constant, phase angle, and resistance has been observed when certain natural crystals are exposed to ultra-violet light.

CHEMICAL ABSTRACTS.

Chemical action of X-rays. P. GUNTHER (Z. angew. Chem., 1928, 41, 1357—1361).—A review of recent work.

A. R. POWELL.

Reaction of excited mercury with oxygen. A. J. LEIPUNSKY and A. W. SAGULIN (Z. physikal. Chem., 1928, B, 1, 362—368).—An investigation has been made of the oxidation of mercury vapour under the influence of light from the mercury arc, and also by bombardment with electrons emitted by glowing platinum and accelerated by different voltages. Only the line 2537 Å. appears to be photochemically active, and the velocity of reaction increases with increasing pressure of mercury vapour. For any given mercury pressure there is an oxygen pressure at which the velocity is a maximum. This is in agreement with the conception of a chain reaction. The velocity of reaction is not affected by electrons accelerated by a field of less than 5 volts, which is the value of the first resonance potential of mercury. The results show that, contrary to the observations of Noyes (J. Amer. Chem. Soc., 1928, 50, 49), the reaction is due to excited mercury atoms only, and the primary formation of ozone has not much influence.

M. S. BURR.

Formation of ozone by cathode rays. A. L. MARSHALL (J. Amer. Chem. Soc., 1928, 50, 3178—3197).—The ozonisation of oxygen by high-velocity electrons is a homogeneous gas reaction independent of the nature or extent of the surface exposed. The energy of the electron beam seems to diminish exponentially after penetrating the window of the oxygen cell; half of the ozonisation occurs within a short distance of the window. For low currents in the cathode-ray tube the logarithm of the rate of flow of the oxygen through the cell is a linear function of the yield of ozone for a given exposure. The rate of formation of ozone increases with the pressure, although at high pressures the yield is independent of the pressure. The ozone is also decomposed by the cathode rays, and eventually a steady state is reached, independent of the tube current, in which one ozone molecule is contained in 1700 oxygen molecules. The attainment of a saturation current observed in the experiments of Kruger and Utesch (A., 1926, 136) could not be confirmed, so that the results of these experimenters are regarded as doubtful.

S. K. TWEEDY.

Combination of hydrogen and oxygen under the influence of cathode rays. A. L. MARSHALL (J. Amer. Chem. Soc., 1928, 50, 3197—3204).—Hydrogen peroxide, water vapour, and ozone are formed as primary products, the rate of formation of the first-named being almost independent of the hydrogen and oxygen concentrations, whereas the rates of formation of the last-named vary very considerably. Since, however, the rates of formation of ozone and of water vapour always parallel one another very closely, the same mechanism is probably responsible for both. This conclusion is supported by the fact that the yield of peroxide decreases as the rate of flow is diminished, the decreases being related linearly to the accompanying increases in the yield of water vapour. The gross rate of reaction parallels that observed by Lind (A., 1919, ii, 210) for the same reaction under the influence of α -particles.

S. K. TWEEDY.

Chemical effects of cathode rays on oxygen, air, nitric oxide, and carbon dioxide. W. F.

BUSSE and F. DANIELS (J. Amer. Chem. Soc., 1928, 50, 3271—3286).—In the ozonisation of oxygen, which proceeds independently of the nature of the surface of the containing cell (cf. preceding abstracts), for short exposures the yield is a function of the voltage and current of the cathode-ray tube, the exposure, the distance between the tube and the reaction cell, and the source of the oxygen, but is independent of the time (within limits) during which the ozone remains in the reaction cell and of the moisture content of the oxygen. Equilibrium is attained when about 0.1 mol.-% of ozone is present. One molecule is formed for each ion pair, which is not in agreement with the results of Kruger and Utesch. The M/C ratio, or the number of molecules formed or decomposed per electron passing through the cathode-ray tube, is 100 for the formation of ozone. When air is used, this efficiency falls to about half the value, but nitrogen oxides are also formed in varying yields (M/C —13.5—16.0). When nitric oxide is exposed, oxygen, nitrogen, and nitrogen dioxide are formed; M/C is 230 for this decomposition. Carbon dioxide yields carbon monoxide and oxygen (ozone), the M/C ratio being 3. The energy of the rays, determined calorimetrically, varied from 3 to 16 g.-cal. per min. The chemical behaviour of high-voltage electrons is essentially the same as that of α -particles. S. K. TWEEDY.

Irradiated quenching of cadmium resonance radiation. J. R. BATES (Proc. Nat. Acad. Sci., 1928, 14, 849—852).—Cadmium atoms in the 2^3P_1 state will not activate hydrogen atoms sufficiently to cause them to react with ethylene, whereas mercury atoms in the same state of activation will promote the reaction. Hydrogen was found to quench cadmium resonance radiation just as effectively as it does that of mercury. Hydrogen atoms cannot be formed by these collisions, but there is an increase in the vibrational energy of the hydrogen molecule. It proved difficult to study the temperature coefficient of the reaction between cadmium atoms in the 2^3P_1 state and hydrogen molecules to give hydrogen atoms owing to the large quenching. The work provides some evidence for the consideration that in the case of activation reactions, the thermal activation of reactants is not so important as the activation of some catalytic substance which may be present.

A. J. MEE.

Chemical inertia of the rare gases. I. Action of helium on platinum. H. DAMIANOVICH (Anal. Fis. Quim., 1928, 26, 365—371; cf. A., 1926, 657).—When a discharge from an induction coil was passed between platinum electrodes in a tube containing helium at about 3 mm. pressure a deposit was formed on the tube and a diminution of pressure was observed corresponding with absorption of 14—34 c.c. per g. of platinum deposited. The deposit, which was dark grey, non-metallic, and of characteristic microscopical appearance, decomposed at a measurable rate in a vacuum between 90° and 160° to yield helium and metallic platinum, and probably consisted of platinum containing adsorbed helium or mixtures of this with definite compounds and excess of metal.

R. K. CALLOW.

Preparation of cuprous sulphate. J. G. F. DRUCE and G. FOWLES (Chem. News, 1928, 137, 385—386).—Copper turnings are dropped into concentrated sulphuric acid heated at 200° and when the reaction has ceased the green solution is decanted from any anhydrous cupric sulphate through an asbestos filter into a mixture of equal volumes of anhydrous alcohol and ether or into methyl alcohol. Cuprous sulphate separates in white crystals which rapidly decompose in moist air into copper and cupric sulphate. A. R. POWELL.

Oxidation of silver under dilute solutions of ammonia. K. A. HOFMANN and U. HOFMANN (Ber., 1928, 61, [B], 2566—2575).—Silver, under aqueous solutions of non-oxidising substances at the ordinary temperature, is much more rapidly oxidised by atmospheric oxygen than is indicated by the literature. Under pure water saturated with oxygen the action on silver is very slight; this effect is not due to the slight solubility of silver oxide since silver is not noticeably oxidised under dilute acetic acid. The oxidisability of silver in presence of dilute ammonia is of a different order of magnitude from that under dilute acid; this is ascribed to the conversion of the oxide into the complex $\text{Ag}(\text{NH}_3)_2\cdot\text{OH}$ and the prevention of the reverse electrochemical reaction. The dissolution of silver in ammonia solutions containing oxygen follows an unexpected course, since the weight of metal dissolved per day depends greatly on the volume of the supernatant liquid and the process comes to a conclusion after some months, long before the solubility of silver oxide in the ammonia has attained the saturation limit. A reverse action leading to re-separation of silver, $\text{Ag}_{\text{diss.}} \rightleftharpoons \text{Ag}_{\text{powder}}$, is not possible under the experimental conditions. The possibility that the paralysis of the change is due to the formation of nitrite as in the case of copper is discounted by the observation that the production of nitrite is too small to account for the effect and that ammonium nitrite is stable in ammoniacal solution in presence of silver powder. Utilisation of the oxygen in other directions, such as formation of nitrogen from ammonia, is not involved, since a quantity of air preserved for months over ammoniacal silver oxide still contained 20.6% of oxygen. If the ammonia solution is renewed after the action has come to a pause, the silver is again dissolved but at a much slower rate. The restriction depends on the compound $\text{Ag}(\text{NH}_3)_2\cdot\text{OH}$ and, if this is transformed into the corresponding salt by addition of ammonium nitrate or sulphate, it becomes operative at a much higher concentration than in the absence of such addenda. An adequate explanation of the restriction is found in the assumption of the slow formation of small amounts of silver fulminate or similar products, e.g., Ag_3N or Ag_2NH , which are gradually precipitated by evaporation of ammoniacal silver oxide solutions. Helped by the surface action in the adsorption layer, the amount of silver nitride can finally become so considerable that restriction occurs. Hence inactive silver powder always appears darker than the active material, although foreign matter is present in quantity which can scarcely be detected analytically. The deposit is gradually removed by

the air under aqueous ammonia, but the process is so slow that the surface of the silver powder remains covered as a consequence of fresh deposition of silver nitride from the solution. Confirmation of this hypothesis is found in the observation that additions of chlorides, bromides, and iodides facilitate restriction in increasing sequence corresponding with the solubility of the silver halides and that the mode of action of these addenda agrees with the limitation caused by the silver nitride. H. WREN.

Magnesia-graphite reactions at high temperatures. F. T. CHESNUT.—See B., 1929, 16.

Reduction of tricalcium phosphate by carbon. K. D. JACOB and D. S. REYNOLDS.—See B., 1929, 16.

Stereochemistry of zinc and cadmium. W. WAHL (Forh. III nord. Kemistmotet, 1928, 172—176).—The following complex salts of *o*-phenylenediamine and *o*-tolylenediamine with the zinc and cadmium halides have been prepared: $[\text{Cd}(\text{o-phen.})_2]\text{Cl}_2$; $[\text{Cd}(\text{o-phen.})_2]\text{Br}_2$ (two isomerides); $[\text{Cd}(\text{o-tol.})_2]\text{Br}_2$; $[\text{Cd}(\text{o-tol.})_4]\text{Br}_2$; $[\text{Zn}(\text{o-phen.})_2]\text{Br}_2$; $[\text{Zn}(\text{o-phen.})_3]\text{Br}_2$; $[\text{Zn}(\text{o-phen.})_4]\text{Br}_2$; $[\text{Zn}(\text{o-tol.})_2]\text{Br}_2$; $[\text{Zn}(\text{o-tol.})_3]\text{Br}_2$. The above salts are all rose-red in colour with the exception of one form of the cadmium di-*o*-phenylenediamine bromide and of the zinc tetra-*o*-phenylenediamine bromide. They usually crystallise well, and can frequently be recrystallised from concentrated aqueous solution, although some decompose when their solutions are heated. The solutions in alcohol are much more stable and can be advantageously employed in preparing the pure salts. Cadmium di-*o*-phenylenediamine bromide also exists in a green modification, crystallising in needles; the two salts of this type are probably geometrical isomerides, the green compound being the *trans*-form. A similar green modification of zinc tetra-*o*-phenylenediamine bromide has also been prepared. The two zinc triammine salts are octahedral, and correspond with the analogous cobalt and chromium compounds. Those of the above compounds which contain four phenylenediamine groups are of special interest, as they represent a class of complex inorganic salts not hitherto prepared. In these octammine salts the eight valencies can be visualised as directed from the centre of a cube towards the corners: in those octammine compounds containing four bivalent groups united to a central atom two isomerides are possible, the two zinc tetra-*o*-phenylenediamine salts being representatives of this class, and geometrical isomerides. If an asymmetrically placed group be inserted in the diamine ring, eight isomerides are possible, and the above cadmium tetra-*o*-tolylenediamine bromide, which possesses a deep rose-violet colour, is probably one of the *cis*-forms. Direct proof of the hexahedral structure of the above compounds is difficult to obtain, but experimental evidence shows that they cannot be diaminophenazine compounds. Both *m*- and *p*-phenylenediamine give rose-red complex salts with the bromides of zinc and cadmium, the latter having the composition $[\text{Zn}(\text{p-phen.})]\text{Br}_2$. A similar compound has also been prepared from *p*-phenylenediamine and copper sulphate, the salt formed being sparingly soluble and very stable.

H. F. HARWOOD.

Action of bromine on strontium oxide and its hydrates. H. B. DUNNCLIFF, H. D. SURI, and K. L. MALHOTRA (J.C.S., 1928, 3106—3111).—Bromine was used both in the form of vapour and in the form of its solution in carbon tetrachloride. No reaction occurs with strontium oxide. The monohydrate reacts incompletely to form strontium bromide and hypobromite. Bromine vapour converts strontium hydroxide octahydrate quantitatively into a mixture of bromide and bromate. The same final result is obtained by using bromine in carbon tetrachloride solution, but it can be shown in this case that in the initial stages of the reaction hypobromite is formed which is subsequently decomposed into bromide and bromate. From the relative proportions of bromide and bromate in the final product it appears that some bromate is formed by the direct oxidation of hypobromite by bromine (cf. Dietzel and Schlemmer, A., 1925, ii, 892).

F. J. WILKINS.

Attempts to isolate new fluoborates. A. TRAVERS and MALAPRADE (Compt. rend., 1928, 187, 982—984; cf. this vol., 38).—Evidence is provided for the decomposition by heat of potassium fluoborate according to the reactions $2\text{KBF}_4 = \text{BF}_3 + \text{BF}_3 \cdot 2\text{KF}$ and $\text{BF}_3 \cdot 2\text{KF} = \text{BF}_3 + 2\text{KF}$, which proceed simultaneously at about 580° and therefore render difficult the isolation of $\text{BF}_3 \cdot 2\text{KF}$. Three crystalline compounds, for which the ratios B/K=1 and F/K=3 were found, were isolated from the action of varying proportions of boric acid on a cold concentrated aqueous solution of potassium hydrogen fluoride. J. GRANT.

Thermal decomposition of aluminium oxide, hydroxide, and nitrate. N. PARRAVANO and G. MALQUORI (Atti II. Cong. Naz. Chim. pura appl., 1926, 1131—1134; Chem. Zentr., 1928, ii, 529).—The heating curve of aluminium nitrate nonahydrate shows three arrests: at 73.5° (fusion with conversion into the hexahydrate), at 140° (formation of $4\text{Al}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_3 \cdot 14\text{H}_2\text{O}$), and at 200° (conversion into Al_2O_3); that of the hexahydrate at 140° and 200°; the tetrahydrate is converted into the oxide at 180°. The hexahydrate can be prepared by keeping the nonahydrate over phosphorus pentoxide in a vacuum or by repeated treatment with hot 100% nitric acid; the tetrahydrate by the action of nitrogen pentoxide on the hexahydrate at the ordinary temperature. The curve for aluminium chloride shows a slight arrest at 122°; conversion into the oxide takes place at 180°. The salt $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ becomes anhydrous at about 105° and affords alumina and sulphur trioxide at about 760°. The thermal dehydration of technical alumina proceeds differently; the production of definite chemical individuals is postulated.

A. A. ELDRIDGE.

Surface oxidation of aluminium, tungsten, and molybdenum. L. C. BANNISTER (J.C.S., 1928, 3163—3166).—A technique has been developed for the preparation, both chemically and electrochemically, of surface films of oxide on aluminium, tungsten, and molybdenum, which vary gradually in thickness. The optical properties demonstrate clearly that the colours exhibited are set up by interference. Tables are given showing the variation of colour with applied

voltage, the number of coulombs used for formation, and the time of oxidation. Films have been isolated from aluminium by volatilising the metal away in hot gaseous hydrochloric acid. They consist mainly of oxide, with 4% of water and a trace of occluded anion from the electrolyte. F. J. WILKINS.

Separation of pure yttrium from yttrium earths. G. CANNERI (*Atti R. Accad. Lincei*, 1928, [vi], 8, 164—167).—Details are given of the separation of yttrium from yttrium earths by the fractional crystallisation of the double carbonates of the elements with sodium. The yttrium so obtained is contaminated with a small percentage of erbium. A final purification is obtained by the fractional precipitation of the crystalline double ferrocyanides with the alkali metals in the presence of a large excess of the alkali metal salt. The presence of the latter eliminates the production of the gelatinous precipitates of the simple ferrocyanides of the yttrium elements and allows of the production of yttrium salts of high purity after four precipitations. F. G. TRYHORN.

Germanium. I. Mode of treatment of germanite, preparation of pure germanium dioxide and of homogeneous germanium tetrachloride. II. Action of carbon tetrachloride on germanium dioxide. L. DEDE and W. RUSS (*Ber.*, 1928, 61, [B], 2451—2459, 2460—2463).—I. If arsenic is to be removed completely from germanium, it is important that as thorough a separation of the two elements as is possible should be effected in the preliminary treatment of the germanite. This is effected by treatment of the finely-divided mineral with a mixture of nitric acid, sulphuric acid, and water in the volume ratio 50 : 20 : 50 (cf. Keil, A., 1926, 589) whereby germanium dioxide, almost free from arsenic and containing as impurities chiefly lead sulphate and gangue, remains. The residue is mixed with fuming hydrochloric acid (*d* 1.19) and distilled in an all-glass apparatus in a stream of chlorine, the condensate being collected in a receiver charged with 20% hydrochloric acid. The lower layer of germanium tetrachloride is hydrolysed to the dioxide by water. The precipitated dioxide contains small amounts of chlorine which cannot be removed by decantation with cold or hot water but are evolved as hydrogen chloride by distillation with steam, thus indicating the probable existence of germanium oxychloride. The germanium in the filtrate is precipitated in the presence of 6*N*-sulphuric acid as the disulphide, which is oxidised to the dioxide by a mixture of nitric acid, sulphuric acid, and water.

The liquid remaining after the preliminary treatment of the germanite (see above) is submitted to electrolysis between a platinum gauze anode and a copper cathode until the deposit on the latter becomes black owing to arsenic. The liquid is concentrated and the germanium dioxide which separates is subjected to treatment with hydrochloric acid and distillation in chlorine as before. The germanium dioxide so prepared is spectroscopically pure.

Germanium dioxide is converted into the tetrachloride by distillation with hydrochloric acid in a current of hydrogen chloride and condensation of the distillate in a receiver cooled by a mixture of ice and

salt. The colourless, lower layer of germanium tetrachloride contains hydrogen chloride, which is mainly removed by aspiration of dry air through it at 18° followed by distillation. The product is preserved over anhydrous sodium carbonate and subsequently distilled. It has b. p. 83°/760 mm.

II. Nitrogen charged with the vapour of carbon tetrachloride is passed over germanium dioxide at temperatures between 500° and 865°. Under constant conditions with respect to the rate of passage of the gas, the diminution in the weight of the dioxide divided by the duration of the experiment is regarded as a measure of the rate of reaction. The change occurs with measurable velocity at 500° and the rate increases rapidly with rise of temperature. Intermediate formation of germanium oxychloride is not observed; hexachloroethane, m. p. 184—187°, appears invariably to be formed. In the behaviour of its oxide towards carbon tetrachloride, germanium appears to be allied much more closely to tin than to silicon. H. WREN.

Constitution of sodium plumbate. A. SIMON (*Z. anorg. Chem.*, 1928, 177, 109—115).—Since sodium plumbate, $\text{Na}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$ liberates all three molecules of water simultaneously at 110°, and there is no evolution of oxygen on dehydration, the salt is derived from metaplumbic acid and does not possess the formula $\text{Na}_2[\text{Pb}(\text{OH})_6]$. This conclusion is supported by the observation that alcohol does not extract sodium hydroxide from the salt. The behaviour of the anhydrous salt at high temperatures (600—800°) is described; at 750° it decomposes into sodium monoxide and lead tetroxide, which rapidly changes to red lead monoxide. The X-ray spectrograph supports the formula $\text{Na}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$.

H. F. GILLBE.

Interaction between nitrogen trichloride and nitric oxide. Reactions of compounds with odd electrons. W. A. NOYES (*J. Amer. Chem. Soc.*, 1928, 50, 2902—2910).—The reaction occurs in a mixed chloroform and carbon tetrachloride solution according to the equations (a) $2\text{NCl}_3 = \text{N}_2 + 3\text{Cl}_2$; (b) $\text{NOCl} + \text{NCl}_3 = \text{N}_2\text{O} + 2\text{Cl}_2$; (c) $\text{NCl}_3 + 2\text{NO} = \text{N}_2\text{O} + \text{NOCl} + \text{Cl}_2$, respectively, according as the temperature is 0°, -20°, or -80°. Reaction (a) is catalysed by the nitric oxide; reaction (b), which is a subsidiary reaction, and occurs slowly at -80°, is accompanied by the decomposition of one quarter of the nitrogen trichloride into nitrous oxide and chlorine, and by reaction (a); reaction (c) probably occurs in two stages: $\text{NCl}_3 + \text{NO} = \text{NOCl} + \text{NCl}_2$, and $\text{NCl}_2 + \text{NO} = \text{N}_2\text{O} + \text{Cl}_2$, although the intermediate compound could not be isolated. In light petroleum at -130° the reaction is $2\text{NCl}_3 + 2\text{NO} = 2\text{N}_2\text{O} + 3\text{Cl}_2$. The nitrogen trichloride also reacts with the petroleum and forms hydrogen chloride which serves to catalyse a reaction like (b). An octet structure for nitrous oxide is suggested in which there is a semi-polar union between the nitrogen and oxygen.

S. K. TWEEDY.

Compound of phosphorus pentachloride with bromine. W. A. PLOTNIKOV and S. JAKUBSON (*Z. physikal. Chem.*, 1928, 138, 243—245).—A reddish-brown compound, $\text{PCl}_5 \cdot 5\text{Br}_2$, m. p. 25° (decomp.),

separates from a solution of phosphorus pentachloride and bromine in carbon disulphide on cooling.

R. CUTHILL.

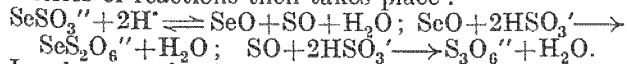
Synthesis of hypophosphoric acid. T. MIEŁOBEŹKI and J. WALCZYŃSKA (Rocz. Chem., 1928, 8, 486—501).—Tetraethyl hypophosphate is obtained by the action of diethyl orthophosphoryl chloride on sodium diethyl phosphite, or of diethoxychlorophosphine on sodium diethyl orthophosphate. Tetraethyl hypophosphate readily dissociates to yield diethyl hydrogen phosphate and metaphosphoric acid. *Tetramethyl hypophosphite*, prepared in a similar way to the ethyl ester, dissociates with the production of menthene and free hypophosphoric acid.

R. TRUSZKOWSKI.

Hydrogen polysulphides. O. VON DEINES (Z. anorg. Chem., 1928, 177, 124—128).—On addition of 100 c.c. of 3*N*-hydrogen chloride solution to 100 c.c. of sodium thiosulphate solution a flocculent yellow precipitate is formed which in the course of some minutes changes to a yellow oil, consisting of a solution of sulphur in hydrogen persulphide. Precipitated "white" sulphur actually consists of hydrogen persulphide containing a large quantity of sulphur. Polysulphides are also formed by the action of acids on sodium hyposulphite solutions.

H. F. GILLBE.

Sulphurous acid and its salts. VI. [With E. HAUFFE.] Autodecomposition of aqueous hydrogen sulphite solutions. VII. [With E. KIRCHHEISEN.] Interaction of hydrogen sulphite and hydro-sulphide. VIII. Inter-relationships of the sulphur acids. F. FOERSTER (Z. anorg. Chem., 1928, 177, 17—41, 42—60, 61—70).—VI. The spontaneous decomposition of hydrogen sulphite solutions, besides being considerably accelerated by the presence of selenium, is autocatalytic, the first products being sulphate and trithionate ions, but not tetrathionate: $4\text{HSO}_3' \longrightarrow \text{SO}_4'' + \text{S}_3\text{O}_6'' + 2\text{H}_2\text{O}$. The slower the reaction the greater is the decomposition of the trithionate according to the equation $\text{S}_3\text{O}_6'' + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4'' + \text{S}_2\text{O}_3' + 2\text{H}^+$. The autocatalytic nature of the main reaction is ascribed to the hydrogen ion, of which the concentration increases more rapidly than is indicated by titration, using methyl-orange as indicator, on account of the disappearance of HSO_3' . The mechanism of the process is as follows: the seleno-dithionate ion, formed rapidly by the action of hydrogen sulphite solution on selenium or on selenious acid, undergoes the decomposition, accelerated by the hydrogen ion, $\text{SeS}_2\text{O}_6'' + \text{H}_2\text{O} \longrightarrow \text{SO}_4'' + \text{SeSO}_3' + 2\text{H}^+$; in presence of more hydrogen sulphite a series of reactions then takes place:



In absence of selenium the hydrogen sulphite ion decomposes very slowly, according to the equation $4\text{HSO}_3' \longrightarrow 2\text{SO}_4'' + \text{S}_2\text{O}_3' + 2\text{H}^+ + \text{H}_2\text{O}$; the resulting hydrogen ions in this case also effect autocatalysis, probably through the formation of polythionates.

VII. On mixing solutions containing respectively 2 mols. of hydrogen sulphite and 1 mol. of hydro-sulphide, thiosulphate is formed immediately and in almost theoretical quantity: $2\text{HS}' + 4\text{HSO}_3' \longrightarrow$

$3\text{S}_2\text{O}_3' + 3\text{H}_2\text{O}$; free sulphur and sulphite ion result as by-products in equimolecular quantities. An excess of hydrogen sulphite causes the formation of trithionate and sulphite in addition to thiosulphate, but the primary reaction is so rapid that the secondary effects may be observed only if the hydrosulphide solution be added to the hydrogen sulphite solution; if the procedure be reversed the excess of hydrogen sulphite remains unchanged. The theory of the reactions involved is discussed, it being assumed that the hypothetical sulphur monoxide plays an important part.

VIII. (Cf. Bassett and Durrant, A., 1927, 843.)

On the assumption of the existence in aqueous solution of the equilibrium $\text{H}_2\text{SO}_3 \rightleftharpoons \text{SO} + \text{H}_2\text{O}$ between sulphylic acid and its hypothetical anhydride, the following equations are suggested to account for the formation of certain other of the sulphur acids: (1) $\text{SO} + \text{H}_2\text{S} \longrightarrow 2\text{S} + \text{H}_2\text{O}$, (2) $2\text{SO} + \text{H}_2\text{O} \rightleftharpoons \text{S}_2\text{O}_3'' + 2\text{H}^+$, (3) $\text{SO} + 2\text{HSO}_3' \longrightarrow \text{S}_3\text{O}_6'' + \text{H}_2\text{O}$, and (4) $\text{SO} + \text{HS}_2\text{O}_3' \longrightarrow \text{S}_5\text{O}_{10}'' + \text{H}_2\text{O}$. New views on the initial stage of the Wackenroder reaction are put forward, based on the occurrence of the reaction $\text{H}_2\text{S} + \text{H}_2\text{SO}_3 \rightleftharpoons \text{S}_2(\text{OH})_2 + \text{H}_2\text{O}$ followed by $\text{S}_2(\text{OH})_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2\text{SO}_2$ and $\text{S}_2(\text{OH})_2 + \text{H}_2\text{S} \rightleftharpoons 2\text{H}_2\text{O} + 3\text{S}$. Bassett and Durrant's equation for the formation of trithionic acid, viz., $2\text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{S} + \text{H}_2\text{S}_3\text{O}_6$, is shown to be improbable, equation (3) being more in accord with the observed facts. H. F. GILLBE.

Decomposition of thiosulphate by hydrogen chloride. O. VON DEINES (Z. anorg. Chem., 1928, 177, 13—16).—Sulphylic anhydride plays an important part in the decomposition of thiosulphate by acids, and the production of hydrogen persulphide has been established.

H. F. GILLBE.

Determination of the m. p. of mineral sulphides and arsenides. L. H. BORGSTROM (Forh. III nord. Kemistmotet, 1928, 169—171).—A knowledge of the m. p. of the ore minerals is of value with regard to the method of origin of such deposits. A number of determinations have been carried out, employing a modification of the usual laboratory m.-p. apparatus, the mineral being heated in a glass or quartz capillary tube immersed in a bath of fused salts contained in a platinum crucible and heated electrically. A Le Chatelier thermo-element is employed to measure the temperature, and this may be inserted directly into the fused salts, no protective tube being necessary. The most suitable salts for the bath are alkali chlorides, sulphates, and nitrates, or mixtures of the two former. An advantage of the method is the small amount of mineral required for a determination. The lowest m. p. are shown by the sulphides of the metalloids, realgar melting at 310°, orpiment at 325°, stibnite at 546°, and bismuthinite at 718°. The sulphides and arsenides of the metals usually melt between 800° and 1200°, but in some cases decomposition with volatilisation of sulphur or arsenic takes place below the m. p. The majority of the mineral sulpharsenides and sulphantimonides melt between 400° and 600°, but the minerals of the tetrahedrite group melt at 600—700°, and some sulpho-salts of bismuth above 800°. The following minerals of the above class have low

m. p.: dufrenoyite 450°, stephanite 470°, and pyrrargyrite 480°, and it is suggested that these minerals may be utilised as "geological thermometers." H. F. HARWOOD.

Corrosive action of sulphur monochloride. E. H. HARVEY.—See B., 1929, 16.

Molybdates and tungstates. Binary systems $\text{Li}_2\text{MoO}_4\text{--MoO}_3$, $\text{Na}_2\text{MoO}_4\text{--MoO}_3$, $\text{K}_2\text{MoO}_4\text{--MoO}_3$, $\text{Li}_2\text{WO}_4\text{--WO}_3$, $\text{Na}_2\text{WO}_4\text{--WO}_3$, $\text{K}_2\text{WO}_4\text{--WO}_3$, $\text{Li}_2\text{MoO}_4\text{--Na}_2\text{MoO}_4$, $\text{Li}_2\text{WO}_4\text{--Na}_2\text{WO}_4$, $\text{Li}_2\text{MoO}_4\text{--K}_2\text{MoO}_4$. F. HOERMANN (Z. anorg. Chem., 1928, 177, 145—186).—The simple molybdate and tungstate of lithium separate from aqueous solution and from fusions as anhydrous trigonal crystals, whereas the potassium salts, which are also anhydrous, crystallise in the monoclinic system; the dihydrated sodium salts form rhombic-bipyramidal crystals. Thermal analysis of the systems $\text{Li}_2\text{MoO}_4\text{--MoO}_3$ and $\text{Na}_2\text{MoO}_4\text{--MoO}_3$ indicates the existence of di-, tri-, and tetramolybdates; in the case of potassium the trimolybdate alone is formed. The salts $\text{Li}_2\text{O}, 2\text{MoO}_3$, $\text{Na}_2\text{O}, 2\text{MoO}_3$, and $\text{K}_2\text{O}, 3\text{MoO}_3$ crystallise in the rhombic system. The rhombic ditungstates of lithium and sodium melt without decomposition, and are probably isomorphous with the corresponding molybdates; potassium ditungstate does not appear to exist. Tetratungstates of lithium and sodium, and tri- and tetra-tungstates of potassium, exist. The following m. p. have been determined:

$\text{Li}_2\text{O}, \text{MoO}_3$, 705°; $\text{Li}_2\text{O}, 2\text{MoO}_3$, (532°);
 $\text{Li}_2\text{O}, 3\text{MoO}_3$, (549°); $\text{Li}_2\text{O}, 4\text{MoO}_3$, (568°);
 $\text{Na}_2\text{O}, \text{MoO}_3$, 687°; $\text{Na}_2\text{O}, 2\text{MoO}_3$, 612°;
 $\text{Na}_2\text{O}, 3\text{MoO}_3$, (528°); $\text{Na}_2\text{O}, 4\text{MoO}_3$, (515°);
 $\text{K}_2\text{O}, \text{MoO}_3$, 926°; $\text{K}_2\text{O}, 3\text{MoO}_3$, 571°;
 $\text{Li}_2\text{O}, \text{WO}_3$, 742°; $\text{Li}_2\text{O}, 2\text{WO}_3$, 745°;
 $\text{Li}_2\text{O}, 4\text{WO}_3$, (800°); $\text{Na}_2\text{O}, \text{WO}_3$, 700°;
 $\text{Na}_2\text{O}, 2\text{WO}_3$, 738°; $\text{Na}_2\text{O}, 4\text{WO}_3$, (784°);
 $\text{K}_2\text{O}, \text{WO}_3$, 921°; $\text{K}_2\text{O}, 3\text{WO}_3$, (660°);
 $\text{K}_2\text{O}, 4\text{WO}_3$, (930°); $\text{Li}_2\text{MoO}_4, 3\text{Na}_2\text{MoO}_4$, (484°);
 $\text{Li}_2\text{WO}_4, 3\text{Na}_2\text{WO}_4$, (511°).

Figures in parentheses are incongruent m. p.

H. F. GILLBE.

Reduction of tungsten by hydrogen. Mechanism of formation of crystals of tungsten of different sizes. G. A. MEIERSON (J. Russ. Phys. Chem. Soc., 1928, 60, 1217—1228).—The growth of crystals of tungsten does not commence below 1200° if the powdered metal be heated in a stream of dry hydrogen. Should the latter contain moisture, growth commences at 1050°, and is accompanied by loss in weight of the sample. These effects are due to the formation of tungsten dioxide, which is volatile at 1050°. This, on being reduced, deposits tungsten on the crystals at the further end of the combustion tube. Similarly, the formation of large crystals of tungsten in the reduction of tungstic anhydride is due to the volatility of the oxides WO_3 and W_2O_5 , which assumes measurable proportions at 850° and 900°, respectively. Where tungsten is prepared by the reduction of the trioxide, the magnitude of the crystals of the latter has no influence on that of the product. It is similarly possible to prepare large crystals of dioxide by slow reduction of trioxide at an appropriate temperature. R. TRUSZKOWSKI.

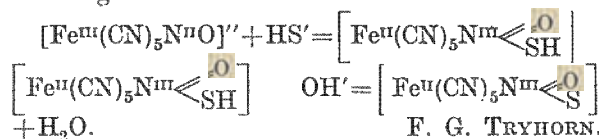
New fluorides, especially chlorine fluoride. O. RUFF [with J. FISCHER, F. LUFT, E. ASCHER, F. LAASS, and H. VOLKMER] (Z. angew. Chem., 1928, 41, 1289—1292).—Electrolysis in a copper vessel at 125° of fused ammonium hydrogen fluoride gives a good yield of nitrogen trifluoride which may be purified by fractional distillation at -160°. Nitrogen trifluoride is a colourless gas, condensing to a colourless liquid, b. p. -119°, f. p. -210°; it is relatively stable, is not decomposed by an electric spark, but yields a mixture of nitric oxide and nitrogen peroxide when sparked with steam. Chlorine fluoride, ClF , is found among the products of the reaction of slightly moist chlorine and fluorine; it is a colourless gas which condenses to a faintly yellow liquid, b. p. -110°, f. p. -150°. Some evidence of the formation of oxygen fluoride or of a hydroxyfluorine compound has been obtained by the fractional distillation of the gases obtained from the interaction of fluorine and water vapour. A. R. POWELL.

Existence of an oxide of bromine. B. LEWIS and H. J. SCHUMACHER (Z. physikal. Chem., 1928, 138, 462).—Experiments on the kinetics of the reaction between bromine and ozone show the presence of some intermediate compound, probably a bromine oxide. In order to test this view, an attempt was made to isolate the product by mixing a small amount of bromine and liquid ozone, and allowing to evaporate in a flask. A thick white deposit of a substance thought to be bromine oxide was formed on the walls of the vessel, but owing to explosion it could not be kept under observation for a sufficient length of time to reach any definite conclusion.

A. J. MEE.

Ferromagnetic ferric oxide. E. F. HERROUN and E. WILSON (Proc. Physical Soc., 1928, 41, 100—111).—A review of recent work.

Reaction between sodium nitroprusside and sulphides. G. SCAGLIARINI and P. PRATESI (Atti R. Accad. Lincei, 1928, [vi], 8, 75—81).—Stable, homogeneous, crystalline compounds of the type $\text{M}_4[\text{Fe}(\text{CN})_5\text{OS}]$ have been obtained by the interaction of the sulphides of potassium, sodium, lithium, and rubidium, with sodium nitroprusside in absolute methyl alcohol. Electro-titrimetric evidence is adduced for the view that the reaction proceeds in two stages:



F. G. TRYHORN.

New green compounds of cobalt. II. A. BERNARDI (Gazzetta, 1928, 58, 743—757; cf. A., 1927, 636).—When very dilute solutions of cobaltous salts and sodium hydroxide react in the cold, the blue basic salts which are first precipitated are rapidly converted into green compounds, which are stable both in solution and in the dry state. The formation of these green compounds depends on the proportions of cobaltous salt and sodium hydroxide used. With cobaltous chloride a green compound is formed only when the mol. ratio $\text{NaOH} : \text{CoCl}_2, 6\text{H}_2\text{O}$

lies within the limits 0.02—0.44. Cobaltous sulphate and nitrate behave similarly but within still narrower limits. The green compounds are not formed in absence of oxygen, but appear when air is bubbled through the solution, and their formation is probably dependent on the oxidation of the cobalt atom from the bivalent state to a higher state. The compounds are of variable composition, which cannot be accounted for on the usual valency principles, and they are considered to be "adsorption compounds."

O. J. WALKER.

Quantitative spectroscopic analysis of alloys. T. NEGRESO (J. Chim. Phys., 1928, 25, 343—362; cf. A., 1928, 501, 929).—The conditions for using spark and arc spectra in the quantitative analysis of binary alloys are described, and precautions as to times of exposure, voltage, and development of plates are given. Two lines, one for each of the metals of the alloy, very close together are selected and their intensities compared either by eye or by a microphotometer. As the proportion of one metal increases relatively to the other, it is found that the line of this metal is first less intense and finally becomes more intense than the neighbouring line of the second metal. Comparison is made with the photographs recording the results of a set of standard alloys, whereby the percentage of the constituents is determined. The accuracy of the method depends on the constancy of the physical conditions employed and also on the nature of the alloy. Examples of the analysis of Sn-Bi, Pb-Bi, Cu-Si, Fe-Si, Cu-Co, and Zn-Cd alloys are given.

J. J. FOX.

Sensitivity of spectral lines. T. NEGRESO (J. Chim. Phys., 1928, 25, 363—407; cf. preceding abstract).—The sensitivity of any spectral line in a given source of emission in an alloy depends solely on its intensity in the pure metal examined under the same conditions. The effect of diminishing the proportion of an element in a mixture is studied and it is concluded that all the spectral lines excited by any particular method diminish in intensity and finally disappear, the last line to vanish being the most intense of the particular spectrum. These last lines are the true "raies ultimes," a definition which differs from that given by de Gramont for these lines. The divergence from de Gramont's conclusions is discussed in detail and sources of error in the results of various observers are indicated. It is shown that in spectra of sources of emission excited by smaller energy, e.g., flames and arcs, the most sensitive lines are emitted by the neutral atom (arc lines); in those of sources excited by greater energy, e.g., spark spectra, the most sensitive lines are given by ionised atoms (spark lines). In both cases the order of sensitivity of the series is sharp, principal, diffuse, Bergmann.

J. J. FOX.

Apparatus for rapid sedimentation analysis. C. J. VAN NIEUWENBURG and W. SCHOUTENS.—See B., 1929, 1.

Wood's metal as cathode in electrolysis. H. A. J. PIETERS (Chem. Weekblad, 1928, 25, 706—707; cf. Paweck and Weiner, A., 1928, 143).—The determination is carried out by finding the increase in weight of a washed and dried quantity of the alloy

after electrolysis; the alloy is kept liquid during electrolysis. The method is most suitable for determination of copper, cadmium, zinc, mercury, nickel, and cobalt present as sulphates. S. I. LEVY.

Fajans' method of titration. H. A. J. PIETERS (Chem. Weekblad, 1929, 26, 6—9).—The use of colour change indicators in titrations in which precipitates are obtained has been investigated. In addition to the fluorescein derivatives employed by Fajans for the silver halide titration, Victoria-violet, chrome-green G, bromophenol-blue, and bromocresol-purple are found to give satisfactory results, both for simple titrations and for determination of chloride and iodide together. Titrations of lead salts with soluble oxalates, ferrocyanides, and phosphates can also be effected by the same method. Close study of the conditions for reaction is necessary in each case.

S. I. LEVY.

Micro-analysis and technical methods of investigation. R. LUCAS and F. GRASSNER (Mikrochem., 1928, 6, 116—132).—A description of the application of micro-analytical methods to technical problems with special reference to the determination of sulphur, halogens, carbon, hydrogen, nitrogen, and phosphorus in organic materials, electro-analysis, and colorimetric methods.

J. S. CARTER.

Spot analysis. W. P. MALITZKY (Mikrochem., 1928, 6, 157—160).—A reply to Feigl (A., 1928, 382).

J. S. CARTER.

Gas analysis apparatus. H. A. BAHR (Chem. Fabr., 1929, 13—15).—Improvements in the construction and manipulation of absorption pipettes are described. A rapid and accurate form of Orsat apparatus, especially suited for the analysis of gases containing hydrogen and methane, is described.

J. S. CARTER.

Hydrogen-ion colorimeter. R. B. H. GRADWOHL (J. Lab. Clin. Med., 1927, 12, 694—701).—The illuminating box slides along a row of glass ampoules containing the selected sterile buffer of known p_H value.

CHEMICAL ABSTRACTS.

"Salt error" of indicators in the colorimetric determination of p_H . I. M. KOLTHOFF (J. Physical Chem., 1928, 32, 1820—1833).—A calculation of the salt correction of indicators on the basis of the Debye-Hückel equation has been attempted. When the ionic strength of the solution is considerably greater than that of the ordinary buffer solutions, the calculated values are higher than the experimental. Furthermore, indicators of the same type vary considerably. The salt corrections for many indicators in citrate solutions and in the presence of neutral salts have been experimentally determined and referred to the hydrogen electrode at 18° as standard. The average salt corrections of the various phthalcins at an ionic strength between 0.1 and 0.0025 are tabulated. The salt correction is also dependent on the properties of the buffer solution. Methyl-orange and methyl-red show small salt errors under different conditions and hence are suitable indicators in the colorimetric determination of p_H . Their behaviour is explained by their hybrid character.

L. S. THEOBALD.

Colorimetric determination of hydrogen-ion concentration in weakly-buffered solutions. E. OEMAN (*Papier-Fabr.*, 1929, 27, 27—30).—The p_H values of unbuffered solutions are accurately determined by plotting the p_H values observed as a function of the number of drops of solution of indicator present and extrapolating to zero concentration of indicator. The slope of the curve may be decreased, and the accuracy of the determination consequently increased, by using as indicator a mixture of the indicator proper and one of its salts.

J. S. CARTER.

Titration of strong acids combined with ammonia or organic amines. Titration of ammonium salts, amino-salts, and amino-acids. C. P. A. KAPPELMEIER (*Rec. trav. chim.*, 1928, 47, 1064—1071).—The method depends on the fact that phenolphthalein paper which has been reddened with ammonia or with an organic amine is rapidly decolorised when warmed owing to the dissociation of the compound of phenolphthalein with the ammonia or amine, whereas the red colour produced by dilute alkalis is stable for a considerable period. The total acid content of a solution containing sulphuric acid and ammonium sulphate may be determined by titrating with dilute sodium hydroxide solution until a piece of phenolphthalein paper which has been dipped in the solution does not lose its colour when warmed. The method can give results accurate to within $\pm 0.3\%$ of the total acid content and is illustrated by titration results for solutions of strong acids containing ammonia and nicotine. It may also be used for the determination of the nitrogen content of ammonium or amino-salts.

O. J. WALKER.

Universal indicator which gives the spectrum colours for a p_H range of 3—11.5. H. W. VAN URK (*Pharm. Weekblad*, 1928, 65, 1246—1249).—The indicator is prepared by dissolving 0.1 g. of methyl-orange, 0.04 g. of methyl-red, 0.4 g. of bromothymol-blue, 0.32 g. of naphtholphthalein, 0.5 g. of phenolphthalein, and 1.6 g. of cresolphthalein in 70% alcohol, and diluting to 100 c.c.

S. I. LEVY.

Use of potassium iodate in back titration for the determination of the hypochlorite content of solutions. J. R. LEWIS and R. F. KLOCKOW (*J. Amer. Chem. Soc.*, 1928, 50, 3243—3244).—Hypochlorite solutions may be analysed by adding excess of a suitable reducing agent and titrating back with potassium iodate, exactly as described for determining hydrogen peroxide (Jamieson, "Volumetric Iodate Methods," 1926). When sodium arsenite is used as reducing agent small amounts of nitrate or chlorate may be present, but chlorates must be absent when sodium thiosulphate or iodide solutions are used.

S. K. TWEEDY.

Detection of "chloramine-T," and its differentiation from hypochlorites. H. W. VAN URK (*Chem. Weekblad*, 1929, 26, 9—10).—Various colour tests by means of which "chloramine-T" may be distinguished are described; the most suitable is the behaviour towards reduced indigo-carmin solution, the yellow colour of which is discharged by the bleaching action of hypochlorites, but changed to blue by the oxidising action of the chloroamine.

The thalleioquinine reaction is not given by the chloroamine, but is recommended as a more delicate and suitable test for hypochlorites than the starch-iodide test.

S. I. LEVY.

Sensitive spot reaction for fluoride. F. PAVELKA (*Mikrochem.*, 1928, 6, 149—151).—The method depends on the fact that the colour of a zirconium alizarin lake is destroyed by hydrofluoric acid. The test-papers are prepared by moistening filter-paper with a solution of basic zirconium chloride to which an excess of an alcoholic solution of alizarin has been added. The dried papers are moistened with a drop of 50% acetic acid and a drop of the suspected solution is added. In presence of 0.01 mg. of fluorine a yellow stain appears on the originally red paper. Sulphates, oxalates, and phosphates interfere. With insoluble fluorides the powdered material is shaken with 5 c.c. of dilute hydrochloric acid containing 0.5—1.0 g. of borax and a drop of the resulting mixture taken for the test. About 0.06 mg. of calcium fluoride may be detected thus. Alternatively, the fluoride may be treated with silica and sulphuric acid and the moistened test-paper held in the vapours.

J. S. CARTER.

Determination of sulphur in copper alloys containing tin. H. LEYSANT.—See B., 1929, 22.

Volumetric determination of sulphate ion. Z. MINDALEV (*Z. anal. Chem.*, 1928, 75, 392—395).—The neutral sulphate solution (10 c.c.) is treated with 10 c.c. of alcohol and 2—3 drops of a cold saturated solution of potassium iodide. The solution is then titrated with 0.1N-lead nitrate solution added slowly with vigorous agitation until a faint yellow colour persists. When these conditions are rigidly adhered to, concordant results very slightly below the theoretical are obtained.

A. R. POWELL.

Determination of selenium in sulphuric acid. Z. REICHINSTEIN.—See B., 1929, 15.

Refractometric analysis of solutions of pure compounds. F. URBAN and V. W. MELOCHE (*J. Amer. Chem. Soc.*, 1928, 50, 3003—3009).—Tables are given which enable the concentrations of solutions of telluric acid, selenious acid, and potassium ferrocyanide to be determined from observations in an immersion refractometer.

S. K. TWEEDY.

Detection of phosphoric acid in minerals and rocks. H. LEITMEIER (*Mikrochem.*, 1928, 6, 144—148).—The sensitive phosphomolybdic acid-benzidine reaction may be applied to the detection of phosphates in minerals etc. A little of the powdered material on a filter-paper or a scratch on a porcelain plate is treated in the manner described (Feigl, A., 1928, 1107). The localisation of phosphates in minerals may be determined by pressing a filter-paper moistened with nitric acid-molybdate solution against a section. This paper is then brought into contact with a second paper moistened with benzidine solution and finally held in ammonia vapour. The blue regions correspond with the positions of the phosphatic constituents.

J. S. CARTER.

Analysis of phosphorite. A. V. KRASNOVSKI (*J. Chem. Ind. Moscow*, 1928, 5, 408—409).—The

insoluble residue is determined by boiling 5 g. with 50 c.c. of aqua regia. In the determination of dissolved silica, nitric acid is employed. The filtrate is diluted to a definite volume; a portion containing <0.1 g. P_2O_5 is used for the determination of phosphate by Woy's method (the molybdate precipitate being kept for 2—3 hrs. in a warm place and at least 12 hrs. at the ordinary temperature before filtration) and another for determining alumina, iron, calcium, and magnesium. This portion is evaporated nearly to dryness and treated on a water-bath with 1 g. pieces of tin and a few c.c. of fuming nitric acid to eliminate phosphoric with metastannic acid. The iron and alumina are determined together by Blum's method; the filtrate is diluted to 300 c.c., and the calcium precipitated twice as oxalate from solutions containing acetic and hydrochloric acids, respectively. Magnesium is determined by Schmitz's method, and moisture and loss on ignition by the usual methods. The determination of fluorine requires examination.

CHEMICAL ABSTRACTS.

Volumetric determination of arsine. H. KUBINA (Z. anal. Chem., 1929, 76, 39—48).—Two titrimetric methods for the determination of arsine are described. According to the first method the gas is introduced into an evacuated absorption vessel containing an excess of a standard solution of bromate and a considerable excess of bromide. After acidification the contents are agitated and oxidation to arsenic acid occurs. An excess of a standard solution of arsenious salt is added and the back titration carried out with the bromate solution. Each c.c. of 0.1N-solution of bromate required during the absorption corresponds with 0.280 c.c. of arsine at 0° and 760 mm.

In the second method the absorbing medium is an acid solution of iodine monochloride, the iodine liberated according to the equation, $AsH_3 + 8ICl + 4H_2O = AsO_3''' + 4I_2 + 8Cl' + 11H'$, being titrated with a solution of potassium iodate in the presence of a cyanide (Lang, A., 1925, ii, 713). Each c.c. of 0.1N-solution of iodate corresponds with 0.187 c.c. of arsine at 0° and 760 mm.

J. S. CARTER.

Decomposition of silicates by strontium salts for the determination of alkali metals. J. KAVINA (Chem. Listy, 1928, 22, 289—294).—The alkali metal content of silicates can be determined with satisfactory accuracy using a fusion mixture consisting of 1 part of ammonium chloride to 6 parts of strontium carbonate.

R. TRUSZKOWSKI.

Determination and separation [of sodium and potassium]. A. THURMER (Chem.-Ztg., 1928, 52, 974—975).—Alcohol (96—99%) is suitable for the separation of sodium and potassium perchlorates. Sodium may be determined in the filtrate by removal of solvent and perchloric acid at 80° and 180°, respectively. In accurate work the resulting sodium perchlorate may be fused with sodium carbonate and potassium nitrate and chloride determined volumetrically or gravimetrically. If the alkali metals are initially present as sulphates precipitation of potassium as the salt $KNa_2Co(NO_3)_6$ should be effected by addition of excess of sodium cobaltinitrite. Sodium and potassium chlorides are appreciably volatile at a bright red heat.

J. S. CARTER.

Determination of potassium. L. GALIMBERTI (Atti II Cong. Naz. Chim. pura appl., 1926, 1396—1397; Chem. Zentr., 1928, ii, 589).—The method depends on the precipitation of potassium sodium cobaltinitrite, reduction therewith of permanganate solution, addition of oxalate, and titration of the excess. It is applicable in presence of considerable quantities of sodium chloride or magnesium sulphate.

A. A. ELDRIDGE.

Indirect detection and determination of alkali sulphates in certain other metallic sulphates.

A. WÖHLK (Dansk Tidsskr. Farm., 1928, 2, 315—319).—The method obviates the necessity for using hydrogen sulphide. The sulphate (1 g.) is dissolved in water (150 c.c.) and a slight excess of a 4% solution of barium hydroxide is added. The whole is boiled for 10 min., the volume being kept constant, and then filtered. Phenolphthalein (0.5 c.c. of a 1% solution) is added to the filtrate, and carbon dioxide passed in until the red colour disappears. The liquid is boiled again until the hydrogen carbonates are decomposed and the red colour returns. After thorough cooling the solution is filtered, 15 drops of methyl-red are added to the filtrate, and the liquid is then titrated with 0.1N-acid until the pink colour of methyl-red appears. If only a qualitative test is desired the solution can be titrated directly, but for quantitative purposes it must first be evaporated to 50 c.c. and refiltered if necessary. Blank determinations require about 0.5—0.9 c.c. of 0.1N-hydrochloric acid for the titration, and the method permits the detection of 1% of alkali sulphate. It is necessary that the sulphates under examination should conform with the requirements of the pharmacopœia as regards freedom from chloride, ammonia, etc.

H. F. HARWOOD.

Nephelometric determination of barium sulphate. J. KREPELKA and A. KALINA (Chem. Listy, 1928, 22, 545—550).—At concentrations of 0.3—1.0 mg. Ba per litre the mean error of nephelometric determinations of the sulphate is 0.5%. The suspension should not be kept longer than 30 min. after preparation; the addition of glycerol to 10% by volume greatly augments the stability of these suspensions. The limiting percentage concentrations of other salts which may be present without affecting the accuracy of this method are: sodium 0.15, hydrogen 0.30, magnesium 0.003, zinc or cadmium 0.006, mercury 0.04, and aluminium chloride 0.002. All these ions, with the exception of magnesium, provoke coagulation of the suspension at higher concentrations than the above, leading to excessively high results, whilst magnesium has a protective influence, so that the results are low.

R. TRUSZKOWSKI.

Radium and geology. C. S. PIGGOT (J. Amer. Chem. Soc., 1928, 50, 2910—2916).—A method of determining the radium content of rocks is outlined very briefly. Preliminary experiments on granites indicate that radium is associated more with those minerals of high than with those of low sp. gr.; it is particularly associated with the micas. A possible method of determining directly the lead derived from uranium by means of the mass-spectrograph is given (cf. Aston, A., 1927, 806).

S. K. TWEEDY.

Determination of zinc as zinc pyrophosphate in the presence of much sodium chloride. L. DEDE (Ber., 1928, 61, [B], 2463—2465; cf. this vol., 43).—The precipitate obtained by the addition of ammonium phosphate to a solution of a zinc salt containing sodium and ammonium chlorides is a mixture of zinc ammonium and zinc sodium phosphate; the proportion of the former can be increased by increasing the relative amount of ammonium chloride, but, contrary to Finlay and Cumming (J.C.S., 1913, 103, 1004), homogeneous zinc ammonium phosphate can only be thus precipitated if the solution contains less than 3% of sodium chloride. If this is not the case, the solution is concentrated until sodium chloride commences to separate, cooled, and saturated with dry hydrogen chloride. The precipitated sodium chloride is removed and washed with highly concentrated hydrochloric acid. After removal of the bulk of the acid from the filtrate by evaporation, the zinc is precipitated as zinc ammonium phosphate in the residue which has been neutralised cautiously by ammonia. H. WREN.

Rapid electrolytic deposition of cadmium and zinc and their separation by regulation of the voltage. E. BRENNECKE (Z. anal. Chem., 1928, 75, 321—371).—The deposition potential of zinc from acid sulphate solutions 0.1—0.5N in free acid using rotating coppered platinum gauze cathodes is 2.7—2.8 volts whilst that of cadmium is 2.28—2.34 volts, but the deposition potential of zinc on cadmium-plated electrodes under the same conditions is 2.92—3.0 volts. The deposition of cadmium from sulphate, acetate, or cyanide solutions is never complete, a fraction of a mg. always remaining in the electrolyte; nevertheless the results obtained for cadmium are invariably high under the conditions usually recommended, owing to oxidation of the surface of the deposit by oxidising agents in the ether used for washing prior to weighing. The use of amalgamated cathodes does not ensure complete precipitation of the cadmium nor does it prevent oxidation. Amalgamated copper electrodes cannot be used for the deposition of zinc from solutions containing ammonium sulphate as ammonium amalgam is formed and the cathode disintegrates, but good results are obtained by deposition from feebly acid acetate solutions using a coppered platinum cathode. For the separation of cadmium from zinc 100 c.c. of the solution are treated with 10—12 c.c. of 2N-sulphuric acid and electrolysed at 2.8 volts for 5—10 min., then at 2.7 volts for 25—35 min. to deposit the cadmium; the solution is then neutralised with ammonia, reacidified with acetic acid, treated with 4 g. of sodium acetate, and electrolysed for 10 min. with 1—2 amp. to deposit the zinc. The results are good by a compensation of errors as the cadmium deposit contains traces of zinc and the zinc deposit traces of cadmium. A. R. POWELL.

Determination of lead by means of 8-hydroxyquinoline. V. MARSSON and L. W. HAASE (Chem.-Ztg., 1928, 52, 993—995).—The hot acetate solution of lead is treated with 30—60 c.c. of a hot solution of 8-hydroxyquinoline (saturated cold), then with dilute ammonia until feebly alkaline, stirred vigorously, and

set aside over-night in a cold place. The precipitate is collected in a porous filter crucible, washed with cold water, dried at 105°, and weighed; it contains 41.85% Pb. As the solubility of the compound in cold water is about 4.5 mg./litre in the presence of excess of the precipitant, the method is unsuitable for the determination of minute quantities of lead, e.g., in drinking water. For the separation of copper from lead the copper is precipitated by means of dibromo-8-hydroxyquinoline in hot dilute hydrochloric acid solution and the lead from the filtrate as described above. A. R. POWELL.

Colorimetric determination of thallium. C. STICH (Pharm. Ztg., 1929, 74, 27).—For the determination of thallium in rat-poisons etc. about 2 g. of material are ashed and the residue is dissolved in dilute sulphuric acid. Thallium is determined colorimetrically as sulphide in alkaline solution. J. S. CARTER.

New salts of nitrosophenylhydroxylamine and their application in microchemical analysis. A. MARTINI (Mikrochem., 1928, 6, 152—156).—The micro-crystalline forms of the *cuprammonium*, *uranyl*, *calcium*, *strontium*, *barium*, and *cadmium* salts of nitrosophenylhydroxylamine (cupferron) are described and photomicrographs are given. The crystal forms of the barium and uranyl salts are sufficiently characteristic for the detection of these cations. The calcium, strontium, and cadmium salts are, however, very similar. Cadmium should therefore be confirmed by treatment with sodium bromide and brucine acetate (A., 1927, 953), and calcium confirmed by conversion into calcium selenite, using a saturated solution of sodium selenite. J. S. CARTER.

Analysis of bauxite and refractories of high alumina content. G. E. F. LUNDELL and J. I. HOFFMAN.—See B., 1929, 19.

Determination of manganese in the presence of silica. C. NEWCOMB (Analyst, 1928, 53, 644—645).—If the ordinary procedure is followed in the colorimetric determination of manganese by permanganate in acid solution in presence of silica it is impossible to extract all the manganese as it is tenaciously adsorbed by the silica. If the ash, fused with alkali carbonate, is dissolved in water and the solution poured into more than sufficient acid to neutralise it, a colloidal solution results; the adsorption then taking place is not in a form that interferes with the oxidation, and a clear pink solution is finally obtained. D. G. HEWER.

Detection of iron as an impurity in reagents by the thiocyanate test. H. W. VAN URK (Chem. Weekblad, 1928, 25, 703—704, 704—706).—The delicacy of the test is influenced by presence of salts. The influence of sodium sulphate has been examined; the test in this case is not more sensitive than the sulphide test, although it can be made sufficiently accurate for examination of the "reagent quality" salt. The presence of chlorides and nitrates is not harmful. The influence of salts is shown to be due to their effect on the hydrogen-ion concentration; by adjustment of this, the otherwise strong effect of salts of weak acids can be completely eliminated. S. I. LEVY.

Stability of ferrous sulphate solutions and their use in standardising permanganate. J. A. N. FRIEND and E. G. K. PRITCHETT (J.C.S., 1928, 3227—3232).—Addition of sulphuric acid in concentrations up to 2*N* greatly increases the resistance of ferrous sulphate solutions to oxidation in air; further increase in acid concentration has little effect. If the precautions described are taken, the results of standardising permanganate with solutions of ferrous sulphate prepared by dissolving iron in sulphuric acid agree to within 0.1% with those obtained by the oxalate method. F. J. WILKINS.

Standard method for examination of [alkali] ferrocyanides. H. MOLL (Chem. Weekblad, 1928, 25, 657—658).—The method selected at the April conference at Berlin (titration against standard zinc sulphate solution) is described in detail.

S. I. LEVY.
Determination of molybdenum. H. A. DOERNER (U.S. Bur. Mines. Inf. Circ., 1928, No. 6079, 2 pp.; also Bull., No. 212).—The sample is dissolved in aqua regia, the solution evaporated with sulphuric acid, and lead sulphate removed; calcium etc. is removed by addition of ammonia solution and sodium carbonate (3 g.) and digestion. Any precipitate produced in the filtrate by tartaric acid and hydrogen sulphide is removed. The alkaline sulphide solution is then acidified and molybdenum disulphide collected. This is dissolved in aqua regia, and lead molybdate precipitated in a properly buffered solution. CHEMICAL ABSTRACTS.

Determination of molybdenum by reduction of molybdic acid with zinc. J. KASSLER (Z. anal. Chem., 1928, 75, 457—466).—About 10 g. of zinc in the form of coarse powder are added to 250 c.c. of the warm solution of molybdic acid containing 30 c.c. of 1:1 sulphuric acid and 5 c.c. of 1:1 hydrochloric acid. If sufficient chloride is present addition of hydrochloric acid is unnecessary. When reduction is effected (about 15 min.) the whole is filtered, conveniently through glass wool covered with a layer of glass beads, and titrated with a solution of potassium permanganate. Precautions must be taken to minimise oxidation between reduction and titration.

To determine molybdenum in steels etc. the solution obtained after dissolution in hydrochloric acid, oxidation with chlorate, and removal of excess of chlorine is neutralised and transferred to a litre flask containing an excess of alkali. After dilution to 1000 c.c., 250 c.c. of filtered solution are neutralised with 1:1 sulphuric acid and a further 30 c.c. added. The solution is boiled and a few c.c. of permanganate solution are added to oxidise organic matter before addition of zinc. If present, vanadium must be reduced by sodium sulphite or ferrous salt before precipitation with alkali. Tungsten and nitrates interfere. The determination of molybdenum in presence of tungsten will be described shortly.

J. S. CARTER.

Analytical chemistry of tungsten. I. Berzelius' method for determination of tungsten as mercurous tungstate. V. I. SPITZIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1229—1235, and Z. anal. Chem., 1928, 75, 433—440).—The use of mercurous

nitrate without the addition of nitric acid gives complete precipitation of mercurous tungstate from neutral tungstate solution, without the necessity of any further treatment of the precipitate, such as addition of alkali. Where precipitation takes place from acid solution even the subsequent addition of alkali does not bring about quantitative separation of tungsten trioxide, owing probably to the formation of soluble mercury metatungstates and of free tungstic acid under the influence of the acidity of the medium.

R. TRUSZKOWSKI.

Analytical chemistry of tungsten. II. Quantitative analysis of tungsten compounds in the dry way. V. SPITZIN and L. KASCHTANOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1333—1349, and Z. anal. Chem., 1928, 75, 440—457).—Sodium tungstate is heated in a platinum boat at 650—700° in a current of pure dry hydrogen for 30 min., and then at 900° for 1 hr.; the tube is then cooled, and again heated at 900° for a further 30 min. The residue in the boat now consists only of tungsten. The preliminary heating at 650° is necessary in order to avoid fusion of acid tungstates, which would interfere with their further reduction. The sodium content is determined similarly by heating in a current of dry hydrogen chloride at 500—550° for 2—8 hrs., when the residue consists of sodium chloride, the tungsten having been volatilised as oxychloride. Tungsten bronzes, of the general formula $x(R_2O)_y(WO_3)_zWO_2$, where R represents one equivalent of an alkali or alkaline-earth metal, are quantitatively converted into tungstates by heating at 400—500°; alternatively, when heated in a current of hydrogen chloride the dioxide is converted into oxychloride: $3WO_2 + 4HCl = W + 2WO_2Cl_2 + 2H_2O$, the residual tungsten, after roasting and volatilisation in hydrogen chloride, affording a measure of that originally present. Metallic tungsten is best analysed for oxides by heating in a current of dry hydrogen chloride, when the oxides are converted into volatile oxychlorides as follows: $3W_2O_5 + 10HCl = W + 5WO_2Cl_2 + 5H_2O$, with a corresponding loss in weight of the sample. R. TRUSZKOWSKI.

Zirconium. II. Detection of potassium by zirconium sulphate in the presence of ammonium ions. R. D. REED and J. R. WITHEROW (J. Amer. Chem. Soc., 1928, 50, 2985—2987; cf. A., 1928, 858).—The sensitiveness of zirconium sulphate as a reagent for the detection of potassium is unimpaired by the presence of ammonium ions. S. K. TWEEDY.

Determination of small quantities of antimony in the form of stibine. J. GRANT (Analyst, 1928, 53, 626—632).—A rapid electrolytic method for determining antimony in solutions containing up to 8 mg. in 10 c.c. of liquid consists in removal of the antimony (from solution in 0.5*N*-hydrochloric acid) as stibine by a swift current of hydrogen, which, as a stream of bubbles, impinges on the point of an inverted cone lead cathode. The stibine is thus removed from the cell before it decomposes. The actual apparatus is an improved form of the electrolytic Marsh type. The antimony in the deposit is determined by a colorimetric method for amounts from 2 to 0.01 mg., and by matching with standard stains for smaller quantities. Any arsenic present is

deposited with the antimony, but since arsenic is sparingly soluble in hydrochloric acid the colorimetric method suggested need not be modified. The deposit is dissolved in 1 c.c. of concentrated hydrochloric acid, diluted with 3 c.c. of water and 1 c.c. of a clear, saturated solution of hydrogen sulphide, and the colour matched against that produced from a known volume of a dilute standard solution of tartar emetic.

D. G. HEWER.

Determination of palladium by means of 6-nitroquinoline. S. C. OGBURN, jun., and A. H. RIESMEYER (J. Amer. Chem. Soc., 1928, 50, 3018—3022).—Boiling palladium chloride solution is precipitated with a hot, saturated, aqueous solution of 6-nitroquinoline. The precipitate is ignited in air and then in hydrogen and, after cooling (preferably in carbon dioxide), the residue of palladium is weighed. Any other platinum metal may be present. The precipitate is $\text{Pd}(\text{C}_9\text{H}_6\text{O}_2\text{N}_2)_2$.

S. K. TWEEDY.

Electric arc in gases at low pressures. F. H. NEWMAN (Phil. Mag., 1928, [vii], 6, 811—817).—The cold electrode arc previously described (A., 1926, 1069) has been modified by the incorporation of water-cooling of the electrodes and the provision of a large reservoir to minimise pressure changes due to the liberation of gases from the electrodes and walls of the containing vessel. The starting of the arc is facilitated by the initial electric discharge through two effects. First, local heating of impurities in the cathode surface gives rise to thermionic emission and, secondly, the gases are modified so as to be more easily ionised than when in the normal state.

A. E. MITCHELL.

Simple modifications of the Kohlrausch bridge for the potentiometric measurement of alternating current resistance. E. DENINA (Annali Chim. Appl., 1928, 18, 529—540).—Descriptions are given of: (1) a simple modification of the Kohlrausch bridge which gives directly the value of a resistance as the mean of two readings; (2) an improved method for elimination of the influence of the contact resistances, and (3) an arrangement for compensating for the capacitance of electrolytic cells.

T. H. POPE.

Microphotometer for comparative measurements of density on X-radiogram spots. K. V. VASILEV (Trans. Inst. Econ. Min. Met. Moscow, 1928, No. 34, 10—19).—Two similar microscopes are used for the examination of the film and a photographic wedge, which is adjusted until the images are indistinguishable. The central portion of the image is that of the spot: its extent depends on the silvered area in the Lummer cube.

CHEMICAL ABSTRACTS.

Method of obtaining X-radiograms. K. V. VASILEV (Trans. Inst. Econ. Min. Met. Moscow, 1928, No. 34, 45—58).—The specimen is mounted in a circular hole in the centre of the film. The plane of the film includes the axis of the beam. The reflected rays are recorded as radial streaks originating at the centre of the film.

CHEMICAL ABSTRACTS.

Microphotometer for the study of spectrograms. I. J. GWINN (Proc. Iowa Acad. Sci., 1927, 34, 279).—The light is focussed by means of a vertical

system of microscope lenses on to a bismuth-silver thermocouple. Measurements of length are made with a micrometer screw.

CHEMICAL ABSTRACTS.

Gas circulating pump. G. BARR (J.C.S., 1928, 3293—3295).—A pump is described for the circulation of gas in a closed system at pressures near that of the atmosphere.

F. J. WILKINS.

Apparatus for micro-gas analysis. C. H. PRESCOTT, jun. (J. Amer. Chem. Soc., 1928, 50, 3237—3240).—An apparatus is described, designed quantitatively to analyse about 0.3 c.c. of gas for carbon dioxide and monoxide, hydrogen, and nitrogen, all reagents being used in solid form.

S. K. TWEEDY.

Stirrer for gas absorption. A. F. BENNING (Proc. Indiana Acad. Sci., 1927, 37, 263—264).—Two short tubular arms are sealed to a tubular shaft near the end, the 4-way junction being constricted and a hole provided at a convenient point in the lower part of the shaft, so that gas is drawn down and mixed with the liquid. A high speed of revolution is necessary.

CHEMICAL ABSTRACTS.

Laboratory devices. Vacuum stirrer, pressure alternator, and a gauge for measuring low pressure of permanent gases in condensable vapours. R. K. TAYLOR (J. Amer. Chem. Soc., 1928, 50, 2937—2940).—The stirrer is used for freeing liquids from dissolved gases. By means of the pressure alternator, which automatically applies alternately a pressure of 1 atm. and a pressure less than 1 atm. by a desired amount, the liquid is continually washed over a column of beads. The gauge is a modified form of McLeod's gauge.

S. K. TWEEDY.

Miscometer. J. HOUSTON (Analyst, 1929, 54, 30; cf. B., 1926, 930).—The measuring device consists of a burette instead of a hollow stopper connected through the top with the air suction, and with a stopcock at the bottom which allows the samples to be drawn in in turn. These are mixed by turning the stopcock to connect the burette with the second chamber in such a way that air is drawn through the mixture. By manipulating the top stopcock (connecting to air-suction and to the second chamber) the mixed sample is drawn into the second chamber, the small burette opening out from this fills up, and the remainder of the sample flows out from a bottom outlet tube by gravity. The stopcocks on each side of the measuring chamber are then closed and the measured sample is drawn out from the small burette.

D. G. HEWER.

Shaker for the Van Slyke blood-gas apparatus. H. F. PIERCE (J. Lab. Clin. Med., 1928, 13, 1048—1049).

Apparatus for the distillation of urea-nitrogen. L. C. MURPHY and R. C. JENKINS (J. Lab. Clin. Med., 1928, 13, 1049—1051).

Separator for continuous fractional distillation under reduced pressure. R. DELABY and R. CHARONNAT (Bull. Soc. chim., 1928, [iv], 43, 1287—1288).—The actual receiver is connected by means of a stopcock with a lower portion fitted with outlet tube and stopcock for distillate. This lower portion

may, by suitable manipulation of stopcocks, be isolated, opened to the air to permit removal of liquid, and re-introduced into the evacuated system without interrupting the distillation. J. S. CARTER.

Laboratory rectifying column. M. J. MARSHALL (Ind. Eng. Chem., 1928, 20, 1379).—The vapour passes up a lagged column filled with beads and out through a small, wide side-tube connected with a vertical condenser. The reflux ratio can be adjusted to any value up to total reflux by operating a small stopcock fitted in the side tube close to the column; a certain fraction is drawn off through the cock and the excess overflows into the fractionation column. Hold-up of reflux liquid is avoided.

E. H. SHARPLES.

Self-adjusting burette. R. C. HOCKETT (J. Chem. Education, 1928, 5, 1131—1132).—The burette is automatically filled to the zero mark by means of a stopcock in the side arm. CHEMICAL ABSTRACTS.

Rapid calibration of burettes. Z. MINDALEV (Z. anal. Chem., 1928, 15, 390—392).—Three burettes are joined to one another by means of T-pieces and rubber tubes below the graduation marks. The first burette serves as a reservoir and the second as a standard for calibrating the third. The volume occupied by 2 c.c. in the second burette is accurately ascertained by weighing, and this volume is marked off in the usual way. By repeatedly transferring this weighed 2 c.c. of water from the standard to the third burette the latter is progressively calibrated and can then be used as a standard for calibrating any number of burettes on the same principle.

A. R. POWELL.

Standardised ground-glass apparatus. J. FRIEDRICH (Chem. Fabr., 1929, 5—6).—Apparatus with interchangeable ground-glass connexions includes reaction flasks for the treatment of one liquid by another, miscible or non-miscible, of a solid by a liquid, Soxhlet extractors, flasks for the generation of gases, etc. It is possible, e.g., to perform an extraction and distil off the solvent without transferring the liquid from one flask to another. C. IRWIN.

Temperature regulator for Carius furnaces. G. B. HEISIG (J. Amer. Chem. Soc., 1928, 50, 3388).—Regulation of the temperature of gas-heated Carius furnaces is facilitated by using a thermostatic control of the type fitted to gas cookers. H. E. F. NOTTON.

Drying oven. F. HAHN (Chem.-Ztg., 1928, 52, 975).—A convenient form of a small aluminium drying oven, which may be supported by a retort stand, is described. The principal feature is that the door is not hinged, but leans against the sloping front. No jolt is then given to the oven on opening.

J. S. CARTER.

Determination of Engler viscosities. S. ERK (Chem. Fabr., 1928, 715—716, and Chem.-Ztg., 1928, 52, 995).—An error is introduced if the volume of liquid is determined by pouring from the flask and draining for 1 min., as viscous liquids will drain more slowly than water. With a liquid of 121° Engler the error is 5.6%. A clean, dry flask should be used, graduated by filling. In the case of determinations at temperatures above atmospheric the water-bath

should not be heated during the determination to counteract a fall in the reading of the thermometer immersed in the oil which is running out. The temperature of the water-bath should be kept constant.

C. IRWIN.

Turbidimeter. W. EWALD (Instruments, 1928, 1, 371—375).—Two pencils of rays from the same source, which have passed respectively through the turbid solution and an adjustable turbid wedge, are reflected on to a divided field, equalised, and the scale reading is recorded.

CHEMICAL ABSTRACTS.

[Filtering] apparatus with fused-in porous glass plates. G. F. HUTTIG (Chim. et Ind., 1928, 20, 1034—1038).—Filters of 25 c.c. capacity made from fritted glass plates fused into ordinary laboratory glass were examined for loss in weight through contact with water, hot dilute hydrochloric acid, and solutions of ammonia, sodium hydroxide (hot), and lead nitrate. In no case was the loss in weight greater than 0.3 mg. except with sodium hydroxide, when 4—8 mg. were lost, the amount depending on the size of pores. The rapidity with which precipitates can be dried on these filters, the loss in weight on heating to 400°, and the increase in weight of a dried filter by absorption of atmospheric moisture were also examined. In their properties these filters compare very favourably with the Gooch and Brunck types. In analytical work care should be taken to choose a filter having pores smaller than the particles being filtered, as otherwise subsequent complete removal of the solid from the filter plate is difficult. H. INGLESON.

Apparatus for testing filtering and decolorising media. A. LINSBAUER and J. VAŠATKO.—See B., 1929, 5.

Attachment for bottles used for storage of standard solutions. A. G. LIPSCOMB (Analyst, 1928, 53, 645).—In order to prevent contamination by carbon dioxide or concentration of the solution being stored, a glass jacket, through the top of which is sealed a tube expanded into three bulbs, is fixed through the cork of the store bottle. The lowest bulb opens into the jacket, and down the centre of the bulbs is a narrower tube, sealed into the lower end of the jacket and passing into the store bottle, and with its upper end sealed through the wall of the centre bulb tube and opening into the top of the jacket. A suitable liquid, such as sodium hydroxide solution, for that solution in store, is poured down the bulb tube; the incoming air is thus freed from carbon dioxide and takes up water vapour to the correct extent.

D. G. HEWER.

Micro-determination of mol. wt. by the ebullioscopic method. A. RIECHE [with F. QUERBERTZ] (Chem.-Ztg., 1928, 52, 923—924).—The advantages and disadvantages of the apparatus of Sucharda and Bobranski (A., 1927, 849) are discussed. The use of the authors' apparatus (A., 1926, 1118) with solvents of higher b. p. is described. F. R. ENNOS.

Atomiser for flame coloration. H. EMDE (Chem.-Ztg., 1928, 52, 1003).—A simple device for the introduction of atomised spray from a salt solution into the air supply of a Bunsen burner is described.

J. S. CARTER.

Geochemistry.

Occurrence of free sulphuric acid in ground-water. E. SCHROEDTER (Chem. Erde, 1928, 4, 70—75).—Analyses of the soils taken at various depths on the moors near Danzig show the presence of small amounts of free sulphuric acid. L. J. SPENCER.

Action of sulphurous gases at high temperatures on basic glasses and rocks and a probable origin of sulphated thermal waters. A. PORTEVIN (Compt. rend., 1928, 187, 1148—1150).—Sulphurous gases, even when dilute, attack basic rocks and glasses superficially at 900° with the formation of a water-soluble deposit consisting principally of sodium sulphate with traces of calcium, potassium, and magnesium sulphates. The dissolution of such deposits in warm springs during the early post-volcanic period is a probable explanation of the origin of alkaline sulphated thermal waters. J. GRANT.

Bearing of base exchange on the genesis of petroleum. E. McK. TAYLOR (J. Inst. Petroleum Tech., 1928, 14, 825—840).—The properties of sodium and calcium clays are described. The p_H values and replaceable calcium and sodium have been determined for samples of shale from Rumania and the West Indies. Under the conditions imposed by a sodium clay roof, oils, fats, waxes, and allied substances, fatty acids which may have been formed by the previous decomposition of oils and fats, and glycerol are decomposed by bacteria, glycerol yielding methane. A theory of the genesis of petroleum involving the formation of sodium clays by base exchange, and the subsequent bacterial decomposition of contiguous organic matter, is advanced.

C. W. GIBBY.

Blue rock salt. F. C. GUTHRIE (Nature, 1929, 123, 130).—That blue rock salt has a slightly greater energy content than the colourless variety is shown by the facts that it glows, with loss of the blue colour, when suddenly heated at 350°, and that it has a slightly smaller negative heat of dissolution.

A. A. ELDRIDGE.

Asphaltite from the Philippine Islands. E. T. HODGE (Philippine J. Sci., 1928, 37, 263—272).—The chemical and physical properties of a sample of asphaltite from the Philippine Islands are described, and show that it lies between manjak and grahamite. Its genesis is discussed.

C. W. GIBBY.

Microscopic characteristics of the oxides of manganese and of the natural manganites. J. ORCEL and S. PAVLOVITCH (Compt. rend., 1928, 187, 1295—1297).—The optical characteristics and behaviour towards etching reagents of a number of anisotropic and isotropic natural manganites and oxides of manganese are tabulated. Neukirchite, ebelmenite, and brostenite are considered to be mixtures of polianite and psilomelane, braunite also being associated with the last-named. Vredenburgite is a mixture of braunite, hæmatite, and polianite.

J. GRANT.

Minerals of the apatite group. G. CAROBBI [with S. RESTAINO] (Atti II Cong. Naz. Chim. pura Appl., 1926, 1156—1181; Chem. Zentr., 1928, ii,

531).—A pyromorphite from Braubach (Nassau) contained lanthanum, neodymium, samarium, yttrium, europium, gadolinium, dysprosium, erbium, ytterbium, and cerium (rare-earth oxides about 0.05%). Pyromorphite from Leadhills (Lanarkshire) contained these elements (0.02% of oxides), except samarium and ytterbium; Cr_2O_3 0.1 (probably as chromate), MnO 0.001, CaO 0.16%, SrO and BaO traces, were also present. Mimetite from Santa Eulalia (Chihuahua, Mexico) contained Cr_2O_3 0.07, MnO 0.008, ZnO 1.37, CaO 0.29, BaO and SrO 0.009%, Cu none. Experimental evidence for the existence of pyromorphites, vanadinites, and mimetites in which rare-earth elements isomorphously replace lead has been obtained. A. A. ELDRIDGE.

Phosgenite of Monteponi. F. RODOLICO (Atti R. Accad. Lincei, 1928, [vi], 8, 171—174).—Twinned crystals of phosgenite, d 6.05, are described, in one of which numerous regular pits occurred. These pits were square in shape with edges parallel to the angles between the planes (001) and (111), and were formed by the facets of a very obtuse bipyramid sometimes truncated and terminating in a square. An analysis of this phosgenite gave PbO 81.73, Cl 13.06, CO_2 7.91, Ag 0.01, less O for Cl 2.99%.

F. G. TRYHORN.

Betafite from Sludianka, E. Siberia. G. TSCHERNIK (Bull. Soc. Franç. Min., 1927, 50, 485—489; Chem. Zentr., 1928, ii, 335).—Betafite, black octahedra, often combined with dodecahedra, d 4.82—4.93, contained: MgO 0.13, CaO 3.93, PbO 0.10, MnO 0.15, FeO 1.20, Fe_2O_3 2.25, Al_2O_3 0.24, ceria earths 1.61, yttria earths 13.11, UO_3 26.37, ThO_2 1.30, SnO_2 0.37, TiO_2 16.51, SiO_2 0.59, Nb_2O_5 37.36, Ta_2O_5 1.46, H_2O 2.47%.

A. A. ELDRIDGE.

Laumontite of Toggiano. P. GALLITELLI (Atti R. Accad. Lincei, 1928, [vi], 8, 82—87).—Two types of laumontite occur associated with the datolite of Toggiano, the one of a rather fibrous structure, with a pearly lustre, the other granular and whitish. Goniometric analyses have been made of these two varieties, which contain, respectively, SiO_2 50.78, 51.43; Al_2O_3 21.09, 22.30; BeO 0.47, 0.40; CaO 12.13, 12.47; H_2O 15.34, 13.74. When heated, laumontite loses water continuously, but there is some evidence of an arrest point between 250° and 300°, leading to the conclusion that there is probably some difference in the nature of the water lost below 300° and that given up at higher temperatures.

F. G. TRYHORN.

Chemical and spectrographic investigations on crocoite from Tasmania and wulfenite from Bleiberg. G. CAROBBI (Annali Chim. Appl., 1928, 18, 485—494).—A Tasmanian crocoite contains (%): Ce_2O_3 0.003; La_2O_3 etc. 0.026; Y_2O_3 etc. 0.008; CaO 0.10; SrO , BaO traces, and wulfenite from Bleiberg: Cr_2O_3 0.47; Fe_2O_3 , Al_2O_3 , and rare earths (less than 0.001) 0.07; CaO , BaO , SrO 0.34; the rare-earth metals include Ce , La , Nd , Sm , Y , Er (cf. A., 1926, 811; 1927, 1164).

T. H. POPE.

Oxidation products derived from sphalerite and galena. P. F. BOSWELL and R. BLANCHARD

(Econ. Geol., 1927, 22, 419—453).—Sphalerite and galena may dissolve without generation of, or attack by, iron-bearing solutions, thus leaving no limonite.

CHEMICAL ABSTRACTS.

Fushun coal and its geological significance. C. IWASAKI (Tech. Rep. Tohoku, 1928, 8, 99—126).—Analyses and microscopic sections of different coals from the Fushun colliery, Manchuria, are given, and the geological significance of the latter is discussed.

C. W. GIBBY.

Composition of coal—its rational analysis. W. FRANCIS and R. V. WHEELER.—See B., 1929, 5.

Chemical weathering in northern Norway. E. BLANCK, F. GIESECKE, and H. KEESE (Chem. Erde, 1928, 4, 76—87).—Analyses are given of fresh and weathered rocks (granite and schist) and of the covering soil on the island of Hindö (cf. A., 1928, 612).

L. J. SPENCER.

Dolomitisation in the Bryozoa reefs of the Zechstein of Thuringia. E. KÖHLER (Chem. Erde, 1928, 4, 42—64).—Many (105) partial analyses are given of the rock taken from different parts of the "coral" reefs in the limestones. They show varying amounts of magnesia from traces up to that required for pure dolomite.

L. J. SPENCER.

So-called kaolinisation of granite under a humus cover in the Black Forest. E. BLANCK and H. KEESE (Chem. Erde, 1928, 4, 33—41).—Analyses of the bleached rock show an increase in silica and a diminution in alumina and alkalis. Kaolin is not formed from feldspar under these conditions.

L. J. SPENCER.

Composition of phonolite from the Heldburg near Koburg. H. JUNG (Chem. Erde, 1928, 4, 23—26).—A detailed chemical analysis of this rock differs appreciably from that of Hilger (1890).

L. J. SPENCER.

Earth cementation by iron and manganese or by alumina and lime. M. HELBIG (Chem. Erde, 1928, 4, 12—22).—Analyses are given of the cementing material in German pebble beds of recent origin. The material is the product of weathering.

L. J. SPENCER.

South European red earths. H. HARRASSOWITZ (Chem. Erde, 1928, 4, 1—11).—Red earths beneath the humus-bearing soil of the Black Forest contain in the hydrochloric acid extract a higher silica/alumina ratio, namely 2.5—2.98, than those from farther south. The ratio is as low as 0.17—0.5 in the red earth from Lake Garda in Italy. The latter, like the "terra rossa" of the Karst region, contains free alumina. The "terra rossa" rests on pure limestones, and the red colour is not confined to the Mediterranean type of weathering.

L. J. SPENCER.

Minerals. V.—VIII. H. COLLINS (Chem. News, 1928, 137, 242—244, 276—278, 338—341, 402—404).

Presence of the rare-earth elements in the sun. C. E. ST. JOHN and C. E. MOORE (Astrophys. J., 1928, 68, 93—108).—Lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, and ytterbium, in the ionised state, are probably present in the sun.

A. A. ELDRIDGE.

Organic Chemistry.

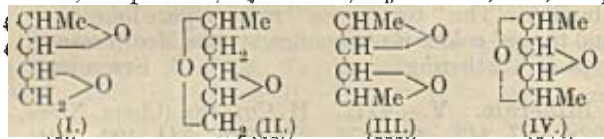
Synthesis of methane from mixtures of carbon monoxide and hydrogen at a nickel surface. H. A. BAHR and T. BAHR (Ber., 1928, 61, [B], 2465—2469).—Observations are recorded of the passage of a mixture of carbon monoxide and hydrogen (1:3) over nickel carbide, Ni_3C , prepared at 250° and stabilised by preservation in nitrogen. The first step in the production of methane is the decomposition of carbon monoxide with production of nickel carbide, $3\text{Ni} + \text{CO} \rightarrow \text{Ni}_3\text{C} + \text{O}$. As secondary changes, the carbide is hydrogenated to methane with re-formation of nickel, $\text{Ni}_3\text{C} + 2\text{H}_2 = \text{CH}_4 + 3\text{Ni}$, and the oxygen, derived from carbon monoxide, is converted into water or carbon dioxide. As long as nickel carbide is present, the production of methane occurs chiefly according to the equation $2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$, which is succeeded by the reaction $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ in proportion as the contact becomes decarbonised.

H. WREN.

Allyl transformations and additive compounds of erythrelic hydrocarbons. III. C. PREVOST (Ann. Chim., 1928, [x], 10, 356—438).—Mainly experimental details of work already published (A., 1928, 1211). The most probable stereochemical formulæ for the various derivatives are deduced and tabulated together with a large amount of physical

data, the following of which appears to be new (or revised). $\Delta^{\alpha\gamma}$ -Pentadiene yields a solid tetrabromide, m. p. 114° (best obtained from the *trans*-hydrocarbon), together with a liquid, b. p. 121—131°/3 mm., d_4^{18} 2.3195, n_D^{18} 1.5915; $\Delta^{\beta\delta}$ -hexadiene yields the known tetrabromide, m. p. 185°, together with two *tetrabromides*, m. p. 108° and 162°, and a mixture of liquid tetrabromides, b. p. 128—133°/3 mm., d_4^{10} 2.1990, n_D^{18} 1.5831, those having m. p. 95—97° and 64—65° (Griner, A., 1893, i, 241) never being obtained. $\beta\gamma$ -Dibromo- $\Delta^{\alpha\gamma}$ -pentadiene (A., 1926, 496) has d_4^{22} 1.8225, n_D^{22} 1.5630; $\gamma\delta$ -dibromo- $\Delta^{\beta\gamma}$ -pentadiene (not quite pure), b. p. 83—86°/12 mm., d_4^{23} 1.6700, n_D^{23} 1.5400, with excess of bromine yields $\beta\gamma\delta\epsilon$ -tetrabromo- $\Delta^{\alpha\gamma}$ -hexene, m. p. 112—113°; $\Delta^{\alpha\gamma}$ -pentadi-ene, b. p. 54—56°, d_4^{21} 0.7375, n_D^{21} 1.4431, the hexa- and hepta-di-enes being obtained only as their *silver* derivatives; α -phenyl- $\Delta^{\alpha\gamma}$ -pentadi-ene, m. p. 22.45°, b. p. 129°/20 mm., d_4^{18} 0.9745, n_D^{18} 1.6368 (optical properties described), adds only 2 mols. of bromine, yielding two *tetrabromides*, m. p. 127—131° and 98°, and with aqueous-alcoholic mercuric chloride yields the compound $\text{CPhCl}:\text{C}(\text{HgCl})\cdot\text{C}(\text{OEt})\cdot\text{CHMe}$. $\Delta^{\alpha\gamma}$ -Pentadiene dibromides have b. p. 70°/11 mm., d_4^{18} 1.6992, n_D^{18} 1.5247, and b. p. 85—86°/11 mm., d_4^{17} 1.7482, 1.5523; the latter yield two diacetates, b. p. 112.5°/11 mm., d_4^{22} 1.0446, n_D^{22} 1.4398 (cf. A., 1926, 496),

and b. p. 104—105°/13 mm., d_4^{25} 1.0386, n_D^{25} 1.4365 (the latter being probably the diacetate of Δ^7 -pentene- $\alpha\beta$ -diol). The dibromide fraction, b. p. 87—88°/12 mm., on hydrolysis yields three glycols, b. p. 109°/14 mm., 1.0147, n_D^{25} 1.4633; b. p. 127°/14 mm., d_4^{25} 1.0234, 1.4730, and b. p. 93°/14 mm., d_4^{25} 1.0082, n_D^{25} 1.4575. From Δ^{68} -hexadiene are obtained the diacetates, b. p. 117—118°/14 mm., d_4^{25} 1.0247, n_D^{25} 1.4460 (65—70%), and b. p. 106—109°/14 mm., d_4^{25} 1.0210, 1.4390, (35—30%), of trans- Δ^7 -hexene- $\beta\epsilon$ -diol, b. p. 117—118°/11 mm., d_4^{25} 0.9865, n_D^{25} 1.4660, and Δ^8 -hexene- $\beta\gamma$ -diol, b. p. 99—100°/11 mm., d_4^{25} 0.9838, n_D^{25} 1.4614, respectively. By the action of an excess of finely-powdered potassium hydroxide on an ethereal solution of the appropriate glycol saturated with bromine the following substituted erythrene oxides are obtained: I, b. p. 146°, d_4^{25} 1.0813, n_D^{25} 1.4382; II, b. p. about 145°: a mixture of the stereoisomerides of III, b. p. 161°, d_4^{25} 1.0312, n_D^{25} 1.4375; IV, b. p.



151°, d_4^{25} 1.0373, n_D^{25} 1.4350. These by hydration yield erythritols, methylerythritol, m. p. 109.5°, s-dimethylerythritol, m. p. 172° (corr.) (not identical with the isomeride obtained by Wagner, A., 1889, 226). $\alpha\zeta$ -Dibromo- Δ^{68} -hexadiene (A., 1927, 337) yields a mixture, b. p. 129—131°/12 mm., d_4^{25} 1.0700, n_D^{25} 1.4760, of the diacetates of Δ^{67} -hexadiene- $\alpha\zeta$ -diol and Δ^{68} -hexadiene- $\gamma\zeta$ -diol, and the diacetate, m. p. 25°, d_4^{25} 1.0762, n_D^{25} 1.4850 (supercooled), of Δ^{68} -hexadiene- $\alpha\zeta$ -diol. Spontaneous decomposition of $\beta\epsilon$ -dibromo- $\beta\epsilon$ -dimethyl- Δ^7 -hexene (A., 1927, 748) yields (?) α -bromo- $\beta\epsilon$ -dimethyl- Δ^{68} -hexadiene, b. p. 64—67°/3 mm., d_4^{25} 1.2230, 1.5522, converted into the acetate, b. p. 77—79°/3 mm., d_4^{25} 0.9570, n_D^{25} 1.4890, hydrolysed to $\beta\epsilon$ -dimethyl- Δ^{68} -hexadien- α -ol, b. p. 77—78°/4 mm., d_4^{25} 0.9197, n_D^{25} 1.5095, which is reduced catalytically to $\beta\epsilon$ -dimethylhexan- α -ol. J. W. BAKER.

New tautomeric phenomena in the allylic series. C. PREVOST (Compt. rend., 1928, 187, 1052—1054).— Δ^4 -Penten- γ -ol (I) and Δ^8 -penten- α -ol (II) are mesomeric at the ordinary temperature, but towards 360° some transformation of I into II takes place. A pseudo-isomeric bromide corresponding with II is formed from either alcohol, but the action of phosphorus trichloride on I yields two chlorides corresponding with I, b. p. 93°, d_4^{25} 0.8966, n_D^{25} 1.4224, and II, b. p. 109.5°, d_4^{25} 0.9095, n_D^{25} 1.4347, respectively. These are mesomeric, becoming desmotropic above 175°. By the action of sodium acetate on these chlorides only the acetate corresponding with II could be isolated, but sodium ethoxide with either chloride yielded a mixture of the mesomeric γ -ethoxy- Δ^4 -pentene, b. p. 102°, d_4^{25} 0.7768, n_D^{25} 1.3986, and α -ethoxy- Δ^8 -pentene, b. p. 123°, d_4^{25} 0.7930, n_D^{25} 1.4099. Some conclusions with regard to synionism (cf. A., 1926, 131; 1927, 851; 1928, 152, 614) are deduced.

B. W. ANDERSON.

[Preparation of nitro- and chloronitroolefines.] E. SCHMIDT (Ber., 1928, 61, [B], 2613; cf. Schmidt and Rutz, A., 1928, 1352).—Substitution

of the hydrogen atom in the system C:CH·NO₂ by chlorine with formation of the system C:CCl·NO₂ causes a depression of the exaltation. H. WREN.

Dodecane- $\alpha\mu$ -diol and linear true diacetylenes, C₁₃H₂₀ and C₂₀H₃₄. R. LESPIEAU (Bull. Soc. chim., 1928, [iv], 43, 1189—1193).—The action of chloromethyl ether on magnesium pentamethylene bromide gives a methyl ether, Me·[CH₂]₅·OMe, b. p. 124—125°, d_4^{25} 0.7897, n_D^{25} 1.4065, some $\alpha\mu$ -dimethoxydodecane, b. p. 182°/35 mm., m. p. 13—14° (Chuit, A., 1926, 499) ($\alpha\mu$ -dibromododecane, m. p. 38.5—39°, and dodecane- $\alpha\mu$ -diol, m. p. 80—81° [acetyl derivative, m. p. 36.5—37.5°], are described), and, mainly, the dimethyl ether of heptamethylene glycol, converted by hydrobromic acid into heptamethylene bromide, b. p. 124—125°/12 mm., d_4^{25} 1.529, n_D^{25} 1.065. The magnesium derivative of the latter with $\alpha\beta$ -dibromo- Δ^8 -propene yields (1) a fraction, b. p. 90°/13 mm., containing β -bromo- Δ^4 -n-decene, (2) and chiefly $\beta\mu$ -dibromo- Δ^{67} -tridecadiene, b. p. 180°/16 mm., d_4^{25} 1.274, n_D^{25} 1.497; (3) $\beta\tau$ -dibromo- Δ^{67} -eicosadiene, b. p. 249—252°/11 mm., d_4^{25} 1.120, n_D^{25} 1.4915, and (4) a liquid fraction, b. p. 300—350°/11 mm. With alcoholic potassium hydroxide the tridecadiene is converted into Δ^{67} -tridecadi-ene, b. p. 115.5°/12 mm., m. p. —3° to —2°, d_4^{25} 0.8262, n_D^{25} 1.454, and the eicosadiene into the hydrocarbon, CH₃C·[CH₂]₁₄·C·CH₃, m. p. 54—56°, the liquid fraction, b. p. 340°/11 mm., affording a similar (impure) product, m. p. 70—75°. Both acetylenes give silver derivatives (cf. A., 1925, i, 225), and further support for the true diacetylene structure of this compound is afforded by the conversion of the undecadi-ene obtained by the action of alcoholic potassium hydroxide on the reaction product of epidibromohydrin on dimagnesium pentamethylene bromide, with magnesium ethyl bromide and carbon dioxide into Δ^{11} -undecadi-ene- $\alpha\lambda$ -dicarboxylic acid, m. p. 111.5—112.5°, giving on hydrogenation behenolic acid, m. p. 110.5—111.5°. R. BRIGHTMAN.

Carbohydrates and polysaccharides. H. HIBERT. XVIII. [With M. G. STURROCK.] *p*-Nitrobenzylidene glycols and glycerols. XIX. [With N. M. CARTER.] Structural, geometrical, and optical isomerism of *p*-nitrobenzylideneglycerols and their derivatives. (J. Amer. Chem. Soc., 1928, 50, 3374—3376, 3376—3388).—XVIII. *p*-Nitrobenzylidene ethylene ether, m. p. 90.5°, and trimethylene ether, m. p. 111.5°, are formed from *p*-nitrobenzaldehyde and the appropriate glycol at 100° in presence of a little sulphuric acid. The reaction between the aldehyde and glycerol is favoured by removing the resulting water under reduced pressure. The product is separated by fractional crystallisation into nearly equal amounts of $\alpha\gamma$ -*p*-nitrobenzylideneglycerol (I), m. p. 88° when freshly prepared, changing to 98°, and $\alpha\beta$ -*p*-nitrobenzylideneglycerol (II), b. p. 177—179°/0.3 mm. (benzoate, m. p. 178°).

XIX. Although the separation of the stereoisomerides of I and II, the presence of which is indicated by the change in the m. p. of I, has not been effected, the four isomeric methyl ethers, benzoates, and *p*-nitrobenzoates theoretically obtainable from I and II have been prepared. Methylation of I yields a mixture from which grey, m. p. 139°, and white,

m. p. 106°, isomeric methyl α -*p*-nitrobenzylideneglyceryl ethers are separated. These are both formed from β -methyl glyceryl ether and *p*-nitrobenzaldehyde in presence of sulphuric acid at 120°. α -Methyl glyceryl ether and *p*-nitrobenzaldehyde give similarly a mixture of yellow, m. p. 47°, and white, m. p. 42°, geometrically isomeric α -methyl β -*p*-nitrobenzylideneglyceryl ethers, which were also isolated with some difficulty from the methylation product of II. Benzoylation of the freshly-prepared acetal, I, in pyridine affords yellow α -*p*-nitrobenzylideneglyceryl benzoate, m. p. 204°, but the samples of m. p. 98° yield, in addition, a white isomeride, m. p. 159°. A greenish-yellow α - β -*p*-nitrobenzylideneglyceryl benzoate, m. p. 115°, apparently isomeric with that described above, is prepared similarly. Yellow, m. p. 208°, and white, m. p. 202°, isomeric α -*p*-nitrobenzylideneglyceryl *p*-nitrobenzoates, and yellow, m. p. 117—118°, and white, m. p. 110°, isomeric α - β -*p*-nitrobenzylideneglyceryl *p*-nitrobenzoates were isolated by manual separation. The pure acetals I and II in presence of a trace of hydrogen chloride at 130° pass into an equilibrium mixture containing 1 part of I and 5 parts of II.

H. E. F. NORTON.

[Configuration of pentaerythritol. II. Optically active dipyrucic acid pentaerythritols.] J. KENNER (Ber., 1928, 61, [B], 2470—2471).—In connexion with the work of Boeseken and Felix (A., 1928, 1213), it is pointed out that chemical methods such as those used by the authors are not suitable for the examination of the Weissenberg principle. H. WREN.

Symmetrical ethers of the alcohols, $\text{CH}_2\text{X}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{X}'$ and $\text{CH}_2\text{X}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OR}$. L. BLANCHARD (Bull. Soc. chim., 1928, [iv], 43, 1194—1204).— α -Dichloropropyl β -*p*-toluenesulphonate, unlike the methyl sulphonate (cf. A., 1927, 853), does not react with dichlorohydrin at 140—190°. With 1 mol. of sulphuryl chloride the dichlorohydrin gives 65% of α -dichloropropyl chlorosulphonate, b. p. 113—114°/13 mm., d^{20}_D 1.592, n_D 1.48325, decomposed above 160°, yielding trichloropropane, probably from the addition of hydrogen chloride to α -dichloropropylene first formed; with 4—5 mols. of dichlorohydrin at 130—140°, sulphuryl chloride affords α -dichloropropyl β -ether, b. p. 141—142°/13 mm., d^{15}_D 1.388. Chlorosulphonic acid and dichlorohydrin yield α -dichloropropyl hydrogen sulphate, crystalline (sodium salt), but when this is heated with potassium cyanide the nitrile is not obtained. α -Chloro- γ -bromopropyl chlorosulphonate decomposed on re-distillation, yielding dichlorobromopropane and α -chloro- γ -bromopropyl β -ether, b. p. 175—177°/20 mm., d^{15}_D 1.806 (yield 85%). Sodium α -chloro- γ -bromopropyl sulphate is described, but the chlorosulphates of dibromohydrin and chloriodohydrin appear to be too unstable to react further with the hydrin. Attempts to obtain the corresponding ethers by the action of sulphuryl chloride on epichlorohydrin, "epimethylene" (γ -methoxypropane α -oxide), and "epithylene" failed. "Epimethylene," b. p. 79—81°/20 mm., at 120—130° gives a liquid of b. p. 190—220°/20 mm., possibly di(chloroamylene) ether. R. BRIGHTMAN.

Influence of poles and polar linkings on course pursued by elimination reactions. III.

Decomposition of dialkylsulphones. G. W. FENTON and C. K. INGOLD (J.C.S., 1928, 3127—3130).—In agreement with the theory that dialkylsulphones should decompose similarly to quaternary ammonium hydroxides (Hanhart and Ingold, A., 1927, 650) into an olefine and an alkylsulphinic acid, it is found that diethylsulphone, m. p. 71°, decomposes in the presence of a concentrated solution of potassium hydroxide at 200° into ethylene and ethanesulphinic acid; ethyl-*n*-octylsulphone, m. p. 68° (prepared by oxidation of ethyl *n*-octyl sulphide, b. p. 102—103°/11 mm., with nitric acid), and potassium hydroxide at 200° gave ethylene and *n*-octanesulphinic acid (ferric salt) but no *n*-octene or ethanesulphinic acid, whilst di-*n*-octylsulphone, m. p. 76° (prepared by oxidation of *n*-octyl sulphide, b. p. 180°/10 mm., with nitric acid, d 1.49), was unaffected by heating under reflux with 90% potassium hydroxide. A. I. VOGEL.

Esters of α -bromopropionic and α -bromoiso-butyric acids. V. DEULOFEU (Anal. Fis. Quím., 1928, 26, 315—319).—By the action of the bromides of the acids on an excess of the corresponding anhydrous alcohols, the following esters have been prepared in yields of 40—54%: isopropyl α -bromopropionate, b. p. 163—165°; allyl α -bromopropionate, b. p. 173—177°; *n*-butyl α -bromopropionate, b. p. 192—196°; *n*-propyl α -bromoisobutyrate, b. p. 92—96°/42 mm.; isopropyl α -bromoisobutyrate, b. p. 91—94°/55 mm.; allyl α -bromoisobutyrate, b. p. 90—93°/42 mm. The esters are oily liquids, denser than water. The allyl esters have pungent and the others fruity odours.

R. K. CALLOW.

Acids derived from chlorohydrins with two β -substituents. E. TROELL (Ber., 1928, 61, [B], 2497—2503).—Ethyl dimethylglycidate is converted into the corresponding sodium salt and transformed by the calculated amount of hydrogen chloride into β -chloro- α -hydroxy- β -methylbutyric acid, m. p. 80.6—81.3°; attempts to prepare salts from it give the metallic chloride and a malodorous, neutral compound which gradually reacts with alkali hydroxide. Decomposition of the acid in aqueous, alkaline solution is not a simple bimolecular change. β -Chloro- α -hydroxy- β -phenylbutyric acid, m. p. 82° (decomp.), is analogously prepared. If benzophenone is condensed with ethyl monochloroacetate and the product is distilled, an ester, b. p. 202°/12 mm., is obtained regarded by Pointet (A., 1909, i, 234) as ethyl diphenylglycidate, $\text{CPh}_2\text{O}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$. It must, however, be considered as ethyl β -diphenylpyruvate, since the acid derived from it forms a phenylhydrazone, m. p. 189° (decomp.); isomerisation occurs during distillation of the ester.

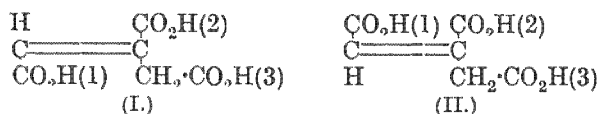
H. WREN.

Esters of α -bromoisovaleric acid. V. DEULOFEU (Bull. Soc. chim., 1928, [iv], 43, 1229—1230).—Propyl α -bromoisovalerate, b. p. 115°/36—38 mm. isopropyl α -bromoisovalerate, b. p. 104°/33 mm., and allyl α -bromoisovalerate, b. p. 117—118°, have been obtained from α -bromoisovaleryl bromide in 38—41% yield. R. BRIGHTMAN.

Mesoxalates from nitrogen tetroxide and esters of malonic acid. E. GILMAN and T. B. JOHNSON (J. Amer. Chem. Soc. 1928, 50, 3341—

3348).—Ethyl malonate and nitrogen tetroxide in presence of metallic sodium at 0° yield 90% of the theoretical amount of ethyl mesoxalate (I) (cf. Curtiss, A., 1911, i, 518). β -Chloroethyl malonate, prepared by an improved method (cf. Bennett, A., 1925, i, 883), is similarly converted into greenish-yellow β -chloroethyl mesoxalate (II), b. p. 148°/3 mm. (oily hydrate); and β -bromoethyl malonate, b. p. 153°/1 mm., from ethylene bromohydrin and malonic acid in presence of hydrogen chloride, is converted into yellow β -bromoethyl mesoxalate, b. p. 155°/0.8 mm. (oily hydrate). The hydrochloride of β -diethylaminoethyl alcohol and malonyl chloride afford in chloroform β -diethylaminoethyl malonate dihydrochloride, m. p. 145° (decomp.), from which the free base (III), b. p. 163°/4.5 mm., is liberated by sodium hydrogen carbonate. This reacts violently with nitrogen tetroxide, yielding an unstable oil from which none of the desired mesoxalate can be separated. The pharmacological effects of compounds I, II, and III are described. H. E. F. NOTTON.

Aconitic acids. I. Stereochemistry of aconitic acids. R. MALACHOVSKI and M. MASLOVSKI (Ber., 1928, 61, [B], 2521—2525).—Aconitic acid occurs in two geometrical isomerides, the ordinary acid, m. p. 194—195°, being the more stable *trans*-form (I). The *cis*-acid (II), m. p. 125°, is prepared by

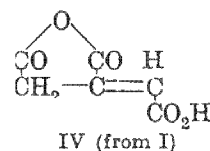
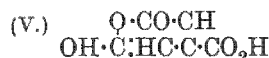
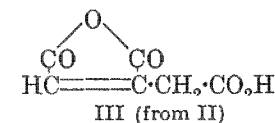


hydrolysis of the so-called "anhydro-acid." It is readily transformed into the *trans*-acid when melted or moderately warmed in aqueous solution. It adds bromine more readily than the *trans*-acid. Its sodium, barium, and copper salts are described. It is converted by dehydrating agents exclusively into the anhydro-acid, the isomeric hydroxyanhydro-acid not being produced even transitively. The anhydro-acid is therefore the actual anhydride of *cis*-aconitic acid. Thorpe's "labile acid" does not appear to be a definite individual. Hydrolysis of the hydroxyanhydro-acid, however performed, yields solely somewhat impure *trans*-aconitic acid. In most of its properties, the "labile" acid differs but little from ordinary aconitic acid. The hydroxyanhydro-acid must be regarded as the true anhydride of *trans*-aconitic acid. The structure of aconitic acid is not symmetrical and its α - and γ -carbon atoms are not equivalent. The production of a single methylaconitic acid by introduction of a methyl group at the α - or γ -carbon atom is readily explained by the hypothesis that a transformation into the more stable form occurs as a secondary process.

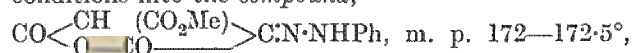
The following new data are recorded: *trans*-aconitic acid, m. p. 194—195° (corr.); the hydro-acid, m. p. 78—78.5° (corr.) [also +0.5C₆H₆]. H. WREN.

Aconitic acids. II. Constitution and mode of formation of aconitic anhydrides. R. MALACHOVSKI, M. GIEDROYC, and Z. JERZMANOVSKA (Ber., 1928, 61, [B], 2525—2538).—Aconitic acid is converted by technical acetyl chloride into the so-called "anhydro-acid," m. p. 78.5°, and by acetic anhydride or acetyl chloride free from phosphorus trichloride into the hydroxyanhydro-acid, m. p. 135°. These com-

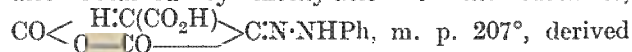
pounds are the anhydrides of the *cis*- and *trans*-aconitic acid (cf. preceding abstract).



To the *cis*-anhydride the structure III is readily assigned, since it gives dark colorations resembling those of citraconic anhydride when mixed with dimethylaniline or quinol in ether (cf. Easterfield and Sell, J.C.S., 1892, 61, 1009). The decision between IV and V for the *trans*-anhydride is less easy, the main reason which has hitherto led to a preference for IV being the isomerisation of the compound by phosphorus pentachloride to the *cis*-anhydride. For the elucidation of the problem the six possible monomethyl esters of the aconitic acids have been prepared. α -Monomethyl dihydrogen *cis*-aconitate (in II, Me at 3), m. p. 101—102° (corr.), is prepared by treating the *cis*-anhydride with ethereal diazomethane, thus giving the anhydro-ester, C₇H₆O₅, b. p. 140—150°/2—8 mm., m. p. 37—38°, d_4^{20} 1.3318, n_D^{20} 1.48350, which is subsequently hydrolysed. Treatment of the *cis*-anhydride with methyl alcohol yields a mixture of γ -methyl dihydrogen *cis*-aconitate (in II, Me at 1), m. p. 126—127° (corr.) (characterised by conversion by acetic anhydride into the ester, m. p. 102°), and β -methyl dihydrogen *cis*-aconitate (in II, Me at 2), m. p. 102—104° (corr.). The *trans*-esters are prepared by isomerisation of the *cis*-derivatives in direct sunlight or in the light of the quartz lamp in presence of bromine. α -Methyl dihydrogen *trans*-aconitate (in I, Me at 3), m. p. 136—137° (corr.), β -methyl dihydrogen *trans*-aconitate, (in I, Me at 2), m. p. 144—144.5° (corr.), and γ -methyl dihydrogen *trans*-aconitate (in I, Me at 1), m. p. 154.5—155° (corr.), are described. As expected, the α -*trans*-ester is not affected by acetic anhydride, whereas the γ -*trans*-ester is relatively easily converted into the anhydro-ester, m. p. 102°. Unfortunately, the behaviour of the *trans*-anhydride towards methyl alcohol affords no clue to the structure, since the sole isolable product is the α -*trans*-ester which can be derived from IV or V. The following method is more successful. The β -*cis*-ester is converted by treatment with acetic acid and acetic anhydride followed by coupling with diazotised aniline under very precise conditions into the compound,



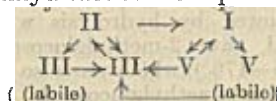
also obtained by methylation of the substance,



derived from the *trans*-anhydride and diazotised aniline. The applicability of structure V to the *trans*-anhydride is confirmed further by the observation that the β -*trans*-ester is converted by mild treatment with acetic anhydride into methyl 6-hydroxy-2-pyrone-4-carboxylate (*trans*-anhydro-ester), m. p. 90—91°, which yields methyl 6-methoxy-2-pyrone-4-carboxylate, m. p. 76.5—78°, obtained also by the action of diazomethane in acetone on the *trans*-anhydride. An unstable tri-bromo-derivative is obtained by the action of bromine

on the *trans*-anhydride. The relationship of the aconitic acids and their anhydrides is most probably

shown by the scheme :



Quantitative investigation of the transformation of the *trans*-anhydride shows the process to be particularly favoured by phosphorus trichloride. Pure acetyl chloride scarcely affects transformation, whereas acetic anhydride and in particular acetic acid have a somewhat more pronounced effect. The action of acetyl chloride or acetic anhydride on *trans*-aconitic acid proceeds simultaneously in two directions, leading to the *cis*- and *trans*-anhydrides, respectively, the production of which occurs independently of the temperature in the ratio 4 : 5. The practical yields are displaced further towards the *cis*-side by secondary changes.

H. WREN.

Carbazylic acids: ammonia analogues of carboxylic acids. E. F. CORNELL (J. Amer. Chem. Soc., 1928, 50, 3311—3318).—The following reactions are adduced to show that the relationship of the acid amidines (carbazylic acids) and nitriles (acid anammonides) to ammonia is similar to that of the carboxylic acids and anhydrides to water (cf. A., 1913, i, 959). Salts of carbazylic acids are formed from metallic amides and amidines or nitriles in liquid ammonia. The following are described: *potassium*, $\text{CMe}(\text{NH})\text{NHK}$, and *sodium ammonoacetates*, *potassium*, *sodium*, and *calcium ammonopropionates*; *potassium* and *sodium ammono-n-butyrate*, *potassium ammono-n-valerate*, *ammonoisohexanoate*, *ammonopalmitate*, *ammonosuccinate*, and *ammono-p-toluate*; *potassium*, *sodium*, *silver* (cf. Pinner, A., 1878, 491), *calcium*, *cupric*, and *cuprous ammonobenzoates*, and the compound $\text{NNa}(\text{CPh}:\text{NH})_2$. Hydrogen cyanide and cyanogen react anomalously with potassamide in liquid ammonia, forming potassium cyanide, and a mixture of potassium cyanide and potassium cyanamide, respectively. In liquid ammonia at 200°, benzonitrile yields with potassium hydroxide benzamide, and with ammonium chloride, a little benzamidine. Propionitrile is similarly converted into potassium propionamide and propionamidine. Dry distillation of a potassium carbazylate, $\text{NH}:\text{CR}:\text{NHK}$, with potassamide yields potassium cyanamide, ammonia, and the hydrocarbon RH. Alkyl carbazylates may be formed and ammonolysed by methods similar to those employed for aquo-esters. The additive product from benzonitrile and magnesium phenyl bromide is converted by liquid ammonia into benzophenoneimine.

H. E. F. NOTTON.

Catalytic hydrogenation under reduced pressure. II. Selective reduction in a vacuum of citral, geraniol, and limonene. R. ESCOURROU (Bull. Soc. chim., 1928, [iv], 43, 1204—1214).—Hydrogenation at 190° under reduced pressure in presence of nickel of citral, b. p. 108—112°/12 mm., n_D^{20} 1.48846, containing about 90% of the terpinolenic form, affords inactive citronellal, b. p. 207—208°, n_D^{20} 1.4591 (semicarbazone, m. p. 80—81°). Under ordinary pressure at 180° the same product is obtained, but at 300° dimethyloctanol, saturated hydrocarbons, and a cyclic product, b. p. 215° (cf. Enklaar, A., 1908,

i, 664, 934). Similarly, Java geraniol, b. p. 114—115°/12 mm., n_D^{20} 1.47628, d^{20}_4 0.908, in presence of platinum oxide at 130°/50 mm. is converted into *r*-citronellol, b. p. 214—215°, 107—108°/12 mm., n_D^{20} 1.4513 (allophanate, m. p. 112.5—113.5°); at 150°/90 mm. in presence of nickel almost the same product, b. p. 213—215°, 1.45037, d^{20}_4 0.850 (allophanate, m. p. 111—111.5°), is obtained (cf. A., 1925, i, 772), these properties agreeing with those of natural citronellol and not those of Barbier and Bouveault's rhodinol. Under 20 mm., *d*-limonene, b. p. 175—176°, d^{20}_4 0.847, n_D^{20} 1.4717, $[\alpha]_D^{25} +116.1^\circ$, containing about 80% of limonene, 12% of terpinolene, and 8% probably of α -terpinene, is hydrogenated only to the extent of about 10%, as shown by the bromine value, the rotatory power being unaltered; hydrogenation is complete only at 150—200 mm. Ozonisation of the product indicates the presence of 88% of the limonene or dipentene form and only 3—4% of terpinolene. These results, which may be attributed to partial isomerisation of the terpinolene into dipentene, or into α -terpinene, which then undergoes reduction and partial isomerisation to β -terpinene, indicate that pure limonene has not been obtained (cf. Braun and Lemke, A., 1923, i, 813).

R. BRIGHTMAN.

"Normal" structure of aldoses and ketoses. H. KILIANI (Z. angew. Chem., 1929, 42, 16—17).—Polemical (cf. Leibowitz, *ibid.*, 1926, 39, 1147).

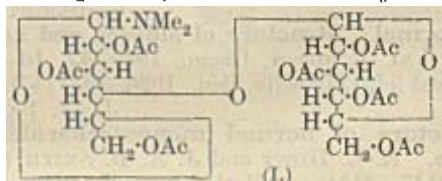
J. W. BAKER.

Structure of normal monosaccharides. V. Lyxose. E. L. HIRST and J. A. B. SMITH (J.C.S., 1928, 3147—3154).— α -Methyl-lyxoside when treated with methyl iodide and silver oxide gave *trimethyl-methyl-lyxoside*, b. p. about 70°/0.02 mm., n_D^{20} 1.4460, $[\alpha]_{D^{20}}^{20} +10^\circ$ in water, which with 6% aqueous hydrochloric acid at 100° yielded *trimethyl-lyxose*, b. p. 90°/0.05 mm., n_D^{20} 1.4629, m. p. 79°, $[\alpha]_D^{20} -22^\circ$ in water. Direct methylation of lyxose with methyl sulphate also gave *trimethylmethyl-lyxoside*, b. p. 70°/0.02 mm., n_D^{20} 1.4471, $[\alpha]_D^{20} -6^\circ$ in methyl alcohol, containing some of the β -isomeride; hydrolysis with 6% aqueous hydrochloric acid gave an 80% yield of *trimethyl-lyxose*, m. p. 79°, $[\alpha]_D^{20} -22^\circ$. Oxidation of *trimethyl-lyxose* with bromine water yielded *trimethyl-8-lyxonolactone*, b. p. 105°/0.02 mm., n_D^{20} 1.4620, $[\alpha]_D^{20} +35.5^\circ$ (initial value) and -9.3° (equilibrium value) in water (*phenylhydrazide*, m. p. 180—181°), which by further oxidation with nitric acid (d 1.42) and esterification of the resultant product with 3% methyl-alcoholic hydrogen chloride furnished *methyl trimethoxyglutarate*, b. p. about 100°/0.1 mm., n_D^{20} 1.4353, $[\alpha]_D^{20} -39^\circ$ in methyl alcohol, $[\alpha]_D^{20} -31^\circ$ in water, in 76% yield [corresponding *trimethoxyglutaramide*, m. p. 230° (decomp.), and the *methylamide*, m. p. 171—172°; in both cases the yields were more than 70%]. *Trimethylmethyl-lyxoside* on oxidation with nitric acid (d 1.42) gave *methyl trimethoxyglutarate*, n_D^{20} 1.4355, $[\alpha]_D^{20} -34^\circ$ in water, which with *methyl-alcoholic ammonia* furnished *trimethoxyglutaramide*, m. p. 230° (decomp.), $[\alpha]_D^{20} -49^\circ$ in water, in 88% yield. From these results the authors assign the pyranose structure to α -methyl-lyxoside and hence also to lyxose. These conclusions are in disagreement with those of Phelps and Hudson (A., 1926, 501), who assign a butylene-oxide formula to α -methyl-lyxoside and its derivatives.

A. I. VOGEL.

Detection of lævulose in presence of other carbohydrates. L. EKKERT (Pharm. Zentr., 1928, 69, 805—806).—A resume of the reactions of lævulose is given. Treatment of 0.01—0.03 g. of lævulose with 3—5 drops of 2*N*-potassium hydroxide solution followed by the addition of 0.5—1.0 g. of solid potassium or sodium hydroxide results in the formation of a blood-red band round the solid alkali and after several minutes the whole liquid assumes a blood-red colour. Other carbohydrates similarly treated behave as follows: arabinose, xylose, maltose, galactose, and dextrin, yellow colour within 1 min.; rhamnose and lactose, lemon-yellow within 1 min.; dextrose, yellow after 2 min.; mannose, yellow after 1 min.; sucrose and glycogen, colourless after 15 min. A. I. VOGEL.

Action of trimethylamine and other bases on acetobromocellobiose. G. ZEMPLÉN and Z. BRUCKNER (Ber., 1928, 61, [B], 2481—2486; cf. A., 1928, 741).—Reinvestigation of the action of alkali hydroxide on the product derived from acetobromocellobiose and trimethylamine (*loc. cit.*) has shown the base evolved to be di- and not tri-methylamine. Support for the conception that the new compound is *hepta-acetylcellobiosidodimethylamine* (I),



m. p. 198—199° (decomp.), $[\alpha]_D^{20}$ -10.51° in chloroform, is found in the observation that it is more readily prepared from acetobromocellobiose and trimethylamine in chloroform at the ordinary temperature, whereby also tetramethylammonium bromide is produced. The same base (together with dimethylamine hydrobromide) is obtained from acetobromocellobiose and dimethylamine. Acetobromocellobiose and triethylamine yield only *hepta-acetylcellobiose* and the mother-liquors are free from diethylamine. The latter base and acetobromocellobiose afford *hexa-acetylcellobiosen*, m. p. 125—126°, $[\alpha]_D^{20}$ -19.78° in chloroform (for nomenclature see Maurer and Mahn, A., 1927, 751). Piperidine and acetobromocellobiose give *hepta-acetylcellobiosidopiperidine*, $C_{31}H_{45}O_{17}N$, m. p. 115—120° (decomp.), $[\alpha]_D^{20}$ -15.28° in chloroform, which appears to absorb two atoms of bromine in chloroform but permits the isolation only of a *monobromo*-compound, m. p. 132—133° (decomp.). H. WREN.

Glucosides. I. Formation of glucosides from 3:4:6-triacetylglucose 1:2-anhydride.

W. J. HICKINBOTTOM (J.C.S., 1928, 3140—3147).—3:4:6-Triacetylglucose 1:2-anhydride (I) (cf. Brigl, A., 1922, i, 1117), most conveniently prepared by the action of dry ammonia on a suspension of dry, finely-powdered 3:4:6-triacetylglucosyl chloride in dry benzene for 3 hrs., reacts with ethyl alcohol with the formation of 3:4:6-triacetyl- β -ethylglucoside, m. p. 121°, $[\alpha]_D^{20}$ $+14.4^\circ$ in ethyl alcohol, which with methyl iodide and silver oxide yielded a *triacetyl*methyl-

β -ethylglucoside, m. p. 95—96°, $[\alpha]_D^{20}$ $+5.0^\circ$ in alcohol. Deacetylation by means of alcoholic ammonia, followed by hydrolysis with aqueous hydrochloric acid, gave 2-methylglucose (*phenylhydrazone*, m. p. 175—176°), which was also prepared from 3:4:6-triacetyl- β -methylglucose by methylation with silver oxide and methyl iodide followed by deacetylation and hydrolysis. Methyl alcohol and I yielded 3:4:6-triacetyl- β -methylglucoside, m. p. 95—97°, $[\alpha]_D^{20}$ $+19^\circ$ (cf. Brigl, *loc. cit.*), which on acetylation in pyridine yielded tetra-acetyl- β -methylglucoside, m. p. 101—103°, whilst isopropyl alcohol and I furnished 3:4:6-triacetyl- β -isopropylglucoside, which with acetic anhydride in pyridine solution gave 2:3:4:6-tetra-acetyl- β -isopropylglucoside, m. p. 134—135°, $[\alpha]_D^{20}$ -23.4° in alcohol. The interaction between benzyl alcohol and I at 100° afforded 3:4:6-triacetylbenzylglucoside, which was converted by alcoholic ammonia into β -benzylglucoside, m. p. 119°, $[\alpha]_D^{20}$ -49° ; acetylation of the latter yielded 2:3:4:6-tetra-acetyl- β -benzylglucoside, m. p. 98—99°, $[\alpha]_D^{20}$ -44° in alcohol (lit. m. p. 96—101°, $[\alpha]_D^{20}$ -48°). When I is heated with menthol at 90—100° for 30 hrs. 3:4:6-triacetylmenthylglucoside, m. p. 144° (sintering at 141°), $[\alpha]_D^{20}$ -10.6° in benzene, is formed; this furnished β -menthylglucoside with aqueous-alcoholic potassium hydroxide (cf. Fischer and Bergmann, A., 1917, i, 467). The interaction between 3:4:6-triacetylglucose anhydride and phenol proceeded less readily than with primary and secondary alcohols; combination was effected in the presence of excess of phenol by heating at 100° for 20 hrs. and 2:3:4:6-tetra-acetyl- α -phenylglucoside, m. p. 112°, $[\alpha]_D^{20}$ $+162^\circ$ in alcohol (lit. m. p. 115°, $[\alpha]_D^{20}$ $+164.9^\circ$ in benzene), was produced which yielded α -phenylglucoside hydrate, m. p. 155—160°, $[\alpha]_D^{20}$ $+157^\circ$ in alcohol, with alcoholic ammonia. The results are regarded as affording independent evidence for the formula I originally assigned to the triacetylglucose anhydride by Brigl (*loc. cit.*). A comparison is made between the chemical reactions of α -glucosan (Pictet and Castan, A., 1920, i, 594) and 3:4:6-triacetylglucose anhydride, and doubts are cast on the structure of the former.

A. I. VOGEL.

Phloridzin and quercitrin. G. ZEMPLÉN, Z. CSÜRÖS, Á. GERECs, and S. ACSÉL (Ber., 1928, 61, [B], 2486—2497).—The synthesis of phloretin from purely synthetic materials is effected in the following manner. β -Phenylpropionic acid is converted by heating with lead thiocyanate into β -phenylpropionitrile, b. p. 132—135°, transformed by nitric acid (*d* 1.48) at 5° into β -p-nitrophenylpropionitrile, m. p. 79.5°, and thence successively into β -p-aminophenylpropionitrile and β -p-hydroxyphenylpropionitrile. The last compound is converted by phloroglucinol and hydrogen chloride through the ketimine hydrochloride into phloretin, $(OH)_3C_6H_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot OH$. Unsuccessful attempts are recorded to condense *p*-hydroxyphenylpropionitrile with the tetra-acetyl derivative of phlorin (obtained from acetobromoglucose and phloroglucinol) and to synthesise phloridzin from phloretin and acetobromoglucose under conditions similar to those leading to the isolation of tetra-acetylphlorin or in presence of quinoline. Glucoside production from free phloretin is rendered difficult by

the ability of acetobromoglucose to react with three different hydroxyl groups and thus furnish a number of isomerides. A phloretin derivative containing a single hydroxyl group is obtained by treating *hepta-acetylphloridzin*, $[\alpha]_D^{25} -41.33^\circ$ in chloroform, with hydrogen bromide and glacial acetic acid at the atmospheric temperature, whereby acetobromoglucose and *triacylphloretin*,

$\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OH})(\text{OAc})_2$ [1 : 2 : 4 : 6], m. p. 188—189°, are produced. The compound last mentioned could not be caused to react with acetobromoglucose, with production of phloridzin.

Quercitrin is converted by acetic anhydride and sodium acetate into *quercitrin hepta-acetate*, $[\alpha]_D^{25} -165.6^\circ$ in chloroform, hydrolysed by hydrogen bromide in glacial acetic acid to *tetra-acetylquercetin* and acetobromorhamnose. The acetyl derivative reacts with acetobromoglucose in the presence of silver oxide and quinoline, giving the acetyl derivative of a quercetin glucoside, presumably *acetylisoquercitrin*. The production of the glucoside is placed beyond doubt, but its isolation has not been effected. H. WREN.

Triacetylstarch and its mol. wt. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1928, 3, 276—285).—Treatment of starch (soluble Merck) with excess of acetic anhydride at about 70° in presence of a saturated aqueous solution of zinc chloride gives a 90% yield of a *triacylstarch* (I), decomp. slowly above 270° after sintering at 258°, $+170.2^\circ$ in chloroform (cf. Pregl, A., 1902, i, 135; Bergmann and Knehe, A., 1927, 342). Hydrolysis of I with sodium ethoxide in toluene gives a phosphate-free soluble starch re-acetylated to I. Cryoscopic determinations of the mol. wt. of I in ethylene dibromide, bromoform, camphor, acetic acid, and phenol, and ebullioscopic determinations in acetic acid, chloroform, and acetone give values ranging from 82 to 8050, but in neutral solvents the value appears to be about 5000, thus demonstrating that the molecule is at least $(\text{C}_6\text{H}_7\text{O}_5\text{Ac}_3)_{18}$ (cf. Pictet, A., 1926, 387).

H. BURTON.

Constitution of flax cellulose. G. W. RIGBY (J. Amer. Chem. Soc., 1928, 50, 3364—3370; cf. Hess and Messmer, A., 1922, i, 988).—Pure cellulose, isolated from flax fibres by the method recommended for cotton cellulose (B., 1923, 825), yields on exhaustive methylation and hydrolysis (cf. Denham, J.C.S., 1921, 119, 77; Irvine, *ibid.*, 1923, 123, 518) only $\beta\gamma\zeta$ -trimethylglucose and a little of the dimethyl derivative. Under the conditions employed by Haworth and Hirst (J.C.S., 1921, 119, 197) cellobiose octa-acetate is obtained in equal yield from both flax and cotton celluloses. Graded acetolysis of flax cellulose by Irvine's method (A., 1926, 823) yields a mixture of trisaccharide and anhydrotrisaccharide acetates identical with the mixture obtained by this author from cotton cellulose. These and other chemical and physical properties are quoted to show the complete identity of the unit structures of flax and cotton celluloses.

H. E. F. NOTTON.

Acetylation of beech wood. O. HORN (Ber., 1928, 61, [B], 2542—2545).—Treatment of beech wood with acetic anhydride containing 0.25% of sulphuric acid gives an acetylated wood (yield 150%) possessing unchanged woody structure and, apart from

its lighter colour, resembling externally the original wood. It does not give the customary colour reactions for lignin; appreciable amounts of substance cannot be removed from it by treatment with organic solvents. A single acetylation gives a product containing 42.2% of acetyl. About 90% of the lignin present in the original wood is found in the acetylated product; hemicelluloses appear to be mainly removed during the acetylation, which does not cause sensible alteration of the methoxyl content. Treatment of the acetylated wood alternatively with chlorine and sodium sulphite followed by potassium permanganate or by Schmidt's chlorine dioxide method leaves 76% of nearly homogeneous cellulose triacetate. The acetylation of beech wood is therefore precisely similar to that of pine (cf. Fuchs, A., 1928, 743; Suida and Titsch, *ibid.*, 1227).

H. WREN.

Influence of poles and polar linkings on course pursued by elimination reactions. II. Mechanism of exhaustive methylation (continued). C. K. INGOLD and C. C. N. VASS (J.C.S., 1928, 3125—3127).—Theory predicts (Hanhart and Ingold, A., 1927, 650) that in the decomposition of quaternary ammonium compounds $\text{CHR}_1\text{R}_2 \cdot \text{CR}_3\text{R}_4 \cdot \text{NMe}_3 \cdot \text{OH} \rightarrow \text{CR}_1\text{R}_2 \cdot \text{CR}_3\text{R}_4 + \text{NMe}_3 + \text{H}_2\text{O}$ (A) or $\text{CHR}_1\text{R}_2 \cdot \text{CR}_3\text{R}_4 \cdot \text{NMe}_2 + \text{MeOH}$ (B) the suppression of (A) in favour of (B) should (i) be governed by R_1 and R_2 much more than by R_3 and R_4 , (ii) should increase tending towards constancy, with increasing R_1 and R_2 , and (iii) should be greater when $\text{R}_1\text{R}_2\text{CH}-$, or any part thereof, is branched than when the corresponding group or part is unbranched but isomeric. Prediction (ii) is here verified, the values for percentage olefine (reaction A) being ($\text{R}_3=\text{R}_4=\text{H}$); and $\text{R}_1=\text{Et}$, 95%; Pr , 84%; Bu , 79%; n -amyl, 77%; n -hexyl, 76%; n -heptyl, 74%; n -octyl, 75%, the constant value being 75%. Prediction (iii) is verified by comparison of n -butyl and isobutyl, 72%. The results differ from these previously described by von Braun (A., 1911, i, 610). Benz- n -amylamide has m. p. 31—32°, b. p. 205—210°/18 mm. (cf. von Braun and Sobecki, A., 1911, i, 128). A. I. VOGEL.

Reaction between sugars and amino-acids.

H. VON EULER and E. BRUNUS (Annalen, 1928, 467, 201—216).—Cryoscopic determinations on mixtures of dextrose and glycylglycine in aqueous solution at p_H 6.0—9.2 show that condensation increases rapidly with increasing p_H . This is contrary to the findings of Waldschmidt-Leitz and Rauchalles (A., 1928, 672), but is similar to the reaction between dextrose and glycine (A., 1926, 822). The decolorisation of methylene-blue solution by a mixture of dextrose and glycylglycine at p_H 9.1 is rather slower than with a mixture of dextrose and glycine. This last mixture decolorises methylene-blue still more rapidly at p_H 10.5 (cf. A., 1928, 1118). A mixture of lævulose and glycine begins to decolorise methylene-blue at p_H 9.1; at p_H 10.3 reduction is more rapid.

H. BURTON.

Amino-acid methionine; constitution and synthesis. G. BARGER and F. P. COYNE (Biochem. J., 1928, 22, 1417—1425).—The amino-acid, $\text{C}_5\text{H}_{11}\text{O}_2\text{NS}$, isolated by Mueller (cf. A., 1923, i, 869, 963) is shown to be γ -methylthiol- α -aminobutyric acid

(methionine) by the following synthesis. β -Methylthiolpropionaldehydediethylacetal, b. p. 89°/14 mm., 96°/20 mm., was prepared by passing methyl mereaptan into alcoholic sodium ethoxide solution and adding β -chloropropionaldehyde acetal. Hydrolysis of the acetal yielded β -methylthiolpropionaldehyde, b. p. 60°/12 mm., which was converted into α -amino- γ -methylthiolbutyronitrile, and finally on boiling the nitrile with hydrochloric acid α -amino- γ -methylthiolbutyric acid, m. p. 281° (decomp.), was obtained. The α -naphthylcarbamido-derivative, m. p. 181—182°, was obtained. The thiohydantoin and the picrolonate prepared from the synthetic product were identical with the corresponding derivatives from natural methionine.

The synthesis of methionine by Erlenmeyer's method failed. The following compounds were prepared. Methylthiolacetaldehydediethylacetal, b. p. 188—190°/760 mm.; methylthiolacetaldehyde; methylthioethylidenethydrantoin, $\text{SMe} \cdot \text{CH}_2 \cdot \text{CH} : \text{C} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$ m. p. 156° (from which methionine could not be obtained by reduction); β -methylthiolpropionic acid, b. p. 235—240°/760 mm.; β -methylsulphonepropionic acid, b. p. 200°/4 mm. S. S. ZILVA.

Specific action of erepsin and trypsin-kinase. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1928, 10, 179—187).—The carbamide derivatives, in which the free amino-group of the polypeptide is replaced by the carboxylamide group, of *dl*-leucylglycine, glycyl-*dl*-valine, and leucylglycylglycine (prepared by the action of ammonia on the corresponding carbethoxy-derivative), are not hydrolysed by either erepsin or trypsin-kinase, but suffer fission when treated with an extract of pancreas powder. Similarly, the phenylurethanes of *dl*-leucylglycylglycine and *dl*-leucylglycine are much more readily hydrolysed with pancreas extract than with trypsin-kinase. The specific action of erepsin, trypsin, and trypsin-kinase on various polypeptides containing *l*-leucine has been investigated. *l*-Leucylglycyl-*l*-leucine, glycyl-*l*-leucylglycyl-*l*-leucine, *dl*-leucylglycyl-*l*-leucylglycine, m. p. 256°, *dl*-leucylglycylglycyl-*l*-leucine, and *l*-leucylglycyl-*l*-leucylglycyl-*l*-leucine are all hydrolysed by erepsin and trypsin-kinase, whilst glycyl-*dl*-leucylglycine, m. p. 216° (decomp.), *dl*-leucyl-*dl*-leucylglycylglycine, *l*-leucylpentaglycylglycine, di-(*l*-leucyltriglycyl)-*l*-leucylpentaglycylglycine, and tri-(*l*-leucyltriglycyl)-*l*-leucylpentaglycylglycine are attacked only by erepsin. *l*-Leucyltetraglycylglycine is hydrolysed by erepsin and slowly by trypsin-kinase, but not by trypsin. Thus, seemingly, trypsin-kinase has an affinity for the carboxyl group of leucine which is absent when the glycine residue is at the end of the chain (but cf. Waldschmidt-Leitz and others, A., 1928, 446, and Abderhalden and Fleischmann, *ibid.*, 1043). Neither *dl*-leucyl- γ -aminobutyric acid nor its phenylurethane, m. p. 166°, is hydrolysed by erepsin or trypsin-kinase. Whilst glycyl- α -aminobutyric acid is hydrolysed by erepsin, the corresponding *l*-compound is unattacked. Chloroacetyl-*dl*-leucylglycine, m. p. 141°, and α -bromoisohexoylglycyl-*l*-leucylglycine, m. p. 180°, are prepared. J. W. BAKER.

Specific action of erepsin and trypsin-kinase; their behaviour with polypeptides and their

derivatives in which β -aminobutyric acid replaces an α -amino-acid, and the action of *N*-alkali on these compounds. E. ABDERHALDEN and R. FLEISCHMANN (Fermentforsch., 1928, 10, 195—212; cf. Abderhalden and Koppel, A., 1928, 1042).—The phenylurethanes of di-(*d*-valyl-*d*-alanyl)-*l*-cystine, decomp. 175°, di-(*l*-leucylglycyl)-*l*-cystine, decomp. 190°, diglycylglycine, m. p. 214—216° (the substance, m. p. 184°, described by Curtius and Wüstenfeld, A., 1904, i, 833, as this derivative being some other compound) (α -naphthylurethane, decomp. 225°), and tri- and tetra-glycylglycine, both decomp. above 220°, have been prepared, and the effect of the substitution of the amino-group on the action of erepsin and trypsin-kinase has been investigated. The first two derivatives are not attacked by erepsin (p_H 7.8) at 37° (although the parent polypeptides are readily hydrolysed), but are hydrolysed by trypsin-kinase (p_H 8.3) at 37°. All are hydrolysed by *N*-sodium hydroxide at 37°. No hydrolysis occurs if the p_H value is increased from 8.1 to 9.2. None is hydrolysed by erepsin and only tetraglycylglycine phenylurethane is attacked by trypsin-kinase. By usual methods tetraglycylglycine is converted successively into *d*- α -bromoisohexoyltetraglycylglycine, decomp. above 220°, $[\alpha]_D^{20} +12.21^\circ$, and *l*-leucyltetraglycylglycine, decomp. above 220°, $[\alpha]_D^{20} +9.41^\circ$. The latter suffers 80% hydrolysis in 3 hrs. with *N*-sodium hydroxide at 37°, and is attacked by trypsin-kinase but not by erepsin (cf. Abderhalden and Schwab, preceding). The influence of the presence of a β -aminobutyric acid group was investigated with the following compounds: *dl*-leucyl- β -aminobutyric acid (I) (phenylurethane, m. p. 188°; benzoyl derivative, m. p. 182°); *dl*-leucyl-*dl*-leucyl- β -aminobutyric acid (II), m. p. 240° (phenylurethane, m. p. 212°) (prepared from *dl*- α -bromoisohexoyl-*dl*-leucyl- β -aminobutyric acid, m. p. 172°); β -aminobutyryl-*dl*-leucine (III), m. p. 265—268° (decomp.) (prepared from β -chlorobutyryl chloride, b. p. 40—41°/12 mm., 65—67°/40 mm., through β -chlorobutyryl-*dl*-leucine, m. p. 132°); β -aminobutyrylglycine (IV), m. p. 248° (from β -chlorobutyrylglycine, m. p. 122°); β -aminobutyryldiglycylglycine (V), m. p. 230° (decomp.) (from β -chlorobutyryldiglycylglycine, m. p. 195°); β -aminobutyryltriglycylglycine (VI), decomp. 249° (from β -chlorobutyryltriglycylglycine, m. p. 227°); β -aminobutyryl- β -aminobutyric acid (VII) (from β -chlorobutyryl- β -aminobutyric acid, m. p. 142°); and β -aminobutyryl-*l*-leucyltetraglycylglycine (VIII) (from β -chlorobutyryl-*l*-leucyltetraglycylglycine, decomp. above 215°). Neither I nor its benzoyl derivative is attacked by *N*-sodium hydroxide, whilst the phenylurethane suffers hydrolysis; II is unattacked, whilst its phenylurethane is readily hydrolysed; III, IV, and VII are not acted on, whilst V, VI, and VIII are hydrolysed. None of these compounds is affected by erepsin, but with trypsin-kinase VIII is hydrolysed, whilst V and VI are not attacked. Trypsin does not act on the amino-group but on the carboxyl group, so that if the terminal amino-acid is not one which occurs naturally (e.g., a β -amino-acid) no attack is possible.

J. W. BAKER.

Hydrolysis of polypeptides and their derivatives with erepsin, trypsin-kinase, and *N*-alkali.

E. ABDERHALDEN and O. HERRMANN (Fermentforsch., 1928, 10, 145—158).—The hydrolysis of a number of synthetic polypeptides and their derivatives with *N*-sodium hydroxide, erepsin, and trypsin-kinase has been investigated quantitatively. By usual methods are obtained *dl*- α -aminobutyrylglycine (I) (*phenylurethane*, m. p. 203°; *o*-nitrotoluene-*p*-sulphonyl, m. p. 170—172°, *p*-nitrobenzoyl, m. p. 188—189°, and *m*-nitrobenzoyl, m. p. 204°, derivatives); *dl*- α -bromopropionyl-*dl*- α -aminobutyrylglycine, m. p. 173°; *dl*-alanyl-*dl*- α -aminobutyrylglycine (II), m. p. 225° (*phenylurethane*, m. p. 208—210°); *dl*-valylglycine, m. p. 245°; *dl*- α -bromopropionyl-*dl*-valylglycine, m. p. 202°; *dl*-alanyl-*dl*-valylglycine (III), m. p. 248° (*phenylurethane*, m. p. 218°; *naphthalene-2-sulphonyl* derivative, m. p. 198°); *l*-leucyl-*l*-phenylalanine + *d*-leucyl-*d*-phenylalanine (IV), m. p. 260° (*phenylurethane*, m. p. 183°), and *l*-leucyl-*d*-phenylalanine + *d*-leucyl-*l*-phenylalanine (V), m. p. 220° (cf. Leuchs and Suzuki, A., 1904, i, 867) (*phenylurethane*, m. p. 193°; *o*-nitrotoluene-4-sulphonyl derivative, m. p. 75°); glycyl-*dl*-phenylalanine (VI), m. p. 260° (decomp.) [*phenylurethane*, m. p. 208°; *naphthalene-2-sulphonyl*, m. p. 100° (decomp.), and *benzoyl*, m. p. 172°, derivatives]; *dl*- α -bromoisovaleryl-*dl*-phenylalanine, m. p. 135°, which by treatment with ammonia yields, not the dipeptide, but an unsaturated substance, m. p. 260° (decomp.). By treatment in 0.1*M*-solution with *N*-sodium hydroxide at 37°, I, II, and III are hydrolysed more slowly than their phenylurethanes; IV, V, and VI, and the *naphthalene-2-sulphonyl* derivative of the last are not hydrolysed, whilst their phenylurethanes and the benzoyl derivative of VI suffer hydrolysis. Thus in all cases the phenylurethanes (this group remaining combined with the amino-acid after fission of the polypeptide) are more readily hydrolysed by alkali than are the parent substances. With erepsin (p_H 7.8 at 37°) fission of the unsubstituted polypeptide occurs in each case, but none of the derivatives is attacked. Conversely, with trypsin-kinase the parents are unattacked, whilst the derivatives suffer enzymolysis in each case.

J. W. BAKER.

Influence of the substitution of the free amino-group of polypeptides by various groups on their fission by *N*-alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN, E. RINDTORFF, and A. SCHMITZ (Fermentforsch., 1928, 10, 213—232).—*dl*-Leucylglycine is more readily attacked by *N*-sodium hydroxide at 37° than is its phthaloyl derivative, m. p. 119—120°, whilst methyl-*dl*-leucylglycine is very resistant to attack. The *trichloroacetyl* derivative, m. p. 172—173°, eliminates trichloroacetic acid under these conditions. Similarly, *methyldiglycylglycine*, m. p. 139—140° (decomp.), is slightly more resistant to attack by *N*-sodium hydroxide than is the parent diglycylglycine. Erepsin (p_H 7.8) at 37° attacks *dl*-leucylglycine, but its acyl derivatives and methyl-diglycylglycine are not affected. On the contrary, all the derivatives of *dl*-leucylglycine with the exception of the methyl compound are hydrolysed by trypsin-kinase (p_H 8.3) at 37°. Ethyl oxalyldi-*d*-glutamate is readily hydrolysed by *N*-sodium hydroxide at 37° with fission of oxalic acid, whilst

ethyl succinyl-d-glutamate is hydrolysed only very slowly. Neither derivative is hydrolysed by erepsin, whilst trypsin-kinase attacks the former but not the latter. From glycyl-*dl*-leucine are prepared its *naphthalene-2-sulphonyl*, m. p. 123° (attacked by *N*-sodium hydroxide only with difficulty); *phenylurethane*, m. p. 177° (much more readily hydrolysed by *N*-sodium hydroxide than the parent dipeptide); *chlorobenzoyl*, m. p. 190°, and *butyryl*, m. p. 182° (both attacked by alkali at a velocity intermediate between that of the phenylurethane and the parent polypeptide), derivatives, and *oxalylglycyl-dl-leucine ethyl ester*, m. p. 163° (readily hydrolysed by alkali). Unlike the parent glycyl-*dl*-leucine, all these derivatives are unattacked by erepsin, whilst trypsin-kinase, which has no action on the parent dipeptide, hydrolyses them all. From glycyl-*dl*-valine, m. p. 240° (decomp.) (prepared from *chloroacetyl-dl-valine*, m. p. 129.5—130.5°), are prepared its *phenylurethane*, m. p. 155°, *dichloroacetyl*, m. p. 151.5—152°, and *benzoyl*, m. p. 135—136°, derivatives, all of which are more readily hydrolysed by *N*-sodium hydroxide than is the parent dipeptide. The dichloroacetyl group is rapidly eliminated by the action of alkali to regenerate the parent dipeptide and not as *dichloroacetyl*glycine, m. p. 125—126°, which was synthesised, and is itself rapidly hydrolysed by alkali at 37°. The phenylurethane is attacked by trypsin-kinase but not by erepsin. These results confirm the view that a free amino-group is essential for attack by erepsin, whilst trypsin-kinase, which does not attack the original polypeptide containing a free amino-group, is able to attack the derivatives in which this group is substituted with a biologically foreign group (e.g., acyl but not methyl).

J. W. BAKER.

Action of *N*-alkali, erepsin, and trypsin-kinase on polypeptides containing *d*-alanine. E. ABDERHALDEN and J. J. DELGADO Y MIER (Fermentforsch., 1928, 10, 251—255).—*d*-Alanyl-*d*-alanine (I) (*phenylurethane*, m. p. 176°; *naphthalene-2-sulphonyl* derivative, m. p. 158—159°) and *d*-alanyl-*d*-alanyl-*d*-alanine (II), m. p. 245°, $[\alpha]_D^{20}$ -15.1° (prepared from *d*-alanine anhydride, m. p. 297°, $[\alpha]_D^{20}$ -28.7°, through *d*- α -bromoisopropionyl-*d*-alanyl-*d*-alanine, m. p. 148°), are both hydrolysed by *N*-sodium hydroxide at 37°, II more rapidly than I. Under the same conditions the phenylurethane of I is completely hydrolysed in 3 hrs. to *d*-alanine and its phenylurethane, whilst its *naphthalene-2-sulphonyl* derivative is only slowly attacked. Erepsin (p_H 7.8) hydrolyses I more rapidly than II, but neither is attacked by trypsin-kinase.

J. W. BAKER.

Action of *N*-alkali, erepsin, and trypsin-kinase on polypeptides containing β -alanine. E. ABDERHALDEN and F. REICH (Fermentforsch., 1928, 10, 173—178).—Glycyl- β -alanine, decomp. 230° (Miyamichi, Chem. Zentr., 1927, i, 1428), *dl*- α -bromoisohexoyl- β -alanine, m. p. 69—72°, and *dl*-leucyl- β -alanine, m. p. 202—204° (*phenylurethane*, m. p. 160—162°), are prepared by the usual methods. With *N*-sodium hydroxide at 37° glycyl- β -alanine is readily hydrolysed and *dl*-leucyl- β -alanine is almost unchanged after 48 hrs., whilst its phenylurethane is rapidly

attacked. In every case fission occurs with erepsin or trypsin-kinase.

J. W. BAKER.

Action of N-alkali, erepsin, and trypsin-kinase on polypeptides containing *dl*- α -aminoisovaleric acid. E. ABDERHALDEN, P. SAH, and E. SCHWAB (Fermentforsch., 1928, 10, 264—273).—By the usual methods the following have been prepared: *dl*-valylglycine (copper salt; phenylurethane, m. p. 188—190°; naphthalene-2-sulphonyl derivative, m. p. 195°); *dl*- α -bromoisovalerylglucylglycine, m. p. 145—146°; *dl*-valylglucylglycine, m. p. 240° (copper salt; benzoyl, m. p. 155°, and naphthalene-2-sulphonyl, m. p. 190°, derivatives; phenylurethane, m. p. 216—217°); chloroacetyl-*dl*-valylglycine, m. p. 141°; glucyl-*dl*-valylglycine, m. p. 239° (phenylurethane, m. p. 197—198°; naphthalene-2-sulphonyl derivative, m. p. 148°). With *N*-sodium hydroxide at 37° only those polypeptides in which the glycine component contains a free amino-group (glucyl-*dl*-valine, glucyl-*dl*-valylglycine) suffer hydrolysis. All the phenylurethanes are attacked, but, contrary to the view previously held that the naphthalene-2-sulphonyl group exerted a stabilising influence against alkaline hydrolysis, all these derivatives suffer hydrolysis, although in two cases the parent polypeptides are unattacked. *dl*-Valylglycine, *dl*-valylglucylglycine, and glucyl-*dl*-valylglycine are all hydrolysed by erepsin, but not by trypsin-kinase, whilst the phenylurethane of the second is hydrolysed by the latter but not by the former enzyme.

J. W. BAKER.

Action of N-alkali, erepsin, and trypsin-kinase on *dl*- α -dileucyl-*dl*-lysine. E. ABDERHALDEN and H. SICKEL (Fermentforsch., 1928, 10, 302—304).—*dl*- α -Dileucyl-*dl*-lysine, an amorphous powder, decomp. 160°, is prepared by usual methods from *dl*- α -dibromoisohexoyl-*dl*-lysine. It is rapidly hydrolysed by *N*-sodium hydroxide at 37—40°. Erepsin and trypsin-kinase both hydrolyse it, the latter more readily than the former.

J. W. BAKER.

Behaviour of α -di-(*dl*-leucyl)-*dl*-ornithine and its phenylurethane with N-alkali, erepsin, trypsin-kinase, pepsin and hydrochloric acid, and arginase. E. ABDERHALDEN and H. SICKEL (Fermentforsch., 1928, 10, 188—194).—*dl*-Ornithine obtained by hydrolysis of *dl*- δ -benzoylornithine; Fischer and Zemplén, A., 1909 i, 303) condenses with *dl*- α -bromoisohexoyl bromide to yield α -di-(*dl*- α -bromoisohexoyl)-*dl*-ornithine, m. p. 126—128° (together with a small amount of a benzoylated monosubstituted substance, m. p. 165°), converted by alcoholic ammonia into α -di-(*dl*-leucyl)-*dl*-ornithine, +H₂O, sintering at 95°, decomp. 150° (phenylurethane, sintering 98°, m. p. 130°). The rate of hydrolysis with *N*-sodium hydroxide at 37—40° is greater for the phenylurethane derivative than for the parent tripeptide, but neither suffers fission with erepsin or trypsin-kinase, nor is the tripeptide attacked by pepsin in 0.1*N*-hydrochloric acid or by arginase.

J. W. BAKER.

Accurate method for the analysis of carbamide. (Miss) M. TAYLOR (J. Amer. Chem. Soc., 1928, 50, 3261—3265).—The use of carbamide as a reference substance in migration and other experiments is suggested. An accurate method of analysis of carbamide solutions is described, depending on the

hydrolysis of the substance under pressure in presence of a small excess of standard hydrochloric acid.

S. K. TWEEDY.

High-molecular condensation products of carbamide and formaldehyde. H. SCHEIBLER, F. TROSTLER, and E. SCHOLZ (Z. angew. Chem., 1928, 41, 1305—1309).—Carbamide and freshly-distilled, neutral formaldehyde solution react, giving hydroxymethylcarbamide (I), m. p. 110°, which on treatment with aqueous acetic acid gives both an insoluble substance, (NH₂·CO·N·CH₂)₁₂·H₂O, and a soluble product, (NH₂·CO·N·CH₂)₁₂·AcOH (cf. van Laer, A., 1921, i, 499). Treatment of I first with acetic acid and then with bromine affords the compound (NH₂·CO·N·CH₂)₃·Br₂, obtained also from the above complexes. *s*-Dihydroxymethylcarbamide, m. p. 133° (cf. Einhorn and Hamburger, A., 1908, i, 141), is converted by the acetic acid-bromine treatment into the compound (II), (OH·CH₂·NH·CO·N·CH₂)₃·Br₂, which after prolonged action passes into the substance (III), [CO(N·CH₂)₂]₃·Br₂. When formaldehyde and carbamide are condensed in presence of a small amount of ammonia hydroxymethylmethylenecarbamide, (OH·CH₂·NH·CO·N·CH₂)₃·H₂O, is obtained. This is converted by the bromine treatment into II.

The product prepared from technical formaldehyde and carbamide is hydrolysed by 20% hydrochloric acid to ammonium chloride, whilst prolonged treatment with hot acetic acid gives, in addition to formaldehyde and methylamine, a water-soluble substance, hydrolysed by phosphoric acid to formaldehyde, carbon dioxide, ammonium salts, and acetic acid. It is converted by the bromine treatment into III, and with a mixture of acetic acid and anhydride yields a chloroform-soluble substance, [CO(N·CH₂)₂]₃·Ac₂O, convertible by bromine into III.

s-Dimethylcarbamide and formaldehyde give hydroxymethyl derivatives and not condensation products, thus indicating that the methylenecarbamide residues are correctly represented as (NH₂·CO·N·CH₂) (cf. van Laer, loc. cit.; Dixon, J.C.S., 1918, 113, 238).

H. BURTON.

Carbylamines. M. PASSERINI (Mem. R. Accad. Lincei, 1927, [vi], 2, 377—398).—A résumé of work previously published (A., 1921, 743, to 1927, 149). The author discusses the reactions of carbylamines with organic acids, aldehydes, and ketones in presence of acids, hydrates of chloro-aldehydes, phenol and naphthols, and pernitroso-derivatives.

E. W. WIGNALL.

Dichloromethylarsine. E. V. ZAPPI and V. DEULOFEU (Bull. Soc. chim., 1928, [iv], 43, 1230—1232).—Dichloromethylarsine, b. p. 130—132°, is obtained in 83% yield (53% after purification) by decomposing sodium cacodylate with hydrochloric acid (*d* 1.19), filtering, evaporating, and then distilling in a current of dry hydrogen chloride.

R. BRIGHTMAN.

New syntheses of organic selenium compounds. Q. MINGOIA (Gazzetta, 1928, 58, 667—673; cf. A., 1927, 134).—The action of acetyl chloride on magnesium bromohydroselenide yields selenoacetic acid, CH₃·COSeH, which has a penetrating, irritating odour and was obtained as ammonium salt, but this is highly unstable and rapidly undergoes partial change

into selenium and ammonium acetate. With salts of the heavy metals, this ammonium salt gives coloured precipitates, which decompose to form the corresponding black selenides.

Ethoxyselenoformic acid, $\text{OEt} \cdot \text{COSeH}$, prepared by the interaction of magnesium bromohydroselenide and ethyl chloroformate, rapidly decomposes into its *anhydride*, b. p. 125–127°, of nauseating odour, carbon monoxide, selenium, and alcohol.

Ethyl iodide and magnesium bromohydroselenide readily react, giving ethylselenomercaptan and magnesium bromoiodide. The action of acetaldehyde or benzaldehyde on magnesium bromohydroselenide, to yield selenoacetaldehyde, m. p. 136° (Vanino and Schinner, A., 1915, i, 117, gave 139°), or selenobenzaldehyde, m. p. 203–205° (Vanino and Schinner, *loc. cit.*), is described. T. H. POPE.

Valency. XII. Isomeric derivatives of diethyl telluride. F. L. GILBERT and T. M. LOWRY (J.C.S., 1928, 3179–3189).— α -Diethyltelluronium diiodide, m. p. 57° (α -tetraiodide, m. p. 98°), yields an α -base, which is converted into a β -base (β -di-iodide, m. p. 42°, β -dibromide, solidifying at –12°, β -dichloride, m. p. –10°), when an aqueous solution is evaporated to dryness at 100°/15 mm. in a stream of nitrogen. The α - and β -salts differ in their behaviour towards alkali; with aqueous ammonia the α -di-iodide gives an α -monoxiodide, $[\text{O}(\text{TeEt}_2)_2]\text{I}_2$, m. p. 104–106°, whilst the β -di-iodide gives a triethyltelluronium iodide. Mercury diphenyl and the α -di-iodide react in chloroform solution to give an additive compound, $(\text{TeEt}_2\text{I}_2)_2 \cdot \text{HgPh}_2$, m. p. 94°; mercury di-*p*-tolyl does not react with α -dimethyl- or α -diethyl-telluronium di-iodide. The absorption spectra of the iodides in cyclohexane exhibit the twin maxima of the “iodoform band” and the bromides exhibit only a step-out. Conductivity measurements show that the β -base has a higher conductivity than the α -base, whereas potentiometric titrations indicate that the β -base is stronger than the α -base during the first half of the process of neutralisation; the curve for the β -base is inflected after half neutralisation and the two curves cross (cf. A., 1928, 1098), proving that the β -base is weaker than the α -base after half neutralisation.

A. I. VOGEL.

Side reactions in the preparation of magnesium alkyl halides. H. GILMAN and R. E. FOTHERGILL (J. Amer. Chem. Soc., 1928, 50, 3334–3341; cf. Fuson, A., 1926, 604, 1237; Gomberg and Bachmann, A., 1927, 245).—The yields of (a) ethylene, hydrogen, methane, and ethane; (b) ethylene, hydrogen, ethane, and butane, and (c) α -butylene and *n*-butane, formed under varying conditions in the preparation of (a) magnesium methyl iodide, (b) magnesium ethyl bromide, and (c) magnesium *n*-butyl bromide, have been determined. The results are in agreement with the view that the production of the Grignard reagent, MgRX , is preceded by the formation of the free radical, $\text{R} \cdot$, from which the by-products, $\text{R} \cdot \text{R}$, RH , and $\text{R}(-\text{H})$ are derived. Similarly, the decomposition of magnesium methyl iodide by means of dilute sulphuric acid yields in addition to methane traces of hydrogen, ethylene, and probably other hydrocarbons. These side-reactions constitute pos-

sible sources of error in the analysis of Grignard reagents and in the determination of active hydrogen by the Zerevitinov method. H. E. F. NOTTON.

Factors influencing yields of magnesium *tert*-butyl and *tert*-amyl chlorides, and preparation of acids from them and carbon dioxide. H. GILMAN and E. A. ZOELLNER (Rec. trav. chim., 1928, 47, 1058–1063; cf. A., 1928, 401).—Magnesium *tert*-amyl chloride is best prepared by the slow addition of *tert*-amyl chloride (0.1 mol.) to finely-divided magnesium (0.1 atom) and ether (0.7 mol.), with stirring, the ether being maintained in ebullition. Details are also given for the preparation of α -dimethylpropionic (55–63%) and α -dimethyl-*n*-butyric acids (about 54%) from the requisite Grignard reagent and dry carbon dioxide at 0–8°.

H. BURTON.

Chlorination of *p*-cymene. W. QUIST (Forh. III nord. Kemistmotet, 1928, 194).—*p*-Cymene when chlorinated under varying conditions behaves essentially in the same way as simpler hydrocarbons under similar treatment. It differs, however, from these in that even when treated with chlorine under the most favourable conditions for obtaining compounds substituted in the side-chain the yield of these is small, chlorination of the heated material even in direct sunlight giving rise largely to products substituted in the carbon nucleus, together with considerable quantities of a viscous material, which is difficultly volatile in steam. Chlorination in acetic or formic acid solution also gave rise to nuclear monosubstitution products. The complete conversion of *p*-cymene into the technically important ω -chloromethyl derivative would thus appear to present considerable difficulties.

H. F. HARWOOD.

Stereoisomerism of disulphoxides and related substances. III. Pairs of aromatic disulphoxides. E. V. BELL and G. M. BENNETT (J.C.S., 1928, 3189–3192).—Oxidation of aromatic disulphoxides, $\text{C}_2\text{H}_4(\text{SR})_2$, Ar being phenyl, *p*-tolyl, and benzyl, and $\text{C}_6\text{H}_4(\text{SR})_2$, R being methyl or benzyl, with 25% hydrogen peroxide in glacial acetic acid solution gave in every case a pair of diastereoisomeric disulphoxides which were separated by fractional crystallisation, and were differentiated by their m. p., crystalline forms, and solubilities. Both forms give the parent disulphide on reduction, the alternative structure of a monosulphone being thereby excluded. Thus *s*-diphenylthiolethane, m. p. 69° (prepared by condensation of thiophenol with ethylene dibromide in the presence of potassium hydroxide), gave an α -disulphoxide, m. p. 166° (decomp.), and a β -disulphoxide, m. p. 123° (decomp.); *s*-di-*p*-tolylthiolethane, m. p. 81°, gave an α -disulphoxide, m. p. 173–174° (decomp.), and a β -disulphoxide, m. p. 126–127° (decomp.); dibenzylthiolethane gave an α -disulphoxide, m. p. 209°, and a β -disulphoxide, m. p. 192° (cf. Fromm and others, A., 1913, i, 44); 1:3-dimethylthiolbenzene (*mercurichloride*, m. p. 108°) gave an α -disulphoxide, m. p. 147°, and a β -disulphoxide, m. p. 102° (cf. Zincke and Kruger, A., 1913, i, 44); 1:3-dibenzylthiolbenzene gave an α -disulphoxide, m. p. 133°, and a β -disulphoxide, m. p. 123° (cf. Zincke and Kruger, *loc. cit.*); 1:4-dimethylthiol-

benzene gave an α -disulphoxide, m. p. 183° [mercurichloride, m. p. 216° (decomp.)], and a β -disulphoxide, m. p. 136° [mercurichloride, m. p. 188° (decomp.)] (cf. Zincke and Frohneberg, A., 1909, i, 643). No crystalline bromide or hydrochloride of the disulphoxides could be isolated. A. I. VOGEL.

Effect of specific compound formation between substrate and enzyme on the hydrolysis of polypeptides. E. ABDERHALDEN and H. BROCKMANN (Fermentforsch., 1928, 10, 159—172).—Colamine (β -hydroxyethylamine) reacts with *dl*- α -bromopropionyl bromide to yield *dl*- α -bromopropionylcolamine, m. p. 78.5° , converted by ammonia into *dl*-alanylcolamine, m. p. 78 — 79° (best isolated through its picrate, m. p. 105 — 108°). Chloroacetanilide, m. p. 138° , is converted by ammonia into glycylaniline, $+2\text{H}_2\text{O}$, m. p. 62 — 63° [picrate, m. p. 186° (decomp.)], and a substance, m. p. 144.5° , probably $(\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2)_2\text{NH}$, which condenses with *dl*- α -bromopropionyl bromide to yield a substance, m. p. 244 — 245° (uncorr.). Similarly are obtained *dl*- α -bromopropionylaniline, m. p. 101° ; *dl*-alanylaniline, b. p. 190 — $196^\circ/15$ — 16 mm. (picrate, m. p. 175°), which reacts with chloroacetyl chloride to yield chloroacetyl-*dl*-alanylaniline, m. p. 156° , converted by ammonia into glycyl-*dl*-alanylaniline, m. p. 80° [picrate, m. p. 186° (decomp.)], and a substance, m. p. 207 — 208° , probably $(\text{NHPh}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2)_2\text{NH}$; *dl*-alanylglycylaniline, m. p. 124 — 125° [picrate, m. p. 198° (decomp.)]. Similarly from diphenylamine is obtained *dl*-alanyldiphenylamine, m. p. 86° . All these substances with the exception of the last are attacked by intestinal crepsin at 37° (p_H 8.0), whilst trypsin (p_H 8.5) is without action (cf. Waldschmidt-Leitz and others, A., 1927, 345; Grassmann and Dyckerhoff, A., 1928, 672). With *N*-sodium hydroxide at 37° , *dl*-alanylglycine, *dl*-alanylglycylaniline, glycylaniline, and glycyl-*dl*-alanylaniline suffer hydrolysis. Erepsin is thus effective if the substrate contains a free amino-group, but no free carboxyl group, whilst in the absence of the latter trypsin has no action. All m. p. are corrected. J. W. BAKER.

Influence of certain substituent groups in the aniline molecule on the formation of carbylamines. M. PASSERINI and G. BANTI (Gazzetta, 1928, 58, 636—640).—The presence in the aniline molecule of the carboxyl, hydroxyl, nitro-, or arsinic group prevents the formation of carbylamine by treatment with potassium hydroxide and chloroform, a halogen atom limits such formation, whilst a ketonic group exhibits no hindering effect. Thus, anthranilic acid gives formylanthranilic acid; *p*-aminophenol gives formyl-*p*-aminophenol; *p*-nitroaniline remains unchanged, as does sodium *p*-aminophenylarsinate; *p*-aminoacetophenone gives *p*-carbylaminoacetophenone, b. p. 80 — $81^\circ/30$ mm., and diphenylformamidine; *o*-bromoaniline yields a small proportion of a liquid having the odour of carbylamine. T. H. POPE.

Compounds of tetryl with hydrocarbons. N. N. EFREMOV and A. M. TICHOMIROVA (Aim. Inst. Anal. Phys. Chem., 1928, 4, 92—117).—Fusion curves are constructed for binary mixtures of tetryl with various other substances. Unstable equimolecular compounds are formed with naphthalene, m. p. 86.4° ,

acenaphthene, m. p. 92.4° , phenanthrene, m. p. 73.2° , fluorene, m. p. 77.5° , and retene, m. p. 95.2° . With picramide, 2 : 4-dinitroaniline, picryl chloride, 2 : 4 : 6-trinitroanisole, 2 : 4 : 6-trinitro-*m*-xylene, and camphor the formation of compounds or solid solutions was not observed. The addition of the above substances to tetryl causes a considerable depression of m. p.

R. TRUSZKOWSKI.

Degradation of quaternary ammonium salts. I. T. S. STEVENS, E. M. CREIGHTON, A. B. GORDON, and M. MACNICOL (J.C.S., 1928, 3193—3197).—With the object of protecting a secondary amino-group by a more easily removable radical than benzyl, quaternary phenacylammonium salts have been prepared by refluxing the base with bromoacetophenone in benzene or alcohol, and isolating the resulting bromide, or converting it into the iodide. The following are described: Phenacylphenyldiethylammonium iodide, m. p. 133° ; phenacyl- β -phenylethyldimethylammonium bromide, m. p. 191° ; diphenacyldimethylpiperazinium dibromide, m. p. 222 — 225° (decomp.); hydrohydrastinine phenacyliodide, m. p. 190° . These all readily lose the phenacyl radical on reduction in aqueous solution by sodium amalgam.

With phenacylbenzyldimethylammonium bromide (I), m. p. 167 — 168° , sodium amalgam reduction is abnormal; a base, $\text{C}_{17}\text{H}_{15}\text{ON}$ (II), is formed, identical with the product obtained by the action of sodium hydroxide. This base is not a product of loss of a methyl group, since its methobromide (see below) is not identical with I, but gives phenyl styryl ketone with hot alkali. It is shown by synthesis from ω -bromo- ω -benzylacetophenone (m. p. 57 — 59° ; obtained by bromination of benzylacetophenone in carbon tetrachloride) and dimethylamine hydrochloride, in presence of sodium methoxide, to be ω -dimethylamino- ω -benzylacetophenone, m. p. 77 — 79° [picrate, m. p. 147 — 149° ; methobromide ($+0.5\text{EtOH}$), m. p. 195 — 197°]. Reduction of I by zinc and sulphuric acid furnishes a crude base, of which the picrate, m. p. 173 — 174° , is identified with benzyldimethylammonium picrate (lit. 168 — 169°).

E. W. WIGNALL.

Action of carbon disulphide on benzidine in presence of metallic oxides. B. CECCHIETTI and U. SARTI (Gazzetta, 1928, 58, 758—760).—The preparation by Krulla (A., 1913, i, 1174) of a compound $(\text{NHPh}\cdot\text{CS}\cdot\text{S})_2\text{Sn}$ suggested that it might be possible to prepare a compound of the type $(\text{NHR}\cdot\text{CS})_2$; actually such a compound, $(\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS})_2$, is formed when benzidine is heated in alcoholic solution with carbon disulphide and stannous oxide. The product can be diazotised and coupled with β -naphthol, when the substance $(\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS})_2$, decomp. 210° , is obtained.

E. W. WIGNALL.

Action of allylthiocarbimide on benzidine. B. CECCHIETTI and U. SARTI (Gazzetta, 1928, 58, 760—763).—When benzidine and excess of allylthiocarbimide are heated together under reflux, a dark product is formed from which a grey substance, $(\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4)_2$, m. p. 243° , is obtained (cf. Schiff, A., 1878, 669). If the reaction mixture contains a large excess of allylthiocarbimide, and

is strongly heated, a different product, 4:4'-dithiocarbimiddiphenyl, m. p. 203°, is obtained, without evolution of hydrogen sulphide; this is identical with the substance obtained by Jaffe (A., 1894, i, 418) by heating benzidine with thiocarbonyl chloride under pressure.

E. W. WIGNALL.

Diphenyl and its derivatives (and dinaphthyls). Scission into optical antipodes of compounds without asymmetric atoms. II. L. MASCARELLI (Gazzetta, 1928, 58, 627—630).—When converted into its salts with various optically active acids, 2:2'-diamino- $\alpha\alpha'$ -dinaphthyl (cf. Mascarelli and Brusa, A., 1914, i, 267) shows definite indications of scission into two optical antipodes, but 1:1'-diamino- $\beta\beta'$ -dinaphthyl exhibits no such indications. This behaviour is in accord with the theory, since with the $\alpha\alpha$ -disubstituted derivatives, rotation of the two naphthyl nuclei round their joining axis cannot be hindered by the presence of the two adjacent amino-groups (cf. Mills and Elliott, A., 1928, 748; Kuhn and Albrecht, *ibid.*, 1015).

T. H. POPE.

Reduction of nitro-compounds by aromatic ketols. II. Some *o*-, *m*-, and *p*-azoxy-compounds. H. B. NISBET (J.C.S., 1928, 3121—3124).—The method previously described (A., 1927, 1063) is successful in the reduction of *p*-nitro-compounds; with *o*- and *m*-nitro-compounds the yields are inferior, owing to difficulty in isolation of the azoxy-compounds. The following are prepared (benzoin being used for each reduction): *p*-azoxybenzylideneacetophenone; *o*- and *m*-isomerides of the latter, m. p. 141—142° (sintering at 135°), and 156—157°, respectively; 2-*o*-, 2-*m*-, and 2-*p*-azoxystyryl-3-methylchromones, m. p. 202°, 275.5°, and 289°, respectively; *o*-, *m*-, and *p*-azoxybenzylidene-*p*-bromoanilines, m. p. 299°, 120°, and 218°, respectively; *m*-azoxybenzylidene-*p*-toluidine, m. p. 150° (sintering at 135°); ethyl *p*-azoxybenzoate; and 2-nitro-3-azoxyltoluene, m. p. 164°. 2-*o*-, 2-*m*-, and 2-*p*-Nitrostyryl-3-methylchromones, m. p. 161°, 212°, and 238°, respectively, were prepared by condensation of 2:3-dimethylchromone with the appropriate nitrobenzaldehyde (cf. Heilbron and others, J.C.S., 1923, 123, 2565), and *m*-nitrobenzylidene-*p*-bromoaniline, m. p. 84°, by condensation of *m*-nitrobenzaldehyde and *p*-bromoaniline.

It was not found possible to isolate *o*-azoxybenzylidene-*p*-toluidine, *m*- or *p*-azoxybenzoates, *o*- or *m*-azoxybenzonitrile, α -azoxynaphthalene, or azoxybenzene itself, but nitrobenzene was found to give with benzoin, anisoin, and furoin, 30—40%, 80%, and 90% yields of benzil, anisil, and furil, respectively.

E. W. WIGNALL.

Metallic complexes [co-ordination compounds] of *o*-amino- and *o*-hydroxyazo-derivatives. G. B. CRIPPA [with F. VICINI, G. LEVI, and A. MANGANO] (Gazzetta, 1928, 58, 716—726; cf. Crippa and Venturini, A., 1927, 1180).—The following compounds are described, all the metallic compounds being of the general type $[X \cdot C_{10}H_7 \cdot N:NR]_2M$: *p*-acetophenoneazo- β -naphthol, m. p. 180° (oxime, m. p. 234—235°); phenylhydrazone, m. p. 165°; semicarbazone, m. p. above 300°, giving a nickel compound, m. p. above 300°, a cupri-compound, m. p. above 300°, and a cobalto-compound (?), m. p. 275°. The corresponding methyl

ether, m. p. 134—135° [oxime, m. p. 250°; phenylhydrazone, m. p. 87—88°; semicarbazone, m. p. 210°], and ethyl ether, m. p. 102° (oxime, m. p. 161—162°; phenylhydrazone, m. p. 64°; semicarbazone, m. p. 190°), form no such metallic compounds, nor does benzeneazo- β -naphthol or *p*-phenolazo- β -naphthylamine.

Nickelo- and cupri- (and in three cases cobalto-) compounds of the following are described: *p*-phenolazo- β -naphthol, *o*-, *m*-, and *p*-nitrobenzeneazo- β -naphthol, *o*-, *m*-, and *p*-nitrobenzeneazo- β -naphthylamine. β -Naphtholazobenzene-*p*-sulphonic acid forms a nickel salt, $C_{32}H_{22}O_6N_4S_2Ni$, and an ammonium-cupri-derivative, $[OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot SO_3]_2Cu(NH_4)_2$; with cobalt the result is uncertain. Potassium β -naphthylamineazobenzene-*p*-sulphonate gives no positive result with nickel or cobalt, but with copper forms an ammino-cupri-derivative, $[NH_2 \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot SO_3]_2Cu(NH_3)_4K_2$, which when heated in aqueous solution is converted into potassium phenyl- $\alpha\beta$ -naphthotriazole-*p*-sulphonate (cf. Witt and Schmitt, A., 1894, i, 608).

The general conclusions are that a *p*-hydroxyl group hinders co-ordination, whilst *p*-nitro- and *p*-acetyl groups have no such action; the small number of cobalt compounds is considered to be due to the nature of the metal rather than that of the organic compounds.

E. W. WIGNALL.

Action of phthalic anhydride on aminoazo-derivatives. G. B. CRIPPA and P. GALIMBERTI (Gazzetta, 1928, 58, 731—738).—In an attempt to protect the amino-group of benzeneazo- β -naphthylamine by condensation with phthalic anhydride, it was found that the latter decomposes the former substance, which loses its benzeneazo-group and gives rise to β -naphthylphthalimide, nitrogen being evolved. *p*-Acetophenoneazo- and α -naphthaleneazo- β -naphthylamines also yield β -naphthylphthalimide. α -Naphthylamine derivatives, on the other hand, condense to the anticipated phthalimido-derivatives, from which the corresponding phthalamic acids are obtained by alkaline hydrolysis of the phthalimide ring.

[With A. BORRONI].—The following are described: 1-benzeneazo-4-phthalimidonaphthalene, m. p. 219° (acid; barium salt); 1-*o*- and 1-*m*-tolueneazo- and 1-*p*-bromobenzeneazo-4-phthalimidonaphthalenes, m. p. 194°, 198°, and 243°, respectively; 4-*p*-acetophenoneazo- α -naphthylamine, m. p. 197°, and its 4-phthalimidonaphthalene derivative, m. p. 249°; potassium 4-phthalimido- α -naphthaleneazobenzene-*p*-sulphonate; and 1- α - and 1- β -naphthaleneazo-4-phthalimidonaphthalenes, m. p. 211° and 257°, respectively.

E. W. WIGNALL.

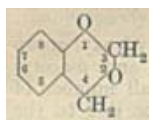
Thiocarbamido-derivatives in the azo series. G. B. CRIPPA [with G. FAINTI] (Gazzetta, 1928, 58, 726—731).—*p*-Aminoazobenzene and carbon disulphide react in alcoholic solution, giving *s*-di-*p*-benzeneazophenylthiocarbamide, m. p. 202°, oxidised by peracetic acid to *s*-di-*p*-benzeneazophenylcarbamide, m. p. 270—271°, and reduced to *pp'*-diaminodiphenylthiocarbamide, which is converted by carbon disulphide into di-*p*-phenylenedithiocarbamide (cf. Bolser and Hartshorn, A., 1924, i, 317). Similarly, *s*-di-4-benzeneazonaphthylthiocarbamide, m. p. 165°, *s*-di-4-*o*-tolueneazonaphthylthiocarbamide, m. p. 160°, and the

corresponding *m*- and *p*-compounds, *m. p.* 172° and 185°, respectively, are prepared. The *p*-compound when subjected to prolonged boiling with acetic acid furnishes a product free from sulphur, *m. p.* 215°. *o*-Aminoazobenzene reacts very slowly with carbon disulphide, yielding *s*-*di-o*-benzeneazophenylthiocarbamide, *m. p.* 100°; similarly, benzeneazo- β -naphthylamine slowly gives *s*-*di-1*-benzeneazo- β -naphthylthiocarbamide.

E. W. WIGNALL.

Mechanism of the formation of 2:4-dinitrophenol from benzene and nitric acid in presence of mercury salts as catalysts. A. I. ZAKHAROV. —See this vol., 152.

Condensation of dichloroacetaldehyde with phenols. F. D. CHATTAWAY and A. A. MORRIS (J.C.S., 1928, 3241—3246).—The condensation of phenols with aldehydes to form a dioxin ring (annexed formula) is not confined to chloral (A., 1928, 632, etc.): dichloroacetaldehyde reacts even more readily. When its alcoholate is added slowly to a cooled solution of *p*-nitrophenol in concentrated sulphuric acid, 6-nitro-2:4-bis(dichloromethyl)-1:3-benzdioxin (I),



m. p. 113.5°, is formed. This may be converted by alcoholic potassium hydroxide into 6-nitro-2(or 4)-dichloromethyl-4(or 2)-chloromethylene-1:3-benzdioxin (II), *m. p.* 108° (which does not, in spite of its apparent unsaturation, form an additive compound with bromine). If the temperature is not controlled, 5-nitro-2-ethoxymandelic acid is formed. The compound I is reduced by iron and hydrochloric acid to 6-amino-2:4-bis(dichloromethyl)-1:3-benzdioxin, *m. p.* 108.5—109.5° [hydrochloride, *m. p.* 210° (decomp.)]; acetyl derivative, *m. p.* 149—150°; diacetyl derivative, formed by the action of boiling acetic anhydride containing sulphuric acid, *m. p.* 145°. 2:4-Bis(dichloromethyl)-1:3-benzdioxin-6-diazonium chloride was prepared, and converted into the *per*-bromide, which decomposed at 128—129° or when heated in acetic acid, giving 6-bromo-2:4-bis(dichloromethyl)-1:3-benzdioxin, *m. p.* 91.5°.

When phenol is dissolved in concentrated sulphuric acid and treated with dichloroacetaldehyde alcoholate, 2:4-bis(dichloromethyl)-1:3-benzdioxin-6-sulphonic acid (+H₂O), *m. p.* 150—155° (decomp.), is obtained (ammonium salt prepared). The monohydrated sulphonic acid dissolved in concentrated sulphuric acid and treated with nitric acid is nitrated to 6:8-dinitro-2:4-bis(dichloromethyl)-1:3-benzdioxin, *m. p.* 133.5—134.5°, also obtainable by nitration of the mononitro-compound. The action of alcoholic potassium hydroxide on the dinitro-compound gives rise to 6:8-dinitro-2(or 4)-dichloromethyl-4(or 2)-chloromethylene-1:3-benzdioxin, *m. p.* 144°; this substance, again, does not combine with bromine. The monohydrated sulphonic acid is converted by phosphorus pentachloride into the corresponding sulphonyl chloride, *m. p.* 105—106°, from which methyl and ethyl 2:4-bis(dichloromethyl)-1:3-benzdioxin-6-sulphonates, *m. p.* 110—111.5° and 148—149.5°, respectively, and, with ammonia and with aniline, the sulphonamide and sulphonanilide, *m. p.* 175.5° and 166—167°, respectively, are obtained.

E. W. WIGNALL.

Steric hindrance in the behaviour of phenyl alkyl ethers and derivatives. L. C. RAIFORD and D. M. BIROSEL (Proc. Iowa Acad. Sci., 1927, 34, 222—223).—Bromination of phenyl allyl ether involves both phenyl and allyl radicals; rearrangement by heat, according to Claisen's method, of the allyl ether may cause loss of bromine.

CHEMICAL ABSTRACTS.

Effect of substituents in the formation and reactions of certain ethers. L. C. RAIFORD and G. THIESSEN (Proc. Iowa Acad. Sci., 1927, 34, 220—221).—The presence of a nitro-group in diphenyl ether interferes with the entrance of bromine to a greater degree than can be ascribed to steric hindrance. Various derivatives of Cook's tetrabromodiphenyl ether have been prepared, but its structure is still doubtful.

CHEMICAL ABSTRACTS.

New derivatives of diphenyl. A. ANGELETTI and D. GATTI (Gazzetta, 1928, 58, 630—635).—The author confirms Bell and Kenyon's view (A., 1927, 145) that the compound, *m. p.* 171°, previously obtained by him is 3:4'-dinitro-4-hydroxydiphenyl and is identical with that described by Schmidt and Schultz (A., 1881, 909) as 4'-nitro-4-hydroxydiphenyl, whilst that with *m. p.* 200—201° is 4'-nitro-4-hydroxydiphenyl (Bell and Kenyon, *loc. cit.*). 4'-Amino-4-cyanodiphenyl, *m. p.* 157°, may be prepared from diazotised benzidine, or tetrazotised benzidine solution may be mixed with benzidine hydrochloride. 4-Iodo-4'-hydroxydiphenyl, *m. p.* 194°, is obtainable either from 4-iodo-4'-aminodiphenyl or from 4-amino-4'-hydroxydiphenyl. 4-Chloro-4'-hydroxydiphenyl, *m. p.* 146—147°; 4-bromo-4'-hydroxydiphenyl, *m. p.* 155—156°; 4-chloro-4'-bromodiphenyl, *m. p.* 151—152°, and 4-chloro-4'-iododiphenyl, *m. p.* 147—148°, were also prepared.

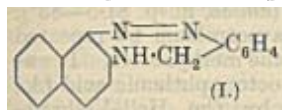
T. H. POPE.

Derivatives of cholesterol. R. L. SHRINER and L. KO (J. Biol. Chem., 1928, 80, 1—8).—Cholesteryl *p*-nitrobenzoate, *m. p.* 188.3—189.8°, [α]_D −6.48° in chloroform, gave, with hydrogen and platinum oxide in ethyl acetate, cholesteryl *p*-aminobenzoate, *m. p.* 237.4—238.5°, [α]_D +3.61° in chloroform (hydrochloride, *m. p.* 210—211°); dihydrocholesterol yielded a benzoate, *m. p.* 135—136.8°, [α]_D +21.4°, *p*-nitrobenzoate, *m. p.* 156.5—157.7°, [α]_D +20.05°, and *p*-aminobenzoate, *m. p.* 191—192°, [α]_D +26.55° (hydrochloride, *m. p.* 182.5—184.5°), all rotations being taken in chloroform. The aminobenzoates and their hydrochlorides are insoluble in water and therefore fail to exhibit antihæmolytic or anæsthetic properties.

C. R. HARRINGTON.

***o*-Aminobenzyl alcohol.** A. REISSERT and K. CRAMER (Ber., 1928, 61, [B], 2555—2566).—*o*-Aminobenzyl alcohol is prepared in 88% yield by the reduction of *o*-nitrobenzyl alcohol with aqueous sodium hydrogen sulphide. The corresponding diazo-compound decomposes with unusual ease, giving saligenin. The diazotised solution couples with *p*-toluidine, giving *p*-toluenediazo-*o*-aminobenzyl alcohol, C₆H₄Me:N:N.NH.C₆H₄.CH₂OH, *m. p.* 108—109°, which passes normally into *p*-toluidine-*o*-aminobenzyl alcohol, *m. p.* 112—113°. Resorcinol and diazotised *o*-aminobenzyl alcohol afford resorcinol-*o*-azobenzyl alcohol, *m. p.* 180—181° (monohydrate,

m. p. 159—160°). β -Naphthol-*o*-azobenzyl alcohol, m. p. 185°, is converted by concentrated sulphuric acid at 70° into the *sulphoanhydro*- β -naphthol-*o*-azobenzyl alcohol, m. p. above 300°. β -Naphthylamine-*o*-azobenzyl alcohol, m. p. 150—151°, and its *anhydro*-



compound (I), m. p. 161°, are described. *o*-Hydroxymethylbenzeneazo-2-naphthol-3-carboxylic acid, m. p. 214—216°, and the

sulphonic acid of its *anhydride*, $C_{18}H_{12}O_6N_2S$, m. p. above 320°, were prepared. Potassium xanthate and diazotised *o*-aminobenzyl alcohol give a very explosive *diazo*-compound, which passes into *ethyl o*-hydroxymethylphenylxanthate. The last-named compound is converted by boiling alcoholic potassium hydroxide into *o*-thiolbenzyl alcohol, which is too unstable to permit purification and is characterised as the *lead* salt; the *S*-benzoyl derivative has m. p. 125—126°. The mercaptan is oxidised by ferric chloride or hydrogen peroxide to *di-o*-hydroxymethylphenyl disulphide, m. p. 144°, in poor yield. Treatment of diazotised *o*-aminobenzyl alcohol with sodium sulphide yields small amounts of *di-o*-hydroxymethylphenyl sulphide, m. p. 164°, but mainly saligenin and *o*-thiolbenzyl alcohol. Under precisely defined conditions *di-o*-hydroxymethylphenyl disulphide is prepared in fairly satisfactory yield from the diazotised aminoalcohol and sodium disulphide. Treatment of the disulphide, preferably suspended in acetic acid, with chlorine affords 6-chloro-2-hydroxymethylbenzenesulphonyl chloride, m. p. 62°, readily hydrolysed by alkalis but volatile unchanged with steam from a suspension in 60% sulphuric acid. With ammonia, the chloride

yields the compound $C_6H_5Cl \cdot \begin{smallmatrix} CH_2 \\ SO_2 \end{smallmatrix} > NH$, m. p. 158° (*methyl* derivative, m. p. 127°), whereas with aniline a normal *anilide*, m. p. 94°, is obtained which is converted by warm, dilute sodium hydroxide into the *sulphinide*, $C_6H_5Cl \cdot \begin{smallmatrix} CH_2 \\ SO \end{smallmatrix} > NPh$, m. p. 151°. 7-Chlorobenzoic sulphinimide, m. p. 153.5°, is prepared by oxidation of the corresponding sulphinide with nitrous acid or potassium dichromate. The position of the chlorine atom in the sulphonyl chloride follows from its conversion by molten potassium hydroxide into 3-chloro-2-hydroxybenzyl alcohol, m. p. 116°, whilst under similar conditions 7-chlorosaccharin affords 3-chlorosalicylic acid, m. p. 170°. Reduction of *o*-nitrobenzyl alcohol by Bamberger's method gave an additive *product*, m. p. 83—84°, of hydroxylamino- and azoxybenzyl alcohol which readily passed into *o*-azoxybenzyl alcohol; later attempts to repeat the process yielded only *o*-hydroxylaminobenzyl alcohol, m. p. 104.5°.

H. WREN.

p-Tolyl triphenylmethyl ether. P. SCHORIGIN and J. MARAKOV-SEMLJANSKI (Ber., 1928, 61, [B], 2519—2521; cf. A., 1928, 59).—Attempts to prepare the ether from triphenylmethyl chloride and sodium *p*-tolyl oxide or from the chloride and *p*-cresol in pyridine gave only the variety, m. p. 114°. Indications of the formation of products of lower m. p. (cf. van Alphen, A., 1927, 660) are obtained only when impure materials are used. Decomposition of *p*-tolyl triphenylmethyl

ether in the presence of molten, anhydrous zinc chloride affords mainly triphenylcarbinol; triphenylmethane is produced only in minor amount. H. WREN.

Condensation of benzhydrol with phenols and cresols. P. SCHORIGIN (Ber., 1928, 61, [B], 2516—2519; cf. A., 1928, 59).—The action of benzhydrol on *p*-cresol in the presence of glacial acetic acid and sulphuric acid at 100° affords 2 : 6-dibenzhydryl-*p*-cresol, m. p. 189—190°. Under similar conditions, *o*-cresol gives benzhydryl-*o*-cresol, m. p. 139°, whereas phenol yields 2 : 4 : 6-tribenzhydrylphenol, m. p. 166°.

H. WREN.

Colour and chemical constitution. XXIV. Complete investigation of the triphenylcarbinol or "aniline" dyes. J. MOIR (Trans. Roy. Soc. S. Africa, 1928, 17, 51—59).—The absorption wavelengths of 23 substances have been determined. 4 : 4'-Dihydroxybenzhydrol (I) (cf. A., 1923, ii, 108) has λ 539 (also $\lambda\lambda$ 487, 450 : wave-lengths on which comparisons are based are given first in each case); assuming the factor for replacement of $\cdot OH$ by $\cdot NH_2$ to be 1.008, and by $\cdot NMe_2$ to be 1.058, the following values are calculated for benzhydrol derivatives, mostly in acid solution, and are compared with the observed values (in parentheses): 4-amino-4'-hydroxy- (II), λ 543 (alkaline, λ 541; also $\lambda\lambda$ 552, 492); 4 : 4'-diamino- (III) λ 548 (half-neutralised, λ 548; also $\lambda\lambda$ 580, 495); 4-dimethylamino-4'-hydroxy- (IV), λ 570 (neutral, λ 571; also λ 563); 4-amino-4'-dimethylamino- (V), λ 574.5 (half-neutralised λ 574; also $\lambda\lambda$ 591, 491); and 4 : 4'-bisdimethylamino- (VI), λ 603 (half-neutralised, λ 603; also $\lambda\lambda$ 565 and 380).

In the triphenylcarbinol series (cf. A., 1921, ii, 6), using the above factors, together with the factor 1.025 for replacement of central $\cdot H$ of benzhydrol by $\cdot Ph$, the values for the six products corresponding respectively with the six substances above are: benzaurin (VII), λ 552.5 (553; also 493, 455); aminofuchson (VIII), λ 556.5 (558; also 564, 499); Doebner's violet (IX), λ 561.5 (562; also 582, 497, 380); dimethylaminofuchson (X), λ 584.5 (neutral, λ 585; also 530, 500); dimethylaminofuchsonimonium chloride $NH_2 \cdot C_6H_4 \cdot CPh \cdot C_6H_4 \cdot NMe_2 \cdot Cl$ (XI), λ 589 (590; also 410); malachite-green (XII), λ 618 (618; also 440). The absorption of 11 compounds has thus been accurately calculated from I by three factors.

In the series of aurin and its analogues, absorption bands in alkali and acid are obtained, which almost correspond with one absorption band of the substances I—VI; thus: aurin (XIII), alkaline, λ 534 (cf. I), acid, λ 485 (λ , 487), also $\lambda\lambda$ 548 and 503; parafuchsin (XIV), neutral λ 543 (cf. III), acid λ 572 (λ_{III} 580), also λ 360; crystal-violet (XV), neutral, λ 596 (cf. VI), also $\lambda\lambda$ 632 and 417 (see below). From the above it is deduced that the factor for calculating λ of a 3-ring compound from λ of the corresponding 2-ring compound is 0.99.

The following are also examined: aminobenzaurin (XVI), alkaline, λ 555, acid, λ 495 (cf. II, acid, $\lambda\lambda$ 552 and 492), also λ 457; diaminofuchson (XVII), acid, λ 556 (cf. II, λ 552), also λ 580, 433, 492; dimethylaminobenzaurin, neutral, λ 575 (cf. IV), also $\lambda\lambda$ 548, 552, 507, and 497; bisdimethylaminofuchson (XIX), alkaline, λ 573 (cf. IV), also $\lambda\lambda$ 605, 505, and 460;

dimethylparafuchsine (XX), neutral, λ 587 (cf. V, acid, λ 590), also λ 455, 549, and 499; tetramethylparafuchsine (XXI), neutral, λ 586 (cf. V), also λ 628, 460, and 420; and dimethyldiaminofuchsone (XXII), neutral, λ 590 (cf. V), also λ 624, 489, 545, 453, and 420. These resemblances, with the additional λ observed, are discussed on the basis of the author's theory (J.C.S., 1921, 119, 1656, 1664), which is now modified by assuming that the orbits described are those of the electrons of the central carbon atom only.

The colour change on acidification of such a substance as crystal-violet (XV) (λ 596, violet \rightarrow λ 632, green) is ascribed to the behaviour of the $\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2^+$ group merely as a loaded benzene ring, not competing for the central electron (cf. iodine-green, λ 634; XII, λ 618; *p*-nitro-, λ 646, *p*-amino-malachite-green, λ 628). The effect of addition of further acid (λ 632 \rightarrow λ 417, yellow) can be considered as due to the behaviour of a second $\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2^+$ group as a loaded benzene ring (cf. XII, acid, λ 440; fuchsone-dimethylmonium chloride, λ 455; tetramethylfuchsine, acid, λ 420 and 460).

The behaviour of other of the above substances is discussed; the large number of absorption bands of XXII is to be attributed to the large number of the theoretically possible quinonoid forms. The author suggests, in addition to his postulated "elliptical" and "trefoil" orbits, a third type, probably a distorted circular orbit, conditioned by the combinations $\cdot\text{ONa}$, $\cdot\text{NH}_2\cdot\text{OH}$ and $\cdot\text{ONa}$, $\cdot\text{NMe}_2\cdot\text{OH}$.

The products of replacement of $\cdot\text{OH}$ by $\cdot\text{NH}_2$ and $\cdot\text{NMe}_2$ in *p*-hydroxybenzyl alcohol (λ 293) have λ 335 and 390, in *p*-hydroxybenzhydrol (λ 320) have λ 350 and 400, and in fuchsone (λ 371) have λ 425 and 455, respectively. E. W. WIGNALL.

Naphthenic acids. VIII. Polymethylene rings of naphthenic acids in Japanese petroleum. IX. Constitution of octanaphthenic acid from Nishiyama petroleum. T. KUWATA (J. Fac. Eng. Tokyo, 1928, 17, 305—310, 311—317).—VIII. Certain fractions of naphthenic acids derived from petroleum from Nishiyama (paraffin base oil) and Kurokawa (asphalt base oil) (cf. A., 1925, i, 1271; 1923, i, 464) were reduced to the corresponding hydrocarbons and the latter compared. A fraction containing undeca- and dodeca-naphthenic acids from Nishiyama oil, b. p. 133—170°/9 mm., d_4^{20} 0.9629, n_D^{20} 1.4649, was converted into the phenyl ester by reaction of the acid chloride with phenol. The ester was then reduced by sodium and alcohol to the naphthene alcohol, b. p. 100—133°/9 mm., d_4^{20} 0.8953, n_D^{20} 1.4592. This was converted by the action of phosphorus and iodine into the iodide, which was then reduced by zinc amalgam in alcohol to the hydrocarbon (C, 85.45; H, 15.04%), b. p. 160—192°, d_4^{20} 0.7930, n_D^{20} 1.4336. When passed over platinum-black at 300° (cf. Zelinski and Pavlov, A., 1923, i, 767) the hydrocarbon was practically unchanged, and cyclohexane compounds therefore appear to be absent. By similar methods a fraction of naphthenic acids (chiefly tridecanaphthenic acid) from Kurokawa petroleum, b. p. 168—198°/9 mm., d_4^{20} 0.9942, n_D^{20} 1.4744, yielded the alcohol, b. p. 126—155°/9 mm., d_4^{20} 0.9270, n_D^{20} 1.4756, and a hydrocarbon (C, 86.66; H, 13.67%), b. p. 203—243°, d_4^{20} 0.8425,

n_D^{20} 1.4548. When passed over platinum-black at 300° a slight change in properties occurred and some gas was formed, indicating the presence of a small proportion of cyclohexane compounds.

IX. Octanaphthenic acid, $\text{C}_8\text{H}_{14}\text{O}_2$, b. p. 231.5—237.5°, d_4^{20} 0.9417, n_D^{20} 1.4318 (*amide*, m. p. 81.5—83°), was isolated from Nishiyama petroleum by repeated fractionation of the acid and the methyl ester. It was not identical with Aschan's octanaphthenic acid (A., 1891, 1452). Bromination by the Hell-Volhard-Zelinski method yielded *methyl α -monobromo-octanaphthenate*, b. p. 95—105°/9 mm., which when heated with dilute potassium hydroxide yielded *α -hydroxy-naphthenic acid*, d_4^{20} 1.023, n_D^{20} 1.4518. This was oxidised by lead peroxide to a substance (? methyl cyclopentyl ketone or dimethylcyclopentanone) (*semicarbazone*, m. p. 89—90°) of ketonic properties, containing some aldehyde, which was oxidised by alkaline permanganate to a neutral substance, m. p. 80—81°, accompanied by a (?) dibasic acid. R. K. CALLOW.

Catalytic reduction of nitriles and oximes. W. H. HARTUNG (J. Amer. Chem. Soc., 1928, 50, 3370—3374).—Hydrogenation of benzonitrile or benzaloxime in alcohol using palladised charcoal yields pure benzylamine if at least 1 mol. and 3 mols., respectively, of hydrogen chloride are present (cf. Braun and others, A., 1923, i, 1087; Rosenmund and Pfankuch, A., 1924, i, 34); otherwise secondary bases and ammonia are also formed. Mandelonitrile is similarly reduced to β -phenylethylamine (52% of the theoretical), whilst its benzoate and acetate yield 84.5% and 74.5% of theory, respectively, of the same product. Attempts to avoid reduction of the hydroxyl group were unsuccessful. H. E. F. NOTTON.

Isomorphous replacement of a chlorine atom by the hydroxyl group in organic compounds. V. VILLIGER (Ber., 1928, 61, [B], 2596—2599).—2:4-Dichlorobenzotrichloride is heated at 70—80° with 95% sulphuric acid until evolution of hydrogen chloride ceases, and the solution, after removal of dissolved hydrochloric acid, is treated with the calculated quantity of 50% nitrating acid at 10°. 2:4-Dichloro-5-nitrobenzoic acid thus produced has m. p. 161—163° after purification through the sparingly soluble calcium salt. The acid is transformed by an excess of sodium hydroxide into 2-chloro-5-nitro-4-hydroxybenzoic acid, m. p. 202—204°, from which any unchanged dichloro-acid is removed by purification through the barium salt. The m. p. of mixtures of the two acids lie approximately on a straight line connecting the m. p. of the individual acids, thus suggesting the formation of an isomorphous series. H. WREN.

Esterification of aromatic and olefinic nitriles. P. PFEIFFER, I. ENGELHARDT, and W. ALFUSS (Annalen, 1928, 467, 158—190).—A review of previous work (Pfeiffer and others, A., 1911, i, 448; 1916, i, 24, 327; 1918, i, 344; 1925, i, 547) and that now recorded leads to the generalisation that a single *o*-substituent inhibits practically completely the conversion of an aromatic nitrile into a carboxylic ester by heating it with methyl or ethyl alcohol and hydrogen chloride. The chemical nature of the substituent plays a minor part, for the methyl, nitro-, chloro-, phenyl, and vinyl

groups all act in the same way. The rule is similar to that which applies to the formation of imino-ethers (Pinner, "Imidoather und ihre Derivate," 1892). Acting on the assumption that aromatic nitriles may be considered as a special class of olefinic nitriles, a number of α -substituted cinnamonitriles were examined. By starting with the *cis*- and *trans*-acids, converting these into the amides, and dehydrating, the *cis*- and *trans*-nitriles were prepared. It was then found that the *trans*-compounds were in all cases easily esterified, but that the *cis*-compounds were esterified not at all or only very slowly under the usual conditions. This accords with the similarity of the configurations of the *cis*-compounds and *o*-substituted aromatic nitriles. Ease or difficulty of esterification is, in the absence of other evidence, indicative of *trans*- or *cis*-configuration, respectively.

Whilst 4-dimethylaminostilbene, the 4'-nitro-derivative, and the 4'-nitro-2'-cyano-derivative, and the amide, acid, and esters corresponding with the last are fluorescent, transposition of the nitro- and cyano-groups yields a non-fluorescent compound (2'-nitro-4-dimethylamino-4'-cyanostilbene), and the corresponding methyl and ethyl carboxylic esters are likewise non-fluorescent.

The esterification of the nitriles was carried out by refluxing with 40 parts of anhydrous alcohol for 2 hrs. while a stream of hydrogen chloride was passed in, and the amount of ester in the washed product was determined from the percentage of nitrogen. The following data are recorded, the figures in parentheses denoting the percentage of methyl or ethyl esters, respectively, found in the product; when only one figure is given it refers to the methyl ester: Benzonitrile (65.4, 35.1); toluonitriles: *o*- (0, 0); *m*- (92.1, 58.7); *p*- (83, 80); nitrobenzonitriles: *o*- (0, 0); *m*- (87, 45); *p*- (both high); *m*-nitro-*o*-toluonitrile (0); *m*-nitro-*p*-toluonitrile (high); chlorobenzonitriles: *o*- (0, 0); *p*- (97, 67.9); *o*-phenylbenzonitrile, b. p. 176—177°/16 mm. (prepared from *o*-phenylbenzoic acid by way of the chloride and amide), (8.4, 5.6); *p*-phenylbenzonitrile (82, 70.4); naphthonitriles: α - (0, 0); β - (77.1, 77); 4'-nitro-2'-cyano-4-dimethylaminostilbene (0); cinnamonitrile (96.2, 85); α -methylcinnamonitrile, b. p. 120°/14 mm. (from α -methylcinnamic acid by way of the chloride and amide) (69.8, 36.8). *cis*- α -Chlorocinnamonitrile, m. p. 19—21°, b. p. 128°/16 mm., and *trans*- α -chlorocinnamonitrile, m. p. 34°, b. p. 138—139°/17 mm., were prepared from the corresponding acids. Both were esterified readily, but inversion of the *cis*-compound occurred, for the *trans*-ester was formed in each case. *cis*- α -Phenylcinnamonitrile was not esterifiable. *trans*- α -Phenylcinnamonitrile, m. p. 49—51°, from the *trans*-acid, was esterified easily (39). From *cis*- α -phenyl-*m*-nitrocinnamic acid were prepared the *chloride*, m. p. 101°, *amide*, m. p. 176°, and *nitrile*, m. p. 133—134°, (0) (identical with the product of condensation of phenylacetone and *m*-nitrobenzaldehyde). From the *trans*-acid were prepared the *chloride*, m. p. 93°, *amide*, m. p. 146°, and *nitrile*, m. p. 96° (51). From *cis*- α -phenyl-*p*-nitrocinnamic acid were prepared the *chloride*, m. p. 88—91.5°, *amide*, m. p. 208.5—210°, and *nitrile*, m. p. 121—122° (0). From the *trans*-acid were prepared the *chloride*, m. p. 95°, *amide*, m. p. 183—184°, and *nitrile*, m. p. 121—

122° (48). The *cis*- and *trans*-*p*-dimethylamino-*p*-nitrophenylcinnamamides (cf. A., 1928, 1132) yielded on dehydration the same (*cis*-)*nitrile*, m. p. 241—242°, which was not esterifiable. From dibenzylidenepropionic acid were prepared the liquid *chloride*, the *amide*, m. p. 178—179°, and (*cis*-)*nitrile*, m. p. 115—116° (0, 0). (*cis*-) α -Benzenesulphonylcinnamonitrile was not esterifiable. From α -phenylcrotonic acid were prepared the *amide*, m. p. 98—99°, and the (*cis*-)*nitrile*, b. p. 125°/13—14 mm. (9.6, 7.9). An attempt to prepare the *nitrile* by condensation of phenylacetone with paraldehyde was unsuccessful. $\alpha\beta$ -Diphenylpropionitrile was readily esterified (64, high). 4'-Nitro-4-dimethylaminostilbene-2-carboxylic acid, m. p. 206° (decomp.) (*methyl* ester, m. p. 158—159°; *ethyl* ester, m. p. 139—140°), was prepared by hydrolysis of the *amide*, m. p. 242—243° (decomp.), obtained by condensation of *p*-dimethylaminobenzaldehyde with *p*-nitro-*o*-toluamide in presence of piperidine. R. K. CALLOW.

Pyridine as a catalyst in Perkin's synthesis of cinnamic acid. G. BACHARACH and F. BROGAN (J. Amer. Chem. Soc., 1928, 50, 3333—3334).—Addition of 8 drops of pyridine to a mixture of 20 g. of benzaldehyde, 30 g. of acetic anhydride, and 10 g. of sodium acetate, refluxed for 8 hrs., increased the yield of cinnamic acid from 60.7% of the theoretical to an optimum value of 85%. H. E. F. NOTTON.

Reactions of nitroso-derivatives with unsaturated compounds. VII. New isomerides of *o*-nitrophenylpropiolates and isatogenates. L. ALESSANDRI (Gazzetta, 1928, 58, 738—742).—A preliminary note on the properties of the colourless isomerides of ethyl and methyl *o*-nitrophenylpropiolates and isatogenates, previously described (this vol., 64). The colourless compound of m. p. 122° can be obtained in considerable quantity by appropriate treatment of ethyl *o*-nitrophenylpropiolate, which it resembles in composition ($C_{11}H_9O_4N$) and mol. wt. When heated, it undergoes, at about 125°, an exothermic and irreversible change into a further yellow *isomeride*, m. p. 150—151°. Methyl *o*-nitrophenylpropiolate similarly yields a colourless *isomeride*, $C_{10}H_7O_4N$, which has two crystalline forms, m. p. 139° and 141°, respectively, and is converted by heating into a yellow *isomeride*, which also exhibits two forms, m. p. 149—150° and 161—162°, respectively. The yellow substances may perhaps belong to the same class as those described by Ruggli (A., 1919, i, 221; A., 1923, i, 833). E. W. WIGNALL.

Diethylaminoethanol esters of diphenyl-2-carboxylic acid and derivatives. F. BELL (J.C.S., 1928, 3247—3249).—In view of the anæsthetic action of diethylaminoethyl diphenate (Roberts and Johnson, A., 1925, i, 816) some similar acids were prepared. Diphenyl-2-carboxyl chloride, b. p. 163°/10 mm. (which has a strong tendency to pass into fluorenone on distillation, and with 2-aminodiphenyl yields diphenyl-2-carboxy-2'-diphenylamide, m. p. 194°), reacts with diethylaminoethyl alcohol to give diethylaminoethyl diphenyl-2-carboxylate, b. p. 183°/1 mm., of which the *hydrochloride*, m. p. 109—110°, has anæsthetic action. Similarly, diphenyl-4-carboxyl

chloride yields *diethylaminoethyl diphenyl-4-carboxylate* (*hydrochloride*, m. p. 183°).

By the action of thionyl chloride on diphenamic acid, 2'-cyanodiphenyl-2-carboxyl chloride, m. p. 84°, is obtained, with some diphenimide; the chloride when heated distils at 222°/15 mm., giving a liquid containing only 3% of 4-cyanofluorenone, m. p. 243—244° (cf. Borsche and Sander, A., 1915, i, 299, whose process for preparing the compound from phenanthraquinone monoxime must depend on the formation of the above acid chloride). *Diethylaminoethyl 2'-cyanodiphenyl-2-carboxylate* forms a *hydrochloride*, m. p. 189°. E. W. WIGNALL.

Derivatives of 2-methylanthracene obtained by the action of oxalyl chloride. D. BUTESCU (Bull. Soc. chim., 1928, [iv], 43, 1269—1272).—Addition of 2-methylanthracene in carbon disulphide in presence of aluminium chloride to nascent oxalyl chloride (a mixture of oxalic acid and phosphorus pentachloride) at the ordinary temperature gives no aceanthrenequinone but about 10% of 10-chloro-2-methylanthracene-9-carboxylic acid, m. p. 158°, oxidised to 2-methylanthraquinone, and 2-methylanthracene-3-carboxylic acid, together with 9:10-dichloro-2-methylanthracene, m. p. 211°, which shows the blue fluorescence characteristic of 9:10-substituted anthracenes. Lower temperatures thus promote chlorination, whilst higher temperatures appear to favour the introduction of the carboxyl group (cf. Liebermann and others, A., 1912, i, 467).

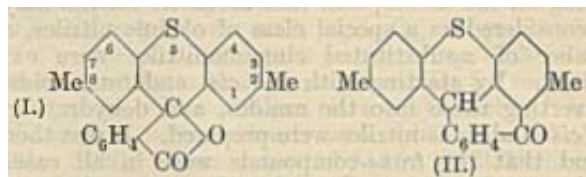
R. BRIGHTMAN.

Lichen products. VI. Synthesis of divaric acid. A. SONN [with J. BURKARD] (Ber., 1928, 61, [B], 2479—2481).—Ethyl acetoacetate and methyl Δ^6 -hexene- α -carboxylate in presence of alcoholic sodium alkoxide afford *ethyl n-propyldihydroresorcinol-carboxylate*, m. p. 85—87°, which is converted successively into *ethyl dibromo-n-propylresorcinol-carboxylate*, m. p. 77—78°, and *dibromo-n-propylresorcinolcarboxylic acid*, m. p. 158—160° (decomp.) after softening. The dibromo-acid is transformed in alkaline solution by hydrogen in presence of palladised calcium carbonate into 2:4-dihydroxy-6-n-propylbenzoic acid, identical with divaric acid.

H. WREN.

Action of phthaloyl chloride on *p*-tolyl methyl ether and *p*-tolyl methyl sulphide. R. WEISS and W. KNAPP (Monatsh., 1928, 50, 392—398).—Phthaloyl chloride reacts with *p*-tolyl methyl ether in presence of carbon disulphide and aluminium chloride, forming 6':6''-dimethoxydi-*m*-tolylphthalide, m. p. 170°, condensation occurring *ortho* to the methoxyl group. Reduction of this with sodium amalgam and alcohol yields 2':2''-dimethoxy-*o*':5''-dimethyltriphenylmethane-2-carboxylic acid, m. p. 212—214°, converted by oxidation with alkaline potassium permanganate into 2':2''-dimethoxytriphenylmethane-2:5':5''-tricarboxylic acid, m. p. 318°—320° (slight decomp.). Treatment of this phthalin with cold, concentrated sulphuric acid gives 1:2'-dimethoxy-9-phenylanthrone-4:5'-dicarboxylic acid, m. p. 340° (decomp.), by way of the corresponding anthranol. With *p*-tolyl methyl sulphide condensation occurs with loss of two methyl groups and a sulphur atom and 2:8-di-

methyl-5-thiofluoran (I), m. p. 228—230°, results. This is reduced by sodium amalgam and alcohol to 2:8-dimethyl-5-thiohydrofluoranic acid, m. p. 192—195°



(gelatinous sodium salt), convertible by treatment with phosphorus pentoxide in boiling benzene into *dimethyl-cæthione* (II), m. p. 188—190° (decomp.).

H. BURTON.

Condensation of phthalic anhydride with *o*-dichlorobenzene. M. TANAKA and N. TANAKA (Bull. Chem. Soc. Japan, 1928, 3, 286—287).—Phthalic anhydride and *o*-dichlorobenzene condense in presence of anhydrous aluminium chloride at 120°, yielding *o*:3:4-dichlorobenzoylbenzoic acid, m. p. 190°, whilst at 150° 2:3-dichloroanthraquinone, m. p. 265—267°, is produced.

Phthalic anhydride and *o*-chlorophenol react in presence of boric and concentrated sulphuric acids at 255° for 3 hrs., giving purpurin (cf. A., 1927, 566).

H. BURTON.

Naphthalic acid derivatives. K. DZIEWONSKI and A. KOCWA [with O. GESCHWINDOVNA] (Bull. Acad. Polonaise, 1928, A, 405—431; cf. Dziewoniski and others, B., 1924, 901; A., 1926, 70, 279).—Compounds obtained from the sulphonation products of acenaphthene and 1:8-naphthalic acid and its anhydride are described. 4-Sulphonaphthalic acid is converted by alkaline fusion into 4-hydroxynaphthalic anhydride, m. p. 350—351°, which when heated with potassium hydroxide at 320° yields 5-hydroxy- α -naphthoic acid, m. p. 235° (benzoate, m. p. 241°), or with phosphorus pentachloride at 200° 4-chloronaphthalic anhydride, m. p. 216—217° (*imide*, m. p. 301—302°), also obtainable from the sulphonic acid by similar means. 4-Bromonaphthalic anhydride, m. p. 219—220° (*imide*, m. p. 286°; phenylhydrazone, m. p. 233—224°), is prepared by the action of phosphorus pentabromide on 4-sulphonaphthalic acid, whilst 4-hydroxynaphthalic anhydride yields a *bromohydroxy-anhydride*, m. p. 266—267°.

3-Sulphonaphthalic acid, m. p. 198° (*aniline salt*, m. p. 297°; *sulphonyl chloride*, m. p. 212—213°; *imide-sulphonamide*, m. p. 348°), is converted by phosphorus pentachloride into 3-chloronaphthalic anhydride, m. p. 223—224° (*imide*, m. p. 315°), which condenses with resorcinol to give a *fluorescein*, m. p. 170°. From 3-hydroxynaphthalic anhydride and phosphorus pentabromide is obtained a *bromohydroxy-anhydride*, m. p. 284—285° (benzoate, m. p. 252—253°; *imide*, m. p. 339°).

2-Sulphonaphthalic acid [*aniline salt*, m. p. 290° (decomp.)] yields on alkaline fusion 2-hydroxynaphthalic anhydride, m. p. 245—246° (*methyl ether*, m. p. 255°; *phenylhydrazone*, m. p. 238—239°; *imide*, m. p. 303—304°); the corresponding acid couples with *p*-nitrodiazobenzene, with loss of the 1-carboxyl group, to give an *azo*-compound readily converted by

warm acids or organic solvents into the *peri-naphthapyridazone* (annexed formula), m. p. 336—337° (decomp.). Mere benzoylation also removes the 1-carboxyl group and yields the *benzoate*, m. p. 196—197°, of 2-hydroxy-8-naphthoic acid, m. p. 257° (acetate, m. p. 221—222°; *anilide*, m. p. 209—210°). From 2-hydroxynaphthalic acid are prepared the 2-chloro-anhydride, m. p. 246—247° (*imide*, m. p. 332—333°), and the 2-bromo-anhydride, m. p. 253—254° (*imide*, m. p. 318°; *phenylhydrazone*, m. p. 251—252°).
C. HOLLINS.

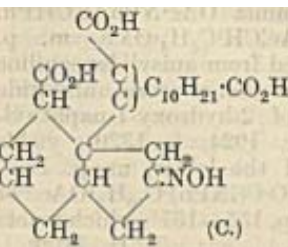
Action of magnesium *o*-tolyl bromide on the dilactone of benzophenone-2:2'-dicarboxylic acid. R. WEISS and S. R. KRATZ (*Monatsh.*, 1928, 50, 429—435).—When the dilactone of benzophenone-2:2'-dicarboxylic acid is treated with magnesium *o*-tolyl bromide in cold benzene solution and the mixture then heated on the water-bath, 2'-*o*-toluoyl-benzophenone-2-carboxylic acid (I), m. p. 188—192°, is produced. If the reaction is performed throughout in boiling benzene there is formed some 2-methylbenzophenone-2'-phthalide (II), m. p. 170—174°, a reduction product of I. Reduction of I with red phosphorus and hydriodic acid in boiling acetic acid solution gives 2-methyl-2'-phthalidodiphenylcarbinol, m. p. 145—147°, whilst oxidation with alkaline potassium permanganate yields the dilactone (III) of 2'-(*o*-carboxybenzoyl)-benzophenone-2-carboxylic acid,

$\text{CO}-\text{C}_6\text{H}_4-\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}-\text{C}_6\text{H}_4-\text{CO}$, m. p. 280—282°, formed also by oxidation of II with chromic anhydride in boiling acetic acid solution. Treatment of III with excess of hydrazine hydrate affords *o*-phenylene-1:1'-di-(4-hydroxyphthalazine), m. p. 350°; aluminium chloride at 200° converts III into 1-benzoyl-anthraquinone-2'-carboxylic acid, whilst reduction with red phosphorus and hydriodic acid in boiling acetic acid solution gives *o*-phenylenedipthalide, m. p. 198—200°. Reduction of this last compound with sodium and absolute alcohol yields 2'-(*o*-carboxybenzyl)diphenylmethane-2-carboxylic acid, m. p. 235—237°.

H. BURTON.

Bile acids. XXII. M. SCHENCK and H. KIRCHHOFF (*Z. physiol. Chem.*, 1929, 180, 107—123).—Bilanic acid monoxime (A., 1928, 1134) undergoes no rearrangement by treatment with sulphuric acid, but dehydrodeoxycholic (α -diketochoholic) acid dioxime (Schenck, A., 1923, i, 678) is converted into the

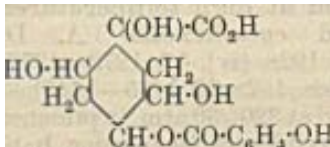
487) when heated for 1 hr. with 20% hydrochloric acid slowly eliminates 1 mol. of hydroxylamine, yielding a substance, decomp. 205° (indefinite), and giving a yellow colour with nitric acid (see below). Hence it seems that an oximino-group attached to ring III does not undergo rearrangement, which is restricted to rings I and II. All oximes and their rearrangement



products which contain an oximino-group in the 12-position give a green or bluish-green colour with nitric acid (*d* 1.4) and this reaction is applied to elucidate the structure of a large number of oximes and their rearrangement products. Thus the green colour is obtained with dehydrocholic acid trioxime and isotrioxime, and with the substance $\text{C}_{21}\text{H}_{33}\text{O}_9\text{N}_2$ (obtained by the action of hydrochloric acid on bilanic acid isodioxime), which is assigned the structure B, fission of the lactam ring having occurred. Positive tests are also obtained with β -diketochoholic acid dioxime and its rearrangement product (Borsche and Wieckhorst, A., 1921, i, 729) and with pseudodeoxybilanic acid oxime, which is therefore given structure C. Negative results (yellow or brown colour only) are obtained with dehydrodeoxycholic acid dioxime, deoxybilanic and isodeoxybilanic acid oximes. Structural formulæ for all the above compounds are suggested.

J. W. BAKER.

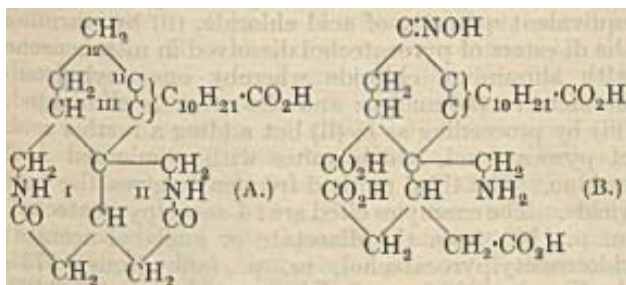
Monoacyl derivatives of quinic acid. III. Synthesis of 4-*p*-hydroxybenzoylquinic acid. K. JOSEPHSON (*Annalen*, 1928, 467, 287—294).—*iso*-Propylidenequinide is converted by *p*-acetoxybenzoyl chloride in presence of pyridine and chloroform into 4-*p*-acetoxybenzoyl*iso*propylidenequinide (I), m. p. 166—167° (corr.), $[\alpha]_{\text{D}}^{20}$ yellow +11.9° in chloroform (cf. Karrer and Link, A., 1928, 63), hydrolysed by hydrochloric acid in acetone solution to 4-*p*-hydroxybenzoylquinic acid (annexed formula), m. p. 108—112°, $[\alpha]_{\text{D}}^{20}$ yellow —9.4° in water. Treatment of this with acetone containing 1%



of hydrogen chloride affords 4-*p*-hydroxybenzoyl*iso*-propylidenequinide, m. p. 191—192° (corr.; lit. 179—180°), acetylated by acetic anhydride in dry pyridine to I.
H. BURTON.

Phloridzin and quercitrin. G. ZEMPLEN and others.—See this vol., 174.

Action of acetic anhydride on Schiff's bases. M. PASSERINI and M. P. MACENTELLI (*Gazzetta*, 1928, 58, 641—646).—To the compound formed by the action of acetyl chloride on benzylidenedianiline, Garzarolli-Thurnlackh (A., 1899, i, 881) ascribed the formula $\text{NPhCl}\cdot\text{CHPh}\cdot\text{OAc}$, but James and Judd (*J.C.S.*, 1914, 105, 1427) consider that the addition of a halogen or an acyl chloride to a Schiff's base takes place solely at the nitrogen atom, bromine and benzylidenedianiline thus giving $\text{NPhBr}_2\cdot\text{CHPh}$. The authors find that benzylidenedianiline (1 mol.) and acetic anhydride (1 mol.) react to give a compound, m. p.



isodioxime (A), sintering at 162°, decomp. 200—202°. Dehydrocholic acid isotrioxime (Schenck, A., 1914, i,

127—129°, which yields benzaldehyde, acetanilide, and acetic acid on hydrolysis, this behaviour being best expressed by the formula $\text{OAc} \cdot \text{NPh} \cdot \text{Ac} \cdot \text{CHPh}$. The compound $\text{OAc} \cdot \text{NPh} \cdot \text{Ac} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, m. p. 89—91°, is similarly obtained from anisylidenaniline and acetic anhydride. The action of acetic anhydride on the dianil derivative of 2-hydroxy-1-naphthylglyoxal (cf. Passerini, A., 1924, i, 1320) yields (1) the acetyl derivative of the latter, m. p. 185°, and (2) a compound, $\text{CHO} \cdot \text{C}(\text{NPh}) \cdot \text{C}_{10}\text{H}_6 \cdot \text{OAc}$ or $\text{NPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OAc}$, m. p. 155—157°, which reacts with phenylhydrazine. T. H. POPE.

Tautomerism of o-nitrobenzaldehyde. III. Action of diazomethane on o-nitrobenzaldehyde. I. TANASESCU (Bull. Soc. chim., 1928, [iv], 43, 1264—1269).—The reactions of "nitraldin" obtained by the action of diazomethane on o-nitrobenzaldehyde (Arndt, A., 1927, 360; 1928, 752) are more readily explained by a dynamic structure analogous to that previously advanced for o-nitrobenzaldehyde (A., 1928, 178; this vol., 66) than by Arndt's o-nitrophenylethylene oxide structure. The formation in acid medium of o-nitrosobenzoylcarbinol and not the o-nitroglycol; of the corresponding acetate, with acetic anhydride, and not the diacetyl glycol; of the chlorohydrin, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Cl}$, and the presence in nitraldin of a mobile hydrogen atom, determined by Zerevitinov's method, are cited in support of the dynamic structure. The formation of methylenedibenzisooxazolone when nitraldin is boiled with formic acid is attributed to the previous formation of formaldehyde and benzisooxazolone which in the nascent state react too rapidly to allow of the isolation of the latter. When the transformation is effected in presence of dimethyldihydroresorcinol, the principal product is methylenebisdimethyldihydroresorcinol, only a little methylenedibenzisooxazolone being formed. Excess of formaldehyde converts the latter into N-hydroxybenzisooxazolone. R. BRIGHTMAN.

Catalytic condensation at high temperatures of cyclohexanone and cyclohexene. A. D. PETROV (Bull. Soc. chim., 1928, [iv], 43, 1272—1276, and J. Russ. Phys. Chem. Soc., 1928, 60, 1435—1445).—cycloHexanone when heated at 320°/30 atm. in presence of alumina affords cyclohexylenecyclohexanone, b. p. 142—144°/0.15 mm., dicyclohexylenecyclohexanone, b. p. 214—219°/0.15 mm., and dodecahydrotriphenylene, m. p. 224—225°, the last-named corresponding with the formation of mesitylene from acetone (cf. A., 1927, 449, 1076, 1172). In presence of zinc chloride dodecahydrotriphenylene is not obtained, and about 15% of the ketone is converted into cyclohexane (cf. Kunze, A., 1926, 1143). cycloHexene in presence of alumina at 400—440° is converted principally into aromatic hydrocarbons. b. p. 75—280°, the fraction of b. p. 75—81° containing about 15% of benzene. R. BRIGHTMAN.

New rearrangement of oximes. II. P. W. NEBER and A. UBER (Annalen, 1928, 467, 52—72; cf. A., 1926, 1247).—When dibenzylketoxime is treated with the appropriate sulphonyl chloride and pyridine it is converted into its benzenesulphonate (I), m. p. 75°, or p-toluenesulphonate, m. p. 80°. When either salt is heated with absolute alcohol it yields benzylamine

benzene- or p-toluene-sulphonate, and ethyl phenylacetate. The action of alcoholic potassium ethoxide on I and treatment of the product with p-toluenesulphonic acid gives rise to benzyl α -aminobenzyl ketone p-toluenesulphonate, m. p. 198°, and the corresponding free base is converted by heating with absolute alcohol into 3:6-diphenyl-2:5-dibenzyl-3:6-dihydro-p-diazine, m. p. 152°, the same compound being synthesised from the amino-ketone obtained by reduction of oximinodibenzylketoxime. The action of alcoholic ammonia on I yields no trace of the diazine, but the products are (1) phenylacetamide benzenesulphonate (II), (2) N-benzylphenylacetamide, m. p. 93° (benzenesulphonate, m. p. 127—130°), (3) benzylamine benzenesulphonate, (4) phenylacetamide, (5) ammonium phenylacetate and benzenesulphonate, and, possibly, phenylacetoneitrile; 1 and 3 are formed by the reactions $\text{CH}_2\text{Ph} \cdot \text{C}(\text{NO} \cdot \text{SO}_2\text{Ph}) \cdot \text{CH}_2\text{Ph} \xrightarrow[\text{change}]{\text{Beckmann}} \text{PhSO}_2 \cdot \text{C}(\text{N} \cdot \text{CH}_2\text{Ph}) \cdot \text{CH}_2\text{Ph} \xrightarrow{\text{NH}_3} \text{NH}_2 \cdot \text{CH}_2\text{Ph} + \text{CH}_2\text{Ph} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2, \text{PhSO}_3\text{H}$ (II), the other products arising by benzylation or hydrolysis of II. Attempts to synthesise the N-benzyl derivative by the action of benzylamine on phenylacetiminooxime yielded only di-(N-benzyl)phenylacetamide, m. p. 100°. Benzylacetoneoxime, m. p. 85° (lit. 80°), is similarly converted into its benzenesulphonate (III), m. p. 80°, and p-toluenesulphonate (IV), m. p. 62°, which by treatment with absolute alcohol are converted into β -phenylethylamine benzene- and p-toluene-sulphonates, respectively, and III is converted by the action of sunlight for 14 days into an unidentified substance, m. p. 86—88°, which is isomeric but not identical with acetyl- β -phenylethylamine benzenesulphonate. By treatment with alcoholic potassium ethoxide III is converted into γ -amino- β -diethoxy- δ -phenylbutane isolated as its p-toluenesulphonate, m. p. 128°, which on hydrolysis yields α -amino- β -phenylethyl methyl ketone, m. p. 175°, both compounds being readily converted into 3:6-dibenzyl-2:5-dimethyl-3:6-dihydro-p-diazine, m. p. 103°. The action of alcoholic ammonia on IV converts it into acetamide p-toluenesulphonate, β -phenylethylamine, and N-(β -phenylethyl)acetamide p-toluenesulphonate, m. p. 125°, which is not identical with β -phenylpropionamide p-toluenesulphonate, m. p. 160° (hydrochloride, m. p. 174°), synthesised for comparison. J. W. BAKER.

Synthesis of polyphenolic ketones. K. W. ROSENMUND and H. LOHFERT (Ber., 1928, 61, [B], 2601—2607).—Simple pyrocatechol ketones are prepared (i) by dissolving pyrocatechol and aluminium chloride in nitrobenzene and gradually adding the equivalent quantity of acid chloride, (ii) by warming the di-esters of pyrocatechol dissolved in nitrobenzene with aluminium chloride whereby one acyl group wanders to the nucleus and the other is eliminated, (iii) by proceeding as in (ii) but adding a further mol. of pyrocatechol, which unites with eliminated acyl residue. The third method frequently gives the best yields. The examples cited are: 4-acetylpyrocatechol, m. p. 116°, from the diacetate or guaiacyl acetate: chloroacetylpyrocatechol, m. p. (anhydrous) 173°, (hydrated) 120°; propionylpyrocatechol, m. p. 146°, from pyrocatechol dipropionate, b. p. 153—157°/14 mm., 281°/760 mm.; butyrylpyrocatechol, m. p. 146°, by all

three methods (*pyrocatechol dibutyrate*, b. p. 305°); *isovalerylpyrocatechol*, m. p. 108°, from *pyrocatechol diisovalerate*, b. p. 153—173°/vac.; *stearylpyrocatechol*, m. p. 70°, from *pyrocatechol distearate*, m. p. 83—85°; *benzoylpyrocatechol*, m. p. 134°, from the *dibenzoate*. Acetylquinol is prepared from quinol and acetyl chloride, quinol diacetate, and quinol diacetate+quinol. Propionylquinol, m. p. 92°, is similarly obtained. Monoketones of phloroglucinol are prepared by allowing the phenol and aluminium chloride to react in presence of nitrobenzene until a complex is formed and complete dissolution ensues and then adding the acid chloride gradually; *butyrylphloroglucinol*, m. p. 179—180°, *hexoylphloroglucinol*, m. p. (anhydrous) 120°, (hydrated) 100°, and *isovalerylphloroglucinol*, m. p. 145°, are thus obtained. *Tribenzoylphloroglucinol*, m. p. 185°, is obtained from the *tribenzoate* and aluminium chloride at 130—140°.

H. WREN.

Syntheses of polyhydroxy-chalkones [-phenyl styryl ketones], -hydrochalkones [-phenyl β -phenylethyl ketones], and -flavanones. I. J. SHINODA and S. SATO. II. Synthesis of naringenin and sakuranetin. J. SHINODA and S. SATO. III. Synthesis of hesperetin. J. SHINODA and M. KAWAGOE (J. Pharm. Soc. Japan, 1928, 48, No. 558, 109—114, No. 560, 117—119, 119—120).—I. Polyhydroxy-derivatives of phenyl styryl and phenyl β -phenylethyl ketones may be prepared by the condensation of cinnamoyl or β -phenylpropionyl chlorides with polyhydric phenols in nitrobenzene under the influence of aluminium chloride at the ordinary temperature. Using phloroglucinol, the isomeric flavanone derivative is the chief product.

Resorcinol and cinnamoyl chloride yield 2:4-dihydroxyphenyl styryl ketone, m. p. 151°, identical with the product obtained by Ellison's method (cf. A., 1927, 880, where m. p. 133—134° is given). Resorcinol and β -phenylpropionyl chloride yield 2:4-dihydroxyphenyl β -phenylethyl ketone (+H₂O), m. p. 84°, also obtained by reduction of the styryl compound or by the method of Bargellini and Marantonio (cf. A., 1908, i, 801, where m. p. 88° is given). 2:4-Dihydroxyphenyl β -4-methoxyphenylethyl ketone, m. p. 82—83°, is prepared similarly, either by condensation or reduction. Phloroglucinol and cinnamoyl chloride yield 2:4:6-trihydroxyphenyl styryl ketone (I), m. p. 189—190°, 5:7-dihydroxyflavanone (II), m. p. 203—204° (*oxime*, m. p. 263°; *monomethyl ether*, m. p. 101°; *diacetate*, m. p. 141—142°; *triacetate*, m. p. 115—117.5°), *tricinamoylphloroglucinol*, m. p. 147.5°, and traces of *substances*, m. p. 243° and 205°. I yields II when fused or heated in acetic acid. II is shown to be a flavanone by the development of a red colour when treated with magnesium and hydrochloric acid. It is converted into I by the action of alkali. Phloroglucinol and β -phenylpropionyl chloride yield 2:4:6-trihydroxyphenyl β -phenylethyl ketone, m. p. 120—121°, the *triacetate* of which, m. p. 76°, is also obtained by reduction of 2:4:6-trihydroxyphenyl styryl ketone *triacetate*. Phloroglucinol and *p*-methoxycinnamoyl chloride yield 2:4:6-trihydroxyphenyl 4-methoxystyryl ketone, m. p. 176°, and 5:7-dihydroxy-4'-methoxyflavanone (*isosakuranetin*), m. p. 193—194°.

The latter yields a monomethyl ether and an acetate of the monomethyl ether identical with sakuranetin monomethyl ether and its acetate. 2:4:6-Trihydroxyphenyl β -phenylethyl ketone, m. p. 201—202°, 3':4'-methylenedioxy-5:7-dihydroxyflavanone, m. p. 220°, and (?) 2:4:6-trihydroxyphenyl 3:4-methylenedioxystyryl ketone, m. p. 213°, are prepared similarly.

II. *p*-Carbethoxybenzaldehyde, b. p. 170—173°/19—20 mm., m. p. 26°, condenses with malonic acid when heated in pyridine containing a little piperidine to give *p*-carbethoxyoxycinnamic acid, m. p. 183°. Condensation of the chloride of this acid with phloroglucinol by the method described above yields a resinous product from which 5:7:4'-trihydroxyflavanone is separated by solution in alcoholic alkali, precipitation with carbon dioxide, and treatment with dilute acetic acid. Two *substances*, m. p. 177° and 267—268°, are also separated in small quantity. The synthetic 5:7:4'-trihydroxyflavanone and its derivatives [*oxime* (+H₂O), m. p. 231°; *dimethyl ether*, m. p. 118°] are identical with naringenin and its derivatives (cf. Asahina and Inubuse, A., 1928, 1020). Methylation of 5:7:4'-trihydroxyflavanone with only one molecular proportion of diazomethane yields 5:4'-dihydroxy-7-methoxyflavanone, identical with sakuranetin and yielding identical derivatives.

III. *iso*Vanillin, prepared by demethylation of veratraldehyde with hydrobromic acid, yields *O*-carbethoxyisovanillin, m. p. 61—62°, which condenses with malonic acid to give *O*-carbethoxyhesperitic acid (3-carbethoxyoxy-4-methoxycinnamic acid), m. p. 199°. Condensation of the chloride of this acid with phloroglucinol by the method described above yields a product from which is obtained 5:7:3'-trihydroxy-4'-methoxyflavanone, m. p. 227—228°, identical with hesperetin and yielding an identical *oxime*, m. p. 229—230°.

R. K. CALLOW.

Dynamic isomerism. XXVIII. Absorption spectra of the ketonic and enolic forms of an α -diketone. T. M. LOWRY, H. MOUREU, and C. A. H. MACCONKEY (J.C.S., 1928, 3167—3179).—The contention of Morton and Rosney (A., 1926, 454) that keto-enol tautomerides exhibit the same wavelengths of maximum absorption, disproved by Lowry, MacConkey, and Burgess (A., 1928, 766) for benzoylcamphor, is now found to be untrue for the isomerides of benzylmethylglyoxal. The ketonic form *A* (Moureu, A., 1928, 419) is obtained by distillation with sodium carbonate and has m. p. 17°, b. p. 104°/10 mm. It has absorption in the yellow, with a maximum $\log \epsilon = 1.5$ at 4300 Å. in alcohol, or 1.8 at 4550 Å. in cyclohexane.

The enolic form *B*, m. p. 70°, b. p. 134°/10 mm., formed by addition of an alkali or base to the liquid, is the stable solid phase, and is colourless, with strong absorption in the ultra-violet, having maximum $\log \epsilon = 4.3$ at 3120 Å. in alcohol, or 4.7 at 3100 Å. in cyclohexane. The inequality in λ between the isomerides is twice as great as with benzoylcamphor (*loc. cit.*), and the intensity ratio is about 600:1.

The absorption bands of *B* may be compared with those of benzylideneacetone and benzoylacetone. Benzylideneacetone has $\log \epsilon = 4.36$ at 2850 Å., closely resembling benzylideneacetone (Lowry and French,

A., 1924, i, 1212). The absorption spectrum of benzoylacetone (Baly and Desch, J.C.S., 1905, 87, 766; Morgan and Moss, *ibid.*, 1913, 103, 78) is now found to have two maxima, with, in alcohol, $\log \epsilon = 4.15$ at 3100 and 3.66 at 2500 Å., in cyclohexane, 4.26 at 3050 and 3.80 at 2450 Å.; by analogy with benzoylcamphor it is assumed that these are due to two isomerides formed in equilibrium mixture when the homogeneous solid is melted or dissolved. The various bands at about 3000 Å. in the above compounds may be considered to be a general ketonic band, reinforced by conjugation of the carbonyl double linking with an olefinic double linking.

The liquid form of benzylmethylglyoxal rapidly develops enolic absorption; if, however, it is examined when freshly prepared, it no longer shows a maximum in the ultra-violet, but only a "step-out," $\log \epsilon = 2.6-2.8$ at 3300—2700 Å. This may be compared with similar behaviour of acetylphenylethylene oxide, at wave-lengths less than 3100 Å.; this compound thus resembles benzyl acetate rather than acetophenone in absorptive properties.

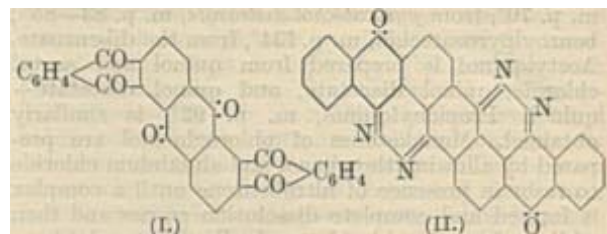
Inter-transformation of the isomerides in solution was not easily effected, and when an equilibrium mixture was obtained the ratio of its components could not be determined. The additive law does not appear to apply, and it is possible that *A* and *B* may combine together. It is, however, noteworthy that the absorption curves for equilibrium mixtures show a minimum rather than a maximum at λ 2450, which is characteristic of the labile form of benzoylcamphor; benzylmethylglyoxal thus does not include a similar form among its tautomerides. E. W. WIGNALL.

Theory of [the colour of] quinhydrones. E. WEITZ (Z. Elektrochem., 1928, 34, 538—546).—The colour of quinhydrones is attributed to salt formation between the "functional groups" of the two components; the functional groups can function as anions or cations and are situated at the ends of a conjugated chain. Owing to the low oxidation or reduction potential of the components, the salts are incompletely heteropolar, the electrons of the cationic group being only partly given up to the anionic group, and to this is directly attributed the colour of the salts. The theory is extended to other classes of compounds, *e.g.*, triphenylmethane dyes and certain coloured inorganic salts containing colourless acid radicals. S. K. TWEEDY.

Dehydrating action of Japanese acid earth in the anthraquinone series. M. TANAKA and S. WATANABE (Bull. Chem. Soc. Japan, 1928, 3, 288—289).—When quinol is condensed with phthalic anhydride at 260° in presence of Japanese acid earth, quinizarin is produced. Pyrocatechol affords a mixture of hystazarin and alizarin, whilst α -naphthol at 250—260° yields α -hydroxynaphthacenequinone, m. p. 303°. H. BURTON.

Indoquinonanthrene (trans-bisang- or 1:2:5:6-diphthalylanthraquinone). R. SCHOLL and H. K. MEYER (Ber., 1928, 61, [B], 2550—2555).—*iso*Violanthrone is oxidised by chromic acid in boiling glacial acetic acid to trans-bisang-diphthalylanthraquinone (I) for which the term "indoquinonanthrene" is proposed to express the similarity of the arrange-

ment of the rings to those of indanthrene. It is a yellow, crystalline material which sublimes at about 400° in a carbon dioxide vacuum and dissolves



sparingly in organic media. The red vat produced by sodium hyposulphite in cold sodium carbonate solution contains hexahydroindoquinonanthrene, since it readily yields a hexa-*p*-bromobenzoyl compound. The hexahydro-derivative is converted by exposure to air or by treatment with boiling trichlorobenzene into the bluish-black quinhydrone ($C_{30}H_{10}O_6 + C_{30}H_{18}O_6$). Indoquinonanthrene is converted by hydrazine hydrate in hot quinoline into the dark blue hydro-derivative of the di-*o*-diazine (II), which is stable towards air, but is readily oxidised by sulphuric acid to the di-*o*-diazine, subliming at 460—480°/20 mm. (carbon dioxide). H. WREN.

Oxidation of "biosterin" [biosterol] by ozone. Z. NAKAMIYA (Bull. Inst. Phys. Chem. Res., Japan, 1928, 1, 1211—1243).—The ozonide of biosterol was separated by light petroleum into soluble (? mono-ozonide) and insoluble (? diozonide) fractions, each of which gave the same products when decomposed with boiling water. From these products were isolated acetaldehyde, formaldehyde, butaldehyde, formic acid, acetic acid, diacetyl, an acidic substance with properties resembling those of a sesquiterpene alcohol derivative, a neutral viscous substance (C 67—72%, H 9—10%), and an acidic viscous substance (C 63—65%, H 8—9%), these last two being the main decomposition products. J. W. BAKER.

Rotenone and degradation products. G. M. WRIGHT (J. Amer. Chem. Soc., 1928, 50, 3355—3360).—The revised constitutions proposed by Takei (A., 1928, 765) are independently confirmed. Rotenone oxime has m. p. 252°, rotenone hydrochloride, m. p. 255° (oxime, m. p. 239°), and rotenone hydrobromide, m. p. 190°. *iso*Rotenone yields a phenylhydrazone, m. p. 230°, but does not combine with hydrogen chloride. Rotenic acid forms a methyl ester, m. p. 39—40°, and a mononitro-derivative, m. p. 187°, and is decarboxylated at 216—225° to a substance, $C_{16}H_{14}O_3$, m. p. 104°, and a phenolic substance. H. E. F. NOTTON.

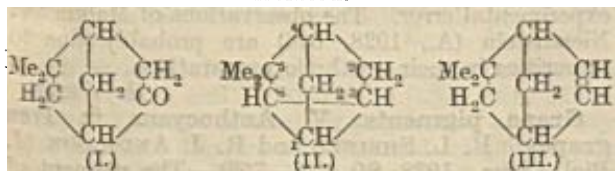
Action of ozone on cyclogeraniolones. R. ESCOURROT (Bull. Soc. chim., 1928, [iv], 43, 1277—1279).—A recapitulation of work already published (A., 1926, 1238). R. BRIGHTMAN.

Camphane-2-carboxylic acid and camphanyl ketones. H. RUPE and H. HIRSCHMANN (Helv. Chim. Acta, 1928, 11, 1180—1200).—Ethyl camphane-2-carboxylate (the acid is obtained in 70—80% yield by the action of carbon dioxide on magnesium bornyl chloride; cf. Houben, A., 1906, i, 21) is reduced by sodium and alcohol to 2-camphanylcarbinol, b. p.

135°/19 mm., m. p. 87—88°, $[\alpha]_D^{20}$ -27.75° in benzene (p-nitrobenzoate, m. p. 123°), also obtained by reducing camphane-2-carboxylamide, m. p. 98° (lit. 138°). Zinc methyl and the acid chloride afford 2-camphanyl methyl ketone (2-acetylcamphane) (I), b. p. 106°/13 mm., d_4^{20} 0.96186, $[\alpha]_D^{20}$ -54.25° (semicarbazone, m. p. 216°; oxime, m. p. 69°), which condenses with benzaldehyde in presence of hydrogen chloride, yielding 2-camphanyl styryl ketone, b. p. (cathode vacuum) 120—121°, m. p. 46°, $[\alpha]_D^{20}$ +25.85° in benzene. Reduction of this with hydrogen in presence of nickel gives 2-camphanyl β -phenylethyl ketone, b. p. 200—201°/13 mm., m. p. 36°, $[\alpha]_D^{20}$ -24.04° in benzene. 2-Camphanyl 2-nitrostyryl ketone has m. p. 77—78°. 2-Camphanyl ethyl ketone (2-propionylcamphane), b. p. 128—129°/13 mm., d_4^{20} 0.9549, $[\alpha]_D^{20}$ -55.69° (semicarbazone, m. p. 186°; oxime, m. p. 97—98°), is prepared using zinc ethyl, and phenyl 2-camphanyl ketone (2-benzoylcamphane), b. p. 178—180°/11 mm., d_4^{20} 1.0391, $[\alpha]_D^{20}$ +12.13°, by the Friedel-Crafts reaction. Treatment of I with ethyl benzoate in presence of ether and sodamide gives 2-benzoylacetylcamphane, m. p. 61°, whilst oxidation with sodium hypobromite yields an acid, m. p. 83—84°, $[\alpha]_D^{20}$ -12.99° in benzene (methyl ester, b. p. 102°/10 mm., d_4^{20} 1.0017, $[\alpha]_D^{20}$ -28.0°), isomeric with camphane-2-carboxylic acid, m. p. 73°, $[\alpha]_D^{20}$ -3.26° in benzene (methyl ester, b. p. 104—105°/11 mm., d_4^{20} 1.002, $[\alpha]_D^{20}$ -14.61°; secondary hydrazide, m. p. 300°). Both acids give the same p-toluidine salt, m. p. 185—185.5°. Magnesium bornyl chloride and benzaldehyde appear to give phenyl-2-camphanylcarbinol, b. p. 170—175°/14 mm.

Optical rotations of the above compounds for different wave-lengths have been measured, and the rotation-dispersions of the acids and their esters are found to be normal or nearly so. H. BURTON.

Camphenilane series. II. apoCyclene, camphenilene, and some of their derivatives. S. NAMETKIN and Z. ALEXANDROV (Annalen, 1928, 467, 191—200, and J. Russ. Phys. Chem. Soc., 1928, 60, 1535—1544; cf. A., 1915, i, 699; 1924, i, 1084).—The structure of α -isocamphenilone (I) has now been determined by preparing it from apocyclene (II) (cf. Komppa and Roschier, A., 1922, i, 1167), and examination of the products of fission of the cyclopropane ring in the latter by hydration has shown that fission probably takes place in all three possible ways, for fission of either the C¹—C⁶ or C²—C⁶ linkings must yield the alcohols corresponding with camphenilone and α -isocamphenilone, and fission of the C¹—C² linking the alcohol corresponding with apocamphor; all these ketones were isolated.



apoCyclene was prepared from camphenilone-hydrazone by oxidation with mercuric oxide in alcohol. Treatment of apocyclene with acetic acid and 50% sulphuric acid yielded a mixture of alcohols, m. p. 51—60°, b. p. 100.5—101°/19 mm. After oxidation of this mixture with chromic acid in acetic acid,

apocamphor was separated by crystallisation of its semicarbazone, and yielded apocamphoric acid when oxidised by alkaline permanganate. After oxidation of the mixture with concentrated nitric acid and then with alkaline permanganate, camphenilone and α -isocamphenilone, m. p. 65—66° (semicarbazone, m. p. 193—194°), were separated by crystallisation of the semicarbazones. cis-apoFenchocamphoric acid, derived from α -isocamphenilone, was separated from the product of the permanganate oxidation. α -isocamphenilone was separated in largest amount, and this reaction provides a convenient method of preparation. Reduction of the ketone with sodium and alcohol yielded a mixture of the stereoisomeric α -isocamphenilols, b. p. 196—198° (corr.). When treated with potassium and carbon disulphide and then with methyl iodide this yielded methyl α -isocamphenylzanthate, which decomposed when heated at 150—160° to yield camphenilene (III), m. p. 27—28°, b. p. 131—132°. Oxidation of III with alkaline permanganate yielded cis-apofenchocamphoric acid.

R. K. CALLOW.

Oxidation of dipinene. L. H. BRIGGS and W. F. SHORT (J.C.S., 1928, 3118—3121).—Application of the method of "dehydrogenating disruption" (Ruzicka), using manganese dioxide and sulphuric acid, to a dipinene, b. p. 183—184°/15 mm., d_4^{20} 0.9260, 1.5174, produced by the action of hydrogen chloride and ferric chloride on pinene, led to benzoic, terephthalic, and trimellitic acids. This result supports the suggestion that certain diterpenes contain two hexagonal nuclei united through a chain of one or two carbon atoms.

R. J. W. LE FEVRE.

New compounds from oil of turpentine. H. WIENHAUS (Forh. III nord. Kemistmotet, 1928, 211—212).—The presence of carene in German turpentine oil has been established. A diterpene, C₂₀H₃₂, m. p. 63°, b. p. 178°/8 mm., $[\alpha]_D^{20}$ +214°, has been isolated from Swedish pine resin. On hydrogenation in presence of platinum it yields a monocyclic (?) octahydroditerpene, C₂₀H₄₀, whilst when boiled with formic acid it affords a tricyclic compound, which on hydrogenation gives a saturated tetrahydroditerpene, C₂₀H₃₈. Its ozonide gives acetaldehyde when boiled with water. A sesquiterpene alcohol, C₁₅H₂₆O, regarded as tertiary, has been isolated from the same source as the previous compounds; when hydrogenated it gives a saturated dihydro-compound, C₁₅H₂₈O. The isonitroso-compound of verbanone has been found to give a dioxime, which yields orange precipitates with nickel salts; by fusion with alkali the first-named substance is converted into pinocamphoric acid. The unsaturated ketone o-menthen-5-one has been prepared by boiling verbanone with acids; when hydrogenated it yields o-menthan-5-one, which forms a crystalline oxime and semicarbazone. The oxime is converted by concentrated sulphuric acid into an isooxime (lactam), m. p. 119—120°. By the reduction of o-menthan-5-one a new secondary alcohol, o-menthan-5-ol, has been obtained. Reduction of the oxime to verbanylamine and subsequent suitable treatment yields dimethylverbanylamine and d-pinene. When oxidised with potassium permanganate the latter gives pinocamphoric acid, but it differs from α -pinene in not giving solid compounds with nitrosyl chloride

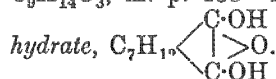
or bromine. *d*-Pinene boils at 156—157°/740.5 mm., and its d_4^{20} (0.8708) and refractive index are higher than those of α -pinene. Sylvestrene on autoxidation yields alcohols and ketones, which may be designated as sylvocarvacrols and sylvocarvones; on hydrogenation of these followed by oxidation *m*-menthanone is obtained.

H. F. HARWOOD.

Tricyclene group. G. KOMPPA (Forh. III nord. Kemistmotet, 1928, 209—210).—The constitution of tricyclenic acid has now been established by its conversion into tricyclene. Its ethyl ester was reduced with sodium and alcohol to *tricyclenol*, m. p. 110—111°, converted by phosphorus pentachloride into the corresponding *chloride*, an oil which on reduction (sodium and alcohol) gives a good yield of tricyclene. Tricyclenic acid is not identical with the teresantallic acid obtained from sandalwood oil as Semmler had suggested, since this latter acid cannot be reduced to tricyclene. The author has also prepared the *dichloro*-compound of tricyclenol, the corresponding *glycol*, and *tricyclenolphénylmethane*, m. p. 86°.

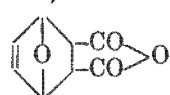
H. F. HARWOOD.

Pinacolin rearrangement of dicyclic ditertiary glycols. J. PALMÉN (Forh. III nord. Kemistmotet, 1928, 195—208).—Contrary to the statement of Semmler and Bartels (1908) that camphenilone is not formed when santeneglycol is subjected to the pinacolin rearrangement, it has been shown that a yield of about 5% of this substance can be obtained by treating santeneglycol with concentrated sulphuric acid below 0°; the simultaneous production of resin prevented following the course of the reaction. Camphenidimethylglycol (dihydroxydimethylcamphane) readily undergoes the pinacolin rearrangement, the dicyclic ring being ruptured with production of a mixture of unsaturated monocyclic compounds. Attempts to prepare the corresponding dihydroxy-diethyl-, -dibenzyl-, and -diphenyl-camphanes from camphorquinone and the appropriate Grignard reagent failed (steric hindrance?), only one of the carbonyl groups reacting, *keto-alcohols* being formed. Those obtained by using magnesium phenyl and magnesium benzyl bromide had m. p. 78—80°, and b. p. 212°/15 mm., respectively. Treatment of santenone with sodamide and amyl nitrite affords *isonitroso*-santenone, converted by formaldehyde into a product, $C_9H_{14}O_3$, m. p. 138—140°, probably a *ketosantenone*



H. F. HARWOOD.

Constitution of cantharidin. Decomposition reaction of cantharidin. F. VON BRUCHHAUSEN and H. W. BERSCH (Arch. Pharm., 1928, 266, 697—702).—Maleic anhydride and furan condense in benzene solution to form *dehydroproto*-cantharidin (annexed formula), which decomposes again above its m. p., 118°, into its original components (cf.



Diels and Adler, A., 1928, 1018). Subsequent treatment with hydrogen and palladised charcoal affords *protocantharidinic acid*, m. p. 117—120° with loss of water, the *anhydride* of which is very stable. The condensation of furan and dimethylsuccinic anhydride to form cantharidin could not be accomplished, but

the latter was broken down into these components when passed over a dehydrogenating catalyst such as palladised asbestos at 280°. This reaction confirms the constitution of cantharidin finally accepted by Gadamer (cf. Coffey, A., 1923, i, 695, 1218).

S. COFFEY.

isoFlavone group. III. Synthesis of genistein. W. BAKER and R. ROBINSON (J.C.S., 1928, 3115—3118).—5 : 7-Dihydroxy-4'-methoxy-2-styryl-isoFlavone gave, on methylation with methyl sulphate and methyl-alcoholic aqueous potassium hydroxide, 5-hydroxy-7 : 4'-dimethoxy-2-styrylisoFlavone, m. p. 245—246° (acetyl derivative, m. p. 203—204°), which was completely methylated only by methyl sulphate and sodium hydroxide in acetone, giving 5 : 7 : 4'-trimethoxy-2-styrylisoFlavone, m. p. 193° (similar treatment of 5-hydroxy-7 : 4'-dimethoxy-2-styrylmethyl-isoFlavone gave 5 : 7 : 4'-trimethoxy-2-styryl-6(?)-methylisoFlavone, m. p. 211°). Oxidation of this compound by potassium permanganate in aqueous pyridine solution led to benzoic acid and 5 : 7 : 4'-trimethoxyisoFlavone-2-carboxylic acid, m. p. 237° (decomp.), which, when heated above its m. p., gave 5 : 7 : 4'-trimethoxyisoFlavone (genistein trimethyl ether), m. p. 162—163°, from which genistein was obtained by demethylation.

R. J. W. LE FEVRE.

Chrysanthemin and asterin. R. ROBINSON and R. WILLSTATTER (Ber., 1928, 61, [B], 2503—2504).—Further purification of asterin has yielded a product identical in all respects with chrysanthemin; the term asterin is no longer necessary. H. WREN.

[Cyanidin. I.] R. ROBINSON and R. WILLSTATTER (Ber., 1928, 61, [B], 2504—2506).—A criticism of the reasons which have led Malkin and Nierenstein (A., 1928, 646) to assume that cyanidin chloride and 3 : 5 : 7 : 3' : 4'-pentahydroxyflavylium chloride differ from one another. H. WREN.

Comparison of natural and synthetic cyanidin. R. KUHN and T. WAGNER-JAUREGG (Ber., 1928, 61, [B], 2506—2508).—Differences are not observable between the cyanidin chloride obtained by hydrolysis of cyanin chloride from dahlias and 3 : 5 : 7 : 3' : 4'-pentahydroxyflavylium chloride from *O*-benzoyl-cyanidin chloride by Robinson's method. Both preparations have the same crystalline form and the same colour in solutions of equal p_H . Their colour reactions with ferric chloride, copper sulphate, and uranyl nitrate are identical with regard to shade and relative permanence. Their extinction coefficients in the ultra-violet are identical within the limits of experimental error. The observations of Malkin and Nierenstein (A., 1928, 646) are probably due to impurities in their synthetic preparations.

H. WREN.

Grape pigments. V. Anthocyanins in Ives grapes. R. L. SHRINER and R. J. ANDERSON (J. Biol. Chem., 1928, 80, 743—752).—The pigment of Ives grapes (a strain of *Vitis labrusca* admixed with a little *V. aestivalis*) was isolated as the picrate, and converted into the chloride which could not be obtained crystalline; the latter was reconverted into picrate and fractionated; the pigment regenerated from the largest fraction, when hydrolysed with hydro-

chloric acid, gave monomethoxydelphinidin chloride, *p*-hydroxycinnamic acid, and dextrose. The methoxydelphinidin yielded an α -tetra-acetate, m. p. 102–104°, and a β -tetra-acetate, m. p. 220–230°, both of which, when oxidised with permanganate, gave syringic acid.

C. R. HARRINGTON.

Interaction of piperidine with nitro- and halogenonitro-derivatives of xanthone and diphenylene oxide. R. J. W. LE FEVRE (J.C.S., 1928, 3249–3252).—Both α - and β -dinitroxanthone formed bright yellow complexes with piperidine in the cold; when boiled with an excess of reagent the former gave an indefinite product, whilst the latter yielded 5 : 5'-dinitro-2'-piperidino-2-hydroxybenzophenone, m. p. 155° (acetyl derivative, m. p. 253–255°), which, when heated at 200°, lost piperidine with regeneration of β -dinitroxanthone. 2 : 4 : 5 : 7-Tetranitroxanthone, m. p. above 300°, did not react with boiling piperidine. Unsuccessful attempts to reveal the orienting influence of oxonium oxygen are described. 2 : 7-Dibromo-4 : 6-dinitroxanthone has m. p. 265–266°.

R. J. W. LE FEVRE.

Dinaphthylene dioxide. I. A. CORBELLINI and F. VIETTI (Gazzetta, 1928, 58, 766–774).—The method of preparation of dinaphthylene dioxide (cf. Pummerer and others, A., 1926, 1135; Inouye, B., 1926, 596; Thyll and Schmid, B., 1927, 470) is simplified and improved by heating crude dinaphthyl with copper oxide at 300–310°, with or without nitrobenzene; the yield is 84–87%. The substance is accurately chlorinated by the method of Zinke, Pongratz, and Funke (A., 1925, i, 384) to a dichloro-derivative, m. p. 259°, is converted by bromine in carbon disulphide into a dibromo-derivative, m. p. 277°, and by excess of bromine into tetrabromodinanaphthylene dioxide, m. p. 349–351°.

In order to avoid the formation of tetranitro- or hexanitro-compounds (cf. Bünzly and Decker, A., 1905, i, 884; Inouye, *loc. cit.*), nitration is effected in carbon tetrachloride suspension. The resulting dinitro-derivative, $C_{20}H_8O_6N_2$, can be reduced by sodium hyposulphite or by stannous chloride, provided that it is first subdivided by dissolving in sulphuric acid and precipitation by water; the reduction product is not yet described. In presence of aluminium chloride, dinaphthylene dioxide readily reacts with benzoyl chloride in carbon disulphide solution to give the dibenzoyl derivative, $C_{20}H_8O_2Bz_2$, m. p. 318.5°, and in benzene with phthalic anhydride to give the aluminium salt of the acid $C_{20}H_6O_2 \cdot CO \cdot C_6H_4 \cdot CO_2H$, decomp. 350°; with excess of phthalic anhydride the acid $C_{20}H_6O_2(CO \cdot C_6H_4 \cdot CO_2H)_2$, decomp. about 350°, is obtained.

E. W. WIGNALL.

Hydroxy-derivatives of thioxanthone dioxide. W. B. PRICE and S. SMILES (J.C.S., 1928, 3154–3160).—Effective methods of preparation of hydroxy-thioxanthone dioxides are described. Equimolecular quantities of 2-sulphinobenzoic acid and *p*-benzoquinone were condensed in aqueous suspension giving 2 : 5-dihydroxydiphenylsulphone-2'-carboxylic acid, m. p. 235° (diacetyl derivative, m. p. 188°; methyl 2 : 5-dimethoxydiphenylsulphone-2'-carboxylate, m. p. 195°; 2 : 5-dimethoxydiphenylsulphone-2'-carboxylic acid, m. p. 223°), which by dehydration in sulphuric

acid passed into 1 : 4-dihydroxythioxanthone dioxide, m. p. 224° (diacetyl derivative, m. p. 174°). The last compound, by oxidation with lead tetra-acetate, yielded thioxanthone dioxide 1 : 4-quinone, m. p. 185°. Similarly, 2-sulphinobenzoic acid with *p*-toluquinone gave methyl 2 : 5-dihydroxydiphenylsulphone-2'-carboxylic acid, m. p. 203°, and with chlorobenzoquinone gave chloro-2 : 5-dihydroxydiphenylsulphone-2'-carboxylic acid, m. p. 210°; both underwent dehydration yielding methyl-1 : 4-dihydroxythioxanthone dioxide, m. p. 175°, and chloro-1 : 4-dihydroxythioxanthone dioxide, m. p. 230°, respectively. 2-Sulphinobenzoic acid and quinizarinquinone gave 2-quinizarinphenylsulphone-2'-carboxylic acid, m. p. 263°, which would not undergo ring closure, whilst 1 : 2-naphthaquinone gave an additive product, $C_{17}H_{12}O_6S \cdot H_2O$ (I), m. p. 156° (decomp.). Dehydration of I led to 1 : 2-naphthaquinone 2'-carboxyphenyl sulphoxide (II), m. p. 236° (phenylhydrazone, m. p. 251°; quinoxaline [from *o*-phenylenediamine], m. p. 292–293°); with boiling acetic anhydride II gave 3 : 4-naphthathioxanthone-1 : 2-quinone, m. p. 244–245°.

The following compounds are also described : 2 : 4-dihydroxy-2'-carboxydiphenyl sulphoxide, m. p. 204°; 1 : 4-dimethoxythioxanthone dioxide, m. p. 193°; 2-hydroxythioxanthone dioxide, m. p. 259° (methyl ether, m. p. 204°); 2 : 3-dihydroxythioxanthone dioxide, m. p. 203° (decomp.) (methyl ether, m. p. 241°).

R. J. W. LE FEVRE.

Carbonylbisamino-acids and their transformation products. II. F. WESSELY and J. MAYER (Monatsh., 1928, 50, 439–448).—(+)-Ethyl carbonylbis- α -amino- β -phenylpropionate (Ia), $CO[NH \cdot CH(CO_2Et) \cdot CH_2Ph]_2$, m. p. 142.5° (corr.) after sintering at 141°, $[\alpha]_D^{25} +42.28^\circ$ in alcohol, prepared by the action of carbonyl chloride on (–)-ethyl α -amino- β -phenylpropionate, is converted by heating with hydrochloric and acetic acids into (–)- α -(5-benzyl-3-hydantoin)- β -phenylpropionic acid (IIa), m. p. 205.5°, $[\alpha]_D^{25} -210.7^\circ$ in alcohol. Similarly, (–)-ethyl carbonylbis- α -amino- β -phenylpropionate (Ib), m. p. 142.5° (corr.) after sintering at 141°, $[\alpha]_D^{25} -42.35^\circ$ in alcohol, from (+)-ethyl α -amino- β -phenylpropionate, yields (+)- α -(5-benzyl-3-hydantoin)- β -phenylpropionic acid (IIb), m. p. 205.5°, $[\alpha]_D^{25} +211^\circ$ in alcohol. Equimolecular mixtures of Ia with Ib and IIa with IIb have m. p. 144.5° (corr.) and 229.5°, respectively (cf. Wessely and John, A., 1928, 530). Whilst the *i*-carbonylbisphenylalanines previously described (*loc. cit.*) are unaffected by heating with 1 or 2 mols. of *N*-sodium hydroxide solution, the corresponding esters, m. p. 145° and 141.5°, respectively, both yield a mixture of the two *i*-acids on hydrolysis with 2 mols. of alkali. With 1 mol. of alkali the former ester gives a mixture of the two isomeric α -(5-benzyl-3-hydantoin)- β -phenylpropionic acids, m. p. 229° and 171°, respectively (*loc. cit.*), whilst the latter ester affords the form of m. p. 229° only. The above hydantoin derivative, m. p. 171°, is converted into its isomeride, m. p. 229°, by treatment with 1 mol. of alkali, and both these compounds are hydrolysed by 2 mols. of alkali, forming the same mixture of *i*-carbonylbisphenylalanines. Ethyl α -(5-benzyl-3-hydantoin)- β -phenylpropionate, m. p. 130° (corr.) after sintering at 125°, is obtained by the action of diazoethane on

the corresponding acid, m. p. (anhydrous or $+1.5\text{H}_2\text{O}$) $171-172^\circ$.

[With E. KEMM.]—When ethyl carbonylbisaminoacetate is hydrolysed with methyl-alcoholic potassium hydroxide solution a mixture of hydantoin-3-acetic acid and carbonylbisaminoacetic acid is obtained.

H. BURTON.

Electrolytic reduction of cyclic imides to hydrogenated cyclic bases. E. SPATH and F. BREUSCH (Monatsh., 1928, 50, 349—356).—Although Tafel (A., 1900, i, 557; *ibid.*, ii, 588) succeeded in converting succinimide derivatives only into pyrrolidones by electrolytic reduction at a lead cathode, further reduction to pyrrolidines is now shown to take place with α - and α' -substituted derivatives and certain other similarly constituted compounds.

The apparatus used was similar to that described by Tafel. The use of specially pure lead is essential. The following compounds were prepared from the corresponding imides in the yields stated: 3-Methylpyrrolidine (32%) (cf. Spath and Prokopp, A., 1924, i, 502); 3-phenylpyrrolidine, b. p. $120-122^\circ/12$ mm. (hydrochloride; picrate, m. p. 166°) (40.3%); 3:4-diphenylpyrrolidine, b. p. $195-200^\circ/14$ mm. (from α,α' -diphenylsuccinimide, m. p. 198°) (1.2%); dihydroisoindole (32%); tetrahydroisoquinoline (15%); dihydroindole (from isatin) (4%); hydrobenzoisoquinoline, m. p. 70° (from naphthalimide) [picrate, darkening at 195° , m. p. 200° (decomp.)] (15%). The imides of pyridine-2:3-dicarboxylic acid and diphenic acid and malonamide could not be reduced to the amines. The formation of pyrrolidone from succinimide appears to take place through γ -aminobutyric acid, ring-closure first occurring on distillation in the ordinary method of working up. R. K. CALLOW.

Piperidine derivatives. VI. 3-Methylpiperidinoalkyl benzoates. J. R. THAYER and S. M. McELVAIN (J. Amer. Chem. Soc., 1928, 50, 3348—3355).—3-Methylpiperidine and chloroacetone in ether yield α -3-methylpiperidinoacetone, b. p. $101-102^\circ/18$ mm., the hydrochloride, m. p. $162-163^\circ$, of which is hydrogenated (platinum) in alcohol to α -3-methylpiperidino- β -propyl alcohol hydrochloride, m. p. $184-185^\circ$ (free base, b. p. $98-100^\circ/18$ mm.). This is converted by benzoyl chloride into the hydrochloride (I), m. p. $165-166^\circ$, of α -3-methylpiperidino- β -propyl benzoate. 3-Methylpiperidine hydrochloride, paraformaldehyde, and acetone in absolute alcohol at 100° yield α -3-methylpiperidinobutan- γ -one hydrochloride, m. p. $151-152^\circ$, which is hydrogenated and benzoylated to α -3-methylpiperidino- γ -benzoyloxybutane hydrochloride (II), m. p. $178-180^\circ$. β,γ -Dibromobutane and silver benzoate (1 mol.) in toluene yield impure β -bromo- γ -benzoyloxybutane (III), b. p. $140-141^\circ/4$ mm. Acetylacetone is hydrogenated (platinum) to pentane- β,δ -diol, which by successive treatment with benzoyl chloride and thionyl chloride gives β -chloro- δ -benzoyloxybutane (IV), b. p. $134-135^\circ/2$ mm., n_D^{25} 1.5074, d_4^{25} 1.1008. Unstable β -chloro- β -methylpentan- δ -one (V), b. p. $50-52^\circ/14$ mm., is obtained from diacetone alcohol and thionyl chloride in dry ether. The products III, IV, and V do not yield tertiary amines when treated with 3-methylpiperidine, but lose 1 mol. of hydrogen

halide. The local anæsthetic action of I and II is much greater than that of the corresponding derivatives with an unmethylated alcoholic residue (cf. A., 1928, 71, 72), II being closely similar in its action to cocaine.

H. E. F. NORRON.

Reduction of cyclohexanoneisooxime (α -keto-hexamethyleneimine). A. MÜLLER and P. BLEIER (Monatsh., 1928, 50, 399—402).—Reduction of cyclohexanoneisooxime, m. p. 69.2° (corr.), with sodium and absolute alcohol gives 18% of hexamethyleneimine (cf. Wallach, A., 1903, i, 103; 1906, i, 175) identified as the hydrochloride, m. p. $236-237^\circ$ (corr.), and the *p*-toluenesulphonyl derivative, m. p. 76.5° (cf. A., 1928, 277), together with high-boiling bases. No ammonia is evolved during the reduction (cf. Wallach, *loc. cit.*).

H. BURTON.

Asymmetric nitrogen atom. LVI. Rates of transformation of stereoisomerides which simultaneously contain an asymmetric nitrogen and carbon atom; parallel to the true autoracemisation of "nitrogen-active" ammonium salts. E. WEDEKIND and G. L. MAISER (Ber., 1928, 61, [B], 2471—2479; cf. A., 1928, 898).—The preparation and separation of the two forms of *l*-menthyl 2-isopropyltetrahydroisoquinolinium iodide acetate, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH} \end{smallmatrix}\rangle\text{NPr}^s\text{I}\cdot\text{CH}_3\cdot\text{CO}_2\text{C}_{10}\text{H}_{19}$, is effected principally according to the method of Wedekind and Ney (A., 1909, i, 514); the more sparingly soluble iodide (β -iodide) has m. p. 161° , the more freely soluble α -iodide, m. p. $146-148^\circ$. Transformation of the α -form occurs mainly in methyl and ethyl alcohol. In acetone and chloroform the α -salt is stable; it is noteworthy that active methylallyltetrahydroquinolinium iodide does not undergo autoracemisation in acetone (*loc. cit.*). The electrical conductivity of solutions of the α -salt in chloroform remains constant over long periods, thus indicating the absence of decomposition. Kinetic measurements of the rate of transformation of the α - into the β -iodide at 25° in methyl alcohol indicate a strictly unimolecular change, the mean velocity coefficient being 0.0050. The velocity is about one tenth of that of the autoracemisation of 1-methyl-1-allyltetrahydroquinolinium iodide. The temperature coefficient of the transformation (2.31) for the interval $25-35^\circ$ is only slightly greater than that of racemisation of the active salt.

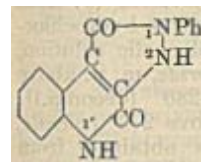
The iodides have been transformed into the corresponding nitrates (α -form, m. p. $125-127^\circ$, $[\alpha]_D^{25} -66.0^\circ$ in methyl alcohol; β -variety, m. p. $153-155^\circ$, $[\alpha]_D -20.3^\circ$), both of which are optically stable in all solvents investigated. In analogy with the behaviour of the active 1-methyl-1-allyltetrahydroquinolinium iodide, the presence of a halogen atom as anion appears essential for transformation into the salt of higher m. p., whilst it may also be noted that precisely similar regularities are observed with compounds containing an asymmetric carbon atom as far as autoracemisation at the ordinary temperature is concerned.

The betaines produced by a type of autohydrolysis when menthyl 1-alkyltetrahydroquinolinium iodide acetates are treated with silver oxide suffer auto-

racemisation in acetone as well as in alcohol but at an appreciably slower rate.

H. WREN.

3-Thiol-2-keto-1 : 2-dihydroquinoline-4-carboxylic acid and some quinolone derivatives. C. GRANACHER and C. KOUNINOTIS (Helv. Chim. Acta, 1928, 11, 1241—1252).—The compound previously described as oxindole-3- α -thiolacetic acid (A., 1923, i, 713), prepared by the action of sodium hydroxide on 3-rhodanylideneoxindole, is now shown to be 3-thiol-2-keto-1 : 2-dihydroquinoline-4-carboxylic acid (I), m. p. 165—167° [(decomp.); S-benzyl derivative, m. p. 230°; S-carboxymethyl derivative, m. p. 218—221° (decomp.)], reduced by Clemmensen's method to 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, m. p. 218—219° (cf. Aeschlimann, A., 1927, 256). Similarly, 3-rhodanylidene-N-methyloxindole gives 3-thiol-2-keto-1-methyl-1 : 2-dihydroquinoline-4-carboxylic acid, m. p. 146—150° (decomp.; S-carboxymethyl derivative, m. p. 210°). When I is treated with phenylhydrazine in boiling methyl alcohol, hydrogen sulphide is eliminated and the pyrazolone derivative (annexed formula) is obtained. Methylation of this with methyl iodide affords the 2-methyl derivative, m. p. 266° (2-ethyl derivative, m. p. 256—258°). Further ethylation of these alkyl derivatives gives the corresponding 2-methyl-1'-ethyl, m. p. 212°, and 2 : 1'-diethyl, m. p. 173—174°, compounds.



The action of aniline on I (loc. cit.) yields the 3-anilino-derivative, hydrolysed to 2 : 3-diketo-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, whilst hydroxylamine gives the anhydride of 3-oximino-2-keto-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid.

H. BURTON.

Pyridinearylimines. II. Elimination and wandering of aryl nitrogen complexes. W. SCHNEIDER and K. WEISS (Ber., 1928, 61, [B], 2445—2451; cf. A., 1924, i, 1108).—Confirmatory evidence is adduced in favour of the authors' formulation of the dark-coloured, anhydro-bases derived from 1-phenylaminopyridinium compounds as pyridine-1-phenylimines. 2 : 4 : 6-Triphenylpyridine, m. p. 138°, is obtained by the action of carbon disulphide or phenylthiocarbimide on 2 : 4 : 6-triphenylpyridine-1-phenylimine; in a single instance the compound $C_{18}H_{10}NS$ was prepared by action of the carbimide. Reduction of 2 : 4 : 6-triphenylpyridine-1-phenylimine in methyl alcohol in presence of spongy platinum affords 2 : 4 : 6-triphenylpyridine and aniline. Treatment of 4 : 6-diphenyl-2-methylpyridine-1-phenylimine with boiling alcohol until the violet colour disappears yields 4 : 6-diphenyl-2-o-aminobenzylpyridine, m. p. 144°, more conveniently prepared by gradual addition of sodium hydroxide to a boiling, alcoholic solution of 4 : 6-diphenyl-2-methylpyridinium iodide followed by treatment of the solution with zinc dust. The monohydrochloride, m. p. 256°, and picrate, $C_{20}H_{20}N_2 \cdot C_6H_3O_7N_3$, m. p. 202°, are described. The base can be diazotised. With methyl iodide it affords 4 : 6-diphenyl-2-o-methylaminobenzylpyridine methiodide hydriodide (+CHCl₃), m. p. 158° (decomp.), in which the solvent of crystallisation is

retained with remarkable tenacity. The salt yields a nitroso-derivative. 4 : 6-Diphenyl-2-o-acetamidobenzylpyridine, m. p. 172°, and 4 : 6-diphenyl-2-o-benzamidobenzylpyridine, m. p. 123°, are described. The last-mentioned compound is converted through its nitroso-derivative, decomp. 105—110°, into an indazole derivative, $C_{24}H_{17}N_3$, m. p. 228°, thus establishing the *ortho*-position of the amino- to the methylene group.

H. WREN.

Attempt to prepare ψ -isoindole. G. W. FENTON and C. K. INGOLD (J.C.S., 1928, 3295—3297).—o-Xylylene dibromide and *p*-toluenesulphonamide, in the presence of the alcoholic sodium ethoxide, gave 2-*p*-toluenesulphonyldihydroisoindole, m. p. 176° (corresponding benzenesulphonyl derivative, m. p. 140°), which by distillation with potassium hydroxide solution in an atmosphere of nitrogen yielded toluene, potassium sulphite, and dihydroisoindole [isolated as the picrate, m. p. 196—197° (decomp.)]. Similarly, 2-*p*-toluenesulphonyl-1-methyldihydroisoindole, m. p. 93° (obtained by toluenesulphonylation of the dihydro-base) gave toluene, sulphite, a tar, and 1-methyldihydroisoindole. ψ -isoIndole thus appears to be less stable than indole, possibly because the elements of unsaturation are more symmetrically distributed in the latter and that aromatic sextuple valency association is peripheral rather than central.

R. J. W. LE FEVRE.

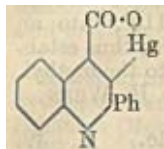
Indole derivatives. II. Synthesis of indole-carboxylic acids. S. KEIMATSU and S. SUGASAWA (J. Pharm. Soc. Japan, 1928, No. 558, 755—761; cf. A., 1928, 1030).—Ethyl β -cyanoethylsodioacetate and benzenediazonium chloride react to give ethyl γ -cyano- α -ketobutyrate phenylhydrazone, m. p. 115°, converted by alcoholic hydrochloric or sulphuric acid into ethyl indole-3-acetate-2-carboxylate [ethyl 3-carbethoxymethylindole-2-carboxylate], m. p. 85—86°. The free acid decomposes at 228°, giving 3-methylindole. Ethyl indole-3-propionate-2-carboxylate, m. p. 95°, is similarly obtained from ethyl δ -cyano- α -keton-valerate phenylhydrazone, m. p. 93°. The free acid, m. p. 195°, loses 1 mol. of carbon dioxide at 220—230°, yielding indole-3-propionic acid, m. p. 134° (cf. Kalb and others, A., 1926, 1151).

K. ISHIMURA.

Indole derivatives. III. Synthesis of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline. S. KEIMATSU, S. SUGASAWA, and G. KASUYA (J. Pharm. Soc. Japan, 1928, No. 558, 762—766).—Ethyl δ -phthalimido- α -acetylvalerate reacts with benzenediazonium chloride in alkaline alcoholic solution, yielding ethyl δ -phthalimido- α -ketovalerate phenylhydrazone, m. p. 146°, which is converted into ethyl 3- β -phthalimidoethylindole-2-carboxylate, m. p. 195° (cf. Manske, Perkin, and Robinson, A., 1927, 265). The latter compound, when heated with alcohol and hydrazine hydrate and then with 10% hydrochloric acid, yields 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline, m. p. 188—189° (cf. Ashley and Robinson, A., 1928, 775), which after heating with alcoholic potassium hydroxide and neutralisation with dilute sulphuric and acetic acids gives 3- β -aminoethylindole-2-carboxylic acid, m. p. 256° (decomp.). It loses carbon dioxide when heated with hydrochloric acid, yielding 3- β -aminoethylindole

hydrochloride, m. p. 243° (decomp.) (acetate, m. p. 136°; picrate, m. p. 245°). K. ISHIMURA.

Action of mercuric acetate on phenylcinchoninic acid. B. CECCHIETTI and E. GODI (Gazzetta, 1928, 58, 764—765).—Phenylcinchoninic acid (2 mols.) reacts in alcohol with 1 mol. of mercuric acetate to give a compound, $C_{32}H_{20}O_4N_2Hg$, probably the mercuric salt, and with 2 mols. to give a compound, $C_{16}H_9O_2NHg$, regarded as having the annexed formula. E. W. WIGNALL.



Carbazole derivatives. I. F. KEHRMANN and F. ZWEIFEL (Helv. Chim. Acta, 1928, 11, 1213—1219).—Acetylation of 3-acetamidocarbazole, m. p. 217°, with excess of acetic anhydride in presence of anhydrous zinc chloride affords a mixture of di- and tri-acetyl derivatives, which when nitrated in acetic acid gives a mixture of α -, m. p. 226°, and β -nitro-diacetamidocarbazoles. Hydrolysis of the α -form with alcoholic sodium hydroxide solution yields 2(or 4)-nitro-3-acetamidocarbazole, m. p. 274°, hydrolysed by alcoholic sulphuric acid to 2(or 4)-nitro-3-aminocarbazole, m. p. 233°. 2(or 4)-3-Diaminocarbazole (benzil condensation product, m. p. 273°) is readily oxidised in air. When the mixture of α - and β -nitro-derivatives is hydrolysed with cold alcoholic sodium hydroxide 4(or 2)-nitro-3-acetamidocarbazole, m. p. 198° (free base, m. p. 177°), goes into solution, and is precipitated by water. The quin-oxaline derivative from benzil and 3 : 4(or 2)-diaminocarbazole has m. p. 261°. H. BURTON.

Biuret reaction. I. Biuret reaction of acid imides of the barbituric acid type. M. M. RISING and C. A. JOHNSON (J. Biol. Chem., 1928, 80, 709—722).—The theory of the biuret reaction is discussed in detail; from the sodium or potassium salt of diethylbarbituric acid there were obtained, by treatment with cupric acetate in alcohol, compounds, $(Na \text{ or } K)_2CuC_{32}H_{48}O_{14}N_8$, which are regarded as having the structure $(Na \text{ or } K)_2Cu(imide)_4 \cdot nH_2O$; in the above two compounds, the water, being firmly bound, is regarded as forming part of the molecular complex. A similar structure is proposed for the compounds prepared by Tschugaev (A., 1907, i, 595) and by Ley and Werner (A., 1907, i, 302), save that in these cases the water is regarded as water of crystallisation. C. R. HARRINGTON.

Determination and characterisation of allantoin. R. FOSSE and (MLLE.) V. BOSSUYT (Compt. rend., 1929, 188, 106—109).—Allantoin is hydrolysed in acid media to give glyoxylic acid (1 mol.) and carbamide (2 mols.). Allantoin may be detected by heating the sample, slightly acidified with hydrochloric acid, for 1 min. at 100° and adding 1% phenylhydrazine hydrochloride (4 drops), followed, after cooling, by 5% potassium ferricyanide (2 drops) and concentrated hydrochloric acid (1.5 c.c.). An immediate red coloration indicates allantoin. G. A. C. GOUGH.

Alkylation of diketopiperazine and peptides. C. GRANACHER, G. WOLF, and A. WEIDINGER (Helv. Chim. Acta, 1928, 11, 1228—1241).—Benzylation of 2 : 5-diketopiperazine with benzyl chloride and

sodium methoxide gives 1 : 4-dibenzyl-2 : 5-diketopiperazine, m. p. 176° (lit. 170—174°), hydrolysed by concentrated hydrochloric acid to *N*-benzylglycine hydrochloride, m. p. 226° (lit. 215°). 1 : 4-Di-*p*-methoxybenzyl-2 : 5-diketopiperazine, m. p. 206°, is obtained similarly. *dl*-Alanine anhydride and benzyl chloride yield a mixture of two diastereoisomeric *NN'*-dibenzylalanine anhydrides, m. p. 144—145° and 89°, respectively, both hydrolysed by hydrochloric acid to *N*-benzylalanine, m. p. 269—270° (decomp.) after sintering at 265°. Similarly, *dl*-leucine anhydride affords two *NN'*-dibenzyl derivatives, m. p. 182—183° and an oil, respectively. Benzylation of hippurethylamide gives *N*-benzylhippurethylamide, m. p. 119°, hydrolysed to benzoic acid, ethylamine, and *N*-benzylglycine, together with *N*-benzylhippurethylethylamide, b. p. 230—240°/1—2 mm., hydrolysed to benzeylethylamine, benzoic acid, and *N*-benzylglycine. *N*-*p*-Bromobenzylhippurethylamide has m. p. 134—136°. H. BURTON.

Substituted guanidines. F. BISCHOFF (J. Biol. Chem., 1928, 80, 345—355).—Piperazine hydrochloride and cyanide, when boiled in alcoholic solution, yielded diguanylpiperazine hydrochloride, m. p. above 310° [chloroplatinate, m. p. 279—280° (decomp.)]; guanylpiperidine sulphate, m. p. above 270° [picrate, m. p. 242—243° (decomp.)], was obtained from piperidine and methylisothiocarbamide sulphate at the ordinary temperature. α -Diguandino-*n*-pentane (cf. Ripke, A., 1911, i, 620) was conveniently prepared from pentamethylenediamine hydrochloride and cyanamide in boiling alcohol; α -diguandino-*n*-octane sulphate (chloroplatinate, m. p. 214—216°, picrate, m. p. 205—206.5°, chloraurate, m. p. 143—144°) was obtained from octamethylenediamine and methylisothiocarbamide sulphate. *p*-Guanidinodimethylaniline, from *p*-aminodimethylaniline hydrochloride and cyanamide in boiling alcohol, had m. p. 117—122°, nitrate, m. p. 185°, sulphate, m. p. 112—112.5°; diguanylbenezidine could not be obtained pure, nor could negatively substituted aromatic amines be brought into reaction with cyanamide (cf. Kampf, A., 1904, i, 534). C. R. HARRINGTON.

Rung, Behrend, and Pinner's reaction. II. G. GASTALDI and Q. TALU (Gazzetta, 1928, 58, 664—666).—Whereas the quaternary ammonium bases formed by glyoxaline and oxypyrazine compounds give, when treated with alkali hydroxide, two molecules of alkylamine (A., 1928, 1027), those formed by oxypyrimidine derivatives yield, under similar conditions, one molecule of alkylamine and one of ammonia. This difference in behaviour depends on the fact that, in the former case, the alkylidides, and in the latter the hydriodides undergo scission. 6-Keto-1 : 2 : 4-trimethyl-1 : 6-dihydropyrimidine hydriodide, $CO \begin{smallmatrix} NMe \cdot CMe \\ \diagup \quad \diagdown \\ CH = CMe \end{smallmatrix} NHI$, m. p. 215° (decomp.), is obtained by treating a methyl-alcoholic solution of 6-keto-2 : 4-dimethylpyrimidine with potassium hydroxide (1 mol.) and methyl iodide (4 mols.). T. H. POPE.

Syntheses of heterocyclic nitrogen nuclei. II. 1 : 3 : 5-Triarylpyrazole-4-carboxylic acids and 1 : 3 : 5-triarylpyrazoles from aldehydehydraz-

ones and ethyl benzoylacetate. G. MINUNNI and S. D'Urso (Gazzetta, 1928, 58, 691—712).—Ethyl benzoylacetate reacts with aldehydephenylhydrazones similarly to ethyl acetoacetate (A., 1925, i, 1175), yielding esters of pyrazolocarboxylic acids, from which the corresponding pyrazoles are prepared. The preparation and properties of the following compounds are described:

[With G. TROIA.]—1 : 3 : 5-Triphenylpyrazole-4-carboxylic acid (cf. Seidel, A., 1899, i, 139); ethyl ester, m. p. 145—146.5°; 1 : 3 : 5-triphenylpyrazole, new m. p. 140—140.5°, which was not found to crystallise with alcohol (cf. Knorr and Laubmann, A., 1888, 725; Moureu and Brachin, A., 1903, i, 581).

[With A. CARNEVALE.]—1 : 5-Diphenyl-3-*o*-nitrophenylpyrazole-4-carboxylic acid, $C_{29}H_{15}O_4N_3$, EtOH, m. p. 232.5—233.5° (decomp.); ethyl ester, m. p. 115.5—117.5°; 1 : 5-diphenyl-3-*o*-nitrophenylpyrazole, m. p. 116—117°. Alkaline hydrolysis of the ester yielded, besides the acid, a secondary product, m. p. above 255°.

[With G. AREZZI.]—1 : 5-Diphenyl-3-*m*-nitrophenylpyrazole-4-carboxylic acid, [\pm EtOH], m. p. 232° (decomp.); ethyl ester, m. p. 126.5—127.5°; 1 : 5-diphenyl-3-*m*-nitrophenylpyrazole, m. p. 137.5—139°. The azoxy-derivative, $C_{44}H_{30}O_5N_6$, of the acid, m. p. 240—247° (decomp.), is formed by prolonged heating of the ester with alcoholic potassium hydroxide.

[With C. VIZZINI.]—The corresponding 3-*p*-nitrophenyl compounds have m. p.: acid, 248—250°; ethyl ester, 166—167°; pyrazole, 153—155°; and azoxy-compound, 285°. In the preparation of the ester a secondary product, m. p. 142—145°, is obtained. E. W. WIGNALL.

Action of diazonium salts on 6-hydroxy-2 : 5-dimethylpyrazine. III. G. GASTALDI and E. PRINCIVALLE (Gazzetta, 1928, 58, 679—682).—The behaviour of 6-hydroxy-2 : 5-dimethylpyrazine (A., 1921, i, 602) when treated with phenyl- or *o*- or *p*-tolyl-diazonium chloride is normal, the products being the corresponding stable, yellow azo-compounds of the constitution, $N \begin{smallmatrix} \diagup CMe \\ \diagdown C(N_2R)CMe \end{smallmatrix} C(OH)N$. The ease

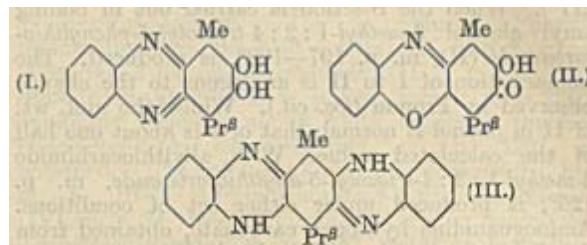
with which this occurs indicates that the pyrazine reacts in the lactimic form, but it is possible that, in its reaction with alkyl halides, the first products are *O*-ethers, which are afterwards transformed into the *N*-derivatives (A., 1928, 1027). The product of the coupling of 6-hydroxy-2 : 5-dimethylpyrazine with *p*-nitrobenzenediazonium chloride has not the characters of the azo-compounds.

3-Benzeneazo-6-hydroxy-2 : 5-dimethylpyrazine, m. p. 208° (decomp.), and its sodium salt; 3-*p*-tolylazo-6-hydroxy-2 : 5-dimethylpyrazine, m. p. 242° (decomp.), and its sodium salt; 3-*o*-tolylazo-6-hydroxy-2 : 5-dimethylpyrazine, m. p. 221° (decomp.), and its sodium salt are described. T. H. POPE.

Fluorindenenes. X. Derivatives of fluorindene and triphenyldioxazine. F. KEHRMANN and C. COLLAUD (Helv. Chim. Acta, 1928, 11, 1028—1034).—When a mixture of 2 : 3-dihydroxy-6-acetamidonaphthaphenazine (A., 1925, i, 1331), *o*-aminodiphenylamino hydrochloride, and benzoic acid is boiled for about 3 min. 6-acetamidophenyl-naphtha-

phenfluorindene is obtained. When the diamine is replaced by phenyl-1 : 2-naphthylenediamine and 4-acetamido-1 : 2-naphthylenediamine the products formed are 6-acetamidophenyl-dinaphthafluorindene and diacetamidodinaphthafluorindene, respectively.

Dihydroxythymoquinone and *o*-phenylenediamine react under the above conditions giving dihydroxythymophenazine (I), decomp. about 240° (acetyl derivative, m. p. 197°), whilst with *o*-aminophenol hydroxythymophenazoxone (II), m. p. 197° (acetyl derivative, m. p. 133°), is formed.



When the quinone, *o*-phenylenediamine, and anthracene are boiled together the product is thymoquinone (III). With *o*-aminophenol hydrochloride in presence of benzoic acid there are formed II and methylisopropyltriphenyldioxazine (in III, NH=O).

2 : 3-Dihydroxynaphthaphenazine and hydroxyisorosindone react with *o*-aminophenol yielding naphthaphenazineoxazine and its *N*-phenyl derivative, respectively. H. BURTON.

Carbocyanine dyes with substituents attached to the three-carbon chain. F. M. HAMER (J.C.S., 1928, 3160—3163).—The condensation of 1-methylbenzthiazole ethiodide and ethyl orthoacetate in the presence of pyridine (or, with less success, acetic anhydride) gave 8-methyl-2 : 2'-diethylthiocarbocyanine iodide (I), decomp. about 280° and m. p. about 290°, which, in alcoholic solution, showed an absorption



band at λ 5400 Å. with a weaker one at λ 5100 Å. In gelatinobromide emulsions the dye was a powerful sensitiser, showing maxima at λ 5900 and 5200 Å.

Similarly, 1-methylbenzthiazole methiodide gave 2 : 2' : 8-trimethylthiocarbocyanine iodide, m. p. about 298° (decomp.), with maximum absorption in alcoholic solution at λ 5400 Å., and 1-methylbenzthiazole allobromide yielded 8-methyl-2 : 2'-diallylthiocarbocyanine bromide, m. p. 260° (decomp.), with principal absorption maximum in alcohol at λ 5450 Å.

R. J. W. LE FÈVRE.

Reactions between phenanthraquinone and magnesylpyrroles. Q. MINGOIA (Gazzetta, 1928, 58, 673—679).—Phenanthraquinone reacts similarly to anthraquinone (A., 1926, 1158) with magnesylpyrrole, but the dipyrrolylphenanthrol formed immediately loses $2H_2O$ from the tertiary alcoholic hydroxyl groups and the iminic hydrogen atoms, giving 9 : 10-dipyrrolyldihydrophenanthrene, m. p. 190°. With magnesylmethylketole, phenanthraquinone reacts similarly to anthraquinone (cf. A., 1927, 158), giving 9 : 10-tetra-(2'-methyl-3'-indolyl)di-

hydrophenanthrene, m. p. 154°, which forms a *tetra-acetyl* compound, m. p. 170°. T. H. POPE.

Reaction between triazoles and thiocarbimides. P. FANTL and H. SILBERMANN (Annalen, 1928, 467, 274—287; cf. Fromm and others, A., 1926, 716; this vol., 199).—5-Amino-3-methyl-1:2:4-triazole reacts with phenylthiocarbimide in cold alcoholic solution forming 5-amino-3-methyl-1:2:4-triazolyl-2-phenylthiocarbimide (I), m. p. 137°, resolidifying with m. p. 197—199° (*picrate*, m. p. 217°). When the reaction is carried out in boiling amyl alcohol 3-methyl-1:2:4-triazolyl-5-phenylthiocarbimide (II), m. p. 197—199°, is produced. The isomerisation of I to II is analogous to the change observed by Fromm (*loc. cit.*). Whilst the mol. wt. of II in phenol is normal, that of I is about one half of the calculated value. With allylthiocarbimide 3-methyl-1:2:4-triazolyl-5-allylthiocarbimide, m. p. 125°, is produced under either set of conditions. Aminoguanidine hydrogen carbonate, obtained from disodium cyanamide and hydrazine in presence of sulphuric acid and subsequent treatment with potassium hydrogen carbonate, is converted by phenylthiocarbimide in alcoholic solution into 5-amino-3-thio-4-phenyl-1:2:4-triazole, m. p. 264° (cf. Arndt and others, A., 1922, i, 375) (*benzyl* derivative, m. p. 172°; *dibenzyl* derivative, m. p. 137°; *tribenzyl* derivative, m. p. 138°). 5-Amino-3-methylthiol-4-phenyl-1:2:4-triazole and phenylthiocarbimide yield a compound, $C_{25}H_{24}(22)N_8S_2$, m. p. 204°. Anilino-guanidinophenylthiocarbimide, m. p. 167°, is identical with the product from phenylthiuret and phenylhydrazine (Fromm and Vetter, A., 1907, i, 982). Allylthiocarbimide and anilino-guanidine give a mixture of anilino-guanidinoallylthiocarbimide (III), m. p. 128°, and a compound, $C_{11}H_{12}N_4S$, m. p. 204° (decomp.), either a triazole or a thiodiazole, formed presumably from the intermediate $NH_2 \cdot C(NH) \cdot NH \cdot NPh \cdot CS \cdot NH \cdot C_3H_5$. Treatment of III with hot aqueous-alcoholic alkali yields 5-amino-3-allylamino-2-phenyl-1:2:4-triazole, m. p. 74° (5-phenylthiocarbimide derivative, m. p. 192°; 5-allylthiocarbimide derivative, m. p. 120°). 1-Phenyl-1:2:4-triazolyl-5-phenylthiocarbimide, m. p. 128°, 2-phenyl-3-methyl-1:2:4-triazolyl-5-phenylthiocarbimide, m. p. 181°, and 5-allylthiocarbimide, m. p. 158°, are described.

Acetamidoguanidine nitrate is an extremely sensitive reagent for trivalent iron. A deep violet coloration is produced with 0.01 mg. and a perceptible coloration with 0.001 mg. The coloration is obtained in presence of other cations, phosphate, or acetate, but is prevented by glycerol or tartaric acid. H. BURTON.

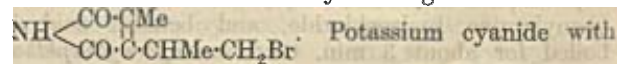
Catalytic hydrogenation of hæmins and porphyrins. R. KUHN and C. SEYFFERT (Ber., 1928, 61, [B], 2509—2516; cf. A., 1927, 784).—Hæmin can be hydrogenated in aqueous-alkaline or pyridine solution in presence of various contacts in such a manner that addition ceases after absorption of 1 mol. of hydrogen (usually 10% less than this amount). Lower values indicate unfavourable conditions which may be due to catalyst or hæmin. Under the experimental conditions, particularly with platinum metals deposited on carriers, a favoured stage of hydrogen-

ation of the hæmin molecule appears to be attained with the introduction of 2 atoms of hydrogen. Spectroscopical examination of the hydrogenated hæmin solutions does not indicate the presence of a considerable proportion of mesohæmin, so that the production of this compound accounts for only a fraction of the hydrogen absorbed. The main amount is not absorbed by the unsaturated side-chain of hæmin. Mesoporphyrin, in which the side-chains are saturated, can be hydrogenated by the same contacts which change hæmin into dihydrohæmin. Mesoporphyrin dihydrochloride in glacial acetic acid does not become changed spectroscopically and the reaction product is identical with the original material. This is true also of mesoporphyrin dimethyl ester, so that it is concluded that the adsorbed hydrogen is only very loosely united and is removed by contact with atmospheric oxygen. In certain cases, dihydrohæmins appear to behave analogously. Formation of porphyrinogens, previously achieved only with sodium amalgam or with hydriodic acid and phosphonium iodide, can be effected catalytically by use of platinum oxide in glacial acetic acid; the isolated products from mesoporphyrin dihydrochloride and mesoporphyrin dimethyl ester are identical with the original materials. Protoporphyrin dimethyl ester is hydrogenated to a leuco-compound with about 5 mols. of hydrogen in presence of platinum oxide and the product is oxidised to mesoporphyrin dimethyl ester, addition occurring thus in the side-chain and the methine bridges. H. WREN.

Addition of bromine to protoporphyrin dimethyl ester and to its complex zinc salt. W. KUSTER and A. GROSSE (Z. physiol. Chem., 1928, 179, 117—138).—The acetylene (A) and vinyl (V) side-chains of protoporphyrin dimethyl ester may exist as such or may form a conjugated ring system, $CH_2 \cdot C \cdot CH \cdot CH \cdot$. These would give the same product after addition of chlorine and hydrobromic acid only if the pyrrole nuclei attached are identical.

Bromination of protoporphyrin dimethyl ester gave a bluish-black product, *A-(αβ)-V-(αβ)-tetrabromoporphyrin ester*, $C_{36}H_{36}O_4N_4Br_4$, showing three bands in the spectrum at 590, 565—545, 530—515 μ . On treatment with methyl alcohol a bluish-black, crystalline substance, *A-α-V-β-dibromo-A-β-V-α-dimethoxyprotoporphyrin dimethyl ester*, showing bands at 620—610, 580—560, 540—525, 515—490 μ , was obtained. When the dibromo-product was treated with zinc acetate in methyl alcohol the methyl was replaced by zinc in the group $-CH \cdot CH \cdot OMe$ in the doubled molecule $(C_{37}H_{37}O_6N_4Br_2Zn)_2Zn$. Similar treatment of tetramethylhæmatoporphyrin gave the salt $C_{38}H_{42}O_6N_4Zn$, absorption bands, 585—570, 550—530 μ . Hydrolysis with aqueous sodium hydroxide removed the two ester methyl groups. On heating the complex zinc salt of tetramethylhæmatoporphyrin with methyl-alcoholic zinc acetate one methyl ether group was hydrolysed and the methyl replaced by a zinc half atom $(C_{37}H_{39}O_6N_4Zn)_2Zn$.

Oxidation of dibromodimethoxyprotoporphyrin ester with chromic anhydride gave the imide,



tetrabromoproporphyrin dimethyl ester gave bluish-black *dibromodicyanoproporphyrin ester*, with bands at 610—600, 580—560, 540—530, 515—495. Hydrolysis gave *A- α -V- β -dibromo-A- β -V- α -dicarboxymethylprotoporphyrin dimethyl ester*, absorption bands, 610—600, 570—560, 540—530, 575—490 μ . The zinc salt showed two absorption bands 590—570, 560—530 μ . Reduction with hydriodic acid and red phosphorus gave *bromomethoxydicarboxymethylprotoporphyrin dimethyl ester*, absorption bands 610—600, 570—560, 535—525, 510—485 μ . The complex zinc salt of protoporphyrin dimethyl ester was brominated. The *tetrabromo-derivative*, $C_{36}H_{36}O_4N_4Br_4Zn$, showed a 4-banded spectrum, 580, 570—540, 530, 510—490. Hydrobromic acid was removed by methyl alcohol, and the whole of the bromine by boiling with secondary sodium phosphate, giving a *product*, $C_{34}H_{26}O_4N_4Zn$; spectrum bands 570—550, 540—520. The complex copper salt of protoporphyrin ester on bromination gave a *product*, $C_{36}H_{34}O_4N_4Br_4Cu$, with bands at 580, 560—555, 530, and 510—490 μ ; the chloro-ferric salt gave a *product*, $C_{36}H_{33}O_4N_4FeClBr_4$, a metallic powder.

J. H. BIRKINSHAW.

Tautomerism of some heterocyclic compounds [oxazolines, thiazolines]. E. FROMM and R. KAPPELLER-ADLER [with W. FRIEDENTHAL, L. STANGELER, J. EDLITZ, E. BRAUMANN, and J. NUSSBAUM] (*Annalen*, 1928, 467, 240—274).—An extension of the work on the tautomerism of amino-oxazolines (A., 1926, 716). Amino-thiazolines react with thiocarbimides, yielding two series of thiocarbimides according to the conditions. No tautomerism is found in either the thiazole, oxazole, or triazole series, in the first two cases presumably because of the aromatic nature of the ring systems. When 2-amino-5-chloromethyl-oxazoline (I) is heated with ammonium chloride (2 parts) and alcohol in a sealed tube at 100°, β -chloro- β -guanidinopropyl alcohol hydrochloride, m. p. 112° (*picrate*, m. p. 147°), is obtained. The *tribenzoyl derivative*, m. p. 178°, of the base is identical with the compound previously described (A., 1925, i, 594) as 2-amino-5-aminomethyliminazoline tetrabenzoate. When I is heated with dilute ammonia at 100° there is formed 2-amino-5-aminomethylloxazoline (*picrate*, m. p. 172°; *chloroplatinate*). Benzenesulphonylation of I yields 2-imino-5-chloromethylloxazolinyl-3-benzenesulphonate, m. p. 111° (2-benzoyl derivative, m. p. 152°), hydrolysed by cold dilute sulphuric acid to 5-chloromethylloxazolidonyl-3-benzenesulphonate, m. p. 106°. Benzenesulphonylation of the reaction product from disodium cyanamide and monochlorohydrin gives the *tribenzenesulphonyl derivative*, m. p. 158°, of 2-amino-5-hydroxymethylloxazoline. Sodium cyanamide and propylenechlorohydrin react, forming 2-amino-5-methylloxazoline (*dibenzoyl derivative*, m. p. 75°), which with phenylthiocarbimide gives 2-imino-5-methylloxazolinyl-3-phenylthiocarbamide, m. p. 98°. When this is heated at its m. p. or in alcoholic solution 5-methylloxazolinyl-2-phenylthiocarbamide, m. p. 152°, is formed, whilst dilute sulphuric acid converts it into 5-methylloxazolidonyl-3-phenylthiocarbamide, m. p. 114°. Similar tautomerism is exhibited by 2-amino-5-benzylthiolmethylloxazoline, m. p. 92° (*dibenzoyl derivative*, m. p. 112°), from I and benzylmercaptan, which gives

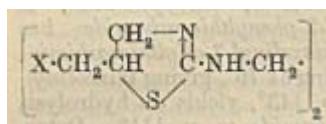
2-imino-5-benzylthiolmethylloxazolinyl-3-phenyl-, m. p. 89°, and 3-allyl-thiocarbimides, m. p. 87°. These last compounds are hydrolysed to 5-benzylthiolmethylloxazolidonyl-3-phenyl-, m. p. 107°, and 3-allyl-thiocarbimides, m. p. 59°, and converted as above into 5-benzylthiolmethylloxazolinyl-2-phenyl-, m. p. 129°, and 2-allyl-thiocarbimides, m. p. 100°, respectively.

p-Toluenesulphonylation of aminothiazoline (II) (Gabriel, A., 1889, 870) (*dibenzoyl derivative*, m. p. 182°) affords 2-iminothiazolinyl-3-*p*-toluenesulphonate, m. p. 143°, since on hydrolysis thiazolidonyl-3-*p*-toluenesulphonate, m. p. 158°, is produced. Phenylthiocarbimide in the cold converts II into 2-iminothiazolinyl-3-phenylthiocarbamide (III), m. p. 60°, resolidifying at 80° with m. p. 129° (*picrate*, m. p. 230°, exploding violently above 300°), whilst in the hot thiazolinyl-2-phenylthiocarbamide, m. p. 130°, is obtained. Thiazolidonyl-3-phenylthiocarbamide has m. p. 103°. 2-Iminothiazolinyl-3-allylthiocarbimide (IV), m. p. 71°, resolidifying at 79°, giving thiazolinyl-2-allylthiocarbamide, m. p. 143°, yields on hydrolysis thiazolidonyl-3-allylthiocarbamide, m. p. 111°. Determinations of the mol. wt. of III and IV in phenol give values which are approximately one half of the theoretical, indicating that they are additive compounds. This possibility is discounted by the formation of thiazolidones by hydrolysis, and also by the observation that diphenylmethylthiocarbamide gives a similar low value. 2-Amino-5-phenylthiazole (Hantzsch and Traumann, A., 1889, 414) (*benzoyl derivative*, m. p. 124—125°; *benzylidene derivative*, m. p. 127°; *p*-toluenesulphonyl derivative, m. p. 150°) does not react with phenylthiocarbimide in the cold, but in the hot yields 5-phenylthiazolyl-2-phenylthiocarbamide, m. p. 213°. 2-Amino-5-methylthiazole (*dibenzoyl derivative*, m. p. 110°) gives 5-methylthiazolyl-2-phenyl-, m. p. 172°, and 2-allyl-thiocarbimides, m. p. 178°, under all conditions.

2-Amino-5-phenyloxazole, m. p. 216° (*benzoyl derivative*, m. p. 182°; *acetyl derivative*, m. p. 184°), from phenacyl bromide and sodium cyanide (cyanamide?), also yields 5-phenyloxazolyl-2-phenylthiocarbamide, m. p. 195°, as the sole product. 3-Amino-5-anilino-1-phenyl-1:2:4-triazole (A., 1907, i, 982) (*monobenzoyl derivative*, m. p. 105°) and phenylthiocarbimide give the corresponding 3-phenylthiocarbamide, m. p. 194° (3-allylthiocarbamide, m. p. 191°). 3-Amino-5-anilino-1:2:4-triazole, m. p. 163° (cf. A., 1922, i, 378), obtained from hydrazine hydrate and phenyl- ϕ -benzylcyanthiocarbamide (A., 1895, i, 461), furnishes the corresponding 3-phenylthiocarbamide, m. p. 203° (3-allylthiocarbamide, m. p. 133°). The *phenyl- and allyl-thiocarbamido-derivatives* of phenylguanazole (Pellizzari, A., 1892, 356) have m. p. 252° and 220°, respectively. 3-Amino-5-thiol-1-phenyl-1:2:4-triazole affords the 3-phenylthiocarbamide, m. p. 264°. The *phenylthiocarbamides* from 3-amino-5-benzylthiol-, 3-amino-5-methylthiol-, and 5-amino-3-benzylthiol-1-phenyl-1:2:4-triazoles (*dibenzoyl derivative*, m. p. 125°) have m. p. 188°, 178°, and 154°, respectively, whilst the corresponding *allylthiocarbamides* have m. p. 129°, 138°, and 138°, respectively. Phenylhydrazine reacts with dimethyl cyanamidodithiocarbonate (Hantzsch and Wolvekamp, A., 1904, i, 718) forming 5-amino-3-methylthiol-1-phenyl-1:2:4-triazole, m. p.

105° (benzoyl derivative, m. p. 118°), whilst dibenzyl cyanamidodithiocarbonate and hydrazine hydrate give 3-amino-4(5?)-benzylthiotriazole, m. p. 109° (hydrochloride, m. p. 100°; dibenzoyl derivative, m. p. 148°). 5-Benzylthioltriazolyl-3-phenyl- and -3-allylthiocarbamides have m. p. 155° and 116°, respectively. The *p*-toluenesulphonyl derivative of 3-amino-5-methylthiol-1-phenyl-1:2:4-triazole (sulphone derivative, m. p. 304° not sharp) has m. p. 142°. Oxidation of 3-amino-5-benzylthiol-1-phenyl-1:2:4-triazole with potassium permanganate in acetic acid solution gives a substance, $C_{30}H_{24}N_8S_6$, m. p. 140°.

Ethylenediamine and allylthiocarbimide react yielding $\alpha\beta$ -di(allylthiocarbamido)ethane, m. p. 102°, which when treated with bromine in cold chloroform solution affords $\alpha\beta$ -di-(5-bromomethyl-2-thiazolinyl-)



amino)ethane (annexed formula, $X=Br$), m. p. 161°. Moist silver oxide converts this into the glycol ($X=OH$), m. p. 108°. The corresponding

dinitrile and dicarboxylic acid have m. p. 118° and 147°, respectively. $\alpha\beta$ -Di-(5-methylene-2-thiazolinylamino)ethane, m. p. 153°, is obtained by the action of alcoholic potassium hydroxide on the above bromo-compound. The 1:4-diphenylthiocarbimide (dibenzyl derivative, m. p. 102°) and 1:4-diallylthiocarbimide (V) derivatives of piperazine have m. p. 263° and 153°, respectively. Treatment of V with bromine in chloroform solution yields 1:4-di-(5-bromomethyl-2-thiazolinyl)-piperazine, m. p. 156° [di-(5-*p*-tolylmethyl) derivative, m. p. 135°], which with alcoholic potassium hydroxide gives the corresponding di-(5-methylene) derivative, m. p. 166°. Hydrobromic acid (*d* 1.49) at 100° under pressure converts V into 1:4-di-(5-methyl-2-thiazolinyl)-piperazine, m. p. 280°.

H. BURTON.

Aldehyde condensations with diphenylisothiohydantoin. S. S. KINGSBURY and K. S. MARKLEY (J. Washington Acad. Sci., 1928, 18, 558—561).—The following condensation products have been obtained from the appropriate aldehydes by the method previously described (Hann and Markley, A., 1926, 623): 5-*o*-Methoxybenzylidene-, m. p. 296—297°; 5-*p*-anisylidene-, m. p. 199°; 5-*veratryl*idene-, m. p. 177—178°; 5-*piperonyl*idene-, m. p. 232°; 5-*p*-tolylidene-, m. p. 197—198°; 5-*p*-hydroxybenzylidene-, m. p. above 300°; 5-*o*-chlorobenzylidene-, m. p. 234—235°; and 5-*m*-nitrobenzylidene-, m. p. 219—220°, -2:3-diphenylisothiohydantoin.

α -Trinitrobenzaldehyde and β -phenylpropaldehyde did not undergo the reaction, nor did isobutaldehyde or citronellal; citral yielded 5-citrylidene-2:3-diphenylisothiohydantoin, m. p. 230°.

E. W. WIGNALL.

[Simplified method for the preparation of substituted μ -methylbenzthiazoles and their transformation into new, heterocyclic polymethine dyes.] R. SCHULOFF, R. POLLAK, and E. REISZ (Ber., 1928, 61, [B], 2538—2541).—An account of work not yet completed, induced by the communication of König (A., 1928, 1385).

[With M. HOPMAYER.]—5-Chloro-2-methylbenzthiazole, m. p. 68°, is prepared by reducing 4:4'-dichloro-2:2'-dinitrodiphenyl disulphide with zinc dust

and hydrochloric and acetic acids, followed by treatment of the zinc mercaptide with acetyl chloride. The chlorothiazole is converted by methyl sulphate into the methosulphate, m. p. 217°, which with *p*-dimethylaminobenzaldehyde affords the polymethine dye, m. p. 245°. 6-Chloro-2:4-dimethylbenzthiazole, m. p. 79°, is analogously prepared from the product of the action of sulphur chloride on *o*-toluidine hydrochloride. 6-Ethoxy-2-methylbenzthiazole, m. p. 56°, gives an ethiodide, m. p. 156°, and amyliodide, m. p. 232°. The ethiodide condenses with anisaldehyde, *o*-methoxybenzaldehyde, and *p*-dimethylaminobenzaldehyde, giving polymethine dyes, m. p. 231°, 231—232°, and 257°, respectively; with cinnamaldehyde and *m*-nitrobenzaldehyde, dyes, m. p. 219—220° and 211°, respectively, are obtained.

H. WREN.

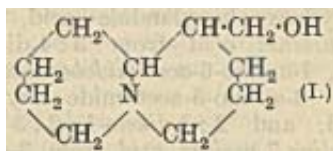
Microchemical reactions of theobromine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 1—5).—The crystal forms and optical properties of the precipitates obtained with the usual reagents are described. Iodine and bromine solutions, and potassium bismuth and potassium antimony iodides all give precipitates with solutions of 1 part of theobromine in 1000 parts, and will detect 1—2 μ g. (0.001—0.002 mg.). S. I. LEVY.

Microchemical reactions of caffeine. M. WAGENAAR (Pharm. Weekblad, 1928, 65, 1334—1339).—The nature of the crystalline precipitates obtained with the common alkaloid reagents is described. The most sensitive test is the salting out from aqueous solution by addition of ammonium phosphate, by which caffeine may be detected at a dilution of 1:5000.

S. I. LEVY.

Lupinine. P. KARRER, F. CANAL, K. ZÖHNER, and R. WIDMER (Helv. Chim. Acta, 1928, 11, 1062—1084; cf. Schopf, A., 1928, 1144).—Details are given for the extraction of lupinine (283 g.) and sparteine sulphate (255 g.) from yellow lupin (100 kg.). Lupinine methiodide (Willstätter and Fourné, A., 1902, i, 557) when converted into the meth-hydroxide and then distilled yields methyl-lupinine, $C_{10}H_{18}ONMe$, b. p. 140—143°/12—13 mm. (this and the compounds subsequently derived from it are probably mixtures of isomerides), reduced by hydrogen and platinum-black to dihydromethyl-lupinine, b. p. 136—141°/12 mm. Conversion of this into the methiodide gives a solid, m. p. 202—203° (30%), and oily fractions (63%), the mixture being converted as above into dihydrodimethyl-lupinine, b. p. 140—145°/11—12 mm., reduced to tetrahydromethyl-lupinine (I), b. p. 140—148°/10—11 mm. The meth-hydroxide from this is decomposed by distillation to a mixture of I and a mixture of unsaturated alcohols (II), b. p. 86—101°/10—11 mm., $d_{20} 0.838$, $n_D^{20} +0.34$ (0.25 dm. tube), of the composition $C_{10}H_{19}OH$. Oxidation of this with zinc permanganate gives the corresponding glycols, further oxidised by chromic anhydride and sulphuric acid, yielding small amounts of formic acid and the lactone, $C_9H_{16}O_2$, b. p. 253—255°, probably β -hydroxymethyloctoleic acid lactone, thus indicating that II contains δ -hydroxymethyl- Δ^8 -nonene. Reduction of II to the saturated alcohols, b. p. 95—103°/11 mm., $n_D^{20} +0.39$ —0.32° (in 0.25 dm. tube), and treatment of these with phosphorus pentabromide gives δ -bromomethylnonane (III), b. p. 100—102°/11 mm., $[\alpha]_D^{20} -3.01$ °. Re-

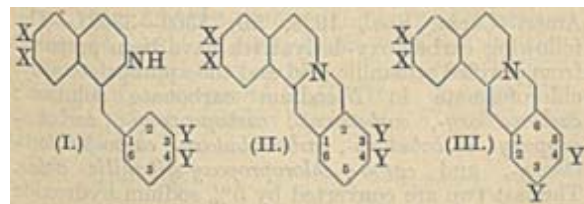
duction of III by zinc dust and alcohol containing a trace of platinic chloride and finally with hydrogen and platinum affords δ -methylnonane, b. p. $54^\circ/12$ mm., $d_{20} 0.723$, $[\alpha]_D^{25}$ about -1.3° . Trimethylamine converts III into the corresponding quaternary ammonium bromide, m. p. $167-170^\circ$, still optically active, but δ -methylenenonene (IV), b. p. $53-54^\circ/11$ mm., obtained with δ -dimethylaminomethylnonane, b. p. $88-89^\circ/11$ mm., by distillation of the quaternary ammonium hydroxide is optically inactive. Treatment of IV with ozone gives formaldehyde and *n*-propyl *n*-amyl ketone, b. p. $76-77^\circ/12$ mm. (semicarbazone, m. p. $60-61^\circ$), synthesised from hexoyl chloride and zinc *n*-propyl iodide. The Beckmann rearrangement of *n*-propyl *n*-amyl ketoxime, b. p. $119^\circ/15$ mm., gives *n*-amylamine and butyric acid. *n*-Amyl isopropyl ketone, b. p. $82^\circ/15$ mm. (semicarbazone, m. p. 75°), and methyldiethylamine picrate, m. p. 168° , are described.



Lupinine is represented best by (I), whilst sparteine is formulated as a condensation product of 1 mol. of lupinine and 1 mol. of piperidine. H. BURTON.

Alkaloids from *Carnegie gigantea* (Engelm.). Britt. and Rose (*Cereus giganteus*, Engelm.). G. HEYL (Arch. Pharm., 1928, 266, 668-673).—The only isolable alkaloid from this cactus is *carnegine*, $C_{13}H_{19}O_2N$, a strongly alkaline syrup, the following derivatives of which are described; *hydrochloride* (H_2O), m. p. 207° ; *hydrobromide*, m. p. 228° ; double salt with mercuric chloride, $C_{13}H_{19}O_2N.HgCl_2.HCl$; *chloroaurate*; *chloroplatinate*. The base contains two methoxyl groups; the salts, which contain one equivalent of acid, are optically inactive. Carnegine resembles lophophorine in physiological action but is not identical with it. S. COFFEY.

Synthesis of bases of berberine type from compounds of the type of tetrahydropapaverine. E. SPATH and E. KRUTA (Monatsh., 1928, 50, 341-348).—All the known natural alkaloids of berberine type contain alkoxy-groups in the positions 3 and 4 in the skeleton formula II (X or Y=OMe, or XX or



$YY=O_2CH_2$). The hypothesis has been put forward that such bases are formed in the plant from bases of tetrahydropapaverine type (I) by condensation with formaldehyde in the 2-position to the tetrahydro-derivative (II), which may then be oxidised to the quaternary base. Attempts to carry out syntheses of this nature have, however, always led to derivatives of type III by closure in the 6-position, viz., tetrahydro- ψ -berberine ($XX=O_2CH_2$, $Y=OMe$) (Haworth, Per-

kin, and Rankin, A., 1924, i, 1098), norcoralydine (X and Y=OMe) (Pictet and Chou, A., 1916, i, 418), and coralydine (Pictet and Malinowski, A., 1913, i, 1224). It is now shown, however, that the tetrahydroxy-derivative, tetrahydropapaveroline (I, X and Y=OH), condenses with formaldehyde to give bases of types II and III in equal amount. It follows, therefore, that the original hypothesis still holds good if it is assumed that in the plant ring-closure occurs before alkylation.

Repetition of the synthesis of norcoralydine as described by Pictet and Chou (*loc. cit.*) gave only 46% yield of the base, m. p. $151.5-152.5^\circ$ (Pictet and Chou give $80-85\%$, m. p. $157-158^\circ$). The yield was improved to 69% by condensing tetrahydropapaverine in hydrochloric acid with formaldehyde (2 mols.) in a sealed tube at 100° . In neither case could any trace of tetrahydropalmatine be detected. Tetrahydropapaveroline was condensed with formaldehyde under similar conditions and the product treated with diazomethane. By careful fractionation of the product norcoralydine and tetrahydropalmatine were separated in equal amounts and in a total yield of 15%, the pooriness of the yield being attributed to the unsatisfactory course of the methylation. R. K. CALLOW.

Strychnine and brucine. VIII. R. CIUSA (Gazzetta, 1928, 58, 774-775).—The preparation of *O*-acetylisostrychnine by Oxford, Perkin, and Robinson (A., 1927, 1208) confirms the presence of a hydroxyl group in isostrychnine, of which the author has prepared a benzoyl derivative (cf. A., 1920, i, 176).

E. W. WIGNALL.

Micro-crystallographic identification of yohimbine. G. DENIGES (Mikrochem., 1928, 6, 113-115).—Yohimbine may be identified by the characteristic micro-crystalline structure of the free base and the hydrochloride. Further confirmation is obtained by addition of a drop of a solution of silver nitrate and a drop of a solution of sodium carbonate to a solution of the substance in a drop of ammonia. With yohimbine a yellowish-brown micro-crystalline mass is obtained. J. S. CARTER.

Alkaloids of Indian aconites. II. ψ -Aconitine. T. M. SHARP (J.C.S., 1928, 3094-3106).—Two reactions of aconitine (cf. Dunstan and Carr, J.C.S., 1894, 65, 176, and later papers) are applied to ψ -aconitine. ψ -Aconitine, when heated in a sealed tube with methyl alcohol, gives *veratroylmethyl- ψ -aconine*, m. p. $206-207^\circ$, $[\alpha]_D +29.8^\circ$ [*hydrochloride*, m. p. $249-250^\circ$ (decomp.), $[\alpha]_D -3.41^\circ$ (in water), $+0.38^\circ$ (in alcohol)]; *hydrobromide monohydrate*, m. p. $237-238^\circ$ (efferv.), $[\alpha]_D +2.15^\circ$, which, by acetylation with acetic anhydride, leads to *monoacetylveratroylmethyl- ψ -aconine perchlorate*, m. p. $240-242^\circ$, whilst with acetyl chloride *diacetylveratroylmethyl- ψ -aconine*, m. p. 160° , $[\alpha]_D +18.43^\circ$, is obtained. Similarly, tetra-acetyl- ψ -aconine with methyl or ethyl alcohol gives only *triacetylmethyl- ψ -aconine*, m. p. $280-282^\circ$, $[\alpha]_D -18.5^\circ$, or *triacetylethyl- ψ -aconine*, m. p. 171° , $[\alpha]_D -26^\circ$. The last compound, on hydrolysis, gives *ethyl- ψ -aconine*, syrup.

ψ -Aconitine when heated above its m. p. loses acetic acid, giving crystalline *pyro- ψ -aconitine* (I),

m. p. 132—135°, $[\alpha]_D^{20} +175.2^\circ$, which is considered to contain a bridged linking, since ψ -aconitine is now shown to contain two hydroxyl groups [acetylation gives *diacetyl- ψ -aconitine*, m. p. 229° (decomp.), $[\alpha]_D^{20} +24.0^\circ$; *monoacetyl- ψ -aconitine perchlorate*, m. p. 225—228° (efferv.)]; benzylation gives only *monobenzoyle- ψ -aconitine perchlorate*, m. p. 236° (efferv.), and I not to possess a double linking, and also since tetra-acetyl- ψ -aconitine when heated loses 1 mol. of acetic acid, giving *triacetylpyro- ψ -aconitine*, m. p. 155—158°, $[\alpha]_D^{20} +156.4^\circ$, which by hydrolysis furnishes *pyro- ψ -aconitine*, m. p. 172°, $[\alpha]_D^{20} +227.5^\circ$, identical with the hydrolysis product from I. Moreover, acetylation of I yields *triacetyldemethylpyro- ψ -aconitine*, m. p. 228°, $[\alpha]_D^{20} +28.4^\circ$, giving, on hydrolysis, a *demethylpyro- ψ -aconitine* different from the analogous product obtained from I or its triacetyl derivative.

The results of Schulze and Liebner (A., 1917, i, 470) are discussed.
R. J. W. LE FÈVRE.

Optical activity of ψ -morphine. A. K. BALLS and W. A. WOLFF (J. Biol. Chem., 1928, 80, 403—411).—The optical activity of ψ -morphine increases with increasing concentration of the base and, to a smaller extent, of potassium ions, but diminishes with increasing hydroxyl-ion concentration; curves are given showing the quantitative relationships observed, which constitute the best available means of identifying the base.
C. R. HARRINGTON.

Optically active isomerides of *N*-phenyl- β -methylglycineamide-*p*-arsinic acid and their use in the resolution of ephedrine. E. FOURNEAU and V. NICOLITCH (Bull. Soc. chim., 1928, [iv], 43, 1232—1264).— α -Bromopropionamide, m. p. 120—121° (yield 81.7% from α -bromopropionyl bromide), with *p*-aminophenylarsinic acid gives *N*-phenyl- β -methylglycineamide-*p*-arsinic acid in 74% yield (cf. Jacobs and Heidelberg, A., 1920, i, 108) (*sodium salt*), resolved by using quinine into the *l*-acid, $[\alpha]_D^{20} -15.83^\circ$, the quinine salt of which crystallises first, and the *d*-acid, $[\alpha]_D^{20} +16.1^\circ$. Attempts at resolution with cinchonine and strychnine were unsuccessful. Both *d*- and *l*-*N*-phenyl- β -methylglycineamide-*p*-arsinic acid readily effect the resolution of ephedrine, the *l*-acid salt of *d*-ephedrine and the *d*-acid salt of *l*-ephedrine separating first in the two cases.

p- α -Bromopropionamidophenylarsinic acid is obtained (yield, 70%) from α -bromopropionyl bromide and *p*-aminophenylarsinic acid. *p*-Nitrophenylacetic acid, m. p. 149.5° (yield 65% on the nitrile), was converted through the chloride into *p*-nitrophenyl- α -bromoacetyl chloride or bromide, and thence into *p*-nitrophenyl- α -bromoacetamide, m. p. 148° (crude). The latter with *p*-aminophenylarsinic acid gave α -*di-p*-nitrophenylsuccinamide, m. p. 212°, the negative result being probably due to the proximity of two negative groups to the bromine atom, since with phenyl- α -bromoacetamide normal condensation gives (yield 56%) *phenylphenylglycineamide-p*-arsinic acid. Attempts to resolve this with quinine failed. Propionyl chloride on bromination at 80° affords only α -bromopropionyl bromide, b. p. 153—155°, other chlorides behaving similarly with the exception of isovaleryl chloride and phenylacetyl chloride. *Diethylacetyl bromide* has

b. p. 153—158°, α -bromodiethylacetyl bromide b. p. 98—100°/25 mm., α -bromoisovaleryl bromide (from isovaleric acid, bromine, and phosphorus), b. p. 90°/10 mm., α -bromoheptyl bromide, b. p. 135°/45 mm., α -bromolauryl bromide, b. p. 180°/45 mm., α -bromo-*p*-phenylpropionyl bromide, b. p. 160°/22 mm., phenylacetyl chloride, b. p. 102.3°/17 mm. (86% yield, using thionyl chloride, 97% with phosphorus trichloride), and bromophenylacetyl bromide, b. p. 150°/26 mm. (yield 84%).
R. BRIGHTMAN.

Heterocyclic arsenic compounds. IV. Carbamido-derivatives of arylarsinic acids. R. W. E. STICKINGS (J.C.S., 1928, 3131—3134).—Sodium *p*-arsanilate reacted with an aqueous suspension of cyanogen bromide to form *p*-carbamidophenylarsinic acid. Similarly, 5-carbamido-2-hydroxyphenylarsinic acid was prepared from 5-amino-3-hydroxyphenylarsinic acid, 1-aminobenzoxazole-4-arsinic acid from 3-amino-4-hydroxyphenylarsinic acid, 2-aminobenzimidazole-5-arsinic acid from 3:4-diaminophenylarsinic acid, 1-amino-6-acetamidobenzoxazole-4-arsinic acid from 3-amino-5-acetamido-4-hydroxyphenylarsinic acid, and 2:4-diketo-1:2:3:4-tetrahydro-1:3-quinazoline-7-arsinic acid from 3-amino-4-carboxyphenylarsinic acid.
R. J. W. LE FÈVRE.

Heterocyclic arsenic compounds. V. Benzimidazolearsinic acids. M. A. PHILLIPS (J.C.S., 1928, 3134—3140).—The following compounds are described: 2-methylbenzimidazole-5(6)-arsinic acid nitrate, 2:2'-dimethyl-5:5'-arsenobenzimidazole, 5:5'-arsenobenzimidazole, 2-ethylbenzimidazole-5(6)-arsinic acid (calcium and magnesium salts), 2- α -hydroxyethylbenzimidazole-5(6)-arsinic acid (magnesium salt), benzimidazole-4(7)-arsinic acid, m. p. 277° (decomp.) (calcium and magnesium salts), 4:4'-arsenobenzimidazole, 2-methylbenzimidazole-4(7)-arsinic acid, m. p. 280—282° (magnesium and calcium salts), 2:2'-dimethyl-4:4'-arsenobenzimidazole, 2- α -hydroxyethylbenzimidazole-4(7)-arsinic acid (magnesium salt), 2:3-dihydroxyquinoxaline-6(7)-arsinic acid, m. p. above 300° (mono- and di-sodium salts; calcium, barium, and magnesium salts), 2:3-dihydroxyquinoxaline-5(8)-arsinic acid, m. p. above 300° (calcium, barium, and magnesium salts).
R. J. W. LE FÈVRE.

Action of alkyl chloroformates on stibanic acid. C. S. HAMILTON and R. E. ETZELMILLER (J. Amer. Chem. Soc., 1928, 50, 3360—3363).—The following carbalkoxy-derivatives have been prepared from purified stibanic acid and the appropriate alkyl chloroformate in *N*-sodium carbonate solution: carbomethoxy-, carbethoxy-, carbopropoxy-, carboisopropoxy-, carbobutoxy-, carboisobutoxy-, carbo- β -chloroethoxy-, and carbo- γ -chloropropoxy-stibanic acids. The last two are converted by 5% sodium hydroxide at 70° into *p*- β -hydroxyethylaminophenylstibinic acid and *d*- γ -hydroxypropylaminophenylstibinic acid, respectively. The products were analysed by a modification of Ewins' iodometric method for arsenic (J.C.S., 1916, 109, 1356).
H. E. F. NOTTON.

Interactions of selenium oxychloride and phenols. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1928, 3260—3270).—Phenol and selenium oxychloride condensed in ether or chloroform solu-

tion to give *tri-4-hydroxytriphenylselenonium chloride*, m. p. 232° (decomp.) [sulphate, decomp. 269—270°; bromide, decomp. 237°; nitrate, m. p. 138—139° (decomp.)]; *chloroplatinate*, decomp. 244°; *methyl ether* (cf. Hilditch and Smiles, J.C.S., 1908, 93, 1384) giving *tri-4-methoxytriphenylselenonium mercuri-chloride*, m. p. 68—70°, which, by dissolving in aqueous sodium hydroxide and reprecipitating by carbon dioxide yielded *tri-4-hydroxytriphenylselenonium oxide*, decomp. 240°; this, by the action of bromine, gave *tri-3-bromotri-4-hydroxytriphenylselenonium bromide*, m. p. 251°, and *tri-3:5-dibromotri-4-hydroxytriphenylselenonium bromide*, decomp. 261°.

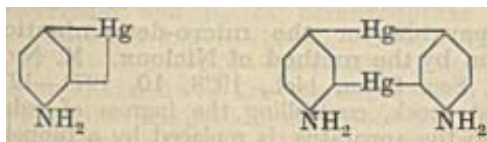
An isomeric *trihydroxytriphenylselenonium chloride*, $(\text{HO}\cdot\text{C}_6\text{H}_4)_3\text{SeCl}_2\cdot 2\text{H}_2\text{O}$, decomp. 125°, was also isolated in the initial condensation.

Selenium oxychloride and *o*-cresol similarly yielded *tri-4-hydroxytri-3-methyltriphenylselenonium chloride*, decomp. 231° (corresponding *nitrate*, decomp. 224°), *tri-4-hydroxytri-3-methyltriphenylselenonium oxide*, decomp. 236°, *tri-5-bromotri-4-hydroxytri-3-methyltriphenylselenonium bromide*, decomp. 253°, and *di-4-hydroxydi-3-methyldiphenyl selenide*, m. p. 98—99°. *p*-Cresol led to *tri-2-hydroxytri-5-methyltriphenylselenonium chloride*, decomp. 260—265°, *tri-2-hydroxytri-5-methyltriphenylselenonium oxide*, decomp. 160°, *tri-3-bromotri-2-hydroxytri-5-methyltriphenylselenonium bromide*, decomp. 195°, *di-2-hydroxydi-5-methyldiphenyl selenide*, m. p. 111°, and *5-chloro-4:4'-di-hydroxy-3:3'-ditolyl*, m. p. 129—130°. Resorcinol and selenium oxychloride produced *tri-2:4-dihydroxytriphenylselenonium chloride*, m. p. 206° (with acetone of crystallisation), whilst β -naphthol and selenium oxychloride gave *di-2-hydroxydi-1-naphthyl selenide*, m. p. 186°. From salicylic acid *di-4-hydroxydiphenyl selenide di-3-carboxylic acid*, sintering at 250° and decomp. 272°, was obtained.

The results indicate that two types of reaction may take place: $3\text{RH}\cdot\text{OH} + \text{SeOCl}_2 \longrightarrow (\text{HO}\cdot\text{R})_3\text{SeCl} + \text{HCl} + \text{H}_2\text{O}$ (e.g., phenol, resorcinol) or $3\text{RH}\cdot\text{OH} + \text{SeOCl}_2 \longrightarrow \text{Se}(\text{R}\cdot\text{OH})_2 + \text{Cl}\cdot\text{R}\cdot\text{OH} + \text{HCl} + \text{H}_2\text{O}$ (e.g., naphthol and salicylic acid); both may occur concurrently (e.g., *o*- and *p*-cresols).

R. J. W. LE FÈVRE.

Formation of a heterocyclic ring closed through mercury atoms. L. VECCHIOTTI (Gazzetta, 1928, 58, 712—715).—Aniline 2:4-dimercuri-acetate (A., 1914, i, 1063) reacts with sodium thio-sulphate similarly to *o*-chloroaniline (A., 1925, i, 1058), giving a compound, $[\text{C}_6\text{H}_5\text{NHg}]_2$, decomp. 162°, m. p. 184°, which probably has one of the two following structures:



E. W. WIGNALL.

Mercuri-compounds from purine derivatives. II. [Caffeine.] L. ROSENTHALER (Arch. Pharm., 1928, 266, 694—696; cf. A., 1924, i, 110).—When a solution of caffeine and mercuric acetate in dilute acetic acid is boiled for 2 days, *acetoxymercuricaffeine*,

sintering at 255°, slight decomp. 280°, unmelted at 300°, is formed. Potassium chloride, bromide, or thiocyanate solutions precipitate the corresponding mercuri-compounds, but potassium iodide converts acetoxymercuricaffeine into *mercuricaffeine*, $(\text{C}_8\text{H}_9\text{N}_4\text{O}_2)_2\text{Hg}$, m. p. above 340°. The acetoxymercuri-derivative furnishes sparingly soluble compounds with tartaric and salicylic acids. It is probable that the mercury atom is attached to the 8-carbon atom.

S. COFFEY.

Serological differentiation of steric isomerides.

K. LANDSTEINER and J. VAN DER SCHEER (J. Exp. Med., 1928, 48, 315—320).—*l*- and *d*-Immune sera, obtained from *l*- and *d*-(*p*-aminobenzoylamino)-phenylacetic acids, diazotised and coupled with proteins, are specific. The *dl*-antigen reacts with both sera. The *d*- and *l*-immune sera also differentiate between the *d*- and *l*-acids when not combined with proteins.

CHEMICAL ABSTRACTS.

Physico-chemical behaviour, as dissolved sodium salts, of electro-dialytically purified protein groups from pathological human blood- and exudate-plasma. I. and II. K. HARTL and W. STARLINGER (Z. ges. exp. Med., 1928, 60, 289—314, 315—335; Chem. Zentr., 1928, ii, 459—460).—I. The isoelectric point of albumin is p_H 4.75, varying between 4.95 and 4.38; for globulin, 5.14 (5.35—4.95); for fibrinogen 4.81. The specific viscosities are 0.109, 0.160, 0.250, respectively, with marked deviations in both directions; specific refractions 0.00151, 0.00173, 0.00209. Similar protein fractions show marked differences in homogeneity. Nephelometry is not suitable for the volumetric investigation of plasma-protein.

II. The base-combination diminished irregularly within the protein concentration 1.4—12.3 g.-% with increasing concentration. The base-combining power diminished with increasing concentration of hydroxide, but considerable individual differences were observed in similar protein fractions. Differences were also observed in conductivity; hence the differences exhibited by the proteins in pathological conditions are very great.

A. A. ELDRIDGE.

Spectrophotometric method of studying hæmoglobin and other coloured substances in solution. G. E. DAVIS (Proc. Iowa Acad. Sci., 1927, 34, 279—280).—The spectrophotometric method for determining hæmoglobin in blood is fairly accurate. Irregularities in the shape of the spectral transmission curve for one of the absorption bands of oxyhæmoglobin were observed.

CHEMICAL ABSTRACTS.

Hydrolysis of ovalbumin by trypsin in relation to the formation of diketopiperazines. A. BLANCHETIÈRE (Compt. rend., 1928, 188, 112—113; cf. A., 1927, 269).—Hydrolysis of crude and denatured ovalbumin with trypsin at 38° and p_H 8.5 leads to the formation of about 38% of diketopiperazines in about 70 days. The reaction is more irregular in the case of the denatured protein, owing possibly to flocculation.

G. A. C. GOUGH.

Mol. wt. of serum-albumin and of serum-globulin. T. SVEDBERG and B. SJÖGREN (J. Amer. Chem. Soc., 1928, 50, 3318—3332).—The partial

specific volumes (0.748 and 0.745) and ultra-violet absorption spectra of serum-albumin and serum-globulin, isolated by a rapid and simple procedure from horse blood, have been determined. Measurements by the sedimentation velocity and sedimentation equilibrium methods (cf. A., 1927, 716; 1928, 783), using isoelectric solutions in an acetate or phosphate buffer medium, show that both proteins are homogeneous with regard to mol. wt. over a wide range of concentration. The mol. wt. of the former, $67,500 \pm 2000$, and that of the latter, $103,800 \pm 3000$, are both simple multiples of that of egg-albumin (cf. A., 1928, 533), and are nearly identical with those of haemoglobin and phycocyan, respectively. At concentrations below 0.5%, serum-albumin undergoes, without change in absorption spectrum, a reversible partial decomposition into non-centrifugable products. Prolonged fractionation of either protein causes a complicated degradation and aggregation of the molecules, with formation of increasing amounts of non-centrifugable matter. These changes account for the apparent heterogeneity of both proteins observed by previous workers. Fractionation products such as the eu- and pseudo-globulins probably differ only in their content of impurity.

H. E. F. NOTTON.

Determination of tryptophan in proteins.

Rate of liberation of tryptophan by enzymes.

I. K. RAGINS (J. Biol. Chem., 1928, 80, 543—550, 551—556).—The accuracy of the vanillin-hydrochloric acid reaction for the determination of tryptophan in protein hydrolysates (A., 1925, ii, 448) is confirmed; whilst native proteins fail to give the reaction satisfactorily, the presence of some of the tryptophan in peptide combination in the material precipitated by mercuric sulphate does not interfere with the determination. For the quantitative precipitation of tryptophan by mercuric sulphate the chloride concentration must not exceed 0.3%. Pepsin does not liberate tryptophan from proteins, nor does erepsin liberate an additional amount of this amino-acid after the action of trypsin; tryptophan is liberated by trypsin very rapidly from caseinogen, less so from edestin and squash-seed globulin.

C. R. HARRINGTON.

Hydrolysis of proteins by hydrofluoric acid.

E. CHERBULIEZ and R. WAHL (Helv. Chim. Acta, 1928, 11, 1252—1255).—Protein substances are hydrolysed with hot 25—50% hydrofluoric acid (cf. Hugounenq and Morel, A., 1909, i, 195, 685) in a lead vessel, and after removal of fluoride ions as calcium fluoride, the hydrolysis products are analysed for total nitrogen. When a comparison is made of the results with those for hydrochloric acid hydrolysis it is found that the percentage of ammonia-nitrogen is higher, the result of partial deamination of the amino-acids formed. The amount of humins formed is relatively large, and it is shown that under the conditions of hydrolysis about 37% of the sugar is destroyed in a mixture of amino-acids and dextrose. The method appears to have no advantage over the usual one.

H. BURTON.

Loosely-bound sulphur in egg-albumin. W. D. TREADWELL and W. EPPENBERGER (Helv. Chim.

Acta, 1928, 11, 1035—1042).—Hydrolysis of a 1.5% solution of egg-albumin with an equal volume of 0.1*N*-sodium hydroxide solution at 78° in rigid absence of air follows the course of a bimolecular reaction. Subsequent determination of the sulphide ions formed, by electrometric titration with lead ions, gives a limiting value of 0.266%, which is about one half the value found by Osborne (A., 1902, i, 250) and one sixth of the total sulphur present. The mol. wt. of ovalbumin is of the order of 12,000.

H. BURTON.

Composition and characteristics of the proteins. S. P. L. SØRENSEN (Forh. III. nord. Kemist. motet, 1928, 72—91).—A review of recent work, mainly 1920—1926, on the determination of the composition and structure of the proteins. H. F. HARWOOD.

Volumetric determination of protein solutions.

W. D. TREADWELL and W. EPPENBERGER (Helv. Chim. Acta, 1928, 11, 1053—1062).—When protein solutions are treated with excess of ferrin the resulting precipitate adsorbs colloidal ferric ferrocyanide, causing decolorisation of the solution, and the end-point is reached when a permanent blue colour remains in the solution. During the titration the mixture is stirred, but not violently enough to cause either disintegration of the precipitate or coagulation of the Prussian-blue. Addition of acid or alkali causes marked diminution in the adsorption (when marked deviations from the isoelectric point are obtained), and the addition of varying amounts of neutral salts gives widely differing results. Protein solutions containing salts should be dialysed before titration. The method needs very careful manipulation. Gelatin-tannin precipitates adsorb more Prussian-blue than egg-albumin precipitates.

H. BURTON.

Determination of peptide and basic forms of nitrogen. C. O. APPLEMAN, W. E. LOOMIS, T. G. PHILLIPS, W. E. TOTTINGHAM, and J. J. WILLAMAN (Plant Physiol., 1927, 2, 497—501).—A report of a Committee of the American Society of Plant Physiologists.

CHEMICAL ABSTRACTS.

Sources of error in organic micro-elementary analysis. II. Determination of carbon and hydrogen. F. BOCK and K. BEAUCOURT (Mikrochem., 1928, 6, 133—143; cf. Friedrich, A., 1923, ii, 788).—A critical discussion. Errors due to the presence of carbon and hydrogen compounds in the oxygen etc. used and impurities given off by rubber connexions may be avoided by the insertion of a platinised asbestos catalyst followed by a bubbler and absorption vessel in front of the combustion tube.

J. S. CARTER.

Apparatus for the micro-determination of carbon by the method of Nicloux. M. NICLOUX (Bull. Soc. Chim. biol., 1928, 10, 1271—1272).—The stopcock, controlling the ingress of sulphuric acid to the apparatus, is replaced by a funnel on a capillary stem fitted with a ground-in plunger (cf. A., 1927, 436, 996).

G. A. C. GOUGH.

Sulpho-chromic oxidation of carbonaceous substances. General wet method of micro-determination of carbon. A. BORVIN (Compt. rend., 1928, 187, 1076—1078).—The carbonaceous

substance is oxidised in solution by heating on a water-bath for 30 min. with sulphuric acid, potassium dichromate, and silver chromate. The apparatus used is that of Nicloux (A., 1927, 436) with the modification that any carbon monoxide present is burnt to the dioxide by an electrically heated platinum filament, the necessary oxygen being supplied by decomposition of the chromic acid.

B. W. ANDERSON.

Determination of nitrogen. M. R. R. SIVAN and M. S. RAJU (Madras Agric. Dept. Yearbook, 1926 (1927), 6—10).—The substance is heated with concentrated sulphuric acid and a platinum spiral as in Kjeldahl's method; the cooled liquid is neutralised with sodium hydroxide, calcium is precipitated as oxalate, the diluted solution is filtered through dry paper, and the ammonia determined by Nessler's method.

CHEMICAL ABSTRACTS.

Determination of maltose and dextrose. W. BRAUN and B. BLEYER [with W. ELHARDT] (Z. anal. Chem., 1929, 76, 1—38).—The various existing methods for the determination of dextrose and maltose have been carefully investigated with special reference to their limitations and to inherent and systematic errors. Methods are given for the determination of dextrose and maltose by the reduction of Fehling's solution, the determination of mixtures of dextrose and maltose by reduction of Fehling's and Barfoed's solutions, the determination of mixtures of dextrose, maltose, and dextrin by reduction of Fehling's and Barfoed's solutions, inversion and

reduction of Fehling's solution, the micro-determination of maltose by reduction of Fehling's solution, and the determination of dextrose, maltose, and their mixtures by reduction of an alkaline solution of iodine. The necessary tables and full details are given, together with actual examples illustrative of the calculations involved.

J. S. CARTER.

Determination of anthraquinone in mixtures with benzanthrone. P. I. SOKOLOV and L. GUREVICH (J. Chem. Ind. Moscow, 1928, 5, 308—309).—Sielisch's method is untrustworthy. The mixture (1 g.) is boiled under reflux with glacial acetic acid (45 c.c.); a mixture of chromium trioxide (5 g.), glacial acetic acid (5 c.c.), and water (5 c.c.) is added during 2 hrs., the liquid boiled for a further 2 hrs., then diluted with cold water (400 c.c.). The benzanthrone is thus oxidised to anthraquinone-1-carboxylic acid, whilst the anthraquinone is unaffected. After 1 hr. the precipitate is collected, washed with water and then with 150 c.c. of 1% sodium hydroxide solution, and treated at 70° with 15 c.c. of a 10% solution of sodium hyposulphite in 10% sodium hydroxide. The red solution of anthraquinone is filtered through a Gooch crucible, the residue washed with a 1% sodium hyposulphite solution, and the filtrate treated at 70° with 5 c.c. of 30% hydrogen peroxide solution to precipitate the anthraquinone, which is collected, washed with water, dried, and weighed. If the sample contains more than 50—60% of anthraquinone, treatment with hyposulphite may be omitted.

CHEMICAL ABSTRACTS.

Biochemistry.

Regulation of respiration. XX. Quinhydrone electrode for determination of hydrogen-ion concentration. R. GESELL (Amer. J. Physiol., 1928, 87, 1—7).—An electrode for use with small quantities of blood or cerebrospinal fluid is described.

B. A. EAGLES.

Regulation of respiration. XXI. Sodium cyanide and p_H of cerebrospinal fluid. R. GESELL and A. B. HERTZMAN (Amer. J. Physiol., 1928, 87, 8—14).—Intravenous injection of sodium cyanide in the dog produces an initial alkalinity of the cerebrospinal fluid followed during recovery by an increasing acidity.

B. A. EAGLES.

Regulation of respiration. XXII. Alveolar oxygen and p_H of cerebrospinal fluid. XXIII. Haemorrhage and p_H of cerebrospinal fluid. A. B. HERTZMAN and R. GESELL (Amer. J. Physiol., 1928, 87, 15—19, 20—23).—XXII. The administration of gaseous mixtures with low oxygen content is accompanied by a decrease in the hydrogen-ion concentration of the cerebrospinal fluid. Re-administration of air is followed by an increased hydrogen-ion concentration exceeding the original level.

XXIII. Haemorrhage produces no change in the hydrogen-ion concentration of the cerebrospinal fluid. Re-injection of the blood always increases it.

B. A. EAGLES.

Regulation of respiration. XXIV. Mechanical asphyxia and p_H of cerebrospinal fluid. R. GESELL and A. B. HERTZMAN (Amer. J. Physiol., 1928, 87, 24—28).—Mechanical asphyxia increases the hydrogen-ion concentration of the cerebrospinal fluid.

B. A. EAGLES.

Method of oxygenating blood. L. E. BAYLISS, A. R. FEE, and E. OGDEN (J. Physiol., 1928, 66, 443—448).—An artificial "lung" consisting of alternate revolving and stationary plates is described. The oxygenator consisting of five pairs of plates has an air volume of 600 c.c. and when revolving at a speed of 200 r.p.m. contains 54 c.c. of blood at any moment. When running in an atmosphere of oxygen it will introduce 19 c.c. of oxygen per minute into the blood flowing through it.

B. A. EAGLES.

Seasonal variation of the carbon dioxide content of the blood of the snail. M. DUVAL (Compt. rend., 1929, 188, 104—107).—The carbon dioxide and sodium hydrogen carbonate contents of the blood of the snail are slightly lower during the periods of hibernation and inactivity. This is in contrast to the sodium chloride content, which increases as the density of the blood increases. The mechanism which tends to oppose these variations is unknown.

G. A. C. GOUGH.

Manganese-copper-iron complex in hæmoglobin formation. R. W. TITUS, H. W. CAVE, and J. S. HUGHES [with H. L. KEIL] (J. Biol. Chem., 1928, 80, 565—570).—The hæmoglobin formation of young rats on a diet of milk supplemented with iron was accelerated about equally by addition of copper and of manganese, and still more by a combination of the two. C. R. HARRINGTON.

Effect of proteins and vitamins on hæmoglobin production in the rat. G. F. CARTLAND and F. C. KOCH (Amer. J. Physiol., 1928, 87, 249—261).—Rats fed on diets containing 10% of gluten or 18% of caseinogen can regenerate their blood satisfactorily after severe hæmorrhage. Vitamins-A and -E and probably -B are not specifically essential for hæmoglobin formation in the rat. B. A. EAGLES.

Sulphur content of the hæmoglobin in the blood of pure-bred dogs and of some other animals. E. TIMAR (Biochem. Z., 1928, 202, 365—379).—The sulphur contents of the hæmoglobin of the blood of cats and of cattle (as well as of some horses) are respectively 0.97% and 0.58%, and hence the proportions of iron and sulphur in the blood are expressed by the ratios Fe:S₅ and Fe:S₃. The value 0.58% is only rarely found in the case of the blood of dogs of ordinary breed, the values usually found being 0.70%, 0.61%, and 0.50%. These three values give no simple relationship between iron and sulphur, but, as in the case of the figures for cats, cattle, and horses, they confirm the findings of Valer (cf. A., 1928, 191). The hæmoglobin of the blood of pure-bred dogs contains 0.57% S (corresponding with the ratio Fe:S₃), and this value is also found in the cases of the ass and the fox. There is 0.71% S in hæmoglobin from the goose. In hæmoglobin which contains 0.58 or 0.97% S all the sulphur must be present as cysteine or cystine. W. MCCARTNEY.

New organic phosphorus constituent of erythrocytes. S. POSTERNAK (Compt. rend., 1928, 187, 1165—1167).—From the so-called acid-soluble fraction of the phosphorus compounds from horse's erythrocytes, a substance, probably α -ketotrihydroxyadipic acid β -diphosphate, [α] +8.8° (after neutralisation with ammonia, +15.04°), has been isolated. When hydrolysed in an autoclave at 125—130° for 6—7 hrs. it gives a product which reduces Fehling's solution more strongly than the original substance. G. A. C. GOUGH.

Phosphoaminolipins and sterols of blood-serum and plasma. M. A. MACHEBŒUF (Compt. rend., 1929, 188, 109—111).—Adjustment of the p_H of blood-serum or -plasma to 3.8 with 0.02N-sulphuric acid after removal of the globulins by the addition of half-saturated ammonium sulphate gives a precipitate which dissolves in a small volume of water on the addition of ammonia (p_H 7.3). Repeated dissolution and precipitation of this product gives a substance consisting of phosphoaminolipins (22.7%), cholesteryl esters (17.7%), and proteins (59.1%). Extraction of a neutral solution of the mixture with ether gives no lipins, whilst addition of alcohol gives a precipitate which dissolves in excess and slowly reappears after boiling. G. A. C. GOUGH.

Cholesterol and lipid phosphorus of the blood in infancy and childhood. M. B. GORDON and D. J. COHN (Amer. J. Dis. Children, 1928, 35, 193—200).—Blood-serum from the umbilical cord at birth contains 89 mg. per 100 c.c. of cholesterol and 4.1 mg. per 100 c.c. of lipid phosphorus; blood-serum in the first week affords similar values. The cholesterol content, which is 136 mg. per 100 c.c. at the end of the first year, increases to 169 mg. in the sixth year. At the end of the first year the lipid phosphorus content is 5.8—6.1 mg. per 100 c.c., remaining constant during the next four years, and reaching 7.8 mg. in the sixth year. CHEMICAL ABSTRACTS.

Cholesterol and cholesteryl ester in the blood-serum of cattle late in pregnancy and during the early lactation period. R. E. SHOPE and J. W. GOWEN (J. Exp. Med., 1928, 48, 25—30).—The total cholesterol and cholesteryl ester of bovine serum during the "dry" period of late pregnancy is low. Following parturition the total cholesterol and cholesteryl ester of bovine serum show a still greater, very transient decrease followed by a gradual rise to reach a fairly constant level 40—50 days *post partum*. This lactation level is very much higher than the "dry" level. CHEMICAL ABSTRACTS.

Biometry of calcium, inorganic phosphorus, cholesterol, and lipin-phosphorus in the blood of rabbits. I. Normal rabbits. A. R. HARNES (J. Exp. Med., 1928, 48, 549—565).—Determinations were made throughout the year on eighty rabbits. The serum contained 14.5 ± 0.10 to 18.5 ± 0.39 mg. of calcium and 4.96 ± 0.20 to 6.82 ± 0.20 mg. of inorganic phosphorus per 100 c.c.; the whole blood contained 51.1 ± 1.18 to 83.3 ± 1.34 mg. of cholesterol and 94.8 ± 1.40 to 168.3 ± 10.18 mg. of lecithin per 100 c.c. Correlation coefficients are as follows: inorganic phosphorus and lecithin, -0.794 ± 0.088 ; calcium and cholesterol, -0.887 ± 0.051 ; cholesterol and lecithin 0.560 ± 0.164 . CHEMICAL ABSTRACTS.

Blood-urobilin. Determination in normal human blood. M. A. BLANKENHORN (J. Biol. Chem., 1928, 80, 477—485).—Blood-serum is treated with zinc acetate and alcohol and kept for 24 hrs. at 0°; the solution is then cleared on the centrifuge and the fluorescence determined by comparison with standard solutions of acriflavine. The average concentration of urobilin in normal human blood-serum is 0.28 mg. per 100 c.c. C. R. HARRINGTON.

Physiology of ergothioneine. B. A. EAGLES and H. M. VARS (J. Biol. Chem., 1928, 80, 615—622).—Out of many samples of pig's blood one was encountered which yielded no ergothioneine; transference of these pigs, which had been fed on garbage, to diets rich in maize led to formation of ergothioneine in the blood. In accordance with this observation, solutions prepared by hydrolysis with sulphuric acid of egg-albumin, various cereal proteins, and, in particular, zein gave a positive reaction for the thiolglyoxaline ring, indicating the probable presence of thiohistidine, whilst caseinogen and gelatin failed to give this reaction. C. R. HARRINGTON.

Blood-chemistry of the albino-rat. A. K. ANDERSON and H. E. HONEYWELL (Penn. Agric.

Exp. Sta. Bull., 1927, No. 213, 7).—Non-protein nitrogen and urea values are slightly higher than for human blood. Creatinine, creatine, uric acid, chlorides, and dextrose were also determined.

CHEMICAL ABSTRACTS.

Yeast feeding and blood-constituents of hens. A. A. HERVATH (Amer. J. Physiol., 1928, 87, 208—220).—Hens fed with active yeast show an increase in the inorganic phosphorus and uric acid of the plasma. Inactive (heated) yeast causes a fall in the inorganic phosphorus and but a small rise in the uric acid of the plasma. The addition of taka-diastase to an inactive yeast ration makes it similar to active yeast in so far as its effect on the phosphorus and uric acid of the plasma is concerned.

B. A. EAGLES.

Serum-proteins and complex ions. S. G. T. BENDIEN and L. W. JANSSEN (Rec. trav. chim., 1928, 47, 1042—1057).—A study of the factors involved in the precipitation of proteins by acidified vanadium salts.

B. A. EAGLES.

Micro-determination of serum-protein. E. FRIED (Z. ges. exp. Med., 1928, 60, 515—520; Chem. Zentr., 1928, ii, 700).—Total protein is precipitated by half-saturation of 0.1 c.c. of serum with ammonium sulphate and addition of 1—2 c.c. of 0.02N-acetic acid, and globulin by half-saturation with ammonium sulphate after five-fold dilution with water, centrifuging, and filtering with suction through asbestos.

A. A. ELDRIDGE.

Catalase number and index of blood of newly-born kittens. F. VON KRUGER (Biochem. Z., 1928, 202, 18—20).—The number of blood-corpuscles and the catalase number are considerably smaller in cats 6 days to 8 weeks old than in fully-grown cats, whilst the catalase index is the same.

P. W. CLUTTERBUCK.

Influence of simultaneous hunger and thirst on the catalase number and index of blood. F. VON KRUGER (Biochem. Z., 1928, 202, 21—28).—During simultaneous thirsting and starving, the blood-corpuscle number per unit volume of blood and the catalase number are considerably increased, but the catalase index is unaltered.

P. W. CLUTTERBUCK.

Relationship of lactic acid to optical activity of blood. S. L. WRIGHT, jun., E. F. HERR, and J. R. PAUL (J. Biol. Chem., 1928, 80, 571—587).—The optical rotation of the ultra-filtrate from blood-serum, both in normal blood and in blood from diabetic subjects, was observed immediately after shedding, and after the blood had been incubated until glycolysis was complete. The initial dextro-rotation was converted during glycolysis into a levorotation of a somewhat lower degree; the phenomenon has been shown to be due principally to the accumulation of the levorotatory salts of *d*-lactic acid. Some such phenomenon may account for the results of Lundsgaard and Holbøll (A., 1925, i, 1494) and others.

C. R. HARRINGTON.

Absorption of lævulose by red blood-corpuscles. G. EISNER and F. LEWY (Biochem. Z., 1928, 202, 91—98).—Dextrose is readily but lævulose is little or not at all absorbed by erythrocytes, and the latter sugar must therefore play a different role in

metabolism from that of the former. Increased absorption under insulin could not be definitely established.

P. W. CLUTTERBUCK.

Determination of blood-sugar. T. L. BYRD (J. Lab. Clin. Med., 1927, 12, 609—613).—The author's micro-modification of Folin and Wu's method is trustworthy; further comparisons have been made.

CHEMICAL ABSTRACTS.

Blood-sugar determination and separation of sugar with live yeast. A. L. RAYMOND and J. G. BLANCO (J. Biol. Chem., 1928, 80, 631).—In view of the work of Benedict (A., 1928, 438) the term "disappearance" is substituted for "adsorption" in the authors' recent paper (A., 1928, 1392).

C. R. HARRINGTON.

Blood-sugar. M. SOMOGYI and H. V. KRAMER (J. Biol. Chem., 1928, 80, 733—742).—Determinations of true sugar in blood (i.e., the difference of the total and non-fermentable reducing substances; cf. A., 1927, 1214) by three independent methods gave practically identical results, so that no evidence is afforded of the existence in blood of a fermentable sugar other than dextrose.

C. R. HARRINGTON.

Blood-sugar. E. R. ORENT (J. Lab. Clin. Med., 1927, 12, 433—438).—Kramer and Gittleman's micro-method accords well with Folin and Wu's method. Results obtained with dextrose solutions, normal and diabetic human blood, and the blood of dogs in convulsions following ligation of the hepatic artery were compared.

CHEMICAL ABSTRACTS.

Colorimetric resorcinol-hydrochloric acid micro-method of blood-sugar determination. B. GLASSMANN and A. ZWILLING (Z. physiol. Chem., 1929, 180, 124—126).—A modification of the method for the determination of blood-sugar (A., 1926, 192, 1169) involving the use of a colorimeter at the ordinary temperature is described. The values so obtained agree, within the experimental error, with those obtained by the Hagedorn-Jensen method.

J. W. BAKER.

Blood micro-analysis. I. TEPUROV (Biochem. Z., 1928, 202, 14—17).—The micro-burette usually used in micro-titrations is replaced by a graduated pipette, the fluid being drawn into and expelled from this by movement of a screw working on a rubber balloon.

P. W. CLUTTERBUCK.

Muscle-hæmoglobin in the fowl. R. P. KENNEDY and G. H. WHIPPLE (Amer. J. Physiol., 1928, 87, 192—195).—Spectrophotometric analysis of chicken-blood hæmoglobin is identical with that of dog-blood hæmoglobin. The muscle-hæmoglobins of the two animals are also identical.

B. A. EAGLES.

Red colouring matter of cardiac and skeletal muscle. R. SCHONHEIMER (Z. physiol. Chem., 1929, 180, 144—148).—Specimens of hæmin isolated respectively from the heart-muscle of an ox and from the skeletal muscle of a dog were each converted into the corresponding mesoporphyrin (by the action of hydrogen iodide in acetic acid), which by comparison of the methyl and ethyl esters are shown to be identical with each other and with that obtained from blood.

J. W. BAKER.

Occurrence and decomposition of pyrophosphate in cells. I. K. LOHMANN (Biochem. Z., 1928, 202, 466—493).—Pyrophosphate is present in fresh muscle to the extent of about 20% of the total acid-soluble phosphate. It can be isolated from frog, rabbit, and crab muscle as well as from baker's yeast by neutralising the trichloroacetic acid extract of the cells with barium hydroxide, precipitating barium pyrophosphate in acetic acid solution, and converting the barium salt by way of the lead or copper salt into the sodium salt. By analysis of the latter, by preparation of roseocobaltic pyrophosphate, and by comparison of the curves of velocity of hydrolysis by acids and of electro-titration with the corresponding curves of authentic pyrophosphate, the identity of the biological material is established. Quantitatively the biological pyrophosphate is determined as the difference between "true" inorganic phosphate plus phosphagen-phosphate and the value obtained after 7 minutes' further hydrolysis by means of *N*-hydrochloric acid at 100°. The electrometric titration curve of pyrophosphoric acid in the region p_H 1.73—12.25 has been determined. In the hydrolysis of pyro- to ortho-phosphoric acid displacement of the reaction towards the alkaline side occurs below 6.8 and to the acid side above this value.

W. MCCARTNEY.

Non-specific pressor principle of tissues. J. B. COLLIP (J. Physiol., 1928, 66, 416—430).—Fresh tissue is thoroughly minced and added to five volumes of boiling water, the mixture is boiled for 5 min., and the filtrate is concentrated in a vacuum to one third of its volume. After removing fatty substances mechanically and by ether extraction, the concentration is continued in a vacuum until the extract is syrupy and the concentrate is extracted with three volumes of acetone. The acetone layer contains much of the pressor fraction. The residue is re-extracted several times. The combined acetone extracts are concentrated in a vacuum to a syrup which is again extracted with acetone. An aqueous or saline solution of the final acetone extract after all traces of acetone have been removed is used for studying its effects after intravenous injection. The pressor effect is enhanced by small doses of ergotamine, antagonised by cocaine, and unaffected by atropine. The height and duration of the response are directly related to the size of dose. Small amounts of the extract have little or no effect on isolated intestine, uterus, or heart.

B. A. EAGLES.

Methionine. G. BARGER and F. P. COYNE.—See this vol., 175.

Normal lipin content of organs. II. B. REWALD (Biochem. Z., 1928, 202, 99—105).—The lipin contents of the acetone-ether and alcohol extracts of the fresh and dried corpus luteum, ovary, testis, thyroid, suprarenal, and pancreas are tabulated. The genital glands are richest and the thyroid and pancreas least rich in lipins (cf. A., 1928, 1154).

P. W. CLUTTERBUCK.

Distribution of unsaturated fatty acids in tissues. III. Vital organs of the ox. W. R. BLOOR (J. Biol. Chem., 1928, 80, 443—454).—Figures are given for the lipin distribution of the

liver, kidney, pancreas, lung, and brain of the ox. Much variability was observed, not only between different organs, but also between the same organ in different animals; the least variable constituent was the phospholipin fraction, which is therefore regarded as fairly characteristic of a given organ. Lecithin and cephalin were found in equimolecular amounts. The iodine values of the lecithin and cephalin fractions of the various organs were closely similar, and a general resemblance was observed in the iodine values of all phospholipin fractions; the unsaturated acids contained large amounts of arachidonic acid, but no trebly unsaturated acid. C. R. HARRINGTON.

Highly unsaturated fatty acid of liver-lipins. Preparation of arachidonic acid. J. B. BROWN (J. Biol. Chem., 1928, 80, 455—460).—Crude liver-fat was hydrolysed, the mixed acids were converted into the methyl esters, and the latter distilled. Bromination of all fractions yielded almost exclusively *methyl octabromoarachidonate*, m. p. 228—231°, which, when reduced with zinc dust in alcohol, gave *methyl arachidonate*, b. p. 200—210°/7 mm.; hydrolysis of the latter gave arachidonic acid with the correct iodine value. The work of Hartley (A., 1909, ii, 597) is thus confirmed.

C. R. HARRINGTON.

Protoplasm and glutathione. A. GIROUD (Compt. rend. Soc. Biol., 1928, 98, 376—377; Chem. Zentr., 1928, i, 2946).—Glutathione is always combined with protoplasm and appears to be specially associated with the chondriosomes.

A. A. ELDRIDGE.

Composition of protoplasm. V. W. LEPESCHKIN (Science, 1928, 68, 45—48).—Protoplasm consists chiefly of proteins and lipins probably in unstable chemical combination; salts, and possibly carbohydrates and the decomposition products of proteins, are also present. Living protoplasm is a hydrophilic colloid, the protein-lipin compounds forming the dispersion medium.

CHEMICAL ABSTRACTS.

Electrical conductivity of protoplasm. S. GELFAU (Protoplasma, 1928, 4, 192—200).—The average conductivity of the various specimens was equivalent to that of 0.05*N*-potassium chloride solution; an exception was that of starfish eggs, equivalent to 0.25*N*.

CHEMICAL ABSTRACTS.

Structure of living matter in the light of colloid research. J. SPEK (Kolloid-Z., 1928, 46, 314—320).—A lecture on the application of the concepts of colloid chemistry to biological problems.

E. S. HEDGES.

Imitation of organic forms by means of albumin and mineral acids. L. A. HERRERA (Atti R. Accad. Lincei, 1928, [vi], 8, 460—464).—Further experiments are described (see this vol., 90).

Normal cerebrospinal fluid in children. D. STEWART (Arch. Dis. Childhood, 1928, 3, 96—108).—Normal cerebrospinal fluid of children contains 15—55 mg. (lumbar), 12—50 mg. (cisterna magna), 5—18 mg. (lateral ventricles) of protein per 1000 c.c.; the protein content does not vary with increasing age. The chloride content is 630—760 mg. per 100 c.c.; the sugar content is 45—66% of the blood-sugar.

CHEMICAL ABSTRACTS.

Tryptophan reactions in the cerebrospinal fluid. B. S. WALKER and F. H. SLEEPER (J. Lab. Clin. Med., 1927, 12, 1048—1052).—The amount of tryptophan in cerebrospinal fluid and egg-albumin varies, although not quantitatively, with the protein content.

CHEMICAL ABSTRACTS.

Cholesterol and cholesteryl ester content of bovine colostrum. R. E. SHOPE and J. W. GOWEN (J. Exp. Med., 1928, 48, 21—24).—The total amount of cholesterol found in colostrum and milk is comparatively low. The amount in colostrum declines at a decreasing rate as milk secretion develops, until at 48 hrs. the cholesterol is nearly the same as that found in milk 3 or 7 months after parturition. The morning milk differs from the evening milk in that the cholesterol present as ester is greater in amount.

CHEMICAL ABSTRACTS.

Lipin content of butter. B. REWALD (Biochem. Z., 1928, 202, 391—393).—The lipin (lecithin) content of butter, deduced from the phosphorus content, is 1.17—1.73%. Differences in different butters may be due to such factors as the nature of the fodder supplied to the cattle, the period of lactation, and the season of the year. Skim milk contains only traces of lipins.

W. MCCARTNEY.

Action of heat on lipins. B. REWALD (Biochem. Z., 1928, 202, 394—398).—Although isolated lipins are very readily decomposed by heat and by atmospheric oxygen, in a natural condition and accompanied by fats they may be boiled or roasted without undergoing any considerable decomposition.

W. MCCARTNEY.

Dextrose content of the vitreous humour. F. ASK (Särl. acta ophthalm., 1928, 5, 23—28; Chem. Zentr., 1928, i, 3084).—In pathological conditions, especially glaucoma, the vitreous humour contains less dextrose than the aqueous humour.

A. A. ELDRIDGE.

Pancreatic secretion. R. CARUSI (Folia Clinica, 1928, 3, 209—255).—An internal and an external pancreatic secretion exist, but changes in the secretions are not always accompanied by corresponding histological changes. The external secretion is composed of trypsin, lipase, and amylase. The internal secretion is produced by the islets of Langerhans and is able to act on carbohydrates. The various methods suggested for determining the enzymes are discussed and a modified method for determining amylase is given.

T. H. POPE.

Does a gastric lipase exist? G. MELLI and M. RADICI (Folia Clinica, 1928, 3, 169—190).—The authors conclude that the lipase, the existence of which in the gastric juice is affirmed by some and denied by others, is actually the lipase which occurs normally in the gastric mucosa and leaves this accidentally as a result of trauma following probing. The functions of this lipase are probably limited to the interior of the individual cells. The stomach plays no part in the digestion of fats.

T. H. POPE.

Elimination of thiocyanate, a source of error in the ferric chloride test for lactic acid. L. A. CRANDALL (J. Lab. Clin. Med., 1928, 13, 1046—1047).—The presence of potassium thiocyanate in

gastric contents, particularly of patients who smoke, affects the ferric chloride test for lactic acid; it is removed by the addition of saturated mercuric chloride solution.

CHEMICAL ABSTRACTS.

Colorimetric determination of inorganic sulphate in urine. B. S. KAHN and S. L. LEIBOFF (J. Biol. Chem., 1928, 80, 623—629).—The urine is treated with benzidine hydrochloride and the precipitate of benzidine sulphate separated on the centrifuge and diazotised; a standard solution of ammonium sulphate is treated similarly. The two solutions are then treated with phenol and excess of sodium hydroxide and the resulting colours compared.

C. R. HARRINGTON.

Effects of sera from normal and anæmic persons on growth of seedlings. L. B. UPJOHN, R. ISAACS, and F. G. GUSTAFSON (Arch. Int. Med., 1928, 42, 909—915).—Seedlings of *Lupinus albus* grown in Shive's nutrient saline solution and containing serum from normal persons show an average rate of growth of 76% of the rate of growth in Shive's solution alone. The growth of seedlings in solutions containing serum from patients with pernicious anæmia did not vary significantly from that in serum taken from normal persons.

B. A. EAGLES.

Utilisation and rate of excretion of ingested creatine by normal and arthritic subjects. F. A. CAJORI, L. M. WRIGHT, and E. STILZ (Arch. Int. Med., 1928, 42, 901—908).—Arthritic patients are as efficient as normal subjects in their ability to retain creatine administered orally. The rate of excretion, however, is slower in the arthritic patients, and this may be due to a disturbance of peripheral blood-flow.

B. A. EAGLES.

Atopy: blood-calcium and gastric analysis. L. H. CRIEP and W. S. McELROY (Arch. Int. Med., 1928, 42, 865—871).—Patients in atopic conditions have a normal blood-calcium value, but frequently show achlorhydria and hypoaclidity.

B. A. EAGLES.

Blood-sugar of corpuscles and plasma in diabetic and alimentary hyperglycæmia. M. SOMOGYI (Arch. Int. Med., 1928, 42, 931—938).—The distribution of blood-sugar between corpuscles and plasma can be determined only from true sugar values. The relative sugar content of corpuscles is the same in the blood of diabetics and normal individuals. The distribution of sugar is unaffected by changes in blood-sugar level caused by ingestion of dextrose.

B. A. EAGLES.

Rational insulin therapy based on daily blood-sugar curves. A. GOTTSCHALK and A. SPRINGBORN (Klin. Woch., 1928, 7, 1129—1133; Chem. Zentr., 1928, ii, 458).—The metabolic picture is best obtained clinically by means of blood-sugar curves extending over 24 hrs.

A. A. ELDRIDGE.

Salabrose (tetraglucosan) in diabetes. E. KAUFMANN (Z. ges. exp. Med., 1928, 60, 116—132; Chem. Zentr., 1928, ii, 367).—Oral administration of tetraglucosan is usually followed in diabetic and in normal subjects by a rise in the blood-sugar, which also follows intravenous injection. With rabbits, tetraglucosan has no effect on insulin hypoglycæmia. The use of tetraglucosan in diabetes is discussed.

After removal of dextrose by fermentation, the substance may be determined polarimetrically or colorimetrically by reduction of picric acid to picramic acid. The latter method is unsuitable for its determination in urine.

A. A. ELDRIDGE.

Clinical calorimetry. XLIII. Thresholds of ketosis in diabetes, epilepsy, and obesity. W. S. McCLELLAN, H. J. SPENCER, E. A. FALK, and E. F. Du Bois (J. Biol. Chem., 1928, 80, 639—652).—The threshold of ketosis (i.e., excretion of 0.1 g. of acetone in 24 hrs.) was reached in normal, diabetic, and epileptic subjects when the fatty acid : dextrose ratio of the food metabolised, calculated by the formula of Woodyatt (Arch. Int. Med., 1921, 28, 125), exceeded 1.5; in a case of obesity the ratio could be raised to 2.4 without producing ketosis.

C. R. HARRINGTON.

Urinary C : N and O : N ratios in phloridzin diabetes. A. R. PESKIN (Biochem. Z., 1928, 202, 5—13).—In phloridzinised dogs and rats, other dysoxidisable substances than sugar are excreted in increased amounts in the urine; the substances are rich in hydrogen and not identifiable with acetone compounds (cf. A., 1926, 639, 642).

P. W. CLUTTERBUCK.

Bile acids in jaundice. I. KATAYAMA (Arch. Int. Med., 1928, 42, 916—930).—Calculated as sodium glycocholate, the bile acids of normal blood-serum vary from 5 to 12 mg. per 100 c.c. Bile acids are absent from normal urine. There is a marked increase in the bile acids of the serum, accompanied by urinary excretion of bile acids in patients with cholecystitis, disease of the liver, catarrhal jaundice, obstructive jaundice, cardiac decompensation, and duodenitis. Changes in concentration of bile acids in the blood bear no relation to variation of bilirubin in the blood. Bile acids appear in the urine when the blood-serum value exceeds 20 mg. per 100 c.c.

B. A. EAGLES.

Determination of bilirubin in blood. H. F. SHATTUCK, J. A. MILLIAN, and M. PRESTON (J. Lab. Clin. Med., 1927, 12, 802—810).—The icterus index was more trustworthy than van der Bergh's method, the latter being unsatisfactory in 50% of the cases of latent jaundice.

CHEMICAL ABSTRACTS.

Urea tolerance test. S. E. KING (Arch. Int. Med., 1928, 42, 877—892).—Following the ingestion of 1 g. of urea per 10 lb. body-weight the blood-urea of normal individuals returns to its control level in 14 hrs. In the cases of impaired renal function investigated, there remained after 14 hrs. an average elevation above the control level of 10.3 mg. of urea-nitrogen per 100 c.c. of blood.

B. A. EAGLES.

Chemical changes in dog's blood in experimental peritonitis. T. G. ORR and R. L. HADEN (J. Exp. Med., 1928, 48, 339—342).—The changes in chloride, urea, and non-protein nitrogen resemble those in pyloric and high intestinal obstructions, but there is no alkalosis.

CHEMICAL ABSTRACTS.

Intestinal p_H in experimental rickets. B. L. OSER (J. Biol. Chem., 1928, 80, 487—497).—In agreement with Shohl and Bing (A., 1928, 1288) the faecal p_H in experimental rickets in rats is variable,

and its measurement is not a sound measure of the vitamin-D content of the diet (cf. Jephcott and Bacharach, A., 1928, 332); the relative alkalinity of the intestinal tract of rachitic rats is most marked in the colon, and is thought to be associated with the decreased reabsorption of phosphorus in these animals, this reabsorption taking place in the normal animal from the colon.

C. R. HARRINGTON.

Trypsin secretion of infants. T. LUKACS (Amer. J. Dis. Children, 1926, 31, 235—240).—In infectious diseases of children the trypsin content of the faeces is decreased, but in rickets it is increased.

CHEMICAL ABSTRACTS.

Coagulation of the blood in parathyroid tetany. J. C. BROUGHER (Amer. J. Physiol., 1928, 87, 221—224).—Blood-coagulation is delayed in parathyroid tetany. One ounce of cod-liver oil given by stomach tube restores the coagulation time to normal after a period of 2—4 hrs.

B. A. EAGLES.

Cholesterol in malignant tumours. A. H. ROFFO (Prensa med. Argentina, 1924, 20 pp.; Chem. Zentr., 1928, ii, 791—792).—The dried substance contains 3% (or up to 10%) of cholesterol. The non-tumour portion of rats contains more cholesterol than normal rats. On a sterol-free diet the cholesterol content of the animals increased with growth of the tumour, which was, however, markedly arrested.

A. A. ELDRIDGE.

Existence of substances resembling insulin in benign and malignant human tumours. A. H. ROFFO and L. M. CORREA (Rev. Soc. Argentina Biol., 1927, 3, 68—71; Chem. Zentr., 1928, ii, 369).—Experiments on rat sarcomata have been extended to human tumours with analogous results, but smaller quantities of substances resembling insulin have been obtained.

A. A. ELDRIDGE.

Chemical changes in the body occurring as the result of vomiting. A. F. HARTMANN and F. S. SMYTH (Amer. J. Dis. Children, 1926, 32, 1—28).—Chloride is lost and hydrogen carbonate retained in compensation; non-protein nitrogen is increased if necessary to maintain the normal osmotic pressure. Excess of non-protein nitrogen and sodium hydrogen carbonate is excreted on administration of sodium chloride, but the excretion of all three substances depends on the total crystalloid concentration of the blood.

CHEMICAL ABSTRACTS.

Chemical changes occurring in the body as the result of certain diseases. I. Effects of diarrhoea, vomiting, dehydration, and oliguria on the acid-base balance of the plasma of infants with mastoiditis. A. F. HARTMANN (Amer. J. Dis. Children, 1928, 35, 557—575).—Vomiting produces a reduction in the hydrogen chloride and base chloride reserve; dehydration an increase in the blood plasma-lactic acid and -protein; oliguria an increase in phosphoric acid and non-protein nitrogen.

CHEMICAL ABSTRACTS.

Metabolism of Eskimos. P. HEINBECKER (J. Biol. Chem., 1928, 80, 461—475).—As compared with inhabitants of temperate zones, Eskimos have a higher basal metabolic rate; they have increased power of oxidising fats which enables them to fast

without developing ketosis; during fasting, the normally high sugar tolerance is reduced, and the respiratory quotient falls to low levels which indicate conversion of fat into carbohydrate.

C. R. HARRINGTON.

Basal metabolism of Australian aborigines. H. S. H. WARDLAW and C. H. HORSLEY (Austral. J. Exp. Biol., 1928, 5, 263—272).

Influence of food on longevity. H. C. SHERMAN and H. L. CAMPBELL (Proc. Nat. Acad. Sci., 1928, 14, 852—855).—Two sets of about 200 rats were fed on separate diets; diet A consisted of $\frac{1}{8}$ dried whole milk, $\frac{5}{8}$ ground whole wheat, 2% of the weight of wheat of table salt, and distilled water *ad lib*. Diet B consisted of $\frac{1}{8}$ dried whole milk, $\frac{3}{8}$ ground whole wheat, and salt and water as in A. The rats were fed on these diets until natural death occurred, and the length of life was noted in each case. It was found that whilst diet A was adequate, diet B was better, the rats fed on B living approximately 10% longer than those fed on A.

A. J. MEE.

Influence of age on the composition of the lipin fraction in the animal organism. V. S. SADIKOV and E. S. GOLOVTSCHINSKAYA (Biochem. Z., 1928, 202, 421—438).—The amount of lipin fraction obtainable from cats when treated according to the process described by Sadikov and Shchegl'ska (A., 1928, 194) varies considerably according to the age of the animals and to other circumstances. Variations according to age are also found in the composition of the fraction. The possible nature and causes of these variations are discussed.

W. MCCARTNEY.

Influence of diet on muscle-haemoglobin. G. H. WHIPPLE, A. H. GROTH, and F. S. ROBSCHERT-ROBBINS (Amer. J. Physiol., 1928, 87, 185—191).—Pups of the same litter were divided into two groups and after weaning were fed on an adequate synthetic bread ration or on a bread ration plus large amounts of cooked liver. After 15—20 weeks on these diets the liver-fed pups had concentrations of blood- and muscle-haemoglobin distinctly greater than those of the bread-fed controls.

B. A. EAGLES.

Respiratory metabolism in infancy and childhood. III. Glycogen storage in children. S. Z. LEVINE, J. R. WILSON, and H. RIVKIN (Amer. J. Dis. Children, 1926, 31, 496—503).—Glycogenesis occurred during high carbohydrate feeding, and glycogenolysis during starvation in all cases (except diabetic) studied.

CHEMICAL ABSTRACTS.

Respiratory quotient of the excess metabolism of exercise. C. H. BEST, K. FURUSAWA, and J. H. RIDOUT (Proc. Roy. Soc., 1929, B, 104, 119—151).—The respiratory quotient of the excess metabolism of very mild exercise is below unity, that of moderate exercise approximates to unity, whilst that of very severe exercise may exceed unity and reach values up to 1.70. The respiratory quotient of the total metabolism for the period of exercise and recovery is below unity for mild or moderate exercise but slightly exceeds unity in the case of very severe exercise.

W. O. KERMACK.

Action of exercise and work on alkali reserve of blood. B. KRAVTSCHINSKI (Russ. J. Physiol., 1928, 11, 415—432).—The alkali reserve of 54 normal individuals varied from 47 to 75 vols.-% of carbon dioxide. Walking, running, or strenuous exercise lowered the alkali reserve. The extent of lowering depends more on the intensity than on the amount of work done. Exercise produces no acidosis in trained subjects but does so in beginners.

B. A. EAGLES.

Free energy of glycogen-lactic acid breakdown in muscle. D. BURK (Proc. Roy. Soc., 1929, B, 104, 153—170).—It is calculated that the free energy of the anaerobic reaction, glycogen \rightarrow lactic acid, is $1\frac{1}{2}$ —2 times the heat of reaction. This conclusion holds whether or not the lactic acid is neutralised by buffer mixtures such as that present in muscle. In the case of aerobic oxidation of glycogen to carbon dioxide the difference between free energy and heat of reaction is negligible because of the large magnitude of the latter.

W. O. KERMACK.

Fate of acetoacetic acid in normal and diabetic dogs before and after evisceration. I. L. CHAIKOFF and S. SOSKIN (Amer. J. Physiol., 1928, 87, 58—72).—Following its intravenous administration sodium acetoacetate disappears rapidly from the blood of normal and eviscerated-normal animals. It disappears at a slower rate from the blood of fasted depancreatized animals, but in eviscerated-diabetic animals the disappearance is as rapid as in normal animals. Since the muscles of fasted depancreatized animals can utilise acetoacetic acid as rapidly as normal muscle, it is argued that ketosis cannot be attributed to an impediment in the normal path of the catabolism of ketonic compounds. It is concluded that the appearance of excess of ketonic compounds in the tissue fluids of the diabetic animal is due to an increased rate of production by the liver.

B. A. EAGLES.

Clinical calorimetry. XLIV. Changes in rate of excretion of acetone substances during the day. W. S. MCCLELLAN and V. TOSCANI (J. Biol. Chem., 1928, 80, 653—658).—Ketosis was induced in normal individuals by exclusive administration of meat; the rate of excretion of acetone substances was highest in the late afternoon and night and lowest in the morning, and thus bears a relationship to the total metabolic rate.

C. R. HARRINGTON.

Behaviour of α -ketovalerolactone- γ -carboxylic acid in the animal body. R. ENGER and H. SIEDENTOPF (Ber. Sachs. Ges. Wiss., Math-Phys. Kl., 1928, 80, 122—126; Chem. Zentr., 1928, ii, 585).—After intravenous injection of α -ketovalerolactone- γ -carboxylic acid into dogs, the urine and blood did not contain increased amounts of acetone, neither was the blood-sugar increased. In perfused surviving liver there was a temporary increase of β -hydroxybutyric acid, and (after 30 min.) an increase in acetone formation. The nature of the decomposition is discussed.

A. A. ELDRIDGE.

β -Oxidation. II. Metabolism of phenyl-substituted acids and of acetophenone in dogs. A. J. QUICK. **III. Fate of γ -phenylbutyric acid in depancreatized dogs.** J. E. SWEET and A. J.

QUICK. IV. Metabolism of conjugated glycuronic acids. A. J. QUICK (J. Biol. Chem., 1928, 80, 515—525, 527—534, 535—541).—II. δ -Phenylvaleric acid was conveniently prepared by boiling cinnamylidenemalonic acid with hydriodic acid and phosphorus. This acid, as also Δ^{α} - and Δ^{β} - α -phenylpentenoic acids, were oxidised in the dog exclusively to benzoic acid, which was excreted in conjugation with glycuronic acid and glycine in the ratio of 2 : 1. Mandelic acid was excreted unchanged, β -phenyl- β -hydroxypropionic acid was excreted for the most part unchanged, the remainder being oxidised to benzoic acid, whilst acetophenone gave benzoic acid and phenylmethylcarbinol, the latter being conjugated with glycuronic acid. Neither acetophenone nor β -hydroxy- β -phenylpropionic acid is therefore a probable intermediate in the physiological oxidation of β -phenylpropionic acid.

III. The depancreatized dog is able to oxidise γ -phenylbutyric acid to phenylacetic acid; it is unlikely, therefore, that the diabetic organism has lost the power to oxidise butyric acid.

IV. Glycuronic acid does not relieve insulin hypoglycaemia in mice. Menthyl glycuronate, bornyl glycuronate, and monobenzoyleglycuronic acid are all partly oxidised in the dog; in the last case benzoic acid appears in the urine; in man the conversion of benzoyleglycuronic acid into hippuric acid is complete. It is thought that, in the dog, all benzoic acid is first conjugated with glycuronic acid, and that a part of the latter is then converted into hippuric acid. C. R. HARRINGTON.

Significance of plant sterols for animal organisms. R. SCHONHEIMER (Z. physiol. Chem., 1929, 180, 1—37). Action of sitosterol [with D. YUASA].—Comparative experiments of the effect of cholesterol and sitosterol and other plant sterols on various animals have been carried out. Morphological examination of rabbits to the food of which have been added similar quantities of cholesterol and sitosterol respectively shows that the usual fatty condition of the liver and other organs is produced in the first case, but, contrary to von Gierke, no effect is produced by sitosterol. These results are confirmed by a chemical analysis of the brains and skins, a large increase in sterol content over that in the normal animals being found in the former case but not in the latter. Similar results accrue from an examination of the blood-serum. Examination of various types of animals, herbivorous, omnivorous, and carnivorous (rats, mice, and cats), all give similar results, the increase in sterol content and pathological effect on the organs occurring only when cholesterol is added to the food.

Deposition of unchanged plant sterols in animal organisms?—In various experiments with rabbits fed on sitosterol the total sterol in the animal was isolated and converted into its acetate, and plant sterols were sought for by Bohmer's method (Abderhalden, "Handb. biol. Arbeitsmeth.," 6, (1), 539). In no case was the m. p. (113—114°) raised to 116° (which is caused by the presence of only 1% of sitosterol in cholesterol), and hence no appreciable deposition of plant sterol occurs.

Presence of plant-sterol esterases in animals? [with D. YUASA].—Cholesterol (0.2—0.3 g.) was introduced under the skin of a dog under aseptic conditions and, after 11 days, examination showed that 9.5—11% had been esterified. In similar experiments with plant sterols (sito-, stigma-, ergo-, and copro-sterols) no trace of esterification could be detected, the plant sterol behaving purely as a foreign substance.

Sterol equilibrium in rabbits fed on sitosterol. —Similar quantities of cholesterol and sitosterol were added to the food of rabbits over the same periods (with careful control experiments), the faeces collected and examined every 3 days, and the sterol content was determined. When cholesterol is added to the food, only about 50% of the excess appears in the faeces, whilst, within the experimental error, the whole of the sitosterol is excreted. By isolation of the sterol present in the fodder and the faeces as its digitonide and determination of its optical rotation, liberation of the free sterol, and comparison of the m. p. of its acetate and benzoate it is shown that the sterols present in the fodder and in the faeces are identical (cf. Dorce and Gardner, A., 1908, ii, 514). It is concluded that cholesterol and plant sterols undergo different metabolic processes, the latter passing through the animal unaltered and totally unabsorbed.

J. W. BAKER.

Relationships between cholesterol metabolism and the production of the bile acids. Y. HORIYE (Biochem. Z., 1928, 202, 409—420).—No experimental support could be found for the view that endogenous cholesterol is involved in the production of bile acids. When a cholagogue was administered orally to rats, the cholesterol content of their livers increased. It is concluded that the liver stores up part of the cholesterol set free in the organism by the action of the cholagogue. W. MCCARTNEY.

Bile salt metabolism. I. Control diets, methods, and fasting output. H. P. SMITH, A. H. GROTH, and G. H. WHIPPLE. II. Influence of foodstuffs. H. P. SMITH and G. H. WHIPPLE. III. Influence of tryptophan, tyrosine, and related substances. IV. How much bile salt circulates in the body? G. H. WHIPPLE and H. P. SMITH (J. Biol. Chem., 1928, 80, 659—669, 671—684, 685—695, 697—707).—I. In dogs on a standard diet the daily output of bile salt is, on the average, 100 mg. per kg., this being secreted at a practically uniform rate; by fasting the output may be reduced to 30—40 mg. per kg. per diem, this residual amount being regarded as endogenous in origin. The bile salts were determined by the method of Foster and Hooper (A., 1919, ii, 376).

II. Variations in the diet of dogs with biliary fistula show that increase of protein in the diet causes increased output of bile salts, whilst alcoholic extracts of meat, yeast, and lipins are without any such effect.

III. Substitution of gelatin for the standard salmon-bread diet of the dogs caused a fall in the secretion of bile salts; supplementation of the gelatin with tyrosine or *p*-hydroxyphenylglycine was without effect, but addition of tryptophan, and to a smaller extent of isatin and indigo, gave increased output;

the indole derivatives produce also increased outflow of bile, and, in combination with a sugar diet, may exercise a cholagogue effect with no simultaneous increase in the output of bile salts.

IV. Re-feeding of the bile salt secreted by a dog with a biliary fistula raises the secretion of bile salts to a steady level of 700–800 mg. per kg. per diem; administration of still more bile salt produces only a temporary increase in secretion. This indicates that the above amount represents the bile salt normally kept in circulation in the dog, additional amounts disappearing from the body in a manner as yet unexplained.

C. R. HARRINGTON.

Metabolism of the bile. III. Enterohepatic circulation of bile acids. C. H. GREEN, M. ALDRICH, and L. G. ROWNTREE (J. Biol. Chem., 1928, 80, 753–760).—After oral administration of bile salts to a dog with a biliary fistula there is a delay in the excretion due to the time taken for absorption from the intestine. Whilst in the normal fasting animal no difference is observed in the bile-salt concentration in different parts of the circulation, injection of bile salts into the duodenum is followed by an increase in their concentration in the portal blood.

C. R. HARRINGTON.

Compounds of lecithin with amino-acids. L. GUERCI (Annali Chim. Appl., 1928, 18, 495–503).—Treatment of lecithin with pancreas extract, the amino-acids of vitellin or egg-protein, or glycine shows that lecithin forms with amino-acids colloidal compounds which are difficult to isolate and represent the first stage in the union of lecithin with albumins. It is thought that lecithin acts as an intermediate substance in the formation of amino-acids from fatty acids.

T. H. POPE.

Effect of protein hydrolysis products on metabolism. III. Specific dynamic effects of protein hydrolysates and amino-acids. D. RAPPORT and H. H. BEARD (J. Biol. Chem., 1928, 80, 413–430).—Glutamic and aspartic acids, arginine, and cystine had definite specific dynamic effects, whilst histidine had no such action. Up to the present this work (cf. also A., 1927, 694) indicates that the specific dynamic effect of a protein is a simple summation of the effects of its constituent amino-acids.

C. R. HARRINGTON.

Behaviour of various protein degradation products in the intermediate region. N. KOTSCHNEV (Pflüger's Archiv, 1928, 218, 635–641; Chem. Zentr., 1928, i, 3087).—Analyses of the portal blood of dogs showed that amino-acids and polypeptides were resorbed from the intestine. The amino-acids were partly resynthesised to polypeptides in the liver and passed into the blood. The kidneys retain amino-nitrogen during the resorption. The spleen, muscle, and intestine participate in the synthesis of polypeptides. In hunger, only the spleen delivers polypeptides to the blood.

A. A. ELDRIDGE.

Biological value of yeast-protein for the rat. E. U. STILL and F. C. KOCH (Amer. J. Physiol., 1928, 87, 225–248).—Young rats will grow on diets containing yeast as the sole source of protein. More satisfactory growth is obtained with caseinogen.

Compared with caseinogen the biological value of dried raw yeast-proteins is 45%. B. A. EAGLES.

Storage of protein by sucking pigs. W. WOHLBIER (Biochem. Z., 1928, 202, 29–69).—Sucking pigs excrete, with increasing age, increasing amounts of nitrogen, and a smaller proportion of the protein absorbed is therefore stored. The nitrogen stored as protein in the first 4 weeks was 89.1, 84.8, 74.7, 67.7% of that absorbed. For an increase in weight of 100 g., 0.957 g. of nitrogen was excreted. Calorific measurements show that for storage of 1 kg., the utilisation in calories increases from 3776 in the first week to 5628 in the fourth week. The daily mean yield of milk for the single test of the sow varies greatly, e.g., from 393 to 721 g. during the first 14 days, the total yield for milk per sow varying daily from 4.5 to 4.9 kg.

P. W. CLUTTERBUCK.

Conditions for the formation of carbamide in the isolated liver. III. P. P. ASTANIN and W. M. RUBEL (Biochem. Z., 1928, 202, 70–74; cf. A., 1928, 669).—Formation of carbamide from ammonium carbonate in the isolated liver occurs only in presence of the perfusing fluid and simultaneously of erythrocytes and serum.

P. W. CLUTTERBUCK.

Origin and fate of uric acid and resorption of nucleic acid in the dog. S. RABINOVICH (Pflüger's Archiv, 1928, 219, 402–406; Chem. Zentr., 1928, ii, 463).

Origin and fate of creatine and creatinine. W. MOCHNATSCHE (Pflüger's Archiv, 1928, 218, 655–660; Chem. Zentr., 1928, i, 3087).—In hunger creatine originates from the liver and kidneys; during digestion only from the liver. A large part of the creatine passed into the circulation is retained in the intestinal wall.

A. A. ELDRIDGE.

Effect of fasting and of creatine feeding on creatine content of rat tissues. A. CHANUTIN and H. SILVETTE [with B. W. RAWLES, jun.] (J. Biol. Chem., 1928, 80, 589–608).—The creatine content of the muscles and kidneys of white rats is increased by fasting, other tissues not being affected. Feeding of large amounts of creatine, particularly after prolonged fasting, causes an increase in the creatine content of the muscles, and, to a smaller extent, in that of the liver and heart. The creatine content of the blood is little affected by fasting, but is much increased by feeding creatine. The results indicate that the greater the rate of endogenous catabolism the greater is the rate of both formation and storage of creatine.

C. R. HARRINGTON.

Effect of dextrose on the metabolism of growing rats. W. ARNOLDI and S. UENO (Z. ges. exp. Med., 1928, 61, 424–437; Chem. Zentr., 1928, ii, 464).—Protein and fat were gradually replaced in the diet by sugar. There was at first increase in weight, positive nitrogen-balance, and diminished urinary elimination of carbon; then (9% protein, 35% fat-cal.) the weight became stationary and afterwards (6%, 2%) fell.

A. A. ELDRIDGE.

Diets and dextrose tolerance. J. S. SWEENEY (Arch. Int. Med., 1928, 42, 872–876).—The antecedent diet has no significant influence on the dextrose tolerance curve in normal men.

B. A. EAGLES.

Action of intravenous injection of lactic acid on alkali reserve of blood. B. KRAVTSCHINSKI (Russ. J. Physiol., 1928, 11, 433—444).—Intravenous injection of lactic acid causes a lowering of the alkali reserve from 10 to 40% of its original value. The degree of lowering depends, not only on the amount injected, but also on the rate of injection. The alkali reserve returns to normal in the course of 2—4 hrs. B. A. EAGLES.

Secretions of digestive glands and blood chemistry. I. Alkali reserve and chlorides in blood. S. I. PRIKLADOVITZKI and M. P. BRESTKIN (Russ. J. Physiol., 1928, 11, 445—469).—Normal digestive activity causes a fluctuation in the alkali reserve depending on the kind of food taken. Feeding with lean meat raises the alkali reserve in the course of the first two hours. It gradually returns to its initial value. It is also raised by feeding white bread. Feeding with fat causes a fall followed by a rise. Fluctuations of alkali reserve in the course of digestion are generally accompanied by inverse fluctuations of the chloride content of the blood. B. A. EAGLES.

Behaviour of the diastase in the blood, urine, and faeces of the dog before and after ligation of the pancreatic ducts. F. GALLI (Folia Clinica, 1928, 3, 120—133).—In dogs with the pancreas intact, the amount of diastase in the blood is always greater than that in the urine, but the maximum and minimum values in the two cases never correspond. Ligation and resection of the pancreatic ducts always cause very great increases of the amounts of the enzyme in the blood and urine, but here again no fixed relationships are observed; with the blood this increase persists a week after the ligation, but the diastase content of the urine gradually diminishes. The lack of pancreatic secretion in the intestine causes the disappearance from the faeces of the amylolytic enzyme, which is not found in the faeces a week after the ligation. T. H. POPE.

Relation between potassium and dialysable and undialysable calcium in the intermediate region. S. NEDSVEDSKY (Pflüger's Archiv, 1928, 218, 647—654; Chem. Zentr., 1928, i, 3087).—Experiments with angiotomised dogs showed that potassium is resorbed in the intestine more quickly than calcium. By passage through the intestinal wall a considerable proportion of the calcium becomes undialysable, but dialysable again after passage through the liver. Calcium is but slightly excreted through the kidneys, whilst 85% of the potassium is eliminated in the urine. A. A. ELDRIDGE.

Mineral food of agricultural animals. II. Influence of calcium carbonate on the development of calves. J. ZAYKOVSKY and A. KRASNOKUTSKA (Biochem. Z., 1928, 202, 239—245).—Feeding of calcium carbonate to calves produces no appreciable effect on their development. W. MCCARTNEY.

Effect of X-radiation on nitrogen and sodium chloride metabolism. A. JUGENBURG (Strahlen-ther., 1927, 25, 288—303; Chem. Zentr., 1928, ii, 463).—The nitrogen content of the blood is reduced, and that of the organs is increased or decreased,

according to the dose. The milk-nitrogen is particularly increased. A. A. ELDRIDGE.

Mitogenetic radiation of stimulated muscle and of other tissues. W. W. SIEBERT (Biochem. Z., 1928, 202, 115—122).—The rate of subdivision of yeast-cells is increased by the action at a distance of the pulp of muscle which has recently been electrically stimulated, but is unaffected by pulp of resting muscle under the same conditions. This effect is due to mitogenetic radiation from the stimulated muscle. The rays may be deflected by a polished metal surface and so directed on to suitable cultures, which then show increased subdivision. Similar experiments with spleen, testes, ovary, skin, and liver pulps showed these to be devoid of radiating power, but bone marrow of both rat and guinea-pig, minced Jensen rat sarcoma, and carcinomatous tissue always showed activity. P. W. CLUTTERBUCK.

Cause of mitogenetic radiation. W. W. SIEBERT (Biochem. Z., 1928, 202, 123—130).—Addition of suitable amounts of lactic acid to resting muscle does not cause it to radiate, but if the muscle is then kept in pure oxygen it becomes active, the radiation being therefore probably associated with the oxidation of lactic acid. Pulp of electrically stimulated muscle becomes active in atmospheric air, pure oxygen being unnecessary. Unstimulated muscle treated with lactic acid and kept in ordinary air can be caused to radiate by addition of copper salts, but not by addition of peroxidase. A similar radiation can be detected with Warburg's charcoal model in which oxalic acid is oxidised on the carbon surface, and in the spontaneous oxidation of laevulose in phosphate buffer (p_H 8) in presence of oxygen and also in the oxidation of pyrogallol to purpurogallin by peroxidase and hydrogen peroxide. The activity of both the charcoal model and the tumour tissue was completely lost by addition of 0.00002N-cyanide. P. W. CLUTTERBUCK.

Effect of hydroxyquinoline [on dogs]. C. GRABBE (Arch. exp. Pharm., 1928, 137, 96—115).—Hydroxyquinoline administered *per os* is excreted by the dog principally through the kidneys as the sulphuric acid ester. It increases the nitrogen metabolism of starving animals. E. A. LUNT.

Action of synthalin. H. STAUB (Z. klin. Med., 1928, 107, 607—658; Chem. Zentr., 1928, ii, 458—459).—Intravenous administration of synthalin causes in fasting rabbits a primary hyperglycaemia and a slight secondary hypoglycaemia. Continued peroral administration also results in no marked reduction of blood-sugar. The incidence of the toxic effect of synthalin is discussed. The liver- and muscle-glycogen is diminished, and the formation of lactic acid is increased. The action of synthalin in no way resembles that of insulin. A. A. ELDRIDGE.

Synthesis of 4(or 5)-glyoxalinyldethylmethylcarbinol and its behaviour towards polyneuritis of pigeons. Y. SAHASHI (Bull. Inst. Phys. Chem. Res., Tokyo, 1928, 7, 1191—1195).—Administration of β -4(-or 5)-glyoxalinyldethylmethylcarbinol [β -4(or 5)-glyoxalinyldbutan- β -ol] temporarily cured the severe spastic form of polyneuritis in pigeons, but the

birds died 7—10 days after the first appearance of spasms. J. W. BAKER.

Has alcoholic extract of polished rice any noxious effect on pigeons? Y. SAHASHI, T. NOGUCHI, and N. HASHIMOTO (Bull. Inst. Phys. Chem. Res., Tokyo, 1928, 7, 1196—1201).—Since a group of pigeons fed on well-washed polished rice and McCollum's salts with the addition of a large quantity of the alcoholic extract of polished rice lived longer than another group fed on the same diet without the alcoholic extract, it is concluded that the latter has no noxious effect on pigeons. Moreover, signs of polyneuritis appeared even earlier in pigeons fed on polished rice powder which had been previously extracted with alcohol than in those fed on the unextracted rice powder. J. W. BAKER.

Variations in the cholesterol content of organs in naphthalene intoxication. D. MICHAEL and P. VANCEA (Compt. rend. Soc. Biol., 1927, 97, 1097—1100; Chem. Zentr., 1928, ii, 791).—During the first ten days the cholesterol content of most of the organs is increased; it is unchanged in the lungs, heart, muscles, and vitreous humour, and falls in the lens and retina. In 30 days it is normal, but subnormal in the suprarenals, spleen, brain, lungs, and heart. In the lens it diminishes until cataract appears, with the growth of which it then increases.

A. A. ELDRIDGE.

Toad poisons. VI. Poisonous constituents of *Bufo bufo japonicus*. M. KOTAKE (Bull. Inst. Phys. Chem. Res., Tokyo, 1928, 7, 1244—1248; cf. A., 1928, 1138).—The species of toad used by the author is now known to be *Bufo vulgaris formosus* and not *Bufo bufo japonicus* as previously stated. Crystals of *bufotalin* have also been separated from the alcoholic extract and converted into the *acetyl* derivative, *bufotaliene*, and *bufotalone*. J. W. BAKER.

Influence of calcium salts on snake-venom hæmolysis. S. KANISAWA (Acta Dermatol., 1927, 479—490; Chem. Zentr., 1928, ii, 460).—In the cases studied, hæmolysis was arrested by calcium chloride or lactate in concentrations >0.025% and accelerated in concentrations <0.01%. A. A. ELDRIDGE.

Catalase system in animal tissues under different physiological and pathological conditions. II. Determination of catalase and anticatalase in the tissues of normal guinea-pigs and white rats. III. Effect of chronic intoxication with morphine, arsenic, and alcohol. E. D. GAGARINA and V. D. YANKOVSKI (Zhur. exp. biol. Med., 1928, 9, 50—57, 59—67).—II. Aqueous extracts of various organs partly lose their catalase activity, especially at 37°, owing to inactivation by an anti-catalase; the inactivation can be prevented by alcohol (1 in 10⁴).

III. Morphine intoxication increases the catalase content of tissues, particularly liver and muscle, and decreases that of the blood. The anticatalase diminishes except in the liver and muscles. Chronic arsenic poisoning causes increase of both catalase and anticatalase, except in the blood, where it is decreased. Chronic alcohol poisoning of rats causes a fall in the catalase and anticatalase content of

the liver and kidneys, and a rise in that of the blood and muscles. CHEMICAL ABSTRACTS.

Determination of morphine in biological material. A. K. BALLS and W. A. WOLFF (J. Biol. Chem., 1928, 80, 379—402).—Finely-divided muscle is extracted with alcohol containing hydrochloric acid, and the extract is evaporated, the alcohol being replaced with water; after removal of fat, the aqueous solution is treated with phosphoric acid, and then adjusted to p_H 9.0 by addition of potassium hydroxide; the morphine is then removed by continuous extraction with chloroform containing 20% of alcohol and a little hydrochloric acid; the residue after evaporation of the chloroform is again dissolved in phosphate solution at p_H 9.0 and re-extracted; finally, the chloroform is evaporated, the residue dissolved in dilute hydrochloric acid, and the morphine determined by precipitation as the silicotungstate. Urine is adjusted to p_H 9.0 and extracted continuously with chloroform; the chloroform is evaporated and the residue dissolved in phosphate solution at p_H 3.0; extraction with chloroform at this stage removes coloured impurities; the morphine is obtained by adjusting the reaction to p_H 9.0 and repeating the extraction, and is then determined as above. Modifications of the method applicable to blood and faeces are also described. The method cannot be used with material containing less than 20 mg.-% of morphine; it avoids the two main disadvantages of existing methods, viz., loss of morphine by adsorption on precipitates or by oxidation. C. R. HARRINGTON.

Physical and pharmacological influences on the action of curare. III. Effect of calcium, barium, and magnesium. IV. Physostigmine and nicotine. S. HORI (Folia pharmacol. japon., 1928, 4, 259—268, 279—280; Chem. Zentr., 1928, ii, 586). A. A. ELDRIDGE.

Action of calcium ions on the frog's heart. A. J. CLARK, G. H. PERCIVAL, and C. P. STEWART (J. Physiol., 1928, 66, 346—355).—The effects produced on the frog's heart by variations in the total calcium content of the perfusion fluid are explained as due to variations in the concentration of calcium ions. The mechanical response of the frog's heart varies directly as the concentration of calcium ions, when the latter falls below a value of 0.43 millimolar.

B. A. EAGLES.

Effect of sulphur on carbohydrate metabolism. E. FOLDES (Z. ges. exp. Med., 1928, 60, 571—582; Chem. Zentr., 1928, ii, 464).—Absorption of sulphur (ointment) through the skin usually causes a diminution of the blood-sugar. With rabbits, the suprarenals became enlarged and contained an increased quantity of sulphur. A. A. ELDRIDGE.

Action of hydrocyanic acid in frogs. V. KARASSIK (Russ. J. Physiol., 1928, 11, 339—350).—The arterial colour of venous blood of frogs poisoned with hydrocyanic acid becomes darker when the frogs are warmed and reappears on cooling them. There is an increase in the absorption of oxygen by the tissues during the period of warming. B. A. EAGLES.

Reducing substances of the blood in lead poisoning. A. MITTLESTEDT (Moskovski med. zhur.,

1927, 7, 1—4).—No abnormality was observed, but in the chronic stage the increase caused by bread feeding was greater than usual.

CHEMICAL ABSTRACTS.

Photochemical dissociation in intermittent irradiation and the absolute absorption spectrum of the respiratory enzyme. O. WARBURG and E. NEGELEIN (Biochem. Z., 1928, 202, 202—228).—A method has been described (cf. A., 1927, 1221; 1928, 537, 549, 851, 1390) for the calculation of the relative absorption spectrum of the respiratory enzyme from the photochemical dissociation of its carbonyl compound using the stationary condition attained during irradiation of cells in mixtures of carbon monoxide and oxygen. The velocity of attaining this condition is now determined and it is shown that the absolute absorption spectrum may be calculated therefrom. The spectrum of the carbonyl compound of the respiratory enzyme is that of an iron-carbonyl group attached to an organic molecule which is the same as that carrying the iron-carbonyl group in carbon monoxide-haemin (tetrapyrrole nucleus).

P. W. CLUTTERBUCK.

Enzyme action. I. Amylase from Cholam (*Sorghum vulgare*). V. N. PATWARDHAN and R. V. NORRIS (J. Indian Inst. Sci., 1928, 11, A, 121—133).—Cholam amylase prepared by making under definite conditions an extract of malted cholam is less active in the production of sugar from starch than is malted barley enzyme, but for the same amount of sugar produced in the same solution much more starch is liquefied by the cholam amylase than by the barley amylase. Sugar production and liquefaction reach a maximum at 50—55°. Dialysis of cholam malt amylase results in a decrease of its activity, but the effect is not so marked as in the case of amylases of animal origin. Sodium chloride activates cholam malt amylase most effectively at a concentration of $N/500$, whilst other chlorides in equivalent proportions have an approximately equal action and affect sugar production and liquefaction to the same extent. Hippuric acid accelerates, whilst asparagine, alanine, glycine, and *l*-leucine inhibit the action of cholam malt amylase. Maltose also has a retarding influence. Precipitated cholam malt amylase shows a peculiar irregular variation in its activity at pH between 4.5 and 5.5, which is exhibited in respect of both its sugar-producing and in its liquefying power. When the enzyme is purified by dialysis no such abnormality is found, both the crude enzyme and the enzyme purified by dialysis showing a maximum activity between 4.86 and 4.66. With excess of substrate the rate of hydrolysis is approximately proportional to the amount of enzyme present. Although it appears probable that the sugar-producing and liquefying properties are due to different enzymes all efforts to separate them have failed.

W. O. KERMACK.

Enzyme action. II. The nature of amylase. D. NARAYANAMURTI and R. V. NORRIS (J. Indian Inst. Sci., 1928, 11, A, 134—139).—Electrodialysis has been applied to purify solutions of cholam malt amylase. The purified enzyme solution shows enhanced activity and gives no protein tests, but a

marked Molisch reaction. By means of electro-osmosis the enzyme has been separated into a fraction relatively more active in liquefying, and a second relatively more active in sugar-producing, the former tending to migrate towards the cathode.

W. O. KERMACK.

Influence of amino-acids on the action of ptyalin. J. T. GROLL (Pharm. Weekblad. 1928, 65, 1315—1922).—The activation of various amylases by amino-acids observed by Sherman (A., 1920, i, 101; 1922, i, 283) has not been confirmed in the case of amylase in saliva.

S. I. LEVY.

Effect of polarised light on starch hydrolysis. A. E. NAVEZ and B. B. RUBENSTEIN (J. Biol. Chem., 1928, 80, 503—513).—The hydrolysis of starch by diastase proceeds more rapidly in the light than in the dark, but no difference could be observed in the effect of ordinary light and of polarised light of similar intensity and wave-length (cf. Baly and Semmens, A., 1925, i, 12).

C. R. HARRINGTON.

Inhibitory action of pancreatic extract on glycolysis. I. Effect of inhibitor on glycolysis of muscle-tissue and extract. E. RONZONI, J. GLASER, and D. P. BARR. **II. Effect of inhibitor on glycolysis of malignant tumours.** D. P. BARR, E. RONZONI, and J. GLASER (J. Biol. Chem., 1928, 80, 309—330, 331—344).—I. Fresh pancreas is minced and twice extracted with water at 0°, the extracts are treated with 2 vols. of 95% alcohol and filtered, the filtrate is freed from alcohol by evaporation at 30°, cleared on the centrifuge, and extracted with ether. The aqueous solution contains the anti-glycolytic factor described by Winfield and Hopkins and others (A., 1916, i, 189); the active substance is partly precipitated by the above treatment with alcohol, but this first fraction is largely contaminated with trypsin. The partly purified material is completely precipitated by increasing the concentration of alcohol to 90%. In agreement with Foster and Woodrow (A., 1924, i, 897) such an extract was found to inhibit the lactic acid formation of excised rabbit's muscle to the extent of 60%; the incompleteness of the inhibition was not due to failure to penetrate the muscle-cells, and, moreover, the inhibition of the loss of carbohydrate was practically complete, indicating the existence of a non-carbohydrate source of lactic acid. Addition of the pancreatic inhibitor to muscle extract entirely inhibits loss of carbohydrate and phosphate and formation of lactic acid, whether sodium fluoride be present or not; formation of lactic acid by muscle extract must therefore proceed through a hexosephosphate, and it is the formation of this ester which is prevented by the pancreatic extract.

II. The glycolytic activity of malignant tumours is reduced by mincing the tissue, and abolished by freezing, grinding, or extraction; glycogen cannot be utilised in the process; the glycolysis is not affected by the pancreatic inhibitor, the reason being that in this case intermediate formation of hexosephosphate does not occur.

C. R. HARRINGTON.

Formation of lactic acid from glycogen with dried muscle and activators. H. VON EULER, E. BRUNIS, and S. PROFFE (Svensk Kem. Tidskr.,

1928, 40, 100—102; Chem. Zentr., 1928, ii, 72).—The formation of lactic acid from glycogen by dried muscle is greatly stimulated by yeast juice, whilst a co-enzyme preparation effected only a slight production of lactic acid. A. A. ELDRIDGE.

Vegetable oxidoreductase. D. MICHLIN (Biochem. Z., 1928, 202, 329—336).—A method of preparing highly purified preparations of potato oxidoreductase is described. These preparations reduce nitrates 250 times as quickly as they reduce methylene-blue. In the presence of potassium cyanide methylene-blue solutions remain coloured even after 8 hrs., although the enzyme is also present. The presence of alkali does not affect the reducing actions on nitrates. The differences between the actions of animal and vegetable oxidoreductases are discussed. W. McCARTNEY.

Enzymic proteolysis. III. P. RONA and E. MISLOWITZER (Biochem. Z., 1928, 202, 453—465; cf. A., 1928, 923).—Trypsin does not reduce the size of the particles in an albumin solution, but in peptic hydrolysis of albumin the particle size is reduced approximately to the same extent as in peptic hydrolysis of caseinogen. The increase of amino-groups during hydrolysis is related to the hydrolysis of the products containing the residual nitrogen. In the colloidal fraction of albumin solution scarcely any increase in the number of amino-groups occurs, but there is an increase in the number of carboxyl groups. W. McCARTNEY.

Behaviour of pepsin. F. GALLI (Folia Clinica, 1928, 3, 191—208).—Gross' caseinogen method for determining the peptic activity of gastric juice is found unsatisfactory and a new method, which depends on the liquefaction of gelatin and gives more certain and exact results, is described. Examination of a number of patients suffering from gastric troubles shows that, although as a rule variation of the pepsin content of the gastric juice is accompanied by variation of the content of hydrochloric acid, there is no fixed relationship between the two. When the free acid is lacking, pepsin also is usually absent but is occasionally present in small proportion. T. H. POPE.

Hydrolytic action of *Ricinus* lipase. II. Hydrolysis of lecithin. III. Hydrolysis of phytin. A. PIUTTI and E. DE' CONNO (Annali Chim. Appl., 1928, 18, 512—519, 520—528; cf. this vol., 99).—II. By a stable emulsion of *Ricinus* lipase, containing about 38% of ricinoleic acid, 4% of proteins, and 58% of water, lecithin is hydrolysed, either in aqueous emulsion or in toluene solution containing 35—40% of water, into fatty acids and glycerophosphoric acid. The latter undergoes no scission, and the realisation of such decomposition by Plummer and Bayliss (A., 1906, i, 325) is regarded as due to the presence of small proportions of other enzymes (glycerophosphatases) in *Ricinus* seeds (cf. Grosser and Husler, A., 1912, ii, 367). The fact that only about 30% of the lecithin undergoes hydrolysis is ascribed to inhibition of the enzymic action by the glycerophosphoric acid formed.

III. *Ricinus* seeds rich in lipase contain also enzymes able to hydrolyse proteins and glyce-

phosphates, together with a small proportion of a phytase. The last is also present in the industrial lipase preparation used in the previous experiments, but the very high lipolytic activity of this preparation exerts an inhibiting influence on the phytase. T. H. POPE.

Uricolysis. I. K. FELIX, F. SCHEEL, and W. SCHULER (Z. physiol. Chem., 1929, 180, 90—106).—The conversion of uric acid into allantoin and carbon dioxide by the action of uricase (in the form of powdered pig's liver) at 37—38° (greatly retarded action below 23°) has been studied quantitatively. The optimum condition for fission of carbon dioxide occurs sharply at p_H 9.9, whilst for the decomposition of the uric acid two maxima appear on the curve at p_H 8.9 and 9.9—10.0, respectively. At the former only a very small quantity of carbon dioxide is evolved (about 20% of the quantity equivalent to the uric acid when the latter has been completely destroyed, the actual volume depending on the duration of the investigation), but at the second point, which is common to both curves, it is always equivalent to the uric acid destroyed. Throughout the whole course of the reaction (p_H 8.6) 1 atom of oxygen is absorbed for each mol. of uric acid decomposed. If the whole of the uric acid is destroyed at the first optimum point (8.9), that is, with evolution of only 20—30% of the equivalent quantity of carbon dioxide, the enzyme then removed, and the effect of hydrogen-ion concentration on the evolution of carbon dioxide by introduction of a fresh sample of liver investigated, the maximum is again found at p_H 9.9 and the evolution of carbon dioxide now proceeds in the complete absence of oxygen. Hence the decomposition occurs in two stages, the first being the oxidation of the uric acid to an unknown intermediate, which, in the second stage, eliminates carbon dioxide. Since uroxyanic acid (Biltz and Robl, A., 1920, i, 883) readily decomposes into allantoin and carbon dioxide, the action of the liver powder on the potassium salt of this acid was studied under similar conditions, but no appreciable quantity of carbon dioxide was evolved. By extracting the liver powder at p_H 8.9 a specimen relatively rich in the oxidase and relatively poor in the decarboxylase was isolated. J. W. BAKER.

Rate of multiplication of yeast at different temperatures. O. W. RICHARDS (J. Physical Chem., 1928, 32, 1865—1871).—The rate of multiplication of *Saccharomyces cerevisiae* increases regularly with a rise in temperature between 4° and 30°, except for a change in the rate which occurs at 9°. A critical temperature for this particular strain of yeast exists at 30°, above which the rate of growth decreases with a rise in temperature. At 30°, abnormal, elongated cells are formed indicating that the process of bud formation is critically affected at this temperature. These abnormal cells are maintained in number only if the temperature is kept constant within limits narrower than those achieved by the usual type of laboratory incubator. The need for precise temperature control of yeast cultures is emphasised. L. S. THEOBALD.

Production of acids by *Aspergillus fumigatus*. R. SCHREYER (Biochem. Z., 1928, 202, 131—156).—

In the course of time the mould loses the power of forming fumaric acid and gives rise to citric and gluconic acids. Citric acid is obtained from sugars having three, five, six, or twelve carbon atoms, from lactose, glycerol, and mannitol. The mould accumulates gluconic acid in young calcium carbonate cultures, and the formation of this acid is favoured by increased oxygen tension, accelerated diffusion, and removal of carbon dioxide. The acid is obtained only in small amount in barium carbonate cultures. The temperature for optimum growth is between 21° and 23°, the minimum about 6° and the maximum 31—32°. Ammonium nitrate is the best source of nitrogen. P. W. CLUTTERBUCK.

Citric acid formation by moulds. III. Theories of citric acid formation and the appearance of acetaldehyde in the mould cultures. K. BERNHAUER and K. SCHÖN (Biochem. Z., 1928, 202, 164—179).—The greatest amount of acetaldehyde obtained in presence of sodium sulphite is about 0.6% of the sugar used. The amount differs with the different sources of carbon, levulose and sucrose giving most, dextrose much less, and glycerol least. In these experiments, owing to the alkaline reaction, the amount of citric acid formed is small, whilst using "dimedon" in place of sulphite, the formation of citric acid is almost completely inhibited. "Dimedon" is attacked by *Aspergillus niger* and is therefore unsuitable as a means of removing aldehyde during its growth. It is concluded that no relationship exists between the processes resulting in the formation respectively of aldehyde and citric acid.

P. W. CLUTTERBUCK.

***Penicillium glaucum*. Production of methyl ketones from triglycerides or fatty acids in the metabolism of the mould.** C. ACKLIN and W. SCHNEIDER (Biochem. Z., 1928, 202, 246—283).—The conditions of growth and of nutrition of *P. glaucum* have been studied. The effects considered were those of different nutrient media, of different sources of carbon and nitrogen, of different hydrogen-ion concentrations in buffered and unbuffered solutions, of change of p_H during the growth of the organism, of maintenance of constant p_H , and of the presence of iron (ionic and in complex form) as a catalyst.

W. MCCARTNEY.

Nutrition of *Polytoma uvella*, Ehrenberg (*Flagella Chlamydomonadinae*), and the synthetic power of heterotrophic protozoa. Mesotrophic protozoa. A. LVOV (Compt. rend., 1929, 188, 114—116).—The synthetic medium of Pringsheim (which contains sodium acetate, glycine, potassium carbonate, magnesium sulphate, and dipotassium hydrogen phosphate; cf. Beitr. z. allgem. Bot., 1921, 2, 88) for the culture of *Polytoma uvella* may be modified by replacing the glycine by any of a large number of amino-acids or amines (glucosamine or histamine). Cystine gives the best results. Whilst this organism is capable of obtaining its carbon and nitrogen from ammonium acetate (heterotrophic), *Glaucocystis pyriformis* requires complex substances such as peptones (mesotrophic). G. A. C. GOUGH.

Fermentation of dextrose by organisms of the genus *Serratia*. C. S. PEDERSON and R. S. BREED

(J. Bact., 1928, 16, 163—185).—*Serratia marescens* produced acetic, formic, succinic, and *l*-lactic acids, ethyl alcohol, acetylmethylcarbinol, β -butylene glycol, carbon dioxide, and a little hydrogen. Similar, but not identical, products were obtained from other strains. CHEMICAL ABSTRACTS.

Respiration and glycolysis of trypanosomes. II. B. VON FENYVESSY and L. REINER (Biochem. Z., 1928, 202, 75—80).—Trypanosomes decompose sugar partly by oxidation and partly by glycolysis, aerobic and anaerobic glycolysis taking place about equally. Hydrocyanic acid and "germanin" do not affect the course of glycolysis. Between p_H 7 and 8 oxidation predominates in the more alkaline and glycolysis in the more acid solutions.

P. W. CLUTTERBUCK.

Determination of caseinogen hydrolysis by *Clostridium botulinum*. G. M. DACK and W. L. WOOD (J. Infect. Dis., 1928, 42, 172—175).—In a medium containing peptone and caseinogen the toxin titre is related to the caseinogen hydrolysis.

CHEMICAL ABSTRACTS.

The *Coccaceae*. XII. Action of streptococci on caseinogen. XIII. Production of carbon dioxide by streptococci. XVI. Biochemical reactions produced by streptococci. G. J. HUCKER (New York Agric. Exp. Sta. Bull., 1928, Nos. 141—143).—XII. Pure caseinogen is not available to the streptococci provided that these are washed free from extracellular enzymes and other impurities, but certain strains of the organisms, particularly those from dairy products, utilise pure caseinogen if large amounts of unwashed cells are present. Pyogenic streptococci do not produce growth under any conditions when pure caseinogen is the only source of nitrogen furnished. Many of the organisms which will not grow in pure caseinogen solutions increase the amount of free amino-nitrogen when grown in milk.

XIII. Of the representative strains of streptococci studied, most produced small amounts of carbon dioxide from peptone and these amounts increased with increased amounts of peptone in the medium. *S. kefir* and *S. citrovorus* produced no carbon dioxide from peptone but formed relatively large amounts from dextrose.

XIV. From the study of 358 authentic strains of streptococci an attempt has been made to classify the organisms on the basis of biochemical behaviour. Two groups can be distinguished according to the type of lactic acid which they produce. One group consists of those strains which generally prefer levulose to dextrose, attack the pentoses, hydrolyse lactose faster than acid is produced, form relatively large amounts of volatile acid, often produce carbon dioxide, and produce always *l*-lactic acid. The strains of the other group (which includes all the commonly encountered types) produce *d*-lactic acid, do not hydrolyse lactose more rapidly than acid is produced, and sometimes produce large amounts of acid from certain sources of carbon. The acids produced by the first group are acetic acid and an acid which is possibly formic acid; those produced by the second group are acetic acid and an acid which is higher in the series and may be propionic

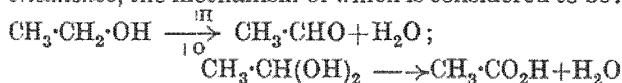
acid. Constant results were obtained in quantitative acid production from sugars if conditions of growth were controlled.

W. McCARTNEY.

Proteolytic bacteria of milk. III. Action on caseinogen and gelatin. W. C. FRAZIER and P. RUPP (*J. Bact.*, 1928, 16, 187—196).—Some of the organisms decomposed the calcium more easily than the sodium compound of caseinogen; in one case the reverse held. Increasing amounts of fermentable sugar up to 0.1% did not in general affect the degradation of caseinogen.

CHEMICAL ABSTRACTS.

Mechanism of oxidative processes. XV. Nature of the acetic acid fermentation. H. WIELAND and A. BERTHO (*Annalen*, 1928, 467, 95—157).—A series of investigations has been carried out on the acetic acid fermentation by *Bacterium orleanense*, the mechanism of which is considered to be:



(cf. A., 1913, i, 1304). It was not found possible to separate the enzymes from the bacteria, and all experiments were carried out with suspensions of the bacteria of known concentrations, buffered to p_{H} 5.6.

With alcohol as substrate the consumption of free oxygen was strictly proportional to time. In presence of 0.0002*M*-hydrogen cyanide the velocity fell to 16% of normal. Titration of the acetic acid formed indicated a greater dehydrogenation of acetaldehyde than would be expected from its concentration relative to alcohol, an effect which is attributed to the preferential adsorption and reaction of aldehyde formed on the surface of the same enzyme which catalyses the first stage of the reaction. When benzoquinone was used as hydrogen-acceptor in absence of free oxygen, the dehydrogenation was more rapid, but the same linear relation with time was found. The bacteria were shown to be unaffected by quinone or quinol in the concentrations used. The reaction was much less sensitive to hydrogen cyanide than the reaction with free oxygen; a concentration of 0.01*M* first produced a noticeable retardation. The rate of hydrogenation of the quinone was only slightly lowered by the presence of free oxygen. On the other hand, the free oxygen began to be consumed only when the quinone was practically used up, and thereafter was taken up at the normal rate. It is concluded that the same enzyme catalyses the reaction with both quinone and free oxygen. The linear relation between reaction and time shows that adsorption on the enzyme surface is more rapid than the chemical reaction. Since quinone displaces free oxygen as hydrogen-acceptor when both are present, quinone must be strongly adsorbed and occupy the surface of the enzyme to the exclusion of oxygen, i.e., it inhibits the oxygen reaction for the same reason as hydrogen cyanide, and the reaction with quinone is less retarded by hydrogen cyanide on account of this strong adsorption of quinone. The hypothesis of activation of both the hydrogen of the substrate and of free oxygen is rejected. Activation of the former alone is considered sufficient. There is no reason why quinone should be able to dispense

with an activation inhibited by hydrogen cyanide if molecular oxygen needs it. Using methylene-blue as hydrogen-acceptor the reaction was very slow and its course was not linear. There was evidence of retardation of the reaction by excess of methylene-blue. The non-linear course of the reaction made observation of times of complete decolorisation quantitatively valueless. Retardation by hydrogen cyanide was first marked at a concentration of 0.01*M*. With methylene-blue in presence of free oxygen the latter was consumed at the normal rate, whilst when sufficient hydrogen cyanide was added normally to inhibit reaction with free oxygen, free oxygen was taken up at about 6% of the normal rate. This rate was increased somewhat by increasing the amount of methylene-blue, and was presumably determined by the rate of reaction of free oxygen with leuco-methylene-blue, which was found in separate experiments to be low and little affected by hydrogen cyanide. It is concluded that the interior of the cell, as well as its external walls, are active in the dehydrogenation process. The methylene-blue is unable to penetrate the wall, and reacts only on its outer surface, whilst molecular oxygen, quinone, and hydrogen cyanide can all diffuse into the interior of the cell, where 90% of the action takes place.

A parallel series of experiments was carried out with acetaldehyde as substrate. The reaction was little retarded by hydrogen cyanide, and addition of acetaldehyde restored the activity of a mixture, containing alcohol as substrate, poisoned by hydrogen cyanide. These effects appeared to be due to formation of cyanohydrin, which was shown to occur rapidly. The cyanohydrin itself, however, had a minor retarding effect. The course of the reaction of acetaldehyde with free oxygen, quinone, or methylene-blue was similar to the reaction of alcohol, although slower. Mixtures of acetaldehyde and alcohol consumed alcohol at a rate which was the mean of the rate of consumption by each separately. The two reactions are, therefore, brought about probably by the same enzyme. Contrary to Neuberg and Windisch (A., 1926, 324), the Cannizzaro reaction plays little part in the formation of acetic acid from acetaldehyde (cf. also Myrback, Euler, and Sandberg, A., 1928, 924). Carefully controlled experiments showed that the rate of consumption of oxygen was actually about forty times that calculated on the basis of dismutation alone, the rate of which was also measured. Similar experiments with *B. pasteurianum* (cf. Neuberg and Molinari, *Naturwiss.*, 1926, 14, 756) showed that these bacteria brought about dehydrogenation of acetaldehyde at 100 times the rate of dismutation.

Salicylaldehyde and *o*-hydroxybenzyl alcohol were not dehydrogenated by *B. orleanense*. Dithioglycollic acid or cystine did not act as hydrogen-acceptors in presence of alcohol. The dehydrogenation of succinic acid by dithioglycollic acid in presence of minced liver previously reported (A., 1924, i, 1172) is erroneous.

The catalase activity of *B. orleanense* was also measured. Hydrogen peroxide was rapidly decomposed in a reaction apparently of high order, retarded

by hydrogen cyanide. This retardation was parallel to that of the dehydrogenation of alcohol. No free hydrogen peroxide could be recognised in any of the reaction mixtures, whether containing hydrogen cyanide or not, so that the inhibitory effect of hydrogen cyanide on the dehydrogenase activity must be of the same order.

R. K. CALLOW.

Precipitation of magnesium ammonium phosphate crystals during the growth of bacteria in media containing nitrogenous substances. S. A. SCUDDER (J. Bact., 1928, 16, 157—161).—Crystals having the composition $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MgNH}_4\text{OP}_2\text{O}_5$, and $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ were isolated from agar cultures of *B. alkaligenes*, *M. catarrhalis*, and *C. diphtheriae*; favourable factors are the presence of meat infusion, peptone, and inorganic phosphate, and a decrease in the amount of sodium chloride and water.

CHEMICAL ABSTRACTS.

Influence of radium on the metabolism of bacteria participating in the nitrogen cycle. J. STOKLASA and J. KRICKA (Zentr., Bakt. Par., 1928, II, 74, 161—183; Chem. Zentr., 1928, ii, 161).— α -Rays in the form of air containing emanation stimulate the nitrogen assimilation of *Azotobacter* although amounts greater than a certain limit retard the assimilation. Hydrolysis of proteins by proteolytic enzymes is not promoted by radium emanation. Denitrification by *B. Hartlebii* or *B. fluorescens liquefaciens* is promoted, by growth stimulation, by weak doses of radium emanation, and inhibited by strong doses. The destruction of dextrose by *Azotobacter* is also increased by radioactive air, unusually large quantities of carbon dioxide, acetic acid, and formic acid being produced. In protein degradation by *B. Hartlebii* the monoamino-nitrogen is specially increased by α -rays. Nitrogen assimilation is retarded in liquid medium by β - and γ -, or by γ -rays, although these rays stimulate the activity of proteolytic enzymes. Denitrification is also increased. In the decomposition of dextrose by *Azotobacter* β - and γ -rays cause greatest formation of alcohol, lactic acid, and acetaldehyde; protein degradation proceeds with special increase of amide-nitrogen.

A. A. ELDRIDGE.

Influence of carbohydrates on the bacterial decomposition of urea. M. ISHIKAWA (J. Infect. Dis., 1928, 43, 67—80).—The decomposition of urea by *Bacillus ammoniogenes*, *B. aërogenes*, *B. Morgani*, *B. proteus vulgaris*, and *Staphylococcus aureus* is accelerated by the presence of a utilisable carbohydrate. Symbiosis of such organisms with one which does not decompose urea, in a medium containing a carbohydrate fermentable only by the latter, increases the amount of ammonia produced.

CHEMICAL ABSTRACTS.

Biochemical production of fats. V. KULIKOV (Oil Fat Ind. Russia, 1928, No. 4, 21—23; Chem. Zentr., 1928, ii, 822).—The bacterial production of fats (36%) consisting of palmitin and stearin, and of waxes, is described.

A. A. ELDRIDGE.

Growth of hæmophilic bacilli with certain iron salts. J. M. BOURN (J. Infect. Dis., 1927, 41, 294—303).—Successive cultures in veal infusion broth

required the presence of sodium aquopentacyanoferrate.

CHEMICAL ABSTRACTS.

Oxidation processes with the iron-containing component of hæmoglobin. K. BINGOLD (Klin. Woch., 1928, 7, 928—951; Chem. Zentr., 1928, ii, 160—161).—Pneumococci, strepto-bacilli, and certain streptococci, when grown on a hæmatin nutrient medium, decompose the hæmatin. In hydrogen peroxide, but not under reductive conditions, decolorisation occurred. In the decomposition of hæmoglobin hæmatin is not necessarily produced, but all oxidases produce a fermentative degradation to hæmatic acid.

A. A. ELDRIDGE.

Physico-chemical behaviour of bacteria. A. E. STERN and E. W. STERN (Univ. Missouri Stud., 1928, 3, 1—84).—Bacteria possess individual characteristic isoelectric points and ranges. The relation between the p_H of reaction, isoelectric point, and retention of anions and cations has been investigated. The toxic action of many bacteriostats, particularly dyes, seems to depend on an ionic equilibrium. Experiments on flocculation by dyes indicate that the same fundamental mechanism is effective as in staining and growth inhibition.

CHEMICAL ABSTRACTS.

Microbiological death rates. C. H. WERKMAN (Proc. Iowa Acad. Sci., 1927, 34, 85—86).—A study of the survivor-curves obtained by subjection of *Staphylococcus aureus* to the action of various bactericidal substances. The toxicity of monohydric alcohols increases with mol. wt.; introduction of hydroxyl groups (e.g., propyl alcohol, propylene glycol, glycerol) causes a diminution of toxicity. Phenyl groups substituted in the alcohol molecule greatly increase the toxicity, but partial oxidation diminishes it. Introduction of an amino-group prolongs the induction period, but does not markedly reduce toxicity. Diminution of surface tension leads to increased toxicity.

CHEMICAL ABSTRACTS.

Effect of metallic salts on the development of bacteria. II. Silver. P. H. ANDRESEN (Zentr. Bakt. Par., 1928, I, 107, 392—397; Chem. Zentr., 1928, ii, 777).—A suitable medium is described, and the effect of silver salts on *Bacillus coli*, *B. proteus*, and staphylococci recorded.

A. A. ELDRIDGE.

Distribution and stability of the antigenic properties of diphtheria toxin. Role of non-specific colloids. P. SÉDALLIAN, A. LEULIER, and (MME.) CLAVEL (Compt. rend., 1928, 187, 1297—1299).—The powers of immunisation of the supernatant liquid and of the precipitate produced at p_H 4.7 have been determined. The former fixes no anti-toxin when placed in contact with it, and the latter fixes only a small amount. The precipitate, however, when dissolved in fresh Martin broth, fixes almost as much as the original toxin, and it is suggested that the broth contains non-specific substances of the protective colloid type, capable of conferring powers of adsorption, and analogous to Ehrlich's toxones.

J. GRANT.

Bilirubin as a potential hæmopoetic hormone. F. VERZAR and A. ZIEH (Klin. Woch., 1928, 7, 1031—1032; Chem. Zentr., 1928, ii, 457).

Interrenin. M. GOLDZIEHER (Klin. Woch., 1928, 7, 1124—1125; Chem. Zentr., 1928, ii, 457).—A physiologically active substance, *interrenin*, which, when injected intravenously, reduces arterial blood-pressure and causes a decrease of blood-lipins, has been prepared from the suprarenals.

A. A. ELDRIDGE.

Physiology of glands. L. ASHER. CXVI. **Respiratory metabolism during work under normal conditions and after adrenaline.** W. H. SCHEUCHZER (Biochem. Z., 1928, 201, 148—164).—Further experiments with Asher's respiration chamber for rats confirmed the results of Curtis (*ibid.*, 1925, 164, 97). Subcutaneous injection of adrenaline causes only a trifling increase of metabolism during work, the body temperature being decreased. The work appears therefore to be performed more economically under the influence of adrenaline.

P. W. CLUTTERBUCK.

Seasonal variations in iodine and thyroxine contents of the thyroid gland. E. C. KENDALL and D. G. SIMONSEN (J. Biol. Chem., 1928, 80, 357—377).—A new method of isolating thyroxine from the thyroid gland is described which consists of a combination of the authors' original sodium hydroxide hydrolysis (A., 1915, i, 600) with subsequent treatment with barium hydroxide (cf. Harington, A., 1926, 644). A seasonal variation of 300% was observed in the iodine content of the glands employed. The thyroxine isolated represented, on the average, 5% of the total iodine. Partly on the basis of this figure, and partly on comparison of physiological activity, it is concluded that the acid-insoluble fraction of the iodine obtained after preliminary alkaline hydrolysis of the thyroid contains iodine compounds other than thyroxine; further, since the whole of the activity of desiccated thyroid cannot be accounted for by the thyroxine which can be isolated from it, it is thought that thyroxine must first be converted into an "active" form, before it can exercise its specific physiological effect.

C. R. HARRINGTON.

Action of thyroxine on the glycogen content of skeletal muscle and of the liver of guinea-pigs. O. BOSL (Biochem. Z., 1928, 202, 299—319).—In young and adult guinea-pigs receiving sufficient food for maintenance of normal body-weight subcutaneous injections of thyroxine cause loss of weight. The glycogen content of the skeletal muscle undergoes no decrease under these conditions, but that of the liver diminishes to an extent which varies according to the individual, so that, in these respects, thyroxine behaves like thyroid gland. The effect of small doses of thyroxine on the glycogen of the liver can be compensated by supplying more food to the animals. The glycogen content of the skeletal muscle of animals treated with thyroxine while receiving only half of the normal amount of food is reduced, on the average, more strongly than that of controls, and under these conditions the livers of the animals receiving thyroxine are free from glycogen. In guinea-pigs receiving normal amounts of food and stimulated to increased activity the glycogen content of the skeletal muscle, and still more that of the liver, is increased as compared with that of resting animals. Control animals

stimulated to activity also show these increases and, on the average, to a greater extent.

W. MCCARTNEY.

Action of thyroxine on the protein, water, and mineral metabolism. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1928, 61, 239—277; Chem. Zentr., 1928, ii, 459).—In dogs, thyroxine causes increased excretion of nitrogen and water; secretion of urea is increased, that of ammonia being at first reduced. In man the effect on the protein metabolism is small; ammonia excretion is increased. In myxœdema the disturbances are counteracted by thyroxine.

A. A. ELDRIDGE.

Carbohydrate metabolism of the white mouse with and without administration of insulin. IV. E. J. LESSER and R. AMMON (Biochem. Z., 1928, 202, 294—298).—When the mouse receives injections of dextrose alone part of this is converted into glycogen and part is burnt in the organism, but when insulin is injected immediately after the injection of dextrose some glycogen (originally present) disappears, and almost all of the injected sugar disappears also. The carbohydrate metabolism is thus greatly accelerated by insulin as a result of the increased oxidation which takes place. The disappearance of glycogen may occur only in the later stages of the action of insulin.

W. MCCARTNEY.

Blood-sugar and respiratory metabolism following simultaneous administration of dextrose and insulin. I. M. RABINOWITCH and E. V. BAZIN (J. Biol. Chem., 1928, 80, 723—731).—Observation of the curves of blood-sugar and respiratory metabolism, following simultaneous administration of dextrose and insulin, indicates that the latter, in normal individuals, inhibits rather than increases the rate of oxidation of sugar.

C. R. HARRINGTON.

Examination of insulin for vitamin-B. C. J. STUCKY (Arch. Int. Med., 1928, 42, 780).—Commercial preparations of insulin contain neither the antineuritic nor the heat-labile growth-promoting factors of vitamin-B.

E. BOYLAND.

Effect of ethylene on the vitamin-B content of celery. M. F. BABB (Science, 1928, 68, 231).—No diminution of the vitamin-B content was observed in ethylene-blanching celery.

A. A. ELDRIDGE.

Vitamin-B content of wheaten bread baked with varying amounts of yeast. A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1928, 202, 380—386).—The vitamin-B content of wheaten bread can be raised by increasing the amount of yeast used in the baking. If the increase amounts to 3—6 times the usual quantity, the bread produced satisfies the vitamin-B requirements of pigeons and of young growing rats.

W. MCCARTNEY.

Relationship between the ability to darken photographic plates and the vitamin-A content of cod-liver oil and pig's fat. L. S. FRIDERICIA and S. V. GUDJÓNSSON (Bibl. for Laeger, 1927, 12 pp.; Chem. Zentr., 1928, ii, 782).—No parallelism was detected.

A. A. ELDRIDGE.

Effect of scurvy-producing diets and tyramine on the blood of guinea-pigs. M. T. HANKE and

K. K. KOESSLER (J. Biol. Chem., 1928, 80, 499—502).—No anaemia was produced in guinea-pigs by subcutaneous administration of tyramine, whether in combination with a normal diet or with one deficient in vitamins-A and -C (cf. Iwao, A., 1914, i, 360).

C. R. HARRINGTON.

Irradiation of sterols; relation between irradiated sterols and antirachitic vitamin. R. FABRE and H. SIMONNET (J. Pharm. Chim., 1928, 8, [viii], 489—506).—A summary of the present state of knowledge regarding vitamin-D. Some experiments on the variation in absorption spectrum of alcoholic solutions of ergosterol after irradiation for varying periods are described. E. H. SHARPLES.

Photochemistry of vitamin-D. S. K. KON (Rocz. Chem., 1928, 8, 502—518).—Ergosterol was completely removed from cholesterol by repeated boiling in acetone solution with potassium permanganate. Cholesterol so purified remains biologically inactive after irradiation. The amount of radiant energy necessary to produce a demonstrable amount of vitamin-D from ergosterol is 700—1000 ergs between 256 and 293 μ , independently of the wave-length of ultra-violet light used. The efficiency of this process is the same when solid ergosterol is used, or dilute or concentrated alcoholic solution, and is the same for ergosteryl acetate as for the free sterol, indicating that the hydroxyl group does not play any part in the formation of vitamin-D. Activation does not take place in acetone solution, as the solvent has itself a strong absorption band in the same region as ergosterol. The formation of vitamin-D from ergosterol is probably a complicated process with low quantum efficiency. R. TRUSZKOWSKI.

Antirachitic substances. IX. Activation of ergosterol. C. E. BILLS, E. M. HONEYWELL, and W. M. COX, jun. (J. Biol. Chem., 1928, 80, 557—563).—Samples of carefully purified ergosterol were subjected to ultra-violet irradiation for various periods in alcoholic solution and then examined both spectrophotometrically and by biological test. The maximum physiological activity was attained before the absorption curve showed any significant alteration; with increasing length of exposure the activity decreased and the band at 248 μ (cf. Heilbron and others, A., 1927, 381, 1123) appeared; the latter band reached its maximum intensity coincidentally with the disappearance of physiological activity, and is associated therefore with the destruction rather than with the formation of vitamin-D. The freer the access of oxygen the more rapid is the development and subsequent fading of the band at 248 μ ; such a band, showing similar behaviour on irradiation, is observed in the spectrum of *iso*ergosterol (Reindel and others, A., 1927, 241). C. R. HARRINGTON.

Destruction of vitamin-E in a diet of natural foodstuffs. J. WADDELL and H. STEENBOCK [with E. VAN DONK] (J. Biol. Chem., 1928, 80, 431—442).—Incorporation of 1% of ferric chloride with an

adequate natural diet leads to destruction of vitamin-E, whilst vitamin-A is not affected.

C. R. HARRINGTON.

Amino-acid synthesis in plants. W. F. LOEWING (Proc. Iowa Acad. Sci., 1927, 34, 115—118).—Fruit formation robs the vegetative structures of tomato plants of nitrates, ammonia, and amino-acids. Nitrates, when absorbed by defruited plants, accumulate at and are reduced to nitrites, ammonia, and amino-acids in the vicinity of the meristem. Alkalinity and the presence of sugars appear indispensable for the reduction, which is not attributed to enzymes. CHEMICAL ABSTRACTS.

Effect of ethylene on the respiration of bananas during ripening. L. O. REGEIMBAL, G. A. VACHA, and R. B. HARVEY (Plant Physiol., 1927, 2, 357—359).—Ethylene (1 in 10³ of air) was allowed to act for 15—20 min. at 25°, aspiration of air free from carbon dioxide then being resumed. Electrometric determination of the rate of production of carbon dioxide showed that the rate of respiration quickly trebled, and then became subnormal, owing either to increase of oxidation or to increase in the permeability of the membranes. Treatment increases the activity of the diastatic and respiratory enzymes. Treated bananas contain 20—25% more sugar (and correspondingly less starch) than untreated. CHEMICAL ABSTRACTS.

Ripening of rice seed and chemical properties of rice of the early-ripening sub-varieties. T. TADOKORO (J. Coll. Agric. Hokkaido, 1927, 20, 333—354).—In ripening, the non-protein nitrogen decreases and the diamino-nitrogen, sodium chloride-soluble and ethyl alcohol-soluble proteins of rice seed increase. The oryzanin increases in specific rotation, in free amino-nitrogen, and lysine, but decreases in arginine and ash until a point is reached when the changes are reversed. In the middle part of the ripening period the ash and phosphorus decrease, the acetyl value of the starch increases, and its specific rotation decreases. Early-ripening varieties are richer in fat, non-protein nitrogen, and water-soluble protein nitrogen, and poorer in ash and protein nitrogen than later-ripening varieties. The oryzanin of the early varieties is lower in free amino-nitrogen than that of the later varieties. CHEMICAL ABSTRACTS.

Action of glycerophosphatase of plant seeds and enzymic synthesis. A. NEMEC (Biochem. Z., 1928, 202, 229—235).—During the after-ripening of seeds, glycerophosphatase action is considerably decreased, and the greater this decrease the greater is the subsequent germinating power. During the germination of maize and barley a slight decrease of glycerophosphatase action is obtained in the first two days followed by a considerable increase, whereas with soya beans and peas there is a continuous increase of glycerophosphatase action. When the seed meal is autolysed with added glycerol and phosphate, the amount of free phosphate decreases, suggesting enzymic union of glycerol and phosphate. P. W. CLUTTERBUCK.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1929.

General, Physical, and Inorganic Chemistry.

Stellar spectra in the far ultra-violet. S. ROSSE-
LAND (*Nature*, 1929, 123, 207).

Ionisation in stellar atmospheres. I. Generalised Saha formulæ, maximum intensities, and the determination of the coefficient of opacity. E. A. MILNE (*Month. Not. Roy. Astr. Soc.*, 1928, 89, 17—49).—Mathematical. W. E. DOWNEY.

Ionisation in stellar atmospheres. II. Absolute magnitude effects. E. A. MILNE (*Month. Not. Roy. Astr. Soc.*, 1928, 89, 157—175).—Formulæ are obtained which determine the variation with g , at constant T , of the number of atoms responsible for the formation of a given absorption line. The behaviour depends on whether the coefficient of general absorption, κ , is constant throughout the stellar atmosphere or is proportional at each point to the electron pressure P . The fact that lines of both neutral and ionised atoms increase in intensity from dwarfs to giants favours the adoption of $\kappa \propto P$. When $\kappa \propto P$ the mass of the reversing layer increases with decreasing pressure and more than counterbalances the reduction in the proportion of neutral atoms due to increased ionisation. The observed strengthening of the Balmer lines from dwarfs to giants now receives theoretical explanation.

C. J. SMITHELLS.

Theoretical contours of absorption lines in stellar atmospheres. E. A. MILNE (*Month. Not. Roy. Astr. Soc.*, 1928, 89, 3—17).—Mathematical. The number of atoms per c.c. in a stellar atmosphere is calculated on the assumption of no surface of demarcation between atmosphere and photosphere.

W. E. DOWNEY.

Relations between the most intense radiations and the highest chemical elements in the luminous atmosphere of the sun. H. DES-
LANDRES (*Compt. rend.*, 1929, 188, 20—24).—The wave-lengths of the ultimate radiations of the chemical elements in the solar chromosphere are tabulated, together with their intensities, heights, and series notations, and the author's conclusion (*ibid.*, 1924, 179, 1066) that the corresponding frequencies are approximate multiples of the same elementary frequency $d_1=1062.5$ is confirmed. The light atoms (H, He, O) show intense radiations but have high excitation potentials, and the effect of the ionised heavy atoms (Ca^+ , Sr^+ , Ti^+) is very marked at great heights.

J. GRANT.

Presence of the absorption line D_α in the solar spectrum. S. B. NICHOLSON and N. G. PERRAKIS (*Compt. rend.*, 1929, 188, 41—43).—Spectrograms of

the sun taken with three Mt. Wilson plates show that the absorption due to helium is relatively strong in the immediate neighbourhood of the plate 3326 (Mt. Wilson notation), and in the interval separating members of the group 3333, whilst it is very faint in the space occupied by the faint markings. The presence of the atmospheric line (λ 5875.603) renders difficult the identification of the absorption line D_α (λ 5785.620). J. GRANT.

Elementary processes in emission and absorption of light. J. STARK (*Ann. Physik*, 1928, [iv], 87, 909—926).—An earlier theory given by Stark is extended and applied to a series of experimental cases. In the process of emission of light three operations may be distinguished. First, the electron in its stationary state in the atom is displaced from equilibrium and approaches indefinitely close to a lower energy level. The time taken for this may be called the "Verweilzeit." Secondly, a light quant is formed in the electronic field. The time taken for this process ("Umformzeit") is independent of the order of magnitude of the period of the light. Thirdly, there is a mutual action between the electron and the light quant resulting in the emission of the quant in a definite direction with the velocity of light, and fixing of the electron in the new energy level. The time taken for this process ("Ablenkzeit") varies between a value of the order of the period and one many times this. The "Verweilzeit" can be estimated (e.g., for H_γ) by examining the effect on spectra of an electric field acting on the given atom for a short time. In a field all energy levels are modified, transitions between a pair of modified levels giving a Stark component of the line concerned; but if the duration of the electric field is less than the "Verweilzeit" an electron may start from a modified and end in an unmodified level, or *vice versa*. In such circumstances components appear between normal and Stark modified lines. The time estimated for this operation for H_γ by this method is 10^{-9} sec. Consideration is given to excitation by cathode rays, and the theory predicts that the emission of characteristic frequencies in consequence of transfers of the atomic electron from one energy level to another is accompanied by the emission of a continuous spectrum in the infra-red or the beginning of the visible spectrum; also, that if the energy of the impinging electron is less than that required to raise the atomic electron to the next higher level an aggregate of atoms will give rise to a continuous spectrum. The theory provides an explanation of the continuous X-ray spectrum. The theory is applied to all kinds of absorption, including con-

tinuous, selective, and photo-electric absorption, and absorption due to scattering. A. J. MEE.

Spectral excitation by recombination in the electric arc. (Miss) J. M. DEWEY (Physical Rev., 1928, [ii], 32, 918—921).—Measurements of electron velocities in arcs indicate that most of the light in the negative glow is due to the recombination of positive ions and electrons. Since the velocities of the positive ions are high, spectral lines emitted in this way should show Doppler broadening. This was measured photometrically for a hot cathode arc in helium in which measurements of electron velocities were also made and results obtained which can be explained by assuming all the light in the negative glow to result from recombination of ions having a temperature about one tenth that of the electrons.

N. M. BLIGH.

Optical behaviour of hydrogen atoms in very strong electric fields. R. VON TRAUBENBERG (Physikal. Z., 1928, 29, 895).—The effect of sudden changes in field strengths up to 420,000 volts/cm. on hydrogen atoms has been studied by means of Stark's arrangement of separated fields, and the Stark effect measured in the second order for Balmer lines. The proportionality with the square of the field strength is confirmed for all components of H_γ . The results for the middle component agree better with the theory of Schrödinger than that of Epstein, but considerable deviations from Schrödinger's values are shown for the higher components. R. A. MORTON.

Theory of the Stark effect in hydrogenic atoms. V. ROJANSKY (Physical Rev., 1929, [ii], 33, 1—15).—Theoretical. Established formulæ give the relativity and spin corrections for a hydrogen-type atom perturbed by a weak electric field, and the energy levels without spin in the case of a strong field. Formulæ are here deduced for the energy levels in either a weak or a strong field, including both the relativity corrections and the Stark effect. The relativity and spin corrections for strong fields are deduced. The methods used are the matrix and wave mechanics. The results are similar, except in form, to those of Schlapp (cf. A., 1928, 806) using Darwin-Dirac wave methods. In the now, as opposed to the old, mechanics there is a linear Stark effect even in weak fields, because of the identity of energy for the ns and np_1 levels in the absence of external fields. This degeneracy is shown to account for the $2s$ level in hydrogen not being metastable. The coefficients are found for the development of the parabolic eigenfunctions in terms of the polar ones, and a set of values of these coefficients is tabulated. Methods are given for the calculation of the relative intensities in the Stark effect in terms of the already available theoretical fine-structure intensities in the absence of fields.

N. M. BLIGH.

Intensity measurements in the helium spectrum. C. HODGES and W. C. MICHELS (Physical Rev., 1928, [ii], 32, 913—917).—The absolute and relative intensities of thirteen lines of the helium spectrum, extending through the visible region, have been measured by the method developed by Ornstein and Dorgelo (A., 1924, ii, 282) modified by comparing each line directly with the known emission from a

tungsten filament, operated under constant conditions. The results for a discharge in a capillary tube, with pressures from 1.92 to 34.3 mm., show that the absolute intensities increase rapidly to a maximum for pressures in the neighbourhood of 2—4 mm., below which they tend to zero. The relative intensities of the singlet system are favoured by lowered pressures, and the higher members of the triplet system are favoured over the lower members. The relative intensities within the singlet series are little affected by pressure.

N. M. BLIGH.

Influence of pressure and addition of foreign gases on the absorption in activated neon. L. ECKSTEIN (Ann. Physik, 1928, [iv], 87, 1003—1034).—The influence of varying the pressure of gas in the absorption tube, keeping that in the emission tube constant, on the absorption of the neon lines 6402, 6266, 6163, 6143, 6096, and 5852 Å. has been investigated. The intensity of the spectral lines was measured by a photo-electric method. For all the above lines, the curves of absorption against gas pressure show maxima at a pressure of 1.2 mm. Hg. The maximum is greatest with the line 6402 Å. The influence of adding foreign gases to the absorption tube on the absorption of the lines 6402, 6266, 6163, and 6143 Å. has also been investigated. All four foreign gases used lowered the absorption, but whereas the decrease of absorption with increasing foreign gas pressure was slow with helium, it was very much quicker with water, nitrogen, and argon.

R. N. KERR.

Experimental proof of "negative" dispersion. H. KOPFERMANN and R. LADENBURG (Z. physikal. Chem., 1928, 139, 375—385).—By increasing the current density of a neon discharge up to 0.1 amp./cm.² a rise in the anomalous dispersion has been found in the yellow-red $s-p$ lines (where p and s are the higher and lower energy levels, respectively). This signifies an increase of the active atoms in the s state. If, however, the current density be still further raised a gradual decrease in the anomalous dispersion in the different s_p-k lines ($k=10, 9, 8, 6, 4, 2$) with increasing current is observed. This is as expected from the dispersion formula of the quantum theory on account of the influence of "negative" dispersion, i.e., due to greater activation of atoms in the p_k state. This is especially borne out by the systematic decrease of the dispersion for the s_p lines combined with different p_k levels; the lower the p level considered and the more strongly it is activated the greater is the decrease of the accompanying anomalous dispersion.

R. N. KERR.

Absorption of ultra-violet light by metastable atoms. W. DE GROOT (Naturwiss., 1929, 17, 13).—Since the ionisation energy of the metastable atoms of neon and argon is only 4.9 and 4.2 volts, respectively; corresponding with 2550 and 2950 Å., it is to be expected that there will be a continuous absorption of ultra-violet light from these wave-lengths up. Apparatus is described to test this. Light from a tungsten spiral at 3400° Abs. was passed through a tube containing the gas at 5 mm. pressure. The spectrum was photographed first of all with the absorption tube dark, and then with a current of

2 amp. flowing through the tube. There was no absorption in the part of the spectrum investigated either with neon or with argon. On the other hand, there was strong absorption corresponding with the $2s-2p$ lines in each gas with 50 milliamp. flowing through the tube.

A. J. MEE.

Spectrum of doubly-ionised krypton. D. P. ACHARYA (Nature, 1929, 123, 244).—A number of regularities have been observed, and three sets of terms are recorded.

A. A. ELDRIDGE.

Spectrum of doubly-ionised fluorine (F III). H. DINGLE (Proc. Roy. Soc., 1929, A, 122, 144—161; cf. A., 1927, 1; 1928, 98).—The lines of the spectrum of doubly-ionised fluorine appear when strongly condensed discharges are passed through silicon tetrafluoride at very low pressure. More than 300 lines, extending from 3267 to 2207 Å., have been measured and tabulated. The spectrum has been partly analysed into quadruplet and doublet systems of terms, which are correlated with the terms to be expected on the Heisenberg-Hund theory, and 82 lines have been classified. The resemblance between the spectrum and that of singly-ionised oxygen, which has the same electron structure as doubly-ionised fluorine, confirms its assignment to F^{++} . Most of the intervals in F III are almost exactly double the corresponding intervals in O II, but there are a few striking exceptions which are discussed.

L. L. BIRCUMSHAW.

Spectrum of doubly-ionised bromine. S. C. DEB (Nature, 1929, 123, 244).—The lines of the spectrum of doubly-ionised bromine have been classified.

A. A. ELDRIDGE.

Absorption spectra of oxygen and of ozone in the ultra-violet region. J. DUFAY (Compt. rend., 1929, 188, 162—164).—The coincidence of bands in the ultra-violet absorption spectra of ozone and of compressed or liquid oxygen may be due to the same bands, enlarged in the latter case by the high density of the absorbing medium. This is supported by the fact that below 2400 Å. the absorption curve of ozone is continuous like that of compressed oxygen.

J. GRANT.

Intercombinations and new terms in the spark spectrum of sulphur (S II). L. BLOCH and E. BLOCH (Compt. rend., 1929, 188, 160—162; cf. A., 1927, 1117; Gilles, A., 1928, 565).—New multiplets in the S II spectrum of sulphur detected by the use of an oscillating electrodeless discharge are recorded and include intercombinations and combinations of old and new terms. A correction of +317.20 must be applied to the doublet terms of Ingram to bring them to the same zero as the quadruplet terms.

J. GRANT.

Structure of the third order spectrum of sulphur (S III). J. GILLES (Compt. rend., 1929, 188, 63—64; cf. A., 1928, 565).—The author has tabulated 40 lines (λ 4527.77—3323.97 Å.) and their intensities, based on the levels of multiplicity corresponding with the electronic configurations $a3d$, $a4s$, and $a4p$ of the S III spectrum. Eight multiplets are involved.

J. GRANT.

Structure of the third order spectrum of sulphur (S III). J. GILLES (Compt. rend., 1929, 188, 320—321; cf. preceding abstract).—Lines of the $4d$ and $5s$ terms of the S III spectrum (2998.27—2442.65 Å.), based on the value 135600 for $4s^3P$, and corresponding with the multiplets ($4p^3S-4d^3P$), ($4p^3P-4d^3P$), ($4p^3D-4d^3P$), ($4p^3P-4d^3D$), ($4p^3D-4d^3D$), ($4p^3S-5s^3P$), and ($4p^3P-5s^3P$), are tabulated with their wave-lengths and intensities and include the line 2665.40 Å., hitherto attributed to the S V spectrum.

J. GRANT.

Further triplets of trebly-ionised arsenic. K. R. RAO (Nature, 1929, 123, 244).—Two additional triplets due to As IV have been found. The values of $5pP_{012}$ are 168010, 167748, 166932.

A. A. ELDRIDGE.

Discontinuities of the K-absorption of simple substances. V. DOLEJSEK and K. PESTRECOV (Compt. rend., 1929, 188, 164—166).—Determinations of the limits of K-absorption of elements of atomic numbers (N) 12—30 in the same chemical state differ from the expression $\nu/R = a' + b'N + c'N^2 + d'N^3 + e'N^4$, where ν/R is the change of the frequencies of the K-level and the coefficients a' , b' , c' , d' , e' are calculated from the frequencies of the rare gases, by amounts which vary periodically with N and show maxima for $N=12, 21$, and 29 and minima for $N=17$ and 25.

J. GRANT.

Diffraction of X-rays by ruled gratings. Spectrographic function of X-rays and ultra-violet rays. J. THIBAUD (Ann. Soc. Sci. Bruxelles, 1928, B, 48, ii, 145—168).—An account of the author's work on the diffraction of X-rays and ultra-violet rays (cf. A., 1925—1928, numerous publications), showing the various stages in the development of the grating method with tangential incidence. This method is compared with the rotating-crystal method, and is shown to be very suitable for the investigation of the region between X-rays and ultra-violet rays. The theory of the diffraction grating with tangential incidence is summarised and a detailed description of the improved form of vacuum spectrograph with glass grating is given (cf. A., 1927, 286).

O. J. WALKER.

D-Line excitation by the green sodium band and the dissociation potential of sodium vapour. E. L. KINSEY (Proc. Nat. Acad. Sci., 1929, 15, 37—41).—The evidence is discussed for the dissociation of molecules into normal and excited atoms by the absorption of light in the fluorescence phenomena of sodium vapour. The conditions under which it is possible to excite the D-lines by the blue-green band of the sodium molecule were determined experimentally. The long and short wave-length limits of the exciting band and the wave-length of the band producing the maximum intensity were measured. The correspondence between the intensity variation of the D-lines and the blue-green bands shows that the process is probably the excitation of the atoms to the $2P$ levels by collisions of the second kind with excited molecules, and not by the dissociation of the molecules; the heat of dissociation is taken as 0.85 volt.

N. M. BLIGH.

Intensity relations in the spectra of titanium. I. Line intensities in the stronger multiplets

of Ti I and Ti II. G. R. HARRISON (J. Opt. Soc. Amer., 1928, 17, 389—416).—The relative intensities of the lines in a number of multiplets in the spectra of Ti I and Ti II have been measured. The apparatus used is described in detail and was capable of separating lines which were 0.24 Å. apart. The sources of error are discussed and are concluded to be less than 1%. Tables are given showing the measured and calculated intensities of these lines, 36 multiplets having been examined in all. J. L. BUCHAN.

Ground-terms in the spectrum of nickel II and proposed standard wave-lengths in the Schumann region. A. C. MENZIES (Proc. Roy. Soc., 1929, A, 122, 134—143; cf. Shenstone, A., 1927, 998).—During previous investigations of fuse spectra (A., 1928, 99, 806) it has been observed that this source is particularly suited to the study of low-level terms, and it is now applied to the analysis of the spectrum of Ni II. It was found that if the wires are mounted horizontally in the vacuum grating spectrograph, and very near the slit, the lines vary greatly in length, in spite of the astigmatic action of the grating, so allowing the application of the method of long and short lines. A number of lines, obviously connected on account of their length and strength, were found on analysis to belong to the hitherto missing ground-terms 2D_3 and 2D_2 of Ni II. Since the combining middle terms are accurately known, a determination of the values of 2D_3 and 2D_2 makes it possible to calculate the theoretical values of the wave-lengths of conveniently spaced lines, which can then be used as standards in the Schumann region. The lines extend from 1317 to 1940 Å.

L. L. BIRCUMSHAW.

Reversals in the arc spectrum of nickel. A. C. MENZIES (Phil. Mag., 1928, [vii], 6, 1210—1216).—An examination of the fuse spectra of nickel in air for the ultra-violet and in a vacuum for the Schumann region has been made to determine if the ground-term of the Ni I spectrum is 1S_0 . Many reversals have been found in the ultra-violet region, but all of these can be accounted for from known data. In the Schumann region no lines attributable to the arc could be found. It is concluded that if the 1S_0 term does exist it must give rise to lines below the region examined. A. E. MITCHELL.

Furnace spectrum of beryllium. R. F. PATON and G. M. RASSWEILER (Physical Rev., 1929, [ii], 33, 16—21).—Observations were made from 2150 to 7000 Å. and up to 2500° Abs., in both absorption and emission, using a specially designed high-temperature vacuum furnace. It is confirmed that the beryllium line 2348.62 Å. is the first line of the principal series of singlets for the neutral atom. The diffuse and sharp series of singlets of the element were discovered and tabulated. N. M. BLIGH.

Spark doublets in the K-series. V. DOLEJSEK and (Mlle.) D. ENGELMANNOVA (Compt. rend., 1929, 188, 318—320).—The experiments previously described (this vol., 225) have been extended to the heavier elements (atomic numbers 23—30) in the same state of valency, and the interval between the spark doublets of the K-series has been found to decrease with increase in atomic number. Dauvill.

ier's results for copper (A., 1922, ii, 243) were confirmed, and the mean value found for the doublet constant ($\Delta\sqrt{\nu}/R$) of 0.0074 is in good agreement with that already obtained (*loc. cit.*). J. GRANT.

Continuous spectrum of mercury vapour. H. VOLKRINGER (Compt. rend., 1929, 188, 321—323).—The changes in the continuous spectrum of mercury vapour excited by an electrodeless discharge in a silica tube, the ends of which may be maintained at different temperatures, have been studied spectrographically. If the whole tube is at 230° the relative intensities of the several bands differ at various points of the tube, and are dependent on the exciting field. The production of the spectrum probably involves association of neutral and excited atoms rather than the simple passage from one atomic state to another. J. GRANT.

Power relation of the intensities of the lines in the optical excitation of mercury. I. E. GAVIOLA (Phil. Mag., 1928, [vii], 6, 1154—1167).—The intensities of the different lines of mercury vapour at the ordinary temperature when optically excited by a water-cooled mercury arc have been calculated as a function of the primary intensities and of the position of the emitting volume element in the tube. The special behaviour of lines like 3650 Å. is then explainable and the absorption laws for 4358, 3650 Å., and similar lines are calculable. A. E. MITCHELL.

Influence of foreign gases on the optical excitation of mercury. II. E. GAVIOLA (Phil. Mag., 1928, [vii], 6, 1167—1191).—The alterations in the intensities of the lines in the optical excitation of mercury vapour caused by the presence of foreign gases are explained on the author's theory (cf. preceding abstract). The examination of the effects of various gases on the absorption of the line 4046 Å. by the metastable mercury atoms has demonstrated the long period of existence of these. The metastable level 2^3P_0 has an existence of 10^{-5} sec. when no foreign gases are present; its existence is, however, sensitive to their presence. In the presence of foreign gases the metastable level has a mean life of 1/300 sec., whilst under ideal conditions (as in stars) it should increase to about 10 sec. The result of Foote (A., 1927, 999) that the efficiency of quenching collisions of nitrogen with excited atoms in the resonance level is approximately 1 has been confirmed. The number of metastable atoms excited by the presence of a few mm. of nitrogen or water vapour is estimated to be about 10^2 times the number of excited atoms in the resonance level. A. E. MITCHELL.

Polarisation of canal-ray light. III. Mercury positive rays of the line 2537 Å. E. RUPF (Ann. Physik, 1929, [v], 1, 289—300).—The polarisation ratio for the line 2537 Å. has been studied for mercury positive rays. Polarisation occurs in the fading light only when disturbances are allowed to occur at the positive-ray slit. By heating the slit the polarisation vanishes, so that it must be a secondary effect. The addition of foreign gases and the application of magnetic fields affect the polarisation ratio for the positive ray in the same way as they influence the resonance fluorescence of the line 2537 Å. The

polarisation disappears when the positive-ray stream is diffused by an obstacle in its path.

R. A. MORTON.

Heat spectrum of solid and liquid iron. R. HASE (Physikal. Z., 1928, 29, 904—907).—The spectral energy distribution of the radiation emitted by solid and liquid iron resembles that from a black body, but the absolute intensity depends largely on surface oxidation. The wave-length of maximum emission for smooth solid iron is shifted in the direction of shorter wave-lengths as the temperature rises, so that Wien's law is obeyed. The intensity E at the maximum varies as CT^6 , T being the absolute temperature and $C=2890$. Matt, slag-free iron emits approximately "grey" radiation approaching the black-body condition as the temperature rises. The heat spectrum of liquid iron closely resembles that of the smooth solid metal both as regards intensity and spectral distribution.

R. A. MORTON.

Excitation of X-ray spectra by means of α -particles. W. BOTHE (Physikal. Z., 1928, 29, 891—893).—The weak X-rays generated by the impact of α -particles on matter have been studied by means of a very sensitive apparatus, using argon in the counter. The following characteristic radiations were identified: K -radiation: Mg, Al, S, Ca, Cr, Fe, Zn; L -radiation: Se, Mo, Pd, Ag, Sb, Sn, Ta, Ir, Au, Bi; M -radiation: Bi. For some elements, the variation of the intensity of X-radiation with the range of the α -particles was determined, and was found to be closely related to the ionisation curve for the inner atomic electrons. The energy of the α -particles (from polonium) was insufficient for the maximum in the differential ionisation to be shown definitely, although the existence of such a maximum can be inferred for the curve obtained with aluminium. The results do not support Thomson's theory of ionisation, but are in agreement with Born's treatment of the quantum mechanics of collision processes.

R. A. MORTON.

Some multiplets of singly-ionised thallium. S. SMITH (Proc. Nat. Acad. Sci., 1928, 14, 951—953).—Some of the lines arising from combinations of singlet and of singlet and triplet terms of $Tl II$ were identified and classified, and compared with the lines predicted by an application of the regular and irregular X-ray doublet laws to the optical spectra of mercury-like atoms and interpolating between data for Hg I and Pb III.

N. M. BLIGH.

Influence of the presence of hydrogen on the L_{111} X-ray absorption edge of palladium. J. D. HANAWALT (Proc. Nat. Acad. Sci., 1928, 14, 953—958).—X-Ray investigation shows that an outstanding distension of the palladium lattice exists due to absorbed hydrogen and corresponding with a compound Pd_2H . To decide whether the hydrogen atoms, are intimately combined with the palladium atoms the L_{111} absorption edge was studied using a vacuum spectrograph. Hydrogen was occluded in the palladium in two ways. Evidence indicates that the complex absorption edge corresponds with the superposition of two simple edges, one due to Pd atoms alone and the other due to Pd atoms combined with H atoms. The compound PdH is indicated,

but the interpretation of the complex edge is inconclusive.

N. M. BLIGH.

Zeeman effect and term arrangement in the spectrum of singly-ionised chromium. E. KROMER (Z. Physik, 1928, 52, 531—548).—Data for some 50 lines are tabulated, and from the results further contributions are made to the term arrangement in this spectrum.

J. W. SMITH.

X-Radiation excited by α -particles. W. BOTHE and H. FRANZ (Z. Physik, 1928, 52, 466—484).—The excitation of the K -, L -, and M -radiation by α -rays from polonium has been observed over the wave-length range 1.1—10 Å. for a number of elements. The relationship between the K - and L -excitation and the range of the α -particles is given graphically for some of the elements and the results are compared with Bragg's curve for the dependence of the ionisation in air on the range of the α -particles. The data obtained for the excitation limit are in opposition to Thomson's theory of ionisation (A., 1912, ii, 410), but not to Born's quantum theory of collision (A., 1926, 1078). The yield of aluminium K -radiation was measured in an absolute manner by an ionisation method, those of the other characteristic radiations being then compared with this. Both in the K - and L -series a general decrease in the yield was observed as the atomic number of the elements under investigation increased. From the observations made it is deduced that the probability of ionisation is essentially smaller for an L electron than for a K electron with equal energy of ionisation.

J. W. SMITH.

Precision measurements in the K -series of the elements zinc (30) to ruthenium (44). B. EDLÉN (Z. Physik, 1928, 52, 364—371).—Using a precision tube spectrometer of the type employed by Siegbahn and by Larsson, measurements have been made of the K lines α_2 , α_1 , β_1 , β_2 of the elements zinc, arsenic, selenium, bromine, rubidium, strontium, yttrium, zirconium, niobium, and ruthenium. The lines of the last six of these elements have also been measured.

J. W. SMITH.

Absolute X-ray wave-length measurements. A. P. R. WADLUND (Physical Rev., 1928, [ii], 32, 841—849).—By means of a speculum metal grating ruled 50 lines to the mm., the wave-lengths of the $K\alpha_1$ line of copper, iron, and molybdenum were determined as 1.5373 ± 0.0008 , $1.937(6) \pm 0.002(3)$, and $0.708(3) \pm 0.001(1)$ Å., respectively. Using the $K\alpha_1$ line of copper the following constants were calculated: the grating space of calcite 3.0290 ± 0.0016 Å., $N = (6.061 \pm 0.009) \times 10^{23}$, and $e = (4.774 \pm 0.007) \times 10^{-10}$. The sources of error involved are discussed, the chief being those due to the settings on the lines of the diffraction pattern and those due to the inexact setting of the grating.

N. M. BLIGH.

Evaporation at the cathode of the mercury arc. J. VON ISSENDORF (Physikal. Z., 1928, 29, 857—864).—By means of a special type of lamp it has been possible to determine the amount of mercury sputtered and vaporised from the cathode of the mercury arc, at various temperatures. The evaporation varies considerably with temperature and to a small extent with current, the whole cathode surface

being apparently involved. Positive and negative limiting values for the vaporisation in the neighbourhood of the focal spot are given and it is shown that the loss of material from the focus is vanishingly small, an actual gain being not improbable owing to the effect of streams of ion. This supports Compton's assumption that, in considering the energy balance, volatilisation from the focus of the mercury discharge is negligible. The amount of mercury sputtered from the cathode shows a roughly linear increase with increasing current strength. The results are considered in relation to the problem of the energy balance at the cathode.

R. A. MORTON.

Transport of matter in the iron arc. H. SCHMICK and R. SEELIGER (*Physikal. Z.*, 1928, 29, 864).—In the theory of the mechanism of the arc cathode, the energy balance plays an important part (cf. Issendorff, preceding abstract). Investigation of the loss of material from the iron arc shows that the phenomenon is complicated, but is definitely not proportional to the current and varies primarily as the degree of cooling of the cathode. In agreement with Issendorff's work, it would appear that the loss of material is not confined to the focal point, but is distributed over the whole neighbouring area.

R. A. MORTON.

Geiger point counter. Influence of cathode material on the sparking potential. O. KLEMPERER (*Physikal. Z.*, 1928, 29, 947—948).—The sparking potential in the Geiger account varies to some extent with the material forming the "point" cathode. In carbon dioxide the limiting voltages were 600—650, no definite effect being traceable to the nature of the cathode. In air, platinum, gold, silver, and copper behaved similarly, but for steel and aluminium the voltage V_0 was lower. In hydrogen, the metals fell into a series, steel, however, being anomalous. The greatest differences in V_0 occurred in argon. The results are discussed in relation to the mode of action of the counter (cf. Curtiss, A., 1928, 985).

R. A. MORTON.

Calculation of the product of the halogen ions by means of their ultra-violet absorption in aqueous solution. G. SCHEIBE (*Naturwiss.*, 1929, 17, 86).

W. E. DOWNEY.

Properties of ionised gases in high-frequency fields. H. GUTTON (*Compt. rend.*, 1929, 188, 156—157; cf. A., 1927, 294).—Determinations of the conductivities corresponding with resonance of an ionised gas for λ 4830, 2528, 1834, and 1324 μ show that the conductivity and elastic force are proportional to the number of ions per cm. and to number of ions to the power 0.75, respectively. The constitution of an ionised gas is analogous to that of a Lorentz dielectric in which the electrons are further apart, and the existence of an absorption band is due to resonance between the oscillations of the electrons and of the field.

J. GRANT.

Passage of the electric current through a Cooper-Hewitt mercury lamp. S. RAY (*Z. Elektrochem.*, 1929, 35, 89—93).—Theoretical. An attempt is made to explain the mechanism of the Cooper-Hewitt mercury lamp in terms of a hypothetical compound HgZ , which is assumed to be

formed in the lamp. The cause of the cessation of the current with time, especially at high voltages, is discussed.

L. L. BIRCUMSHAW.

Nature of streamers in electric sparks. M. MIYANISHI (*Japan. J. Phys.*, 1928, 5, 67—82).—The streamers emanating from the anode and cathode of a spark have been examined spectrographically and found to consist of positively and negatively charged particles respectively. Their velocity and duration of luminosity have also been measured.

J. L. BUCHAN.

Ionisation through electronic collision. A. VON HIPPEL (*Ann. Physik*, 1928, [iv], 87, 1035—1086).—A theoretical discussion of the ionisation of atoms by electronic collision on the basis of classical theory is given. An ionisation function representing the probability of ionisation taking place through a collision is deduced. Under certain limiting conditions this function for a single atomic electron shows a maximum at a collision-electron speed corresponding with double the ionisation potential of the atom. Former experimental methods are critically discussed and a new one is described. A stream of electrons of homogeneous velocity hits perpendicularly a stream of atoms; the ions formed are carried on with the stream of atoms and are separated from the non-ionised atoms by passage through a mass spectrograph. The deflected ray of ions is then collected on a suitable ion collector. Mercury vapour has been examined afresh by this method, and the existence of a maximum of ionisation yield for an electronic speed in the neighbourhood of double the ionisation voltage of mercury is demonstrated. The measured collision yield, however, at this maximum is 8.3% compared with that predicted of 15%. A short description is also given of a high-frequency method suitable for the qualitative study of collision ionisation and also for experiments with streams of ions.

R. N. KERR.

Secondary electron emission produced by positive caesium ions. J. M. HYATT (*Physical Rev.*, 1928, [ii], 32, 922—928).—Experiments were made to determine the number of electrons emitted from a caesium-covered grid and plate as a function of the accelerating potential, by positive caesium ions from a tungsten filament maintained at about 1200 Abs. in the presence of caesium vapour. The number of electrons emitted per positive ion was found to increase uniformly from 0.01 at 100 volts to 0.15 at 600 volts. The ratio, positive-ion current to plate/total emission current, was found to be independent of the plate and grid potentials for plate potentials greater than 0.2 of the grid potential. This ratio, 0.72, is the same as the ratio, total area of plate less projected area of grid/total plate area. Assuming the same distribution of electrons as positive ions, the ratio, plate current/grid current, in the type of tube used can be calculated.

N. M. BLIGH.

Critical photo-electric potential of clean mercury and the influence of gases and of the circulation of the mercury on it. W. B. HALES (*Physical Rev.*, 1928, [ii], 32, 950—960).—Experiments were made to test the theories of photo-electric fatigue after eliminating every possible source of

contamination of the metal surface, using a reconstructed form of the apparatus of Kazda and Dunn (A., 1926, 3; 1927, 603). The long wave-length limit for running mercury was found to be 2735 and the critical frequency for stationary mercury 2735 ± 10 Å., in agreement with Kazda for flowing mercury. It is now found that a four-fold increase of photo-current is not reached until 80 hrs. after turning off the still, and remains constant indefinitely thereafter. The long wave-length limit for this maximum sensitivity was found to be 2910 Å. Traces of hydrogen, helium, argon, nitrogen, and water vapour had no influence on the photo-electric behaviour or on the rate of rise of sensitivity, except for a cleansing effect in reducing impurity which slowly contaminates the surface. Oxygen reduced the threshold value to 2555 Å. in 18 hrs. N. M. BLIGH.

Ion-rays. J. KAHRA (Ann. Physik, 1929, [v], 1, 135—156).—In conformity with the view of Schmidt (A., 1924, ii, 727; 1925, ii, 251; 1926, 877) that only those ions capable of wandering in electrolysis are emitted on heating, it is found that at 400° lead bromide, iodide, and fluoride emit negative ions only. Experiments designed to increase the emission as a result of irreversible loosening of the crystal lattice were unsuccessful. The introduction of gases into the salt converted the falling portion of the emission curve into a rising portion, the change being due to irreversible processes. A number of glasses were found to emit positive ions exclusively, a separate negative emission being observed only at the highest temperatures. The data again support Schmidt's theory. The increase in emission with time arises from loosened structure following irreversible processes. R. A. MORTON.

Change in emission of ion-rays with time. O. BIRKENBERG (Ann. Physik, 1929, [v], 1, 157—168).—Dissolved or fused salts heated on a wire until the emission becomes constant maintain this constant value indefinitely in a vacuum or in contact with dry gases. In the presence of water vapour the emission from soluble salts is increased, whilst the emission from salts insoluble in water is unaffected. Salts which have been sublimed in air on to a wire and heated until the emission becomes constant revert to the normal in a vacuum or in contact with moist or dry gases, whereas if the sublimation has been carried out in a vacuum, reversion does not occur. The phenomena are all explained on the assumption that the salts can occlude foreign matter which results in the formation of loosened ions. R. A. MORTON.

Photo-electric behaviour of mercury during the transition from the liquid to the solid state of aggregation. (FRL.) M. GRUTZMANN (Ann. Physik, 1929, [v], 1, 49—73).—The total photo-electric emission of mercury remains constant for temperatures on either side of the m. p., in contrast with the electrical behaviour of mercury in other respects. An electrical effect at the m. p., and independent of light, is shown to occur, and it is suggested that the phenomenon may be related to the liberation of mercury vapour.

R. A. MORTON.

Influence of hydrogen on the photo-electric electron emission of potassium. R. SUHRMANN and N. THEISSING (Z. Physik, 1928, 52, 453—463).—Thoroughly purified and dried hydrogen exerts no influence on the photo-electric sensitivity of potassium in bulk. When the latter was in the form of a unimolecular film on the surface of platinum-black, the sensitivity was considerably reduced on admitting hydrogen. This effect diminished, however, as thicker films of potassium were built up. Hence it is concluded that the spectral maximum of the sensitivity curve observed with potassium is not attributable to the action of hydrogen molecules. J. W. SMITH.

Theory of photo-electric action. H. WOLFF (Z. Physik, 1928, 52, 158—160).—The difference between limiting energies required to eject electrons from the surface of two metals equals e times the contact $P.D.$ of the metals, and lightly bound electrons should suffer only Compton scattering. This, and other inconsistencies, suggests that photo-electric emission is caused by atoms, raised to a metastable state by light absorption, losing their energy to colliding and slowly moving electrons of the "electron-gas," which are then ejected as photo-electrons. A. B. D. CASSIE.

Thermionic emission from clean platinum. L. A. DUBRIDGE (Physical Rev., 1928, [ii], 32, 961—966; cf. A., 1927, 391; 1928, 340).—Owing to previous inconsistent results for platinum, a greater precision and range of temperature and currents has been attempted. The thermionic emission from thoroughly outgassed platinum in high vacuum was measured to 0.5% over the temperature range 1360—1750° Abs. The values obtained for the thermionic constants of the equation $I = AT^2 e^{-b/T}$, when corrected for the Schottky effect, are: $b = 72820$ Abs., $\phi = 6.27$ volts, $A = 17000$ amp./cm.²deg.² The value of the thermionic work function ϕ is correct to 1% and agrees within 0.5% with the value of the photo-electric work function previously obtained. The value of A is confirmed to be 250 times as great as the theoretical value of 60.2 amp./cm.²deg.² (cf. Bridgman, A., 1928, 682). N. M. BLIGH.

Secondary electron emission from molybdenum. J. M. HYATT and H. A. SMITH (Physical Rev., 1928, [ii], 32, 929—935).—The secondary electron emission from a clean molybdenum plate in a simple three-electrode tube was studied. The number of primary electrons striking the plate was calculated by the positive-ion calibration method (cf. this vol., 228). The number of secondary electrons per primary reaches a maximum of 1.15 at 600 volts and then decreases to 1.00 at 2000 volts. Petry (A., 1925, ii, 1017) reported discontinuities in the secondary emission curve at several accelerating potentials. One definite discontinuity is now found at 13.5 volts; the others are very small and not reproducible. The emission increases about 3% within a few minutes after heating if the gas pressure is very low and then remains constant for some time; it decreases with time when there is more gas present. The secondary emission appears to increase by about 4% when the temperature of the target is raised from that of normal operation to 1600° Abs. N. M. BLIGH.

Thermionic emission constant A . R. H. FOWLER (Proc. Roy. Soc., 1929, A, 122, 36—49).—The relation between the constants A and γ of the thermionic emission formula, recently recorded by DuBridge for severely outgassed platinum (A., 1928, 340), is explained by the application of Nordheim's theory of the emission coefficient of electrons from metals. The necessary conditions for the proper application of the theory are formulated. Apart from the absolute value of A in certain cases, the theory gives a most satisfactory account of the whole range of thermionic emissions by clean surfaces, or surfaces so contaminated that the true work function is diminished. Certain apparent discrepancies in absolute magnitude between the observed and theoretical values of A are discussed.

L. L. BIRCUMSHAW.

What happens during an electron jump? D. S. VILLARS (Nature, 1929, 123, 240).—It is considered that in an electron "jump" the electron does not suddenly change its position, but merely undergoes a change in momentum and obeys a new force law; its behaviour is compared with that of a vibrating molecule after absorbing light. By Pauli's interpretation of Schrodinger's theory the electron orbit represents a cloud in space, the centre of gravity being the locus of a Bohr orbit. A. A. ELDRIDGE.

Polarisation of the light emitted in electron collisions in inert gases. K. STEINER (Z. Physik, 1928, 52, 516—530).—The degree of polarisation of the light produced by electron collisions in neon and helium has been investigated experimentally. In the case of neon, very definite effects were observed, the lines of some of the spectral series showing a tendency to become polarised parallel to the electron beam, and others at right angles to it. Indications of a similar effect have been obtained with helium.

J. W. SMITH.

Absorption of X-rays. H. R. ROBINSON and C. L. YOUNG (Nature, 1929, 123, 203—204).—By a method of "magnetic spectrometry" it is shown that the two K -electrons of a zinc atom absorb probably more (almost certainly not less) X-radiation of wave-length 0.56 Å. than the eight L -electrons of tungsten. Simplifying assumptions associated with all theories so far proposed may account for the deviations between experimental and theoretical values.

A. A. ELDRIDGE.

Some transient effects with ions of low mobility. H. P. WALMSLEY (Mem. Manchester Phil. Soc., 1927—1928, 72, 29—41).—The mathematical theory of the motion of ions of low mobility is discussed and approximate equations are derived which lead to curves for the time variation of the saturation exhibiting the same type of distortion from the normal as do the author's experimental curves relating to ions of low mobility. R. W. LUNT.

Range of H -particles. W. BOTHE (Z. Physik, 1928, 51, 613—617).—Calculations based on the energy exchanges which take place when a α -particle collides with a neutral molecule resulting in the liberation of an H -particle lead to values of the range of H -particles in agreement with experiment if it be assumed that after collision the α -particle becomes attached to the

nucleus of the atom with which collision has taken place. Such an hypothesis was suggested by Blackett in order to account for the apparent disappearance of α -particles after collision in nitrogen. R. W. LUNT.

Dispersion electrons of lithium. J. HARGREAVES (Proc. Camb. Phil. Soc., 1929, 25, 75—96).—Mathematical. The method of Hartree (cf. A., 1928, 216) has been used to determine the number of dispersing electrons corresponding with the lines of the principal series of the optical spectrum of lithium, and also to the continuous spectrum at the head of the series. W. E. DOWNEY.

Measurement of the life of the metastable mercury atom. M. L. POOL (Physical Rev., 1929, [ii], 33, 22—26).—An interrupted optical excitation method was used for measuring the life of the metastable 2^3P_0 state. The line 4047 Å. (2^3P_0 — 2^3S_1) showed strong absorption when a few mm. of nitrogen were introduced into the resonance tube, whilst the lines 4077, 4358, 5461, 5770, and 5790 Å. showed no measurable absorption. The rate of decay of the amount of 4047 Å. absorbed with respect to the delay after excitation of the mercury vapour was taken as the rate of decay of the metastable 2^3P_0 state. The life or half-value time of the state varied markedly with the pressure of admixed nitrogen. The maximum life, 4.2×10^{-4} sec., occurred for 6.8 mm. of nitrogen. No absorption of 4047 Å. was observed on introducing hydrogen, argon, neon, or helium into the resonance tube. N. M. BLIGH.

Counting of α -particles by Wulf's method. (Mlle.) M. DESMET and (Mlle.) M. VAN HAEPELEN (Ann. Soc. Sci. Bruxelles, 1928, 48, B, i, 100—113).—A comparison of the improved ionisation chamber method of counting α -particles of Wulf (Physikal. Z. 1925, 26, 382) with the scintillation method. Using as a constant source of α -particles a small sphere of polished steel activated by means of radium emanation, the optical method gave 15 particles/min. Wulf's method gave values of 10—13 in the most favourable cases using dull-pointed needles, and only 3—5 with fine-pointed needles. Particular attention was paid to the cleaning of the needles, shape of the point, and sign and magnitude of the voltage applied. Since the scintillation method almost certainly gives a low result, Wulf's method is not considered suitable as an accurate quantitative method.

O. J. WALKER.

Diamagnetism of ions of the rare gas type. H. KULENKAMPEFF (Ann. Physik, 1929, [v], 1, 192—194).—The value of c_1 in the work of Ikenmeyer (cf. this vol., 247) can be obtained as follows: the susceptibility $\chi = \Sigma r_i^2 (e^2 L / 6mc^2) = Z_E \bar{r}^2 e^2 L / 6mc^2$, r_i being the distance from the nucleus of the i -th electron, \bar{r}^2 the mean distance for all electrons, and Z_E the number of electrons. As a first approximation, \bar{r}^2 is independent of Z_E and $\bar{r}^2 = 0.282 \times 10^{-16} = (0.531 \times 10^{-8} \text{ cm.})^2$, agreeing with $a_1 = 0.532 \times 10^{-8} \text{ cm.}$, where is the ground orbit of the Bohr hydrogen atom. It is then shown that $\bar{r}^2 = a_1^2 [1 + (1/Z_E)(c_2' - c_1)/c_1] = a_1^2 [1 + (7.35/Z_E)]$ for halogen ions. For alkali ions and alkaline-earth ions the values 3.0 and 4.35, respectively, replace 7.35, $2c_1$ replacing c_1 in the numerator in the latter case. R. A. MORTON.

Motion of electrons in pentane. J. D. MCGEE and J. C. JAEGER (Phil. Mag., 1928, [vii], 6, 1107—1117).—The method of Bailey (A., 1925, ii, 1019) has been employed to investigate the motion of electrons in pentane vapour. The phenomena observed are very similar to those previously obtained with ethylene. The fraction of the energy lost in collision rapidly approaches a maximum as the agitation velocity increases and then decreases rapidly. It is suggested that this may be due to the formation of ions. The "ageing" effect of the gas, when left in the apparatus, reported by Wellish (Phil. Trans., 1909, A., 209, 249) was absent. A. E. MITCHELL.

Capture of electrons by molecules. V. A. BAILEY and J. D. MCGEE (Phil. Mag., 1928, [vii], 6, 1073—1089).—The apparatus previously described by Bailey (A., 1925, ii, 1019) has been modified to simplify the procedure of measurement. The measurements of Bailey and Higgs (to be published later) on ammonia have been repeated and it is shown that the probability of attachment of an electron at a collision with a molecule may vary very considerably with the energy of the electron. This result is in disagreement with that of Loeb and others, who consider the probability of attachment to be a characteristic constant for a gas.

A. E. MITCHELL.

Electronic waves and electrons. (SIR) J. J. THOMSON (Phil. Mag., 1928, [vii], 6, 1254—1281).—It is shown that if the structure of the electron were such that the usually accepted point charge, or something analogous to it, formed a nucleus surrounded by a system made up of parts which can be set in motion by electric forces and when in motion produce the effects of electric currents, then the motion of the electron would, from the ordinary laws of electro-dynamics, give rise to a train of waves, the relationship between the wave-length of this train and the velocity of the electron being exactly as indicated by the experiments of G. P. Thomson. This surrounding structure might comprise either a distribution of discrete lines of force or of a number of positively and negatively charged particles which would behave like free particles. The sphere surrounding the nucleus will have a definite period of vibration, the frequency of which is proportional to the square root of the number of electrified systems per unit of volume. The vibrations form an oscillating electric field in which there is no transmission of energy. Both the nucleus and the sphere can vibrate, and in the steady state of the electron the vibrations are in resonance. The total energy of the electron is that due to the charge on the nucleus plus that due to the oscillating field, the importance of which conception is pointed out in connexion with the calculation of the size of the electron.

A. E. MITCHELL.

Wave mechanics of rotating electrons and the fundamental equation of the electromagnetic field. J. FRENKEL (Z. Physik, 1928, 52, 356—363).—Mathematical. In continuation of a previous communication (A., 1928, 570) the fundamental equation of the wave mechanics of an electron is shown to be a generalised form of Maxwell's equation and the

corresponding d'Alembert equation. By modifying slightly the previous work, a system of eight equations is obtained which may be combined into pairs yielding the four equations of Dirac's theory.

J. W. SMITH.

Anomalous magnetic rotation of excited neon. R. N. JONES (Nature, 1929, 123, 278).—Erroneous values of the dispersion constants determined from the anomalous magnetic rotation in excited neon (A., 1928, 1310) are replaced by corrected values.

A. A. ELDRIDGE.

Charge of an electron. A. S. EDDINGTON (Proc. Roy. Soc., 1929, A, 122, 358—369).—The ratio of hc to e^2 is a pure number, and although the usual methods of macroscopic physics break up this number so that its dimensionless character appears curious, in the wave theory of the interaction of electrons the number is kept intact. In the wave equation for two electrons (or an electron and a proton) e occurs in the expression $hc/2\pi e^2$ as the coefficient of certain terms. The present investigation of the interaction of two electrons is based on the exclusion principle and the Fermi-Dirac statistics, and it is not considered necessary to postulate electric charge. A wider principle of relativity is conceived, which allows, in addition to a rotation of space and time, a "rotation" which will interchange the identity of two electrons; or the two electrons become two indistinguishable entities. This treatment leads to an equation containing $2\pi e^2/hc$ as a coefficient of one term, which according to the theory must have the value $1/136$. The experimentally determined value of e gives, however, 137.1 for $hc/2\pi e^2$. L. L. BIRCUMSHAW.

Longitudinal magnetic actions on beams of slow electrons (periodic concentrations and dilatations). J. THIBAUD (Compt. rend., 1929, 188, 54—56).—The blue fluorescence shown by a beam of electrons traversing an evacuated cylinder containing a wire-wound coil in a high vacuum and at a voltage below 500 shows periodic variations between a thin, bright uniform thread of light (state of concentration) and a luminous cone (state of dilatation) when varying magnetic fields are applied. The phenomenon is unaffected by the sense of the field and the type of coil used to generate it, and a linear relation exists between the spread of the electrons and the field strength producing concentration (or dilatation) for each successive phase.

J. GRANT.

Concentration and dilatation effect produced by a longitudinal magnetic field on a beam of slow electrons. J. THIBAUD (Compt. rend., 1929, 188, 158—160).

Diffusion of slow-moving electrons in the inert gases. H. POSE (Z. Physik, 1928, 52, 428—447).—The diffusion of electrons in an inert gas has been investigated by passing a beam of thermally emitted electrons through a hole in the centre of one plate, and measuring the ratio of the number of electrons striking an opposite parallel plate to the number returning to the plate through which the electrons enter, both plates being maintained at the same potential. According to the diffusion theory of Hertz (Z. Physik, 1925, 32, 298), this ratio should

be equal to $4\lambda/3a$, where a is the distance between the plates and λ the mean free path of the electrons. After correction for the dimensions of the source, which were necessarily large compared with the mean free path of the electrons, the values obtained for the mean free path in the gases investigated, viz., neon, argon, and a mixture of neon and helium, were in good agreement with those obtained by direct measurement. They also showed very clearly the phenomenon observed by Ramsauer (A., 1921, ii, 324) of the strong dependence of the mean free path in argon on the electronic velocity.

Measurements were also carried out with an electrostatic field between the two plates, the dependence of the above-named ratio on the potential between the plates being measured. In this case, also, the results were in good agreement with the diffusion theory. The deviations observed, especially at high electronic velocity, are explainable on the ground of reflexion at the plates. In argon the deviations were of the order to be anticipated according to the diffusion theory from the change in the mean free path with electron velocity. It is concluded that, to the degree of accuracy obtainable, the motion of slow-moving electrons through the inert gases is correctly expressed by the diffusion theory.

J. W. SMITH.

Polarisability of an electron pencil. F. WOLF (Z. Physik, 1928, 52, 314—317).—If an electron is a magnetic dipole an electron pencil must come into a state of polarisation when it is passed through a magnetic field. Experimental analysis of such a pencil carried out by allowing it to impinge on a metallic reflector with its face at an angle of 45° to the pencil and connected to an electrometer failed to show any such effect.

J. W. SMITH.

Theory of electron scattering and excitation by collision. J. HOLOMARK (Z. Physik, 1928, 52, 485—495).—Mathematical. These phenomena are discussed from the point of view of wave mechanics.

J. W. SMITH.

Refractive index of electrons and diamagnetism. L. ROSENFELD (Naturwiss., 1929, 17, 49—50).—By further application of the principles of wave mechanics to the considerations of Bethe (A., 1928, 1303) a relationship is deduced connecting the diamagnetic susceptibility of an element with its refractive index with respect to electrons. The experimentally observed susceptibility can be regarded as the difference between a paramagnetic component and a diamagnetic component. Since the former can also be calculated from wave mechanics, this difference can be deduced theoretically. Calculations have been made for six metals, and the theoretical figures compared with practical data. In the cases of copper, silver, gold, and lead, values of the right order of magnitude are obtained, but considerable discrepancies are found in the cases of chromium and aluminium.

J. W. SMITH.

Magnetism and nuclear structure. D. ENSKOG (Z. Physik, 1928, 52, 203—220; cf. A., 1928, 343).—Both kinetic and potential terms of the classical Hamilton energy function are modified when electrically-charged particles, moving under their

mutual influence, are supposed possessed of magnetic doublets. The energy of emission of an α -particle, as measured by Rutherford and others, from radioactive atoms seems given by this modified expression for closed quantised orbits. A non-magnetic planet moving in a magnetic field has kinetic modification, and the maximum core charge suggested by considerations of stability of this system is two electronic units. Larger nuclei ought, therefore, to be formed of helium and smaller nuclei. The positive energy of this non-magnetic-planet system disagrees with Aston's results on "packing." Magnetic-planet systems may have negative energy, and a planet with two magnetic units gives quantitative agreement with experiment. The decrease in energy is greater when a second single proton planet is added to a two-proton core, indicating stability of the helium group. The magnetic number for the helium nucleus is 2, for an α -particle 1, indicating instability of binding for an α -particle. The formation of more complex nuclei is considered.

A. B. D. CASSIE.

Free and bound electrons in metals. R. RUEDY (Physical Rev., 1928, [ii], 32, 974—978).—Theoretical. It is found when the theory of dispersion in an absorbing medium is applied to recent values for the optical properties of different metals (copper, gold, nickel) that bound electrons exist inside the metal comparable in number with that of the free electrons.

N. M. BLIGH.

Number of recoil electrons and intensity of modified scattering. E. J. WILLIAMS (Mem. Manchester Phil. Soc., 1927—1928, 72, 1—16).—Scattered radiation consists of modified and unmodified radiation; the modified radiation, according to the quantum theory, should be accompanied by production of β -rays or recoil electrons. X-Ray properties of the elements show a periodicity, and on this basis the coefficients of modified scattering for oxygen and nitrogen and radiation of wave-length 0.6 Å. have been calculated from results for carbon and aluminium. The values agree to within the experimental error (10%) with those determined experimentally from the expression $\tau \times N_R/N_P$, where τ is the coefficient of photo-electric absorption, and N_R and N_P are the numbers of recoil and photo-electrons, respectively. This proves that β -rays are produced distinct from the photo-electrons and equal numerically to the number of modified quanta scattered. Comparison of σ_m calculated from the wave mechanics with values of $\tau \times N_R/N_P$ shows discrepancies of 10%. The error is greater in the case of carbon.

G. E. WENTWORTH.

Ninth report of the German Commission on atomic weights. M. BODENSTEIN, O. HAHN, O. HÖNIGSCHMID, and R. J. MEYER (Ber., 1929, 62, [B], 1—23).—The report is divided into three sections dealing respectively with atomic weights determined by physico-chemical methods, with those dependent on chemical processes, and with progress in the question of isotopes of non-radioactive elements. Under their respective headings, detailed consideration is given to neon, argon; potassium, caesium, copper, silver, barium, cerium, erbium, titanium, uranium, rhenium; neon, potassium, zinc, and germanium.

New determinations of the ratio Ag:O are regarded as establishing the value $Ag=107.880$ with an uncertainty not exceeding ± 0.001 . Atomic weights on the silver basis, in so far as they have been determined with all the refinements of the halogen process, have been re-calculated to the adopted at. wt. of silver and are now given to so many decimal places that the last figure may be regarded as accurate at any rate to within a few units. Changes are adopted for the following elements, to which the at. wts. assigned are: Ba=137.36; Cd=112.41; C=12.000; Ce=140.13; Co=58.94; Dy=162.46; Er=167.64; H=1.0078; He=4.002; I=126.93; Li=6.940; Ne=20.18; Ni=58.69; P=31.02; Pb=207.21; Pt=195.23; S=32.06; Sm=150.43; U=238.14; V=50.95; Zn=65.38; Zr=91.22. H. WREN.

Numerical regularities in the atomic weights of elements. S. M. LOZANIC (Bull. Acad. Sci. Boheme, 1928, Reprint, 9 pp.).—Regularities of the type $a=2m+b$, where a is the at. wt., m the atomic number, and b is 0, 1, 2 or 3, appear in the first part of the periodic table. As the at. wt. increases, regularities of the same type appear to persist, with high values for b . These considerations are regarded as supporting the view that the at. wts. are whole numbers. The number of isotopes possessed by a given element is connected with its place in the table.

R. A. MORTON.

Isotopy of lead. (MME.) B. PERRETTE-MONTAMAT (Ann. Physique, 1928, [x], 10, 349—407).—The behaviour of two samples of lead, one from galena and having an at. wt. of 207.2, the other from pitchblende from the Belgian Congo and having an at. wt. of 206.14, has been investigated. The carefully purified samples were spectroscopically examined and the line at 4058 Å. was found to vary by 0.0076 ± 0.0008 Å. between the two specimens. The ordinary lead had $d\ 11.336 \pm 0.0004$, the pitchblende lead, 11.278 ± 0.0004 . The nitrates, crystallised at 0°, had $d\ 4.536 \pm 0.0005$, 4.523 ± 0.0005 , respectively. The values of n_{5890} for the two nitrates do not vary by more than 0.00015 from 1.78185 at 10°.

W. E. DOWNEY.

Is there a stable radium isotope in barium minerals? O. KAHN and K. DONAT (Z. physikal. Chem., 1928, 139, 143—150).—Since calcium, strontium, and barium, of even atomic numbers, occur in large quantities and since uranium and thorium occur in amounts comparable with those of their next lower homologues tungsten and hafnium, the possibility of the existence of a stable isotope of radium is discussed. A concentration of the active isotope, a stable element of atomic number 88, was attempted by methods of radium-fractionation using barium bromide; the product was examined spectroscopically for radium lines, but no such lines were recognisable.

G. E. WENTWORTH.

γ-Rays of radium. J. A. GRAY (Nature, 1929, 123, 241—242).—It is concluded that the theory of Cave and Gray (A., 1927, 1004) can be employed in the interpretation of cosmic-ray experiments; Dirac's theory of scattering is considered to be incorrect. The results of cosmic-ray experiments

have been examined. The author's method for the determination of γ-ray wave-lengths is outlined.

A. A. ELDRIDGE.

Measurement of the active deposit of radium by the penetrating γ-radiation. (MME.) I. CURIE (Compt. rend., 1929, 188, 64—66; cf. A., 1928, 810).—The number of millicuries of radium-C in a source of radium (B+C) in radioactive equilibrium may be determined from the fraction of ionisation (K) attributable to radium-B. The correction to be applied is obtained from the electrometric measurement of the difference in the ionisation currents produced in two chambers, in one of which the β-radiation of radium-B is absorbed by a lead sheet 27 mm. thick. The correction is applied by division by $[1-K(1-\alpha)]$, where $\alpha=bB/cC$, B and C being the number of atoms of radium-B and radium-C, and b and c their radioactive constants, respectively. At equilibrium $(1-\alpha)=0.735$. J. GRANT.

Quantum mechanics of radioactive nuclei. G. GAMOW and F. G. HOUTERMANS (Z. Physik, 1928, 52, 496—509).—Mathematical. From the point of view of Gamow's previous theory (this vol., 7) the disintegration constant of an α-radiator is calculated from the energy of the α-particle, the atomic number, and the characteristic nuclear radius. In each radioactive series the observed rate of disintegration of the emanations was assumed and hence the nuclear radius was calculated. Using these values the disintegration constants of the remaining α-ray emitters in the series could be calculated without any supposition as to the change of potential in the immediate neighbourhood of the nucleus. The results obtained are in approximate agreement with the experimental values. They are also compared with the values calculated from the Geiger-Nuttall relation. A qualitative view of the mechanism of radioactive disintegration is also developed.

J. W. SMITH.

Blue rock salt. K. PRZIBRAM (Nature, 1929, 123, 243).—Guthrie's observations (this vol., 168) confirm those of the author (Sitzungsber. Akad. Wiss. Wien, 1923, IIa, 132, 261), whose recent principal results concerning the coloration of salts are summarised.

A. A. ELDRIDGE.

Passage of α-rays through matter. S. ROSENBLUM (Ann. Physique, 1928, [x], 10, 408—471).—The effect of passage through matter on α-rays has been examined by the method of the magnetic field. The total distance traversed by α-rays from thorium-C' is equal to $36.3K$, where K is a constant characteristic of the metal and is a function of the atomic number of the metal. The power of various metals in stopping α-rays is found to be expressed by $N/\sqrt{N+4}$.

W. E. DOWNEY.

Positive ion currents in the positive column of the glow-discharge in the noble gases. W. UYTERHOEVEN (Proc. Nat. Acad. Sci., 1929, 15, 32—37).—Langmuir's method for the use of collectors in gas discharge was employed to study the positive column of the glow in neon, argon, and helium. The positive ion current increased with decrease of the potential of the collector, and there was a difference between the measured and calculated values of the

positive ion current amounting to one half of the former. A number of possible explanations of these discrepancies are summarised and discussed.

N. M. BLIGH.

Discharge of canal rays and the influence of metal walls. J. KOENIGSBERGER (Z. Physik, 1928, 51, 565—569).

Yield of H -particles. G. KIRSCH and H. PETTERSON (Z. Physik, 1928, 51, 669—695).—Elaborate experiments are described by means of which the authors have sought an explanation of the discrepancies in the yields of H -particles between their results and those of Bothe and Franz. It is claimed that the experiments establish that the scintillation counting method is free from the objection that β -particles may be confused with H -particles, and counter-objections are made to the Geiger counter method.

R. W. LUNT.

Passage of β -rays through matter. C. E. EDDY (Proc. Camb. Phil. Soc., 1929, 25, 50—61).—The form of the absorption curves of homogeneous β -rays in aluminium has been investigated by means of a Geiger counter. The main portion of the curve is linear with pronounced initial and final flattenings. Similar initial flattenings were found for copper and silver, but not for gold. The range of β -rays emergent at different angles has been determined, and it appears that the loss of range is due to the increased path consequent on scattering. Some evidence of the angular distribution of plurally scattered particles was obtained; also evidence of a most probable angle of scattering, similar to that found for α -rays by Geiger.

W. E. DOWNEY.

Light from hydrogen canal rays. B. DASANNA-CHARYA (Ann. Physik, 1929, [v], 1, 74—92).—A simple deduction is given of Wien's formula for the intensity of the positive-ray Balmer spectrum of hydrogen for equilibrium between rays and pressure in an observation space behind the cathode. A correction factor applicable to earlier work by the author (*ibid.*, 1925, [iv], 77, 613) is introduced. A new magnitude c_0 , the free path of the total disturbance in a collision, is introduced and values are calculated for H_β and H_γ and compared with those for H_α . It is calculated that the ratio of the intensities of the hydrogen lines is H_α/H_β , 8.4—21.5; H_β/H_γ , 4—5.8; and H_γ/H_β , 2.8—3.4.

R. A. MORTON.

Refraction of material waves from the point of view of special relativity theory. H. BAUER (Z. Physik, 1928, 52, 221—224).

Transference of energy in collisions between nuclei. W. KUHN (Z. Physik, 1928, 52, 151—155).—Mathematical.

Laws of scattering of canal-rays in their passage through solid bodies. C. GERTHSEN (Ann. Physik, 1928, [iv], 87, 1000—1002).—The units used in calculating the most probable angle of deflexion should not be rings of a plane as taken by Honma (A., 1926, 880), but spherical zones. On correction of that author's results in this way the resemblance obtained between these laws and the laws of scattering for α -particles disappears.

R. N. KERR.

Structure of the helium atom. J. STARK (Ann. Physik, 1928, [iv], 87, 927—934).—Consideration of the results of experiments on the splitting of helium lines in an electric field enables a generalisation to be made concerning the displacement of lines belonging to either an ortho series of one of the groups $2p^2$ or $2s$ or a para series of one of the groups $2P^2$ or $2S$. Measured with reference to a common zero, the displacement depends on the product of the field strength at the higher energy level of the emitting electron inside the atom, and a parameter characteristic of the atomic structure, whether the field is applied externally or is intrinsic. In the case of the helium atom the parameter is opposite in sign for the para and ortho cases. The parameter might describe the direction of rotation of the electron; this would then be opposite for para and ortho. The work is in agreement with a structure proposed earlier by Stark, and with the observations of Ishida and Kamijima on the splitting of helium lines.

A. J. MEE.

Isobaric elements. H. HERSZFINKEL (Naturwiss., 1929, 17, 50—51).—With reference to the work of Meitner (*ibid.*, 1926, 30, 719) it is pointed out that it is uncertain whether any neighbouring atoms are isobaric with caesium, so predictions cannot be made concerning its radioactivity. In the case of elements of medium at. wt. it is important whether the isobars are among the principal isotopes of their respective elements. Isobars of bromine and iodine certainly exist, and although these elements are practically non-radioactive it may be assumed that they possess a certain instability and may give rise to a β -ray change. Such changes would produce the inert gases krypton and xenon, which are much more readily detectable than, e.g., calcium, which is the product of the disintegration of potassium. Assuming the radioactivity of these elements to be one hundredth of that of potassium, it is calculated that compact bromine and iodine minerals 10^6 — 10^7 years old should contain 10^{-5} — 10^{-6} mg. of krypton or xenon per gram; this is quite a detectable amount.

J. W. SMITH.

Quantum theory of atomic disintegration. G. GAMOW (Z. Physik, 1928, 50, 510—515).—From the point of view of wave mechanics it is shown that atomic disintegration may be brought about by α -particles with an energy lower than the potential maximum of the atom struck. An upper limit is deduced for the amount of atomic disintegration produced in dependence on the energy of the α -rays and the nuclear charge of the scattered atom. The results obtained are in good agreement with practical data.

J. W. SMITH.

Fusibility and atomic number of the elements. P. VINASSA (Atti R. Accad. Lincei, 1928, [vi], 8, 121—125).—The ratio of the absolute fusion temperature of helium to its at. wt. is 0.5. Referred to this coefficient as unity the analogous ratios for the great majority of the elements are integers. Attempts have been made to correlate this regularity with the electronic configuration of the elements.

F. G. TRYHORN.

Electromagnetic equations in the quantum theory. C. G. DARWIN (Nature, 1929, 123, 203).—Mathematical.

A. A. ELDRIDGE.

Nuclear motions associated with electron transitions in diatomic molecules. E. U. CONDON (Physical Rev., 1928, [ii], 32, 858—872).—Theoretical. A mechanism for the direct dissociation of molecules by light absorption has been proposed by Franck (cf. A., 1925, ii, 1077), and extended by Condon to the theory of intensity distribution in band systems (cf. A., 1927, 89). Franck's postulate has been derived from the new quantum mechanics, and is here described, and discussed with reference to wave mechanics. It appears that Heisenberg's indetermination principle gives the clue to the inexactitude of the earlier method of predicting electron transitions and intensities based on Franck's postulate, since its strict application calls for a violation of the principle. The quantum-mechanical formula is applied, for the halogens, to the continuous spectrum accompanying molecular dissociation, and additional applications to band systems are made. The existence of an entirely new type of band spectrum due to the wave nature of matter is predicted, and the interpretation of Rayleigh's mercury band at 2476—2482 Å. (cf. A., 1928, 806) as of this type is suggested. It is shown that although Franck's postulate is also true for electron jumps in atoms, it is of minor interest because its inexactitude is much greater for the electrons than for the heavy nuclei.

N. M. BUGH.

Molecular constants of hydrogen. H. H. HYMAN and R. T. BIRGE (Nature, 1919, 123, 277—278).—New observations show that the $B-A$ system bands consist of R and P branches only. A complete verification of the combination principle has been obtained. For the zero vibrational level of the B state, it is computed that $B_0 = 19.46 \pm 0.04$, whence $I_0 = 1.423 (\pm 0.003) \times 10^{-40}$ g.cm.², a value of the moment of inertia which is considered to be trustworthy.

A. A. ELDRIDGE.

Intensity measurements in the secondary spectrum of hydrogen. II. W. KAPUSCINSKI and (Miss) J. G. EYMERS (Proc. Roy. Soc., 1929, A, 122, 58—68).—An extension of previous work (Ornstein, Kapuscinski, and Eymers, A., 1928, 678). The intensities of 1427 lines in the secondary spectrum of hydrogen have been determined over the region 3652 to 6441 Å. The whole spectrum was taken at a pressure of hydrogen of about 0.17 mm., the times of exposure ranging from $\frac{1}{2}$ min. to 5 hrs. It was found that, on taking several photographs on the same plate, only differing in time of exposure, the ratios of the intensities of the lines on each pair of photographs were dependent on the density. A correction was made for this phenomenon, which is probably due to "developer-effects," causing the density curves (obtained by means of continuous density marks) to have a too small inclination at high intensities and a too large inclination at lower intensities.

L. L. BIRCUMSHAW.

Interpretation of the atmospheric absorption bands of oxygen. R. S. MULLIKEN (Physical Rev., 1928, [ii], 32, 880—887).—Theoretical. The atmospheric oxygen absorption bands can be attributed to a $^3S \rightarrow ^1S$ transition from the normal 3S to a metastable excited state of O_2 . This accounts for all the

strong lines and explains missing lines, without conflict with existing theory. Certain very weak series are, however, not yet explained. Of the three rotational levels for each value of j_k in the 3S normal state, the two for which $j = j_k \pm 1$ show only a very small separation, which increases slowly with j_k , whilst the third is separated from the other two by an interval of about two wave numbers which does not change with j_k . The 3S and 1S states involved in the atmospheric bands are probably both due to the same electron configuration (cf. A., 1928, 1067). If so, it is likely that a metastable 1D state derived from the same configuration also exists, and that infra-red atmospheric bands corresponding with the transition $^3S \rightarrow ^1D$ should be found.

N. M. BUGH.

Infra-red emission spectra of Bunsen and allied flames. C. R. BAILEY and K. H. LIH (Trans. Faraday Soc., 1929, 25, 29—32).—Using a rock-salt prism spectrometer the emission spectra of the Bunsen and Méker flames have been examined in the infra-red (1—7 μ) and compared with those of the carbon monoxide, hydrogen, and methane flames. Particular attention was paid to constancy of atmospheric temperature and of source of radiation. The more important maxima in the flame spectra are tabulated. The ratio of the intensities of radiation from the two most prominent bands at 4.46 and 2.8 μ varies greatly from flame to flame. Measurements of the spectra from known mixtures of carbon monoxide and hydrogen show that this ratio passes through a maximum at about 10% of hydrogen and falls to zero for the hydrogen flame.

O. J. WALKER.

Infra-red emission spectra of separated cones in methane and Bunsen flames. C. R. BAILEY and K. H. LIH (Trans. Faraday Soc., 1929, 25, 32—36).—By means of a modified Smithells separator provided with a rock-salt window the emission spectra of the inner and outer cones of the methane and Bunsen flames have been examined in the region 0.5—8 μ . The radiation from the outer cone is more intense in spite of its lower temperature. There is no trace of emission from new-formed molecules of carbon monoxide in the inner cone, but the water-vapour spectrum is much more prominent than in the outer cone. A band in the Bunsen and inner cone flames of methane at 3.35 μ is attributed to thermal emission from heated methane.

O. J. WALKER.

Infra-red emission spectra of flames in nitrous oxide. C. R. BAILEY and K. H. LIH (J.C.S., 1929, 51—56).—Examination of the infra-red emission spectra of flames of hydrogen, carbon monoxide, and coal gas in nitrous oxide supports the assumption that, as far as the end-products are concerned, the combustible gas burns in oxygen furnished by the decomposition of nitrous oxide. Hydrogen presents anomalous features in that, whilst carbon monoxide and coal gas give the same spectra whether they are mixed with nitrous oxide or burned directly in an atmosphere of it, the spectra obtained from hydrogen differ in the two cases. Further, the spectrum obtained by burning hydrogen directly in an atmosphere of nitrous oxide is different in type from those obtained with carbon monoxide and coal gas. The new spectrum

is attributed to some form of stimulation by the burning hydrogen molecules.

F. J. WILKINS.

Absorption of ultra-violet light by liquid carbon dioxide. G. HARIQ (Physikal. Z., 1929, 30, 8—20).—A method has been devised for the quantitative determination of the absorption spectra of liquefied gases, using high pressures and temperatures and small thicknesses of liquid. Carbon dioxide, whether liquid or gaseous, is quite transparent to visible light; the gas under ordinary conditions shows no measurable absorption of wave-lengths greater than 2195 Å., in agreement with Kreusler (Ann. Physik, 1901, [iv], 6, 412). Liquid carbon dioxide, however, absorbs in the region 2195—2552 Å. about 10^3 times as strongly as the gas at the same pressure. The data are interpreted by assuming the existence of two kinds of carbon dioxide molecules, differing widely in absorptive power, the "gas" molecules showing negligible absorption, whilst the molecular species present in the liquid shows a broad absorption band with a maximum near 2265 Å., and a second weaker band with maximum at 2435 Å. Both types of molecules can exist in the supercritical state, the reversible transformation occurring at the points where the isotherms and isobars intersect. The absorptive power of the liquid remains about the same at constant temperature, although the pressure may vary, but near the critical temperature a very sudden, but not discontinuous, change occurs.

R. A. MORTON.

Band spectrum of lanthanum oxide. R. MECKE (Naturwiss., 1929, 17, 86—87).—Seven band systems at 4372, 4418, 5600, 7380, 7403, 7877, and 7910 Å. have been observed and ascribed to lanthanum oxide.

W. E. DOWNEY.

Change in the cathode-rays spectrum of nitrogen by cooling with liquid air. J. AARS (Ann. Physik, 1929, [v], 1, 216—228).—Investigation of bands belonging to the second positive system of N_2 and the negative band system of N_2^+ shows that, under the conditions obtaining in the work, the distribution of line intensities depends solely on the temperature and not on pressure or on the velocity of the cathode rays.

R. A. MORTON.

Absorption spectrum of vitamin-D. T. A. WEBSTER and R. B. BOURDILLON (Nature, 1929, 123, 244).—The observation that irradiation of ergosterol produces three substances in succession is confirmed; the first shows intense absorption at 2500—2900 Å. and great antirachitic power, the second shows intense absorption at 2400 Å. and no antirachitic power, whilst the final product (or products) shows no absorption and has no antirachitic power. Intensity of absorption of irradiated ergosterol between 2700 and 2900 Å. is parallel with its antirachitic activity; moreover, further irradiation of such solutions with exclusion of radiation of wave-lengths less than 2600 Å. affords a product showing intense absorption at 2400 Å., but no antirachitic activity.

A. A. ELDRIDGE.

Structure and activation of the molecules of aliphatic aldehydes. I. Analysis of the spectrum of the vapour of formaldehyde. S. A. SCHOU (J. Chim. phys., 1928, 25, 665—721).—The absorption spectrum of formaldehyde in the gaseous

state has been measured by means of two quartz spectrographs of high dispersion. For a concentration of vapour of 60 mg. per litre the spectrum consists of 35 bands between 3700 and 2500 Å. The intensity of these bands varies periodically throughout the range of wave-length. The bands consist of large numbers of fine lines arising from rotation of the molecule. The structure of each band in the middle and in the part nearest the visible is very complicated, but towards the ultra-violet both the distribution and intensity of the lines show a distinct regularity. The band in this part is made up of two series of lines and this double structure is attributed to the molecule of formaldehyde having a rotation about two axes, the first a line joining the carbon and oxygen atoms and the second a line perpendicular to this. The theoretical formula for a molecule of this type having two different moments of inertia has been worked out from the quantum theory and good agreement is obtained between the wave-lengths of the lines calculated from it and the observed values.

R. N. KERR.

Infra-red arc spectra. H. AUERBACH (Naturwiss., 1929, 17, 84—85).—A group of bands believed to be due to lanthanum oxide has been observed between 7876 and 8638 Å.

W. E. DOWNEY.

Absorption spectra of certain organic liquids in the near infra-red. J. W. SAPPENFIELD (Physical Rev., 1929, [ii], 33, 37—47).—Absorption spectra were studied from 0.8 to 2.5 μ with an accuracy of 0.002 μ for nine alcohols, six esters, two ethers, two aldehydes, and five other organic liquids, and the bands tabulated and plotted. The sources of absorption and relative intensities of the band heads are discussed. An attempt is made to obtain a relation between different band heads of a particular compound. The anharmonic oscillator and a relation due to Gapon (cf. A., 1927, 1007) modified to $\nu_n = \nu_0/(n)^{1/2}$ were applied with moderate success.

N. M. BLIGH.

Combination frequencies of the infra-red bands of quartz. E. K. PLYLER (Physical Rev., 1929, [ii], 33, 48—51).—Two new bands at 2.72 and 3.18 μ have been found. By combining the frequencies, assumed to be fundamental, of bands at 9, 12.5, 20, and 26 μ , six bands in the region 3—9 μ in addition to the new bands are accounted for. This gives a total of eleven absorption bands, the remainder being at 2.96, 3.75, 4.10, 4.35, and 8.40 μ , for the ordinary ray of quartz, the frequencies agreeing, with only small differences, with the calculated values.

N. M. BLIGH.

Absorption spectra and fluorescence of fats. W. SPROESSER.—See B., 1929, 101.

Energies of dissociation of cadmium and zinc molecules. J. G. WINANS (Nature, 1929, 123, 279).—The difference in energy between the limiting band at 2212 Å. and the atomic line at 2288 Å. gives the value 0.200 volt for the energy of dissociation of the normal Cd_2 molecule. The value for Zn_2 is 0.246 volt.

A. A. ELDRIDGE.

Diffraction of X-rays by aqueous solutions of sucrose, lævulose, and dextrose. P. KRISHNAMURTI (Indian J. Physics, 1928, 3, 209—223; cf. A., 1928,

1079).—Dilute solutions give an outer ring due to the water, and a corona surrounding the central spot, due to relatively intense scattering at small angles, and increasing in intensity with increasing solution concentration. The corona is attributed to molecules of the solute distributed at random in the solvent, thus giving direct experimental verification of the well-known analogy between the gaseous and dissolved states as deduced by van 't Hoff. At higher concentrations the corona develops into a halo on account of a diminution of the intensity of scattering at small angles, and interpreted as due to the molecules acquiring a roughly uniform spatial arrangement. As concentration increases the halo develops into a ring of increasing diameter, the pattern ultimately resembling that for the powder. The angular radius of the disc round the central spot is a measure of the average size of the dissolved molecule. The influence of the hydration of the molecules is considered.

N. M. BLIGH.

Continuous spectrum of mercury. J. K. ROBERTSON, K. A. MACKINNON, and W. H. ZINN (J. Opt. Soc. Amer., 1928, 17, 417–427).—Two methods for producing the continuous spectrum are described. In the first a drop of mercury was caused to move to and fro in an evacuated cylindrical quartz tube which was heated by a small electric oven. The intensity of the glow increased as the temperature was raised, reaching a maximum at about 200° and finally disappearing at red heat. Three characteristic bands were observed, two broad and with maxima at about 4600 and 3340 Å., respectively, and one narrow band ending abruptly at 1942 Å. A method is also described for producing the continuous spectrum by means of an electrodeless discharge. The appearance of the spectrum at various temperatures is described. In general the same three bands as before were found and in some cases also one at about 2650 Å. The origin of the spectrum is discussed and it is concluded that it is molecular.

J. L. BUCHAN.

Band spectra of the alkaline-earth halides.
I. Calcium fluoride, strontium fluoride. II. Barium fluoride, magnesium fluoride. R. C. JOHNSON (Proc. Roy. Soc., 1929, A, 122, 161–188, 189–200).—I. An extension of Mecke's work (A., 1927, 495). The whole of the known band spectra of the fluorides of calcium and strontium have now been completely analysed and ordered in regard to their gross structure. A re-measurement of about 250 band-heads has been made from first-order plates taken on a 21-foot Rowland grating, and the sequences have been fitted to cubic formulæ by the method of least squares. A notable feature of these spectra is the existence of unusually prolonged sequences in which the lines are packed close together. The sequence $\Delta n=0$ is always dominant, and $\Delta n=\pm 1$ sometimes occur but are much weaker. This is explained by the fact that the vibration frequencies in the initial and final states of the molecule differ very little. The characteristic "tail" phenomenon exhibited by many of the sequences has been shown to accord with theoretical expectations. In each case the molecules give rise to at least three band systems, one in the ultra-violet, one in the green, and one in the

orange. The first two groups are degraded to the red side and the third to the violet. They appear to arise from the electronic transitions $3^2S \rightarrow 1^2S$, $2^2S \rightarrow 1^2S$, and $2^2P \rightarrow 1^2S$, respectively. All the systems exhibit minor doublet intervals due to the presence of *Q* branches, and the *Q* heads are always stronger than the associated *P* or *R* heads. Several exceptional features are observed, such as the occurrence of strong *Q* branches in $2^2S \rightarrow 2^2S$ transitions, and a definite discrepancy in (n'') as evaluated from $2^2S \rightarrow 2^2S$ and $2^2P \rightarrow 2^2S$ systems. Applying the methods of Birge and Sponer (A., 1926, 993), the energy of dissociation of the CaF molecule, evaluated from the vibrational structure of the various electronic levels, has been found to be approximately 3.36 volts (77460 g.-cal.), and that of SrF is of the same order. The value found gives a satisfactory explanation, in the case of CaF, of the sudden fall of intensity and termination of the *B*₁ sequence with the 20th member.

II. A quantum analysis has been made of the gross structure of the band spectra of barium and magnesium fluorides, and for BaF new measurements have been made from first-order plates taken on a 21-foot Rowland grating. In the case of magnesium fluoride, Datta's experimental data (cf. A., 1921, ii, 529) have been used. The familiar BaF bands in the green region are believed to represent two systems, arising respectively from the electronic transitions $2^2S \rightarrow 1^3S$ and $3^3D \rightarrow 1^3S$. A number of bands measured by George (A., 1913, ii, 646) and attributed by him to barium oxide have been analysed, and their final state has been identified with that determined for BaF, thus proving their fluoride origin. This system is attributed to the transition $2^2D \rightarrow 1^2S$, since it is found in about the expected region and has the same structural characteristics as the $3^2D \rightarrow 1^2S$ transition. The suggested $2^2D \rightarrow 2^2S$ transitions are discussed; they are believed to be new to band spectra. The system $2^2P \rightarrow 1^2S$, which is so dominant in CaF and SrF, is unrecorded in BaF. It is possible that the 2^2P level lies below the 2^2D level in the BaF molecule. The recorded emission bands for MgF constitute a $2^2P \rightarrow 1^2S$ system in which $\Delta 2^2P=18.6v$. The vibrational constants for these two states are given. Evidence of the vibrational isotope effect occurs in the *D*₁ sequence, and the theoretical value of the isotope coefficient, calculated on the basis of two isotopes of magnesium of masses 24 and 25, agrees satisfactorily with the experimental value.

L. L. BIRUMSHAW.

Band spectra associated with zinc, cadmium, and mercury. J. M. WALTER and S. BARRATT (Proc. Roy. Soc., 1929, A, 122, 201–210; cf. A., 1928, 812).—With the view of determining the origin of the extensive band systems ascribed to zinc, cadmium, and mercury (cf. Mohler and Moore, A., 1927, 917), the vapours of these metals have been examined spectroscopically, using the apparatus previously described (*loc. cit.*). Criteria are given for true metal spectra, and the non-metallic origin of most of the spectra under investigation was proved by observing their total disappearance on the introduction of a trace of sodium or potassium vapour into the absorbing column. This indicated that the molecules responsible for the repressed bands contained electronegative

elements, and the impurities were identified by increasing the quantity of each probable electro-negative element in turn until every one of the band spectra had been obtained in an enhanced form. It was thus found that the majority of the supposed band spectra of zinc and cadmium (with the exception of two weak and diffuse bands, one at 2212 Å. for cadmium and one at 3050 Å. for zinc), and one band system previously attributed to mercury (3000—2750 Å.), were probably oxide and chloride spectra. There is, however, no doubt that mercury vapour contains diatomic molecules. The bromides of the three metals and the iodide of cadmium all yield absorption band systems analogous to the chloride bands.

L. L. BIRCUMSHAW.

Band systems of the fluorides of beryllium and magnesium. W. JEVONS (Proc. Roy. Soc., 1929, A, 122, 211—227).—Evidence is cited in support of the following interpretation of the band-heads of the BeF doublet system, those in parentheses being missing: $R_2, R_1, Q_2, (Q_1)$, with a doublet separation of the order $R_2 - R_1 - 3 \text{ cm.}^{-1}$, rather than $R_2, Q_2, (R_1), Q_1$, with a separation $Q_2 - Q_1 = \text{about } 35 \text{ cm.}^{-1}$, as suggested by Mulliken (cf. A., 1926, 8). With this interpretation there is now a steady increase of the origin separations $\Delta\nu$, with the number of electrons in the alkaline-earth fluoride molecules BeF to BaF. The spectra given by the flame surrounding the arc between carbon poles fed with several beryllium salts have been examined under varying conditions. With the fluoride, for a few minutes after charging the arc is surrounded by a yellow flame, showing the band systems of both BeO and BeF, the latter being specially well developed. Subsequently a bright blue flame appears, with the visible BeO system strongly developed and scarcely a trace of the BeF system, and the region between the CN λ 3590 sequence and the 0 sequence of the BeF system is now occupied by a new set of bands which, like the BeF bands, are also degraded towards the red. Other beryllium salts tested give similar results, although less satisfactorily. The new bands do not form a number of regular sequences such as characterise the known band systems of diatomic emitters, but they occur in separate groups not wholly unlike those sequences. The emitting molecule is considered to be either an oxide or a fluoride of beryllium, possibly BeO or BeF₂. No bands attributable to BeCl and no further bands of BeF have been detected. The data for the BeO band-system are extended by the recognition of four bands of the hitherto unrecorded sequence $n'' - n' = -2$, of which the strongest band-head occurs between the λ 4216 and 4197 heads of the CN violet system. With magnesium fluoride in the carbon arc in air the outer flame develops, in addition to the MgF doublet system, a new more refrangible system of three sequences of bands degraded to the further ultra-violet from heads at 2741.6, 2689.3, and 2636.4 Å., respectively, the middle sequence being the strongest. The heads appear single under the dispersion used. P -head data and n', n'' values are tabulated for the new system, which is also due to MgF, and may have for its final state the initial state for the doublet system. If $-P \rightarrow {}^2S$ is assumed for the doublet system, the

new system may be ${}^2P \rightarrow {}^2P$. The spectrograms of the new system show no evidence of the vibrational Mg-isotope effect.

L. L. BIRCUMSHAW.

Structure of the violet bands of silicon nitride. F. A. JENKINS and H. DE LASZLO (Proc. Roy. Soc., 1929, A, 122, 103—121; cf. Mulliken, A., 1925, ii, 1020).—The spectrum of the luminescence produced when silicon tetrachloride vapour reacts with glowing active nitrogen has been investigated, using an instrument of high resolving power. The wave-numbers (in vacuum) of the lines of the ten strongest bands due to the molecule containing the most abundant isotope, Si²⁸N, are tabulated. The line structure of the bands is in accord with that to be expected for a ${}^2S \rightarrow {}^2S$ system. One line is missing at the origin, and the members of each branch are resolved into narrow doublets at higher rotational quantum numbers. The components of these doublets are in general of equal intensity. Several interesting perturbations occur, as in the analogous CN bands, which usually take the form of an exceptionally wide or narrow doublet, and faint satellite lines are often visible in the immediate neighbourhood of the perturbed line. These irregularities are connected in every case with the initial electronic state. One of them is of a new type, and suggests an intimate connexion between the perturbations and the rotational doubling. The combination relations between P and R lines are applied to find the term differences, from which the rotational constants are evaluated. The moment of inertia of the vibrationless molecule is found to be 38.29 and $37.89 \times 10^{-40} \text{ g.cm.}^2$ in the initial and final states, respectively. Assuming this molecule to be Si²⁸N, the corresponding internuclear distances are 1.576 and $1.568 \times 10^{-8} \text{ cm.}$ Accurate values are obtained for the band origins, and an equation is derived from these, giving the vibrational energy in the initial and final states. The isotope effect is well marked for Si²⁸N, Si²⁹N, and Si³⁰N. From this effect in three bands of the strongest sequence, quantitative evidence is adduced in support of the quantum mechanics formulation for the vibrational energy, which is developed in powers of $(n + \frac{1}{2})$.

L. L. BIRCUMSHAW.

Excitation of solid bodies by slow-speed electrons. S. ZIEMECKI (Bull. Acad. Polonaise, 1928, A, 367—375).—The cathodo-luminescence of calcium oxide, zirconium oxide, calcium sulphide, willemite, and a samarium preparation has been examined using slow-speed electrons. The excitation potentials are found to be of the same order as the excitation potential of gases.

W. E. DOWNEY.

Absorption of ultra-violet light by the inversion products of sucrose. L. KWIECŃSKI and L. MARCHLEWSKI (Biochem. Z., 1929, 204, 192—196).—See this vol., 9.

Energy increase in elementary processes. H. BEUTLER and B. JOSEPHY (Z. physikal. Chem., 1928, 139, 482—496).—A study of energy exchange between activated atoms and molecules. The fluorescence of irradiated mercury vapour to which nitrogen has been added shows spectrum lines derived from atoms containing double the energy of metastable mercury atoms; this corresponds with $A^* + A^* = A^{**} + A$.

The chemiluminescence produced in the reactions $\text{Na} + \text{HgCl}_2$, $\text{Na} + \text{Cl}_2$, and $\text{K} + \text{Cl}_2$ has been studied. Mercury vapour was added and the spectrum obtained showed the presence of mercury atoms of greatly increased energy, the amount being characteristic of each reaction. It is shown that the energy change may be represented by $A^* + A^* + B = B^{**} + 2A$. Evidence of the transfer of energy from several molecules to a single atom has also been obtained.

R. N. KERR.

Alkali halide phosphors containing copper. A. M. MACMAHON (Z. Physik, 1928, 52, 336—341).—Sodium chloride and potassium chloride phosphors containing copper as the active cation are rather unstable when the lattice is strongly mechanically disturbed by high copper concentration. The excitation bands show a strong depression after some time. The influence of cooling on the absorption bands of phosphors containing copper is generally similar to that in the case of phosphors containing thallium and lead (cf. Lorenz, A., 1928, 347). It was found, however, that the relatively broad bands emitted by phosphors containing copper were split up on cooling into two or three components. The narrowing of the band widths by cooling is not always associated with a rise in the absorption constant at the maximum. In sodium chloride phosphors the bands were both narrower and less intense on cooling.

J. W. SMITH.

Structure of colouring matter. N. NYBERG (Z. Physik, 1928, 52, 406—419).—A new theory is given of the structure of pigments, based on Helmholtz' theory of light sensitivity. Ostwald's theory of colour is criticised mathematically.

J. W. SMITH.

Electronic states and band spectrum structure in diatomic molecules. VII. $^2P \rightarrow ^2S$ and $^2S \rightarrow ^2P$ transitions. A correction. R. S. MULLIKEN (Physical Rev., 1928, [ii], 32, 997; cf. A., 1928, 1166).

N. M. BLIGH.

Visible absorption bands of colourless liquids and their relation to infra-red bands. J. W. ELLIS (Physical Rev., 1928, [ii], 32, 906—912).—The absorption of ten representative organic liquids, hexane, cyclohexane, benzene, toluene, *m*-xylene, chlorobenzene, chloroform, acetone, ethyl acetate, and aniline, was studied in the visible spectrum by photographic means, with cell-lengths up to 6½ metres. The effect of unsaturation and substitution in the molecule was examined. The near infra-red spectra of these substances was obtained. A good correlation of the bands of the two regions has been secured. The bands of the visible region seem to be higher members of series previously detected in the infra-red.

N. M. BLIGH.

Infra-red absorption spectra of the methyl halides. W. H. BENNETT and C. F. MEYER (Physical Rev., 1928, [ii], 32, 888—905).—The molecules are considered as symmetrical tops having one low moment of inertia. Two types of bands are expected, arising from vibration parallel to and perpendicular to the axis of symmetry, \parallel and \perp bands, respectively. The appearance of each type is described. There are seven bands for each of the four compounds. The

twenty-eight bands fall into seven series, *A* to *G* inclusive. Two of the four bands of series *A* lie beyond the range of observation. Series *A*, *C*, *E*, and *F* are made up of bands of the \parallel type, and series *B*, *D*, and *G* of the \perp type. The series converge towards the known bands of methane with decrease in the atomic weight of the halogen in the halide. The envelopes of the \parallel type bands show the existence of *P*, *Q*, and *R* branches. With the possible exception of the chloride, the doublet separations for the various bands of the same compound appear to be the same, increasing from compound to compound with decreasing atomic weight of the halogen in the halide. The methyl fluoride *A* series band has been resolved and the *P* and *R* branches have been shown to consist of a single series of lines. Strong convergence in the spacing is present. The bands of the \perp type have all been resolved. Every third line is more intense than the others. The spacing converges in series *B* towards lower frequencies, and in series *D* and *G* towards higher frequencies. The mean frequency intervals from band to band of the same compound show a marked and unexplained variation. N. M. BLIGH.

Red band system of sodium. F. W. LOOMIS and S. W. NILE, jun. (Physical Rev., 1928, [ii], 32, 873—879).—The red band system of Na_2 is found to extend into the infra-red, and terminates in a fairly sharp edge at 8150 Å. This edge, which is not an ordinary convergence limit, can be explained by an unusual distribution of intensities of vibrational transitions which can be deduced from the Franck-Condon theory of intensity distribution, when account is taken of the shape of the potential energy curves as dissociation is approached. The same theory explains a head of the red system in the yellow-green, the reappearance of the orange cathode-ray fluorescence series in the infra-red, and the observed asymmetry in the two branches of the Condon parabola.

N. M. BLIGH.

Photosensitised band fluorescence of OH, HgH, NH, H₂O, and NH₃ molecules. E. GAVIOLA and R. W. WOOD (Phil. Mag., 1928, [vii], 6, 1191—1210).—A more detailed study of [the photosensitised band fluorescence previously examined by Wood and Gaviola (A., 1927, 1117, etc.) has been made. The fluorescence of HgH, OH, NH, Hg-H₂O, and Hg-NH₃ molecules has been observed and the conditions for the exhibition of the various bands and the most probable chemical processes causing them have been suggested. The concentration of OH and NH in the fluorescence tube is, under the best conditions, of the same order as that of excited mercury atoms (10^{-5} mm.). The dissociation energy of a water molecule into H^+ and OH^- is probably about 5.2 volts and not less than 4.9 volts as given by Senftleben and Rehren (cf. A., 1926, 768), whilst the corresponding dissociation energy of the nitrogen molecule is approximately 9.8 volts and not 11.4 volts as calculated by Spöner and Birge. Collisions of excited mercury atoms in the resonance level 2^3P_1 with normal water vapour molecules may lead to three different results. In most cases the mercury atom is reduced to the metastable 2^3P_0 level, in about 1 per 10,000 collisions the water molecule is disso-

ciated to H^+ and OH^- , and in less than 1 per 1000 collisions a quasi-molecule $Hg-H_2O$ is formed which emits the continuous band at 2800 \AA . when dissociating. Such collisions with nitrogen molecules reduce the mercury atoms to the metastable state, whilst collisions of two such mercury atoms with nitrogen molecules may give dissociation of the nitrogen molecule.

A. E. MITCHELL.

Deterioration of quartz mercury-vapour lamps and the luminescence of fused quartz. A. E. GILLAM and R. A. MORTON (Phil. Mag., 1928, [vii], 6, 1123—1132).—The factors operating in the deterioration of quartz mercury-vapour lamps are found to be a shortening of the spectrum confined to the extreme ultra-violet and a non-selective loss in transmission. The first factor exhibits itself in a rapid fall in output and preponderates for the first 150—200 hrs. of use. It is suggested that it is due to the formation of silicon monoxide vapour within the lamp. The second factor manifests itself more slowly, but plays an increasingly important part in the subsequent history. Its origin is suggested in the gradual deposition of a film of opaque elementary silicon. No exact connexion between this deterioration and the luminescence properties of fused quartz has been found. Transparent fused quartz has been shown to exhibit three types of luminescence: a brief visible phosphorescence, a phosphorescence of long duration, and a thermoluminescence, the origin of which is attributed to traces of impurities in the material.

A. E. MITCHELL.

Relation between luminosity and concentration in luminescent solid solutions. J. EWLES (Proc. Leeds Phil. Soc., 1929, 1, 341—345).—The relation between the intensity of luminescence of a solid solution of bismuth oxide in calcium oxide, illuminated by a mercury-vapour lamp, and the concentration of the solution has been studied. On the assumption that a luminescent solid solution consists of a number of active particles distributed in accordance with the laws of chance in a transparent lattice, and that the luminescent centre consists of one atom of an active metal associated with a definite number (n) of lattice points (this number being characteristic of a given band), the expression $I = Ace^{-nc} + Bce^{-nc} + \text{etc.}$ is deduced, where I —intensity of luminescence, $c = N/M$ —the atomic concentration, and A and B are constants (cf. Bruninghaus, Compt. rend., 1909, 149, 1375). In the example studied the observed points lie closely on the theoretical curve so plotted ($A = 2.34 \times 10^4$, $B = 1.58 \times 10^3$, $n_1 = 5012$, $n_2 = 331$) which shows two maxima (at $c \text{ Bi/Ca } 0.03233$ and 0.034000). The range of action of the first centre extends across about 11 unit cells and of the second across 4—5 unit cells each way.

J. W. BAKER.

Phosphorescence of fused quartz. A. C. BAILEY and J. W. WOODROW (Phil. Mag., 1928, [vii], 6, 1104—1107).—Many samples of fused quartz are shown to possess the property of phosphorescence, emitting phosphorescent radiation when heated after illumination by ultra-violet light. Heating at a red heat completely deactivates the material. Quartz crystals may be made to exhibit the phenomenon after being heated slowly to 1600° . Similar phos-

phorescent activity is exhibited by pyrex glass, calcite, and fluorite, but not by gypsum.

A. E. MITCHELL.

Phosphorometer for the rapid measurements of the intensities of phosphorescences. R. COUSTAL (Compt. rend., 1929, 188, 326—327).—The intensity or decrease of phosphorescence of the substance to be examined is matched by means of mixtures, in known proportions, of varying amounts of two zinc sulphides from the same batch, of which one only has been rendered phosphorescent. The surface densities of such mixtures are proportional to the concentrations of the active sulphide. The intensities of phosphorescence show the same rates of decrease with time and the Güntz formula was confirmed.

J. GRANT.

Raman effect in quartz. M. CZERNY (Naturwiss., 1929, 17, 12—13).—The transmissibility of quartz in the long-wave infra-red has been determined by means of a grating spectrometer, and absorption was found at 38 and 78μ as is required by the Raman effect. There is no anomaly in the transmissibility curve at 48μ which others appear to have observed. There is considerable deviation between the relative intensities of the infra-red absorption bands and the corresponding Raman lines. According to Pringsheim and Rosen the Raman lines corresponding with 80 and 48μ should be equally strong, and the 38μ line weaker, but it is found that in the infra-red spectrum the 38μ band is apparently stronger than the 80μ band, whilst the 48μ band is so weak that it is not measurable.

A. J. MEE.

Secondary radiations in the molecular diffusion of light (Raman effect). P. DAURE (Compt. rend., 1929, 188, 61—62).—Solutions of antimony chloride in hydrochloric acid show Raman spectra, in which the lines spread out with increasing dilution so that beyond the dilution of 50% the b band is completely covered by the a band, and the spectrum is comparable with that of dissolved bismuth trichloride. Aqueous solutions of magnesium or aluminium chloride, of calcium bromide, or of liquid oxygen showed no Raman effect, whilst liquid ammonia and methane gave wide bands and a single fine line, respectively.

J. GRANT.

Production of new radiations by light scattering. I. C. V. RAMAN and K. S. KRISHNAN (Proc. Roy. Soc., 1929, A, 122, 23—35).—Further studies have been made on the radiations previously described (A., 1928, 1075). Spectrograms are reproduced of the scattering of monochromatic light by benzene, toluene, and carbon tetrachloride. The characteristic infra-red frequencies of the molecules, calculated from the frequencies of the modified lines, are in satisfactory agreement with the values obtained from direct measurements of infra-red absorption. Whilst most of the modified lines have frequencies lower than the exciting line, there appear in all three spectrograms (and particularly conspicuously in that of carbon tetrachloride) some relatively feeble lines of which the frequencies exceed that of the exciting line by an infra-red frequency of the molecule. It is considered that the existence of these lines of enhanced frequency yields the first direct experimental proof of induced

emission (or negative absorption) of radiation by molecules. A visual examination with a direct-vision spectroscop of benzene, toluene, and some other liquids showed a nebulosity or continuous spectrum accompanying the prominent lines in the scattered spectrum, extending unsymmetrically on the two sides of the exciting line. Its origin is discussed; it is possibly due to a combination of the rotational frequencies of the molecule with the frequency of the incident radiation. The modified radiations scattered at 90° exhibit striking polarisation, the lines corresponding with different frequency shifts being polarised to different extents. The intensity of the weaker component varies from almost zero to about 40 or 50% of that of the stronger line. The negative lines (of enhanced frequency) are polarised to the same extent as the corresponding positive lines. A tentative explanation of these results is suggested. The usefulness of light-scattering as a convenient and accurate method of exploring molecular spectra is indicated, and some preliminary remarks are made with regard to the dependence of the intensity of the modified radiation on the wave-length of the exciting lines.

L. L. BIRCUMSHAW.

Raman spectra for certain substances. M. KIMURA and Y. UCHIDA (Japan. J. Physics, 1928, 5, 97—101).—The Raman spectra have been examined for commercial xylene, calcite, water, and salts of neodymium. Tables are given showing the wave-lengths of the Raman lines and the calculated infra-red absorption bands derived from them.

J. L. BUCHAN.

Raman lines under high dispersion. R. W. WOOD (Phil. Mag., 1928, [vii], 6, 1282—1283).—Previous work (A., 1928, 1306) has been extended by photographing the spectra scattered by benzene and carbon tetrachloride under very high dispersion. The line at 4618 \AA. , excited by the mercury line 4046 \AA. , is shown to be a strong line about 1 \AA. wide with a faint line 2.5 \AA. wide close to it on the violet side. The wave-lengths of the strongest Raman lines of benzene are 4686.74 , 4682.11 , 4659.30 , 4618.36 , 4554.87 , 4525.0 , and 4476.0 \AA. It is concluded that the high resolving powers employed are not necessary owing to the considerable width of most of the lines. The range of frequencies covered by the benzene line 4554.87 \AA. , when translated into the range of the corresponding infra-red absorption band, gives one very much narrower than that observed by Coblentz close to 10μ .

A. E. MITCHELL.

Raman effect with hydrogen chloride; the "missing line." R. W. WOOD (Nature, 1929, 123, 279).—With hydrogen chloride at 100° and at atmospheric pressure a modified line of wave-length 4581 \AA. , presumably excited by the mercury line 4046 \AA. , was observed. The frequency difference corresponds with the frequency in the infra-red which would represent a line at 3.47μ . The line thus appears to be the "missing line" corresponding with a vibration transition unaccompanied by change of rotation, which does not appear in the absorption spectrum of the gas.

A. A. ELDRIDGE.

Breadth of the spectral lines of the Raman scattered radiation of benzene. W. GERLACH

(Ann. Physik, 1929, [v], 1, 301—308).—The Raman effect results in new diffuse lines and also in a definite broadening of some lines which are scattered without large change of frequency. This broadening occurs on both the long-wave and short-wave sides of the lines. The breadth and structure of scattered lines of both types have been determined for benzene. Different scattering processes are possible, an incident frequency ν_0 giving a Raman line $\Delta\nu'$ and differences $\pm\Delta\nu_1''$, $\Delta\nu_2''$, . . . accounting for the breadths of the modified and "unmodified" lines. The results permit the breadth of an infra-red band to be determined; e.g., a benzene band near 3μ would be 0.2μ wide, in accordance with experience. Infra-red bands of benzene would appear not to be made up of unresolved neighbouring similar bands, but rather to be governed by a central frequency increased or decreased by a number of secondary frequencies.

R. A. MORTON.

Raman effect with alcohols. S. VENKATESWARAN and A. KARL (Z. physikal. Chem., 1928, B, 1, 466—474).—The radiation which is scattered when a beam of monochromatic light is passed through methyl, ethyl, amyl, or allyl alcohol or water has been examined. The secondary spectra have the usual characteristics of the Raman effect (A., 1928, 685), that of allyl alcohol consisting of lines only, and that of water of a band. Amyl alcohol gives a continuous spectrum, as well as lines, the presence of the former probably being connected with the relatively high viscosity of the liquid. From the difference in frequency between the primary lines and the lines to which they give rise the infra-red frequencies of the molecules have been calculated. In the scattered light the unmodified lines, the new lines, and the continuous spectrum are all polarised, but in different degrees.

R. CUTHILL.

Apparently anomalous Raman effect in water.

J. W. ELLIS (Nature, 1929, 123, 205—206).—The view that the band at 3.0μ in the infra-red spectrum of water is composed of an overtone of the band at 6.1μ and a fundamental of wave-length 2.9μ does not require that the modified frequency afforded by Raman scattering by water molecules, corresponding with an infra-red band at 2.90μ , should be regarded as anomalous. The width of the water band at 1.46μ is 800 cm.^{-1} , a value which is somewhat greater even than that of the band at 2.9μ of the Raman spectrum.

A. A. ELDRIDGE.

Raman effect in gases. F. RASETTI (Nature, 1929, 123, 205).—Carbon monoxide shows two Raman lines at 4432 and 4810 \AA. , respectively, evidently corresponding with the same quantum transition, excited by both 4046 and 4358 \AA. of mercury; the differences in frequency between the Raman lines and the exciting lines correspond with an infra-red absorption band at 4.64μ . In the Raman spectrum of carbon dioxide no lines corresponding with the infra-red absorption bands at 2.7 , 4.25 , and 14.7μ were observed; two doublets, at 4639 , 4616 , and 4289 , 4268 \AA. , excited respectively by 4358 and 4046 \AA. , were, however, observed. The corresponding transitions, 1284 and 1392 cm.^{-1} , coincide, within the limits of experimental error, with the differences in fre-

quency between the two components of the double band at $2.7\ \mu$ and the band at $4.25\ \mu$.

A. A. ELDRIDGE.

Ionisation processes in methane interpreted by the mass spectrograph. T. R. HOGNESS and H. M. KVALNES (Physical Rev., 1928, [ii], 32, 942—945).—The apparatus for ionisation by controlled electron impact and method of analysis were those of Hogness and Lunn (A., 1925, ii, 839). CH_4^+ and CH_3^+ are the only ions formed, and from their relative intensities under different conditions of pressure and voltage, were both found to be formed directly by electron impact. The ionisation processes are: $\text{CH}_4 = \text{CH}_4^+ + e^-$ (14.5 volts); $\text{CH}_4 = \text{CH}_3^+ + \text{H} + e^-$ (15.5 volts). Neon was used as a calibrating gas, and the existence of a third neon isotope of mass 21, in addition to isotopes of mass 20 and 22, was definitely determined.

N. M. BLIGH.

Ionisation of carbon monoxide by controlled electron impact, interpreted by the mass spectrograph. T. R. HOGNESS and R. W. HARKNESS (Physical Rev., 1928, [ii], 32, 936—941).—Ionisation processes may be accompanied by a dissociation of a gas molecule, either simultaneous with the ionisation by electron impact or resulting from the secondary collision of the ionised molecule with a neutral one as illustrated by the ionisation of nitrogen. The ionisation of CO molecules by electrons of definite energy was studied with the mass spectrograph (cf., this vol., 114). The variation of the relative intensities of the ions CO^+ , C^+ , and O^+ with changes of pressure and changes of the electric fields leads to the conclusion that the principal processes occurring are: (1) $\text{CO} = \text{CO}^+ + e^-$; (2) $\text{CO} = \text{O}^+ + \text{C} + e^-$; (3) $\text{CO} = \text{C}^+ + \text{O} + e^-$; (4) $\text{CO} + \text{CO}^+ = \text{CO}_2 + \text{C}^+$. No negative nor doubly-charged positive ions were found. Contrary to expectation, the ionisation processes were found not to resemble those of nitrogen.

N. M. BLIGH.

Dependence of dielectric constant of liquid helium on temperature. M. WOLFKE and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 800—806).—A discontinuity in the values in the dielectric constant of liquid helium is found at 2.295° Abs . The helium molecule probably does not undergo any change in internal structure at this point. The results are in agreement with optical data.

C. W. GIBBY.

Dielectric constant of supercooled sulphur and of some solutions of sulphur. S. ROSENTHAL (Bull. Acad. Polonaise, 1928, A, 1, 377—395).—The dielectric constant of sulphur, molten and supercooled between 150° and 95° , is found to obey the Clausius-Mossotti law. At the moment of solidification the dielectric constant suddenly increases. Solutions of sulphur in benzene and in carbon disulphide also obey the Clausius-Mossotti law.

W. E. DOWNEY.

Dielectric constants of methylene chloride and bromide. P. C. MAHANTI and D. N. SEN-GUPTA (J. Indian Chem. Soc., 1928, 5, 673—681).—The dipole moments of methylene chloride and bromide, 1.621 and 1.914×10^{-18} e.g.s.u., respectively, have been determined in the vapour state by the authors' heterodyne method (cf. this vol., 243). The higher

value for the bromide is explained by assuming that the bromine atoms are more inclined to each other than the corresponding chlorine atoms: the resultant moment in the direction opposite to that developed in the CH_2^{++} ion is, therefore, smaller for the bromide. The bromide has a larger polarisation than the chloride owing to less distortion in the atomic orbits.

H. BURTON.

Anomalous dispersion, absorption, and Kerr effect in viscous dielectrics. D. W. KITCHIN and H. MÜLLER (Physical Rev., 1928, [ii], 32, 979—987).—The temperature variation of the dielectric constant and power factor of castor oil and rosin, measured at different frequencies from 10^7 to 60 cycles, shows that, in accordance with Debye's theory of polar molecules, the region of anomalous dispersion shifts with decreasing temperatures into the long-wave radio region and even down to audio frequencies, whilst its existence in these regions explains the complicated dielectric behaviour of many insulating materials and makes it possible to observe an anomalous behaviour of the Kerr effect. As expected, the regions of anomalous Kerr effect and anomalous dispersion were found to coincide. The influence of viscosity in solutions of rosin in different oils which have no polar molecules was found to agree with Debye's theory.

N. M. BLIGH.

Kerr constant for nitrobenzene. R. MÖLLER (Physikal. Z., 1929, 30, 20—24).—The lack of agreement between the published values for the Kerr constant for nitrobenzene has been traced to instrumental defects and impurities. Nitrobenzene readily absorbs enough moisture from the air to increase greatly its conductivity. A special arrangement for filling the Kerr cell with dry liquid is described. Two different methods lead to the value $B = 3.46 \times 10^{-5}$ at 20° for the line 546.

R. A. MORTON.

Molecular refraction and non-polar linking. R. SAMUEL (Naturwiss., 1929, 17, 13—14).—In non-polar bound molecules there is a negative and a positive group or atom. It is, therefore, possible to give a group or an atom a different refraction constant according as it is positive or negative, instead of a single mean value as is usual. If this is done, many of the abnormalities in molecular refraction data vanish, exaltation and depression disappear, and the molecular refraction of the primary, secondary, and tertiary amines can be calculated by using one value for the atomic refraction of nitrogen instead of three. If this hypothesis is accepted it is possible, conversely, to arrive at the structure of non-polar molecules from observations of their molecular refraction.

A. J. MEE.

Formula for the optical rotatory dispersion of quartz. I. BRADSHAW and G. H. LIVENS (Proc. Roy. Soc., 1929, A, 122, 245—250; cf. Lowry and Coode-Adams, A., 1927, 813).—Lowry's revised formula for the rotatory dispersion of quartz (*loc. cit.*) does not represent the experimental results obtained by Duclaux and Jeantet (A., 1926, 886), and accordingly a formula of a different type is suggested. In the case of a medium with three absorption bands at

λ_2 , and λ_3 , it takes the form $\alpha = \sum_{r=1}^3 \{A_r / (\lambda^2 - \lambda_r^2) +$

$B_r/(\lambda^2 - \lambda_r^2)^2$. It is found by trial that with $\lambda_1^2 = 0.01274912$, $\lambda_2^2 = 0.01208$, $\lambda_3^2 = 80$, the values of the six constants A_r , B_r can be so chosen that the discrepancies between the calculated and observed values of α for quartz (including those of Duclaux and Jeantet) are practically within the limits of experimental error. This formula provides an explanation of the practically constant effect of the infra-red band. On comparison with that proposed by Lowry, it appears that the new formula is in general the more satisfactory.

L. L. BIRCUMSHAW.

Structure of caesium and ammonium sulphates. W. TAYLOR and T. BRYER (Mem. Manchester Phil. Soc., 1927—1928, 72, 125—137).—These salts crystallise in the didigonal equatorial class of the orthorhombic system, being pseudo-hexagonal, the c axis the pseudo-hexagonal axis. A complete survey was made, in the case of ammonium sulphate, of the relative intensities of X-rays reflected from planes of the type (hko), (hol), (okl), and the space-group V^{10} assigned. This was confirmed in the case of caesium sulphate, there being 4 mols. to the unit cell. The dimensions of the unit cell previously given by Ogg and Hopwood have been redetermined. The structure of the crystals is very similar, the positions of the constituent atoms having been allotted taking into consideration the determined and calculated values of the sum of the scattered amplitudes.

G. E. WENTWORTH.

Heats of linking of C-H and N-H linkings from vibration spectra. J. W. ELLIS (Physical Rev., 1929, [ii], 33, 27—36).—Theoretical. The frequency formula for an anharmonic vibrator is applied to visible and near infra-red absorption data for several molecules, previously obtained (this vol., 239), and the mechanical frequencies associated with each stationary state are evaluated and plotted. Assuming that these frequencies originate in oscillations between a hydrogen atom and the remainder of the molecule, the restoring force residing in the C-H and N-H linkings, the heats of linking, i.e. the heats of dissociation of these linkings are calculated, using the methods of the old quantum theory for non-polar, diatomic gaseous molecules. The values obtained for the C-H linking are, hexane, 97,000 (cf. 92,500, obtained thermochemically for methane); cyclohexane, 94,000; benzene, 117,000; chloroform, 108,000; aniline, 117,000; aniline N-H linking, 113,000 g.-cal./mol. The last is believed to agree with 101,000 obtained thermochemically for an ammonia N-H linking. A possible explanation of the doubleness of the absorption bands of several substances, notably hexane and cyclohexane, is sought in two types of carbon valency, the doubleness indicating a slight inequivalence in the energy content of two types of C-H linking (cf. Lonsdale, A., 1928, 1079).

N. M. BUGH.

Chemical valency and spectral multiplicity. A. T. WILLIAMS (J. Chim. phys., 1928, 25, 722—726).—The valency V can be connected with the multiplicity r of the spectrum of an element by the relation $V = r \pm 1$, the sign of which depends on connexions between x , the number of electrons in the outermost sub-group, N , the total number of electrons

which can be present in that sub-group according to the rule of Stoner, and k , the azimuthal quantum number of that sub-group. The relationship holds for all elements except the rare earths, iron, cobalt, and iridium. Preliminary results are given of the application to elements of variable valency.

R. N. KERR.

Electric moments of methyl chloride, ethyl chloride, and chloroform. S. C. SIRCAR (Indian J. Physics, 1928, 3, 197—208).—The permanent moments of methyl chloride, ethyl chloride, and chloroform measured by the heterodyne null method were 1.69×10^{-18} , 1.98×10^{-18} , and 1.05×10^{-18} , respectively, in complete agreement with Debye's dipole theory. Slight divergences from the values deduced from optical data and from the results of other investigators are attributed to the many sources of experimental error.

N. M. BUGH.

Electric moment and its relation to chemical constitution. P. C. MAHANTI and D. N. S. GUPTA (Indian J. Physics, 1928, 3, 181—196).—The heterodyne beat method was used to determine the permanent dipole moments and polarisability of methyl iodide, ethyl bromide, and ethyl iodide. The values found for the moments were 1.31×10^{-18} , 1.78×10^{-18} , and 1.62×10^{-18} , and for the polarisability 0.005761, 0.0022, and 0.007839, respectively. Such organic halides have gradually weakening dipole moment with increasing atomic weight of the halogens. It is suggested that the permanent dipole moment in compounds of this type is due to the deformation of the electron orbits of carbon and halogen which give rise to the permanent moment of the molecule, and that the polarisability of the molecule itself due to applied field increases with the increasing atomic weight of the halogen due to weakening of the linking of the shared electron.

N. M. BUGH.

Dipole moments of some aliphatic ketones. K. L. WOLF and E. LEDERLE (Physikal. Z., 1928, 29, 948—950).—Determinations carried out on ten saturated aliphatic ketones show that the dipole moment is $\mu = 2.75 \pm 0.05 \times 10^{-18}$, this value being independent of the length and structure of the side-chain. The carbonyl group thus shows a much greater dipole moment than gaseous carbon monoxide ($\mu = 0.108 \times 10^{-18}$). The difference is ascribed to different electronic structures.

R. A. MORTON.

Dipole moments of some mono- and di-substituted benzene derivatives. P. WALDEN and O. WERNER (Z. physikal. Chem., 1929, B, 2, 10—26).—The dipole moments of fluoro- and iodo-benzene, o -, m -, and p -dibromobenzene, o -, m -, and p -bromiodobenzene, o -, m -, and p -chlorotoluene, and o -, m -, and p -chloronitrobenzene were obtained from their dielectric constants in pure benzene solution, and their molecular refractions. There is a variation in the moment for isomeric compounds, the moment in some cases increasing, and in others decreasing in value from the *ortho*- to the *para*-compound, according to the nature of the substituent. It is to be expected that for compounds which have two electrically equivalent substituents, e.g., dibromobenzene, the p -isomeride, possessing the greatest symmetry, will have the smallest moment, and the value actually

obtained for *p*-dibromobenzene is zero. If both substituents are not electrically equivalent but are similar, there will be a decrease in the moment from the *o*- to the *p*-isomeride. This is found to be the case with bromiodobenzene and chloronitrobenzene. Since bromine and iodine are very similar, the moment of *p*-bromiodobenzene would be expected to be small; this is so. The introduction of the nitro-group seems to cause an extraordinary increase in the moment. The moments of *o*-, *m*-, and *p*-chloronitrobenzene are much greater than those of the corresponding chlorotoluenes. If the substituents have opposite electrical natures, the moment decreases from the *p*- to the *o*-compound. In chlorotoluene the methyl group is positive and the chlorine negative; it would be expected that in the *p*-compound where the two groups are diametrically opposite the greatest moment would be found. This was found to be so. The actual numerical values obtained for the moments are in good agreement with those arrived at from Thomson's theory. The values derived by Syrlan on the basis of the critical data are also compared with those obtained by experiment. A. J. MEE.

Dipole moments, association, and ultra-violet absorption of aliphatic ketones and their solutions. I. Influence of solvent and mechanism of reaction from the point of view of the dipole theory. K. L. WOLF (Z. physikal. Chem., 1929, B, 2, 39—76).—The effect of various "indifferent" solvents on the structure and ease of reaction of dissolved molecules, and the effect of steric hindrance can be investigated by determinations of the ultra-violet absorption and the molecular polarisation of solutions. A characteristic homologous series of ketones was used and the relationship between these properties and concentration and temperature was determined, using solvents varying from neutral (dipole-less), such as hexane and benzene, up to strongly dipolar liquids. The relationship between molecular refraction, absorption, molecular polarisation, and the forces depending on solution is discussed, and various examples of non-ionic reactions which can be explained by the effect of the solvent are given. The value of the dipole moment of a saturated aliphatic ketone is independent of the length of the hydrocarbon chain, and is equal to 2.74×10^{-18} . The ultra-violet absorption of the series of ketones was investigated, and the bands were found to be displaced owing to the influence of the solvent, the amount of displacement being dependent on the polar group. There is a parallelism between the displacement of the bands and the amount and type of association in the ketone itself. Both these phenomena, as well as the ease of formation of sulphite compounds and oximes, appear to be entirely or mainly determined by the size of the dipole moment and the amount of hindrance of the polar group by indifferent (electrosymmetric) CH_2 groups. The position of the carbonyl group in the hydrocarbon chain is discussed. A. J. MEE.

Electrical dipole moments of organic molecules. II. I. ESTERMANN (Z. physikal. Chem., 1928, B, 1, 422—426; cf. A., 1928, 1309).—The dipole moments of methyl phthalate and tere-

phthalate are practically the same, but are greater than that of the benzoate. Lengthening the side-chain by a CH_2 group has no appreciable effect. Compared with benzophenone, *as*-diphenylethylene has only a very small moment, so that it appears that a double linking is not in itself sufficient to give rise to a high dipole moment. R. CUTHILL.

Relation between polarisation and association. J. W. WILLIAMS (Proc. Nat. Acad. Sci., 1928, 14, 932—936).—A short review of the theories of associated liquids and a criticism of the conclusion by Rolinski (cf. A., 1928, 1181) that the greater the dipole moment the larger is the degree of association of the substance in question. Certain substances, including phenol and benzoic acid, which on chemical evidence are associated, would show a zero degree of association according to Rolinski's treatment. Other factors in addition to the presence of a dipole moment influence the degree of association. N. M. BLIGH.

Application to the allotropic varieties of phosphorus of Smits' theory. P. JOLIBOIS (Compt. rend., 1929, 188, 174—176).—Polemical against Smits' theory (this vol., 127; cf. A., 1916, ii, 317). The author considers that there are four varieties of solid phosphorus, white, red, black, and pyromorphic, all of which may coexist at the ordinary temperature and pressure, although only the pyromorphic and, possibly, the black varieties are stable. Smits' results may be explained by the slow transformation of one variety into another. J. GRANT.

Intensity measurements on X-rays scattered by crystalline powders. J. BRENTANO (Physikal. Z., 1928, 29, 893).—A preliminary account of work designed to yield quantitative data on the scattering of X-rays by very finely-divided crystalline powders. The importance of such data is indicated. R. A. MORTON.

Constitution of hydroxides and hydrates. III. Strontium hydroxide octahydrate. G. NATTA (Gazzetta, 1928, 58, 870—882; cf. this vol., 15).—An X-ray examination, by means of the Laue, rotating-crystal, and powder methods, of strontium hydroxide octahydrate was made in order to determine the exact position of the molecules of water of crystallisation in the lattice. The hydrate crystallises in the hexagonal system, with a unit cell containing 1 molecule of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (a 6.41, c 5.807 Å., d_{calc} 1.85), defined by the following co-ordinates: Sr (0, 0, 0), O of hydroxide ($\frac{1}{2}$, 0, 0) (0, 0), and O of water molecules (u , u , v) (u , $-u$, v) ($-u$, u , v) ($-u$, $-u$, v) (u , u , $-v$) (u , $-u$, $-v$) ($-u$, u , $-v$) ($-u$, $-u$, $-v$), where u has a value of 0.29—0.30 and v is 0.25. The structure is also shown diagrammatically. O. J. WALKER.

Determination of the orientation of crystal axes by X-rays. S. TAKEYAMA (Mem. Coll. Sci. Kyoto, 1928, 11, 469—479).—In a rotating-crystal spectrometer a V-shaped frame of lead wires is inserted between the crystal and the photographic plate, and rotated with the crystal. From the positions of the shadows cast by the lead wires on the spectral lines the angle through which the crystal must be rotated to reflect these spectral lines can be

calculated. If X-rays of known wave-length are used the orientation of the crystal axes can be determined. The method is suitable for thick crystals, or crystals on the surface of thick specimens. A polished surface of copper examined by this method indicated a preferred orientation in which (111) or (100) planes were nearly parallel to the surface.

C. J. SMITHELLS.

Form of the lattice of some monoclinic compounds of the magnesium tungstate type. E. BROCH (Z. physikal. Chem., 1928, B, 1, 409—421).—X-Ray examination shows ferrous, manganous, zinc, cobalt, nickel, and magnesium tungstates and also wolframite to form an isomorphous series. The lattice of magnesium tungstate is of the type $\gamma_{11}^{\prime}22^{\prime}33$, and has the dimensions $a=4.67$, $b=5.66$, $c=4.92$ Å., $\beta'=89^{\circ}35'$, $\beta=90^{\circ}25'$, the unit cell containing 2 molecules.

R. CUTHILL.

Higher fatty acids. III. X-Ray measurements. G. T. MORGAN and E. HOLMES (J.S.C.I., 1928, 47, 309—311r).—X-Ray measurements have been made on a series of pure saturated fatty acids, C_{17} — C_{26} , and on a number of fractions of acids obtained from hydrogenated whale oil, and also from arachis oil. The latter fractions have given anomalous results which suggest that the ester-distillation method of separation is to be preferred to the ordinary crystallisation methods. Normal hexacosic acid has a main X-ray spacing $d_1=56.6$ Å. for the bimolecular unit crystal cell, whilst examination of the so-called cluytinic acid suggests that it is of much higher mol. wt. than hitherto supposed.

Röntgen diagrams of cellulose. R. O. HERZOG and W. JANCKE (Z. physikal. Chem., 1928, 139, 235—262).—From a survey of previous work and also from interference photographs of native and mercerised ramie, now reported, the following conclusions are reached. The cellulose crystals always take up positions with one and the same principal axis either in the axis of the fibre or for spiral fibres as a tangent to the spiral. The spiral angles determined from X-ray diagrams are, within the limit of experimental error, in agreement with those obtained from data on double refraction, striations, and directions of cleavage. All natural cellulose gives the diagram of native cellulose, but mercerised products or those strongly dispersed in solution give that of cellulose hydrate. The difference between the two types of diagrams can be explained by the existence of two modifications of cellulose of which one (native cellulose) crystallises as far as possible in a monoclinic and the other (cellulose hydrate) in a rhombic system. Native and mercerised fibres give fibre diagrams with the same identity periods in the direction of the fibre.

R. N. KERR.

Structure of the crystalline part of cellulose. II. H. MARK and K. H. MEYER (Z. physikal. Chem., 1929, B, 2, 115—145).—Work on the X-ray diagrams of cellulose has shown that it is made up of elementary cells, monoclinic in form. An atomic model is here put forward for the structure of cellulose which will give values for the intensities of the diagram in agreement with those observed. The size and form of the

cellulose micelle are calculated. It has a length of about 500 and a width of about 50 Å. The mechanisms of reactions into which cellulose can enter are considered. The micellary structure of cellulose leads to two types of reaction, (a) the micellary surface reaction, and (b) the "permutoid" reaction. The latter is the more important. By the use of Hudson's rule, the rotations of various cellulose derivatives are calculated and found to agree with the observed values. An X-ray method for the comparison and identification of cellulose preparations is given and the question of small structural elements of cellulose is discussed. (See A., 1928, 621.) A. J. MEE.

X-Ray investigation of the mixed crystal system $BaSO_4 + KMnO_4$. G. WAGNER (Z. physikal. Chem., 1929, B, 2, 27—38).—Barium sulphate and potassium permanganate possess the properties necessary for the formation of mixed crystals. The Debye-Scherrer diagrams were obtained for ten preparations of varying permanganate content. Comparison of the lines obtained with those given by barium sulphate and potassium permanganate alone shows a displacement. By plotting the lattice space against the permanganate content it is shown that the displacement is proportional to the latter within experimental error. These facts are evidence for the mixed crystalline nature of the barium sulphate-potassium permanganate system. A photograph of barium sulphate with adsorbed barium nitrate gave no displacement of the barium sulphate lines.

A. J. MEE.

Nature of martensite. N. SELJAKOV (Nature, 1929, 123, 204—205).—Honda and Sekito's result (A., 1928, 594; B., 1928, 753) that the ratio (1.07) of the axes of the lattice of tetragonal martensite is independent of the carbon content, is criticised; it is considered that the carbon content of the surface layers was the same in all cases. The presence of carbon atoms in the lattice will cause a decrease in the intensity, but not a broadening, of the spectral lines.

A. A. ELDRIDGE.

Metallic filaments. R. SCHENCK, R. FRICKE, and G. BRINKMANN (Z. physikal. Chem., 1928, 139, 32—46).—Artificially-prepared as well as naturally-occurring metallic filaments have been investigated by means of X-ray analysis. The artificial trichites of silver were prepared by means of the reaction between silver sulphate and sulphide and by the reduction of silver sulphide with hydrogen at 400—500°. The copper trichites were obtained in a similar manner by reduction with hydrogen at 500—600°. The silver threads show only isolated interference spots and those prepared by reduction are assumed to possess a uniform crystal orientation. When the material is heated at 900°, this uniformity disappears and simultaneous enlargement of the grains takes place. Natural silver trichites show no kind of orientation. With copper, the X-ray pattern changes from one preparation to another and heating is accompanied by re-orientation. The mode of formation of metallic trichites is discussed and the significance of the presence of sulphide is emphasised. In all probability, the former is to be ascribed to an electrolytic process arising from a short-circuited thermoelement between

the metal and the sulphide. Photographs and data are reproduced. L. S. THEOBALD.

Crystal structure of anhydrous silicotungstic acid and related compounds, and their probable molecular formulæ. A. G. SCROGGIE and G. L. CLARK (Proc. Nat. Acad. Sci., 1929, 15, 1—8).—An X-ray diffraction analysis was made of the crystal structure of the anhydrous acid obtained from the hydrated forms at 220°, and combined with chemical data to deduce the molecular structure. A series of modified acids with 7, 8, and 10 tungsten atoms was isolated by stepwise addition of alkali to the acid. The crystal form of the acid was shown by the X-ray examination to be a body-centred cube, with a 12.16 Å. This dimension applies to the acids with 8, 10, and 12 tungsten atoms, and to the modifications of the latter which contain 2 or 8 molecules of water, i.e., $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 2\text{H}_2\text{O}$ or $(\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 6\text{H}_2\text{O})_2\text{H}_2\text{O}$, but not to the anhydride, $\text{SiO}_2 \cdot 12\text{WO}_3$. Phosphodecimolybdic acid similarly forms a body-centred cube with a 14.31 Å. A modified formula for the acid $(\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 6\text{H}_2\text{O})_2\text{H}_2\text{O}$ or $\text{H}_4[\text{SiO}_4 \cdot \text{W}_{12}\text{O}_{30}(\text{OH})_{12}]$ and a new spatial structure were deduced to correlate the X-ray and chemical data. N. M. BLIGH.

X-Ray analysis of cadmium arsenide and arsenious anhydride. L. PASSERINI (Gazzetta, 1928, 58, 775—781).—Cadmium arsenide, examined by the powder method, is shown to have a cubic structure with a non-ionic lattice of the zinc arsenide type (cf. A., 1928, 1313). The length of the unit cell is 6.29 Å., $d_{\text{calc.}} = 6.495$ and the distance As—Cd is 2.723 Å. The structure of the cubic modification of arsenious oxide determined by Bozorth (A., 1923, ii, 632) is confirmed by the powder method. The length of the unit cell containing 16 molecules of As_2O_3 is 11.08 Å. ($d_{\text{calc.}} = 3.851$). The distance As—O is calculated to be 2.016 Å., which gives a value of 0.696 Å. for the radius of the As^{+++} ion. O. J. WALKER.

Form of the central carbon atom in pentaerythritol tetra-acetate as shown by X-ray crystal analysis. (Miss) I. E. KNAGGS (Proc. Roy. Soc., 1929, A, 122, 69—76).—X-Ray examination of pentaerythritol tetra-acetate by taking rotation, oscillation, and Laue photographs, indicates that it crystallises in the tetragonal bipyramidal class. There are two molecules in the unit cell, which has $a = 11.98$, $c = 5.47$ Å. The crystals are built on a simple tetragonal lattice, Γ_1 , and the space-group is C_{4h}^1 ; this necessitates each molecule having a four-fold alternating axis of symmetry. The conclusions reached by Gerstacker, Moller, and Reis (Z. Krist., 1928, 66, 355), that the space-group is C_{4h}^2 and that the molecules possess a simple tetragonal axis of symmetry, are criticised. The evidence for the space-group C_{4h}^1 is very slight. A probable structure is suggested, from which it follows that the symmetry of the central carbon atom may be tetrahedral, although a slight departure from true tetrahedral symmetry is possible. L. L. BIRCUMSHAW.

Nature of interference lines in X-ray photographs of many crystalline materials. I. H. MOLLER and A. REIS (Z. physikal. Chem., 1928, 139, 425—438).—The influence exerted by the nature of

the cross-section of the powder rod on the interference lines obtained in X-ray photographs taken by the Debye-Scherrer method is examined mathematically assuming that a parallel primary radiation is used. The shape, dimensions, and absorption of the rod are considered and results are given for three different shapes—flat slab, wedge, and cylinder. Weakening of intensity of the lines through increase in the coarseness of the particles is considered.

R. N. KERR.

X-Ray diffraction of crystal powders and liquids in relation to their constitution. P. KRISHNAMURTI (Indian J. Physics, 1928, 3, 225—240).—Results for a number of organic liquids confirm those of a previous investigation (cf. A., 1928, 691). Geraniol and terpineol showed some differences, the former giving a broader and more diffuse halo, and a smaller inner ring due to double molecular spacing, indicating the existence of longer molecules than in the case of terpineol, for which, also, the halo was clearly defined. Some benzene derivatives with a long side-chain gave rings of about the same size as in a long-chain aliphatic derivative. Examination in both powder and liquid states was made of *o*- and *m*-nitrobenzaldehyde, *o*-nitrophenol, *o*-nitroaniline, and *p*-toluidine. In both states the *o*- and *m*-compounds showed two rings, the outer one contracted in the case of the liquid, for which both were broader and more diffuse at the edges. The outer ring is explained generally, with supporting evidence, as being due to the thickness of the molecule, and the inner to its length and breadth. The *p*-compound showed a number of rings close together in the powder, joining up into one broad ring in the liquid, when only the spacing due to the average thickness of the molecules is obtained. N. M. BLIGH.

New type of alum. W. R. C. CURJEL (Nature, 1929, 123, 206).—The salt $\text{K}_2\text{BeF}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ crystallises in the cubic system, normally as octahedra, and is a true alum; the salt $\text{K}_2\text{ZnCl}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ is also an alum. Hence potassium sulphate and potassium beryllium fluoride are truly isomorphous. Rubidium beryllium fluoride is isomorphous with the potassium salt.

A. A. ELDRIDGE.

Influence of traces of foreign ions on the absorption of alkali halide crystals. I. MASLAKOWEZ (Z. Physik, 1928, 51, 696—706).—Measurements of the ultra-violet and infra-red absorption of crystals of potassium chloride, bromide, and iodide, and of sodium chloride, containing traces of potassium nitrate, or nitrite, show that nitrate and nitrite ions may be introduced in the alkali halide grating forming mixed crystals. Carbonate and sulphate ions cannot be introduced without producing very considerable distortion. R. W. LUNT.

Relationship between grain size and magnetic properties in pure iron. G. J. SIZOO (Z. Physik, 1928, 51, 557—564).

Experimental study of the growth of zinc crystals by the Czochralski-Gomperz method. A. G. HOYEM and E. P. T. TYNDALL (Physical Rev., 1929, [ii], 33, 81—89).—Conditions for the growth of single zinc crystals of any desired orientation were

determined experimentally. For a constant rate of growth and given initial orientation the successful growth of a single-crystal rod 10 cm. or more in length was found to depend on the temperature gradient in the column of liquid zinc just below the growing crystal. The appropriate temperature gradient is plotted as a function of the orientation. Attempts to grow crystals outside the region of successful growth result in changes to new orientations.

N. M. BLIGH.

Phase rule and Euler's law. O. RUDEL (Z. Elektrochem., 1929, 35, 54).—A parallelism exists between the phase-rule equation and Euler's equation relating the faces, edges, and corners of a crystal, and the number of phases, degrees of freedom, and components of the former equation may be identified with the number of faces (or corners), corners (or faces), and edges, respectively, of the latter.

L. L. BIRCUMSHAW.

Form and potential energy of the isomorphous crystals ruby (Al_2O_3) and hæmatite (Fe_2O_3). J. TOPPING (Proc. Roy. Soc., 1929, A, 122, 251–273; cf. Topping and Chapman, A., 1927, 96; Lennard-Jones and Dent, *ibid.*).—To determine the equilibrium configuration of a crystal, as given by the minimum value of the potential energy of the crystal, it is necessary to calculate the electrostatic potential energy of an infinite array of point-charges, arranged according to the crystal pattern, and the potential energy due to the intrinsic repulsive forces between the ions. From a consideration of these forces, a very good account can be given of the observed size and shape of the isomorphous crystals ruby and hæmatite, the structures of which involve three parameters. It is indicated that theoretically, in terms of the electrostatic and intrinsic repulsive ionic forces which have been considered, an exact hexagonal close-packed arrangement of the oxygen ions is not compatible with the observed size and shape of the crystals, and that there must be some slight distortion from the exact arrangement. This distortion is indicated by the mutual distances of the ions of the Al_2O_3 groups which surround the lattice-points—*i.e.*, by the value of the distance $2d$ between the aluminium ions and the distance $b\sqrt{3}$ between the oxygen ions of such an Al_2O_3 group. These results are in good agreement with experiment (cf. Bragg and Brown, A., 1926, 227). It is further found that, in order that the theoretical series of possible configurations of the crystal might include the observed configuration, it is necessary to adopt a value of $\mu_{22}=11.0$ for O^{--} , which is considerably lower than the value 17.6 obtained by Lennard-Jones and Dent (A., 1926, 888). Using this revised value of μ_{22} , crystalline sodium nitrate has been reconsidered (cf. Topping and Chapman, *loc. cit.*) and fairly satisfactory results have been obtained.

L. L. BIRCUMSHAW.

Molecular theory of crystals. K. WEISSENBERG (Z. physikal. Chem., 1928, 139, 529–583).—Crystal structure is discussed from the point of view of the Schoenflies–Fedoran symmetry laws. It is shown that not only may morphological and physical properties thus be explained, but also the chemical constitution of crystals. From these laws a new hypothesis is deduced which is applicable to crystals

in the same manner as Avogadro's law to gases and leads to a new type of space-lattice. A survey of different space-lattices has been made and examples of the new type are given. The hypothesis was tested for 459 substances; in 401 cases the mol. wt. of the crystal unit calculated from this hypothesis agrees with that of the simple chemical formula and in the remainder it is a simple multiple of that.

R. N. KERR.

Quantum mechanics of electrons in a crystal lattice. F. BLOCH (Z. Physik, 1928, 52, 555–600).—Mathematical. The motion of an electron in a crystal lattice is discussed in relation to Fermi's statistics. An expression is deduced for the component part of the specific heat of crystals due to this motion. It is also shown that the order of magnitude of the electrical conductivity of metals and its dependence on temperature, as deduced from these considerations, are in qualitative agreement with experimental observations.

J. W. SMITH.

Hall effect in steel-nickel alloys. U. SALERNO (Rend. Accad. Sci. Fis. Mat. Napoli, 1928, [iii], 34, 159–165).—The Hall effect is exhibited by steel-nickel alloys with the same characteristics as with ferromagnetic metals, invar showing a moderately high coefficient of rotation. The phenomenon is influenced to some extent by the nature of the secondary electrodes. Asymmetry, which is observed in all the alloys examined, is especially marked in that containing 22% of nickel (the least magnetic), but almost absent from the highly magnetic 49% alloy. The contribution of steel to the effect is greater than that of nickel, the presence of 80% of which is necessary to reverse the sign of the effect. Analogies are shown between the variation of the Hall effect and those of specific heat, thermo-electric power, electrical conductivity, and electrical resistance with the composition of the alloys.

T. H. POPE.

Comparison of the Corbino and Hall effects in silver and brass. K. K. SMITH and H. M. O'BRYAN (Physical Rev., 1929, [ii], 33, 66–74).—An improved electromagnetic torque method was used to measure the Corbino effect, which was compared with the Hall effect, in rectangular silver sheets. To avoid magnetic impurities, navy brass was used for the suspended system and the two effects were measured also for this metal. The values obtained for the Corbino coefficient c , the Hall coefficient R , and the resistivity ρ , were, for silver $c=-5.0 \times 10^{-7}$, $R=-8.6 \times 10^{-4}$, $\rho=1.72 \times 10^3$, and for the brass $c=-0.14 \times 10^{-7}$, $R=-0.96 \times 10^{-4}$, $\rho=6.7 \times 10^3$ e.m.u. Probable causes of the differences of c for circular and rectangular plates and in previous experiments are discussed.

N. M. BLIGH.

Magnetic susceptibility of alkali and alkaline-earth halides. K. IKENMEYER (Ann. Physik, 1929, [v], 1, 169–191).—The diamagnetic susceptibility of the halides of the alkali and alkaline-earth metals in aqueous solution has been determined by a differential method involving small rotating rods of material in an inhomogeneous field. Throughout the measurements the susceptibilities show a linear variation with respect to concentration, so that no apparent reciprocal action occurs between ions. The molecular

susceptibility varies approximately linearly with the sum of the atomic numbers of atoms in the molecule Z_m , i.e., $-\chi_m = c_1 Z_m + c_2$, the constants having the values, $c_1 = 0.803 \times 10^{-6}$ and $c_2 = 8.30 \times 10^{-6}$. Using values of χ_m corrected to conform with this relation, the ionic susceptibilities have been calculated. The relation, $-\chi_{\text{ion}} = c_1 Z + c'_2$ agrees well with the data if the following values of c'_2 are adopted: halogen ions 6.70, alkali ions 1.60, alkaline-earth ions -51.0×10^{-6} . The value of c_1 remains unchanged.

R. A. MORTON.

Chromites and ferrites of nickel and of cobalt. (MLLE.) S. VEIL (Compt. rend., 1929, 188, 330—332).—The magnetisation coefficient—composition curves of mixtures of chromic or ferric oxide with nickelous or cobaltous oxide, prepared by calcination of the precipitate obtained on the addition of sodium hydroxide to solutions containing corresponding mixtures of the sulphates, show maxima at the points corresponding with the formation of the respective chromites and ferrites. The magnetisation coefficients of the ferrites are more than 1000 times as great as those of their pure constituents.

J. GRANT.

Magnetic properties in relation to chemical constitution. L. C. JACKSON (Nature, 1929, 123, 279).—After allowance is made for the diamagnetic properties of the sulphur atoms in iron pyrites, the iron atom possesses a small residual positive magnetic moment, and the susceptibility is independent of the temperature. These properties are in agreement with what would be expected for a twofold co-ordination compound of ferrous iron, but differ from those associated with simple ferrous salts (cf. Lowry and Gilbert, this vol., 127).

A. A. ELDRIDGE.

Hall effect in galena and molybdenite. C. W. HEAPS (Phil. Mag., 1928, [vii], 6, 1283—1286).—A specimen of galena from Missouri gave a Hall coefficient of -108.3 independent of the orientation of the crystal, whilst another specimen of unknown origin gave the value $+4802$. This great discrepancy in values for the same mineral is attributed to the presence of different proportions of different impurities. The average Hall coefficient for molybdenite was found to be -1907 . The isothermal Hall coefficient for molybdenite is about 6% smaller than the adiabatic. In galena the two coefficients do not differ by more than 2%.

A. E. MITCHELL.

Magnetostriction of a single iron crystal. N. AKULOV (Z. Physik, 1928, 52, 389—405).—Mathematical. A general formula is deduced for the calculation of the energy of expansion of the dipole lattice and the electrostriction and magnetostriction of any crystal. The curve for the magnetostriction of an iron crystal, calculated from this formula, is compared with the experimental curve of Honda and Mashiyama (A., 1927, 299). The positions of the maxima and minima as well as the period of the effect coincide exactly with the experimental data, whilst the absolute values of the magnetostriction calculated by the formula are also of the same order as those found experimentally. It is concluded that the ions of iron have no perceptible electrical dipole moment, and that, for the calculation of the magnetic coupling

force, the iron ion can be treated, as a first approximation, as a single magnetic dipole. J. W. SMITH.

Resistance and thermo-electric phenomena in metal crystals. P. W. BRIDGMAN (Proc. Nat. Acad. Sci., 1928, 14, 943—946).—Some experimental results are summarised briefly. An improved method has been evolved for making single metal crystals and for measuring their thermal *E.M.F.*, some results being given. It is concluded that the Kelvin-Voigt law for thermal *E.M.F.* is approximate only. Some theoretical considerations are briefly discussed.

N. M. BLIGH.

Pyro- and piezo-electricity. A. MEISSNER (Naturwiss., 1929, 17, 25—31).—The pyro- and piezo-electric properties of quartz have been studied in detail. From the characteristic oscillations excited in a quartz disc it is possible to calculate the dimensions of the unit cell in the crystal lattice, and the structural dimensions obtained macroscopically agree closely with those obtained from X-ray data. The properties of quartz are connected with the orientation of the electric axes in the unit cell. At constant temperature the electric moment is constant, but increases with increasing shifts in the atoms, i.e., with rise in temperature. The pyro-electric coefficient has been determined for quartz, sucrose, tartaric acid, sodium potassium tartrate, tourmaline, topaz, zinc blende, pyrites, and pentaerythritol.

R. A. MORTON.

Slip-bands produced when crystals of aluminium are stretched. II. Extension at high temperatures. K. YAMAGUCHI and S. TOGINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 9, 277—292).—The deformation of single crystals of aluminium under tension, above the recrystallisation temperature, is studied. Slip takes place on the same planes and in the same crystallographic direction as at the ordinary temperature, but does not result in increased hardness. The distortion takes place by simple shear throughout the crystal, and not by a succession of slips on different planes. Instead of slip bands appearing on the surface, uneven wavy stripes having no relation to the direction of the crystal axes are produced.

C. J. SMITHELLS.

Recrystallisation of metals. II. R. KARNOP and G. SACHS (Z. Physik, 1928, 52, 301—313; cf. A., 1927, 504).—The influence of previous stretching and annealing on the temperature of crystallisation and the size of crystals formed in rods of commercial aluminium (99.3% Al, 0.4% Fe, and 0.2% Si) has been investigated. Comparisons have also been made between the effects of extension, compression, and a combination of these two on the recrystallisation. The application of a stress during the recrystallisation process is found to exert a marked effect on the product.

J. W. SMITH.

Molecular association and molar concentration. G. G. LONGINESCU and G. CHABORSKI (Bul. Chim. pura Appl., 1927, 30, 3—29; Chem. Zentr., 1928, ii, 1175).—The number of g.-mols. of a liquid or solid contained in 1 litre (the "molar concentration," C_m) is determined for 350 organic compounds. In homologous series C_m diminishes with increasing mol. wt.; isomerides have similar values.

The values lie between 55.5 (water) and 0.09 (tristearin). All organic liquids which are considered to be associated have $C_m > 10$, whilst normal liquids have $C_m = 10$ (approx.). The difference between normal and "associated" liquids is not ascribed to an association of single molecules, but to an accumulation of single molecules in a given volume. The conception of molar concentration leads to an explanation of cryoscopic anomalies and of anomalous values of the temperature coefficient in Ramsay and Shields' formula. A. A. ELDRIDGE.

Relations between physical constants of liquids. V. PERSCHKE (Z. Elektrochem., 1929, 35, 13—17).—See this vol., 21.

Magnetism of hydrated zirconia. F. BOURION and (ILLE.) O. HUN (Bull. Soc. chim., 1929, [iv], 45, 49—60).—A more detailed account of work already published (this vol., 20).

Change in the intensity of magnetisation of an iron wire on stretching. J. B. SETH, C. ANAND, and M. DAYAL (Z. Physik, 1928, 52, 382—388).—Application of stress to a piece of iron wire suspended in various weak magnetic fields caused a change in the intensity of its magnetisation, which was followed by a ballistic differential method. The curves obtained for the change with extension are analogous for different field strengths and are similar in form to the stress-strain curves for such a wire. J. W. SMITH.

Anomaly in the diamagnetism of gases. H. BUCHNER (Ann. Physik, 1929, [v], 1, 41—48).—Glaser's anomaly (A., 1925, ii, 82, 642) in the diamagnetism of gases at low pressures, namely, a triple increase in the susceptibility, is ascribed to an error in the temperature correction. R. A. MORTON.

Electrical conductivities of dilute liquid amalgams of gold and copper at various temperatures. T. C. WILLIAMS and E. J. EVANS (Phil. Mag., 1928, [vii], 6, 1231—1253).—The electrical conductivities of liquid gold amalgams at concentrations up to the saturation at 11.5° have been determined at 11.5°, 100°, and 300°. Similar measurements have been made with copper amalgams, the concentrations being varied up to saturation at the temperature of experiment. In both cases the temperature coefficient of resistivity is less than that of pure mercury. The ratio of the increase of conductivity relative to mercury to the concentration has been determined at each temperature for each concentration, and at infinite dilution both series of amalgams gave the same values at the same temperatures. These values are equal to those obtained for silver amalgams by Johns and Evans (A., 1928, 244). The results show that, atom for atom, the effect on the conductivity of the different metals of group I(b) of the periodic table is the same. A. E. MITCHELL.

Dissociation of pure mercury. E. S. KEEPING (Nature, 1928, 122, 728).—Bradley's results (A., 1928, 1302) are criticised. Values of p/q , where p and q are the average numbers of free electrons per atom of the metal X and mercury, respectively, are recorded for indium, magnesium, thallium, germanium, antimony, yttrium, cerium, gallium, copper, cadmium, and silver. A. A. ELDRIDGE.

Tribo-electricity and friction. IV. Electricity due to air-blown particles. P. E. SHAW (Proc. Roy. Soc., 1929, A, 122, 49—58; cf. A., 1928, 467).—An apparatus has been devised for studying the charges developed by the impact of two unlike metals, of two like metals, of sand on sand, or ice on ice. Particles of the materials are driven by means of a rapid stream of air on to surfaces of one material only, and the charges arising on the particles, on the surfaces, and on the issuing air are measured separately. Copper, iron, zinc, and brass are found always to receive charges of sign, and to some degree of amount, in accordance with the Volta effect, the photo-electric effect, and the thermionic effect. But the fact that considerable charges arise when the particles and surfaces are chemically identical, as with copper/copper, zinc/zinc, brass/brass, sand/sand, and ice/ice, indicates that the Volta effect alone will not account for all the charges developed. Physical differences of the surfaces—i.e., strain differences—are suggested as contributory factors to tribo-electric charges. The effect of the cleanliness of the filings and of the temperature, speed, and direction of the air blast was studied. Fresh, clean filings yield as much as 30% more charge than old. On reducing the speed of the blast, the charges were reduced, whilst in some cases they were doubled by raising the temperature from 18° to 58°. The use of an oblique air blast also caused a considerable increase in the charges. The results for sand and ice provide a key to the meteorological effects observed in electric sand- and snow-storms. L. L. BIRCHSHAW.

Dependence of the susceptibilities of glasses on temperature. W. GERLACH and N. LITTLE (Z. Physik, 1928, 52, 464—465).—The magnetic susceptibility of glass is dependent to a remarkable extent on temperature. All the types of glass investigated had a temperature coefficient of the same order of magnitude, independently of the absolute value of the susceptibility. This temperature coefficient is ten times the order of magnitude found in the case of gases. The phenomenon is attributed to the paramagnetic components present in the glass. J. W. SMITH.

Electrical resistance and magnetic permeability of iron wire at radio frequencies. G. R. WAIT, F. G. BRICKWEDDE, and E. L. HALL (Physical Rev., 1928, [ii], 32, 967—973; cf. Wait, A., 1927, 505).—Further efforts to detect a reported anomalous change in the permeability of iron, and to observe a critical variation in the resistance of iron wire reported by Mitiaev (A., 1926, 1086), were unsuccessful. N. M. BLYTH.

Changes in the resistance of nickel wire with stretching. J. B. SETH and C. ANAND (Physikal. Z., 1928, 29, 951—952).—In most cases metallic wires exhibit a steady increase of electrical resistance with stretching. Nickel, however, shows at first a decrease followed by the customary increase. The minimum occurs when the elongation is 15% of that observed just before the wire breaks. A detailed investigation of the elongation process up to the stage of minimum resistance shows that the change in resistance is not truly reversible since the curve obtained by plotting elongation against change in resistance is looped, one

branch representing the change as the resistance is increased and the other branch representing the reverse process. The shape of the loop depends not only on the number of times the wire has been stretched, but also on the previous history of the specimen.

R. A. MORTON.

Measurements with the aid of liquid helium.
III. Resistance of metals. Superconductivity of tantalum. Contribution to the explanation of superconductivity. Specific heat of gaseous helium. W. MEISSNER (Physikal. Z., 1928, 29, 897—904).—The electrical resistances over the temperature range 1.29—273.20° Abs. have been determined for aluminium, beryllium, cobalt, molybdenum, rhodium, palladium, tantalum, tungsten, iridium, antimony, German silver, carbon, and various kinds of iron. Although some elements exhibit quite small resistances when highly purified, the only one among those listed which shows superconductivity is tantalum, the phenomenon commencing at 4.36° Abs. Attention is directed to the fact that all the known superconductors, including tantalum, occupy neighbouring places in the periodic table. German silver, like constantan and manganin, shows little decrease in resistance with fall in temperature, the value at 1.32° Abs. being 90% of that at 273.2° Abs. Carbon, on the other hand, shows an increase in resistance of 19% over the same temperature interval.

The superconductivity of tin at the temperature of liquid helium is not eliminated when the metal is enclosed in a tightly-fitting sheath of German silver, from which it is concluded that superconductivity is a volume- rather than a surface-effect. From other experiments it is concluded that the current is carried by electrons distributed at random, the disappearance of resistance being due to the failure of the electrons to give up their energy to the atoms, *i.e.*, to elastic reflexion of electrons. Experiments on the specific heat of gaseous helium show that at 5.5° Abs. and 0.75 atm., the molecular heat at constant volume is 1.94, *i.e.*, 65% of the normal classical value.

R. A. MORTON.

Disturbance of the superconductivity of thallium by magnetic fields. W. TUYN (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 687—691).—The superconductivity of thallium has been measured at temperatures of 1.82—2.21° Abs., in fields of 22.3—67.8 gauss. Hysteresis is shown.

C. W. GIBBY.

New superconductors. W. J. DE HAAS (Naturwiss., 1929, 17, 85—86).—Antimony and zinc, and bismuth and thallium yield superconducting alloys, the latter metal in each case being a superconductor. It is now found that the combination gold-bismuth is superconducting although neither metal is a superconductor *per se*. The resistance of the alloy at 2.2° Abs. is 0.7 of the resistance at the ordinary temperature, whilst 0.05° lower the alloy has no resistance. At 1.5° Abs. neither gold nor bismuth is superconducting.

W. E. DOWNEY.

Excitation of frictional electricity between metals and non-conductors in relation to the pressure of the surrounding gas and the outgassing of the metal. W. KLUGE (Ann. Physik, 1929, [v], 1, 1—39).—An experimental technique is

described for the quantitative study of static electrification in a vacuum. It is shown that the polarity of the electrification produced by rubbing platinum, gold, and palladium in a high vacuum is reproducible. The magnitude of the charge depends on the condition of the metallic surface, outgassing by heating to redness causing an increased effect. When the metal is allowed to take up gas again, the original phenomena are reproduced. If platinum is heated to whiteness, friction against silk results in a marked positive polarity of the metal. This effect arises from the formation of a film of "sputtered" platinum, since a little volatilisation occurs with strong heating. The film is readily polished away by the silk, whereupon the normal negative polarity reappears on the metallic surface. The influence of the pressure of the surrounding air on the sign and magnitude of the electrification has been studied.

R. A. MORTON.

Excitation of frictional electricity. L. WOLF (Ann. Physik, 1929, [v], 1, 260—288).—Frictional electricity arises largely from the transference of metallic ions in solution in the film of water on the insulator. Friction of an earthed metallic "needle" against a rotating plane surface of specially prepared shellac results, in the absence of an electric field, in an equilibrium between solution tension and the pressure of dissolved ions. Application of an electric field sets up a new equilibrium characterised by a smaller concentration of ions in the film, reversion to the first equilibrium being possible by reducing the field strength. The sign of the frictional electricity can be reversed by adjusting the field to neutralise the pressure of the ions. Artificially increasing the ionic concentration also reverses the sign. By increasing the surface of contact, the amount of electricity excited with constant capacity increases to a limiting value. It is also shown that the speed of the moving surface has no influence on the quantity of electricity excited.

R. A. MORTON.

Analogous properties and analogous radiometer curves of nitrogen and carbon monoxide, and of carbon dioxide and nitrous oxide. E. BRÜCKE and W. LITWIN (Z. Physik, 1928, 52, 334—335; cf. this vol., 251).—It has been shown that, in common with the majority of the other physical properties of these pairs of gases, the radiometer curves of nitrogen and carbon monoxide are almost identical, as are those of carbon dioxide and nitrous oxide.

J. W. SMITH.

Dynamic allotropic state of selenium. G. BRIEGLER (Naturwiss., 1929, 17, 51).—A preliminary account of experiments on the allotropic modifications of selenium, all of which have been shown by X-ray investigations, to contain two pseudo-components. Although the absolute solubilities of the constituents are almost identical, they dissolve at different rates in carbon disulphide, and use has been made of this property to effect some separation. By spectroscopic methods it has been shown that two forms of selenium exist in equilibrium in this solution, but that the equilibrium changes with temperature. The results are discussed in relation with the observations of previous investigators.

J. W. SMITH.

Radiometer question. E. BRUCHE and W. LITWIN (*Z. Physik*, 1928, 52, 318—333).—With an improved form of measurement radiometer, the radiometer curves of twelve gases have been measured under various conditions. In low-pressure regions the radiometric effect appears to be a surface effect, independent of the type of gas and the geometrical relations of the instrument, being proportional only to the number of molecules in unit volume of the gas. With moderate pressures the effect attains a maximum in each gas which in pressure and magnitude is proportional to the free path of the molecules. In the regions of higher pressure it becomes an edge effect which is directly proportional to the square of the free path and inversely proportional to the pressure.

J. W. SMITH.

Birefringence and dichroism of thin layers of iron obtained by distillation. M. CAU (*Compt. rend.*, 1929, 188, 57—58).—The component of the vibration parallel to the axis is less absorbed than the normal component by the birefringent, dichroic layers of iron obtained in the axial zone in the author's experiments (*A.*, 1928, 695). In the middle of the visible spectrum the dispersion is normal for the ellipticity, and abnormal for the rotation of the emergent vibration. The effect, which increases with the thickness of the deposit and with decrease in distance between the wire and the deposition surface, was also studied by reflexion, a rectilinear incident vibration then being transformed into an elliptical vibration having a different azimuth. J. GRANT.

Gaseous state of low-boiling substances. K. WOHL (*Z. physikal. Chem.*, 1929, B, 2, 77—114).—The critical data for the permanent gases and normal substances are collected and compared. The two virial coefficients which express the deviations from the ideal gas state when reduced with the critical data correspond well with each other within the range neon, nitrogen, argon, and oxygen, whilst with normal substances there is a certain degree of correspondence above the critical temperature. This more or less close relationship holds in general up to the neighbourhood of the critical volume, although at the furthest extreme from the ideal gas state the compressibility of the permanent gases is markedly greater than that of normal substances. The dependence of the van der Waals constant b on temperature was investigated. The temperature coefficient of b is of the same order of magnitude for all permanent gases and decreases inversely with the critical temperature from helium to argon. The dependence of the van der Waals constant a on temperature is very small for all permanent gases above the critical temperature, and diminishes with falling temperature, so that no degeneration effect will be noticed in the rarefied gas. It is possible from the value of b to calculate the packing density of the molecules of the liquefied gases at 0° Abs. For neon and argon there is the closest packing, and there is a considerable decrease in packing density from neon, through hydrogen, to helium, which can be explained only by the existence of energy at 0° Abs. It can be shown that the ratio of this energy at 0° Abs. to the potential energy of the liquid for low-boiling substances must

be large. For hydrogen and helium, and to a smaller extent neon, the values of the critical data are influenced by the energy at 0° Abs. By the use of "idealised" critical data it is possible to arrive at a value for the second virial coefficient which shows a good degree of correspondence for similar permanent gases. The difference between the permanent gases with the higher critical temperatures and normal substances lies in the fact that for the latter there is a somewhat larger temperature effect on the van der Waals attraction. Attempts to explain the van der Waals attraction on the basis of the old quantum theory lead to large deviations from practice. In particular the assumption that for polyatomic substances the attraction at medium and low temperatures rested ultimately on the orientation of the molecule is in contradiction with the good correspondence between monatomic and diatomic substances. A. J. MEE.

Multiplicative properties. M. TRAUTZ (*Z. angew. Chem.*, 1929, 42, 89—94).—A theoretical paper concerned with the physical properties of gases and based mainly on the results of the author's work on the specific heats, friction, and thermal conductivities of gases. J. S. CARTER.

Heat capacity of methyl alcohol from 16° to 298° Abs. and the corresponding entropy and free energy. K. K. KELLEY (*J. Amer. Chem. Soc.*, 1929, 51, 180—187).—The method previously described was used (Giauque and Wiebe, *A.*, 1928, 228). Methyl alcohol exists in two crystalline forms having a transition point at 157.4° Abs. and a heat of transition of 154.3 g.-cal./mol. The heat of fusion of the substance is 757 g.-cal./mol. at 157.22° Abs.; the molal entropy at 298° Abs. is 30.3 g.-cal./1° and the molal free energy of formation —44,000 g.-cal.

S. K. TWEEDY.

Heat capacities at low temperatures of "ferrous oxide," magnetite, and cuprous and cupric oxides. R. W. MILLAR (*J. Amer. Chem. Soc.*, 1929, 51, 215—222).—The molal heat capacities of "ferrous oxide" (83% FeO; 16% Fe₃O₄), magnetite, cuprous and cupric oxides are recorded for the range 70—300° Abs. Except in the case of cuprous oxide, the specific heat curves exhibit discontinuities. The smoothed curves are represented by the sum of Debye and Einstein functions, whence the respective molal entropies (g.-cal./1°) at 25° are calculated to be 12.7±2; 34.69; 21.7±1; 9.75. S. K. TWEEDY.

Heat capacities at low temperatures of the oxides of tin and lead. R. W. MILLAR (*J. Amer. Chem. Soc.*, 1929, 51, 207—214).—The molal heat capacities of stannous and stannic oxides, red lead, and lead dioxide are recorded for the range 70—300° Abs. (cf. Millar, *A.*, 1928, 936). Except in the case of red lead the specific heats are represented as the sum of Debye and Einstein functions, whence the respective molal entropies at 25° are calculated to be (g.-cal./1°): 13.56, 12.51, 60.53, and 18.27. The molal free energies (ΔF) at 25° are —123540, —147270, —52010, and the heats of formation (g.-cal. evolved) 137800, 172440, and 65960, respectively, for the last three oxides. The molal entropies (g.-cal./1°), free energies (g.-cal.), and heats of formation (g.-cal. evolved) are,

at 25°, 16.41, —44887, and 51960, respectively, for yellow litharge, and 15.62, —45050, and 52360, for the red modification. S. K. TWEEDY.

Absolute zero of temperature ; specific heats of gases ; and deductions respecting quanta. F. H. LORING (Chem. News, 1928, 137, 370; 1929, 138, 18—22, 81).—Speculative. C. W. GIBBY.

Specific heat of lead at the temperature of liquid helium. W. H. KEESOM and J. N. VAN DEN ENDE (Physikal. Z., 1928, 29, 896—897).—The work of Keesom and Andrews (A., 1927, 1131) has been repeated using an improved technique. For the region 10—20° Abs. the earlier data are confirmed. The present work is in agreement with the Debye curve with $\theta=88$ even in the region 3—6.5° Abs. to which the T^3 law applies, so that discrepancies in the earlier work now disappear. At 7° Abs. a marked deviation persists, but since a similar deviation occurs when bismuth is studied instead of lead, the discrepancy may be due to an instrumental defect.

R. A. MORTON.

Supercooled water. L. HAWKES (Nature, 1929, 123, 244).—Water remains liquid at —9°, but when suddenly cooled to —12° or —17° it solidifies without crystallisation. A. A. ELDRIDGE.

Surface tension constants in an homologous series from the point of view of surface orientation. K. W. HUNTEN and O. MAASS (J. Amer. Chem. Soc., 1929, 51, 153—165).—The surface tensions (capillary-rise method) and densities of some fatty acids and of dicetyl were measured up to about 150° and, in the cases of hexoic and propionic acids, down to —20° and —36°, respectively. The acids exhibit zero angle of contact with glass. The total surface energy of fatty acids rapidly reaches a series constant. The series constant for the paraffins is apparently reached much more slowly. These two series constants approach one another. The surface orientation of pure liquids, unlike that of water, is probably incomplete, and it is unlikely that abnormally high values of the Ramsay and Shields constant, K , can be accurately interpreted in terms of complete orientation. A partial orientation may be the cause both of the high values of K and of the regularities in the series constants. The value of K for a fatty acid containing n atoms of carbon is given by $\times 2.12/3.95$. The deviations from the normal values both of K and of the parachor parallel one another in the case of the fatty acids and may be due to the same cause.

S. K. TWEEDY.

Determination of the density of liquids. J. GRINDLEY (J.C.S., 1928, 3297—3298).—The method of Hartley and Barrett (*ibid.*, 1911, 99, 1072) has been modified in order that the densities of more expansible liquids may be derived over a range of temperature.

F. J. WILKINS.

Density and temperature. VII. W. HERZ (Z. Elektrochem., 1928, 34, 857—858; cf. A., 1927, 718, 927).—For 33 substances of widely different types, the ratios of the density of the liquid to the density of the saturated vapour at $\frac{1}{2}T_c$ and at $\frac{3}{2}T_c$ have been calculated from published data. In the first case the ratios are fairly concordant about an average value of

10, being highest for the alcohols (methyl alcohol 14.86) and lowest for gases (argon 6.88). At $\frac{3}{2}T_c$, the ratios are larger and become too divergent for a mean value to be given. The sequence also changes.

L. S. THEOBALD.

Approximate prediction of vapour pressure. J. CHIPMAN (J. Physical Chem., 1929, 33, 131—135; cf. A., 1928, 1315).—Relationships between the heat of vaporisation, ΔH , the apparent heat of vaporisation, L' , obtained from vapour-pressure data, and the heat of vaporisation ΔH_K derived from the Kistiakovski equation have been investigated. For a given class of liquids, the ratio between any two of these quantities at the b. p. is approximately constant. The ratio $L'/\Delta H_K$, called the "slope factor," g , can be estimated for most liquids from the tables which are given, and this factor and the normal b. p. suffice to establish an approximate vapour equation which is given as $\log P_{atm} = \log (82.07T_b)/T + g \log (82.07T_b)$. A method for correcting observed b. p. to normal pressure is also indicated.

L. S. THEOBALD.

Vapour pressures of related compounds and the application of Dühring's rule. A. R. CARR and D. W. MURPHY (J. Amer. Chem. Soc., 1929, 51, 116—121).—The use of Dühring's rule for constructing vapour-pressure curves is discussed. The Dühring lines (the locus of points obtained by plotting the b. p. of a substance as ordinate against the b. p. of a reference substance at the same pressure) for a family of substances intersect in a common point. Graphs are given showing line families for aliphatic hydrocarbons, alcohols, anilines, esters, etc. In the case of organic acids the lines are parallel.

S. K. TWEEDY.

New equation of state. H. J. BRENNEN (Proc. Nat. Acad. Sci., 1929, 15, 11—18).—Van der Waals' equation is criticised, and a parameter is shown to be missing. The equation is modified by substituting a/V^n for the term a/V^2 due to the cohesive pressure of the molecules, and n is regarded as the missing third parameter. It is shown that the reduced values a_r , b_r , and n are interconnected by simple relationships, and are definite single-valued functions of the critical ratio K . An exponential function is proposed for a , and it is shown that two substances will exactly obey the law of corresponding states only when they have the same values for both K and $\partial P/\partial T_r$ at the critical point.

N. M. BLIGH.

New equation of state for fluids. II. Application to helium, neon, argon, hydrogen, nitrogen, oxygen, air, and methane. III. Normal densities and compressibilities of several gases at 0°. J. A. BEATTIE and O. C. BRIDGEMAN (J. Amer. Chem. Soc., 1928, 50, 3133—3138, 3151—3157).—II. The equation of state previously proposed (A., 1927, 819) is applied to the above gases between —252° and +400° and up to 100—200 atm. The average deviation between the observed pressures and those calculated from the equation is 0.18%. A method of converting compressibility results in the form of isothermals into the form of isometrics is given, which smooths the results with respect to volume. A method of evaluating the constants in the equation is outlined.

III. The equation of state is used to calculate the compressibility coefficients of the above gases and of carbon dioxide at 0°, and thence their mol. wt. The results agree well with the accepted values. The agreement is also good in the cases of carbon monoxide and nitrous oxide when the mol. wt. of these gases are calculated using in the equation the constants of their isosteres, nitrogen and carbon dioxide, respectively (cf. Langmuir, A., 1919, ii, 506). S. K. TWEEDY.

Allotropic modifications of phosphorus. A. SMITS (Compt. rend., 1929, 188, 390—391; cf. this vol., 127).—The possible forms of the vapour pressure-density curves of phosphorus are discussed on the assumption of the existence of four or three of the allotropic modifications proposed (cf. Nicolaïev, A., 1928, 827). J. GRANT.

Compressibility of thallium, indium, and lead. T. W. RICHARDS and J. D. WHITE (J. Amer. Chem. Soc., 1928, 50, 3290—3303).—The following compressibilities (in megabar⁻¹ × 10⁶) are recorded for pressures between 100 and 500 megabars and at 24.84°: toluene, 70.9; lead, 2.40; thallium, 2.83; indium (*d* 7.296), 2.55; indium containing 3% of zinc (*d* 7.292), 2.51 (the value calculated by the mixture rule is 2.52). Details for the preparation of the metals in the pure state are given. The periodic variations of thermal pressure, internal pressure, and other properties of the elements, as calculated by Richards' equation of state, are discussed with particular reference to the gallium, indium, and thallium group. These elements seem to occupy sub-maximum points in the upward slope of the periodic curves previously given (A., 1915, ii, 518).

S. K. TWEEDY.

Compressibility of sodium, barium, and beryllium. T. W. RICHARDS, L. P. HALL, and B. J. MAIR (J. Amer. Chem. Soc., 1928, 50, 3304—3310).—The following compressibilities (in megabar⁻¹ × 10⁶) are recorded for 25° for the following very pure metals: barium (*d* 3.661) 10.48; beryllium (*d* 1.85) 0.927. The preliminary value of 7.22 is recorded for strontium (*d* 2.737), whilst the value previously recorded for sodium (15.6) is confirmed. Special methods of weighing barium and strontium, and of measuring their densities pycnometrically, are described.

S. K. TWEEDY.

Tube correction in measurements of the velocity of sound in gases. R. E. CORNISH and E. D. EASTMAN (Physical Rev., 1929, [ii], 33, 90—96).—The validity of the Helmholtz-Kirchoff equation for the velocity change of sound in a tube is examined, and it is concluded to be correct for fairly high frequencies and large tube diameters, but not wholly satisfactory for low frequencies and small tubes. An approximation is deduced for the variation of the correction with temperature. N. M. BLIGH.

Internal friction of atomic hydrogen. P. HARTECK (Z. physikal. Chem., 1928, 139, 98—106).—An apparatus is described by which the internal friction of a mixture of atomic and molecular hydrogen and the concentration of atomic hydrogen in the mixture may be determined. Experiments have been carried out at -80°, 0°, and 100° with mixtures con-

taining 58—67% of atomic hydrogen. The values found for the internal friction of atomic relative to that of molecular hydrogen are 0.925 at -80°, 0.792 at 0°, and 0.775 at 100°. From these the absolute value at 0° is calculated to be $(690 \pm 25) \times 10^{-7}$. The temperature coefficient of the internal friction for atomic hydrogen is very small. The following values have been calculated for atomic hydrogen: the free path 130×10^{-7} cm., the active cross-section of the atoms present in 1 c.c. under normal conditions 1.36×10^4 sq. cm. R. N. KERR.

Viscosity and flow-orientation. S. KYROPULOS (Physikal. Z., 1928, 29, 942—947).—Viscosity-temperature curves have been determined for several saturated hydrocarbons. The curves show that in addition to the normal effect due to change in density the breakdown of complexes must be an important factor. The types of complexes and the influence they exert on viscosity are discussed. It is shown that the flow-orientation of the molecules of liquids is of importance to lubrication and other stream processes.

R. A. MORTON.

Variation with direction of the capillary constant of smectic substances. R. GIBBAT (Compt. rend., 1929, 188, 183—185).—Gauss' theory of capillarity is applied to smectic substances, and expressions are obtained for the capillary constant which indicate the existence of two minimum values, corresponding with planes passing through the axis and perpendicular to it. J. GRANT.

Equation of state for gaseous mixtures. I. Application to mixtures of methane and nitrogen. J. A. BEATTIE (J. Amer. Chem. Soc., 1929, 51, 19—30).—The equation of state previously proposed (cf. A., 1927, 819) applies to mixtures of methane and nitrogen, those constants in the equation containing the dimension of density to the first power being linearly combined in proportion to the relative amounts of each gas, e.g., $b_{\text{mix}} = b_1(1-x) + b_2x$, where x is the mol. fraction of the second constituent, whilst the A constant is given by $A_{\text{mix}} = [\sqrt{A_1(1-x)} + \sqrt{A_2}x]^2$. A general algebraic equation in thus obtained for gaseous mixtures, and this can be thrown into the virial form (cf. A., 1928, 1315). S. K. TWEEDY.

Pressures of gaseous mixtures. II. Helium and hydrogen, and their intermolecular forces. C. W. GIBBY, C. C. TANNER, and I. MASSON (Proc. Roy. Soc., 1929, A, 122, 283—304; cf. Masson and Dolley, A., 1923, ii, 462).—Full details are given of measurements of the compressibilities, up to 125 atm., of helium, hydrogen, and ten mixtures of the two gases at 25°, and of both pure gases and an equimolecular mixture at seven temperatures from 25° to 175°. All the mixtures deviate from Dalton's partial pressure law, in the sense of yielding actual pressures higher than the additive figures. The deviation is at a maximum in equimolecular mixtures, where it reaches, at 25°, about 4% of the ideally additive pressure. Within a certain range of compositions, mixtures of the two gases are more incompressible than either constituent. The data may be expressed by $pv = a + bp$, and values of a and b are recorded for each gas and each temperature. Values of b are

plotted against gas composition, and, applying Lennard-Jones' partial pressure equation (A., 1927, 727), the measurements are shown to support the assumption that the intermolecular forces in helium and hydrogen are spherically symmetrical about each molecule. The influence of temperature on the constants of the isotherms was studied, and the results confirm Lennard-Jones' theory of superposed forces of attraction and repulsion around each molecular centre in an encounter. The distance indices of these forces have been evaluated for encounters between 2He, between 2H₂, and between He and H₂. If the distance index for the attractive component is -5 , then the index for the repulsive component is found to be -10 or -11 in all three cases. The force constants are evaluated; regarding the constants for the attractive components of force, that between 2He is only about one fourth of that between 2H₂, and that between He and H₂ is slightly larger than the value for 2He. The "cohesion energy" for each type of encounter is defined and tabulated, together with the kinetic diameter (the distance of closest approach) appropriate to various temperatures. The joint kinetic diameter when a helium atom meets a hydrogen molecule is practically the average of the respective kinetic diameters when each molecule meets its own kind.

L. L. BIRCUMSHAW.

Viscosity of mixtures of rare gases. I. A. NASINI and C. ROSSI (Gazzetta, 1928, 58, 898—912).—With the apparatus previously described (A., 1928, 1084) the viscosities of mixtures of helium and krypton containing 10.21—94.54% Kr have been measured at 16—27° and at 100° approx. A simple device for ensuring intimate mixture of the small quantities of gases used is described. The viscosity-composition curves show a maximum viscosity for 38% Kr at 16° and 43% at 100°. These are considered to be in fair agreement with the theoretical maxima at 30 and 35% Kr, respectively, calculated by means of Thomsen's modification of Puluj's formula (cf. following abstract). In the case of mixtures of helium and neon no maximum is possible from the formula, and preliminary measurements of the viscosities of such mixtures confirm this.

O. J. WALKER.

Viscosity of gaseous mixtures. A. NASINI and C. ROSSI (Gazzetta, 1928, 58, 912—921).—The relationship of Puluj connecting the viscosity of a gaseous mixture with those of the constituent gases has been critically examined with reference to the explanation of the gradual disappearance of the maxima in the viscosity-composition curves as the temperature is raised. The partial pressure (x) of the constituent with the higher mol. wt. (m_2) in the mixture of maximum viscosity is given by the expression derived from Puluj's formula $x = 3/(c-1) - 4/(a-1)$, where $a = m_2/m_1$ and $c = (\eta_1/\eta_2)^{3/2} (m_2/m_1)^{3/4}$ (cf. Thomsen, A., 1912, ii, 23). Since $1 > x > 0$ and $a > 1$, the limits of between which a maximum is possible can be determined. The variation of η_1/η_2 with temperature is discussed. Using the Sutherland function connecting temperature and viscosity, the temperature limits between which a maximum viscosity is possible can be calculated. The maximum is restricted to

definite temperature limits only in the case of certain mixtures. In other mixtures there is either a maximum at all temperatures or no maximum is possible. The experimental results bear out these conclusions.

O. J. WALKER.

Viscosity of supersaturated solutions. II. I. K. TAIMNI (J. Physical Chem., 1929, 33, 52—68; cf. A., 1928, 578).—The viscosities of supersaturated solutions of sucrose, carbamide, acetamide, citric acid, and sodium thiosulphate in water, of resorcinol, acetamide, and urethane in ethyl alcohol, and of phenanthrene and urethane in toluene have been measured by means of the apparatus previously employed (*loc. cit.*). The most pronounced supersaturation occurs with the solvent of greatest association. The curves viscosity-concentration, viscosity-temperature, $\log \eta$ -temperature, and $\log \eta$ -concentration and data for 10—50° are reproduced. The Arrhenius equation $\log \eta/\eta_0 = 0C$ is not applicable to these solutions, but either of the equations $\eta = mC + n$ or $\log \eta = 0C + \phi$, where θ , ϕ , m , and n are constants depending on temperature, can be applied. The temperature coefficients of viscosity for all solutions increase with increasing concentration and with a fall in temperature. Under certain conditions, relative viscosity, concentration, and temperature can be connected by an equation of the type $\log \eta' = (kt + k')/c$, which, in this instance, holds for solutions of sucrose in water.

L. S. THEOBALD.

Theory of concentrated solutions. VI. Application of thermal analysis to the determination of the f.-p. curves of binary mixtures of organic compounds of low m. p. J. TIMMERMANS (Bull. Soc. chim. Belg., 1928, 37, 409—423).—Using a thermo-couple the f.-p. curves of the binary mixtures of benzene with *n*-hexane and chloroform, cyclohexane with methylcyclohexane, *n*-hexane, toluene, carbon tetrachloride, and chloroform, ethylene bromide with ethyl bromide and aniline, nitrobenzene with carbon disulphide and ethyl acetate, aniline with carbon tetrachloride, toluene, and acetone, carbon tetrachloride with chloroform, carbon disulphide, and acetone, and chloroform with *n*-hexane, toluene, and carbon disulphide have been investigated. Additive compounds are formed by chloroform with benzene and toluene, and by acetone with aniline. cycloHexane has a transition point at -91° .

J. S. CARTER.

Solutions. II. F.-p. diagrams and latent heats of evaporation of binary mixtures of volatile liquids. III. The transition point of carbon tetrachloride and compounds of carbon tetrachloride or chloroform with acetone, ether, and benzene. W. F. WYATT (Trans. Faraday Soc., 1929, 25, 43—48, 48—53; cf. A., 1928, 1085).—II. F.-p. curves have been determined for the systems methyl alcohol-chloroform, ethyl ether-carbon tetrachloride, ethyl acetate-carbon tetrachloride, and ethyl bromide-benzene. Cryoscopic evidence is found for the existence of the compounds MeOH·CHCl₃, Et₂O·CCl₄, CCl₄·2Et₂O, and CCl₄·2Me·CO₂Et. The f.-p. diagrams are considered in relation to the curves for the latent heats of vaporisation of the systems. The form of the latent heat curves for systems containing carbon tetrachloride indicates that compounds

of this substance are not stable at elevated temperatures. The latent heat curve for the system MeOH-CHCl₃ shows two maxima and two minima.

III. The transition point at about -48.5° in the systems ethyl alcohol-carbon tetrachloride, ethyl ether-carbon tetrachloride, and ethyl acetate-carbon tetrachloride has been observed also in mixtures of acetone and of carbon disulphide with carbon tetrachloride. It is inferred from this and from the data of other workers that the break is due to the existence of two crystalline modifications of carbon tetrachloride, and it is suggested that observations of this transition point in a binary mixture would be preferable to the use of the pure substance as a fixed temperature in thermometry. The f.-p. curves for the systems benzene-carbon tetrachloride and ethyl ether-carbon tetrachloride have been determined, and in conjunction with curves for other systems evidence has been obtained for the existence of the following compounds: C₆H₆.2CCl₄, stable only in mixtures containing more than 71% of carbon tetrachloride; C₆H₆.CCl₄, stable only in the presence of more than 52% of carbon tetrachloride; COMe₂.CCl₄, stable only in the presence of more than 61% of acetone; CHCl₃.3Et₂O, unstable except in mixtures containing more than 84% of ether; CHCl₃.2Et₂O, more stable than the 1:3-compound, but only in the presence of more than 75% of ether; CHCl₃.Et₂O, stable, m. p. -99.5° ; and 2CHCl₃.Et₂O, stable at its m. p. -89.5° , and in excess of ether but not in excess of chloroform. The oxygen compounds are accounted for by supposing that a co-ordinate linking is formed by the oxygen atom of the one substance donating a lone pair of electrons to the chlorine atom of the halogen derivative. The etheric oxygen atom is seen to be a more powerful donator than a ketonic oxygen atom and the chlorine atoms of chloroform are more powerful acceptors than those of carbon tetrachloride. With benzene as a second component it is found that chloroform does not combine with it, although carbon tetrachloride is able to do so.

F. G. TRYHORN.

Determination of vapour and liquid compositions in binary systems. I. Methyl alcohol-water. J. B. FERGUSON and W. S. FUNNELL (J. Physical Chem., 1929, 33, 1-8).—A description is given of a new type of apparatus by means of which the composition of the vapour in equilibrium with a binary liquid can be determined using only a small sample of liquid. Vapour is circulated over a weighed sample of liquid until equilibrium is obtained, the pressure is then measured, and finally a known volume of vapour is condensed and weighed. Data for the system methyl alcohol-water at 39.90° have been obtained and are critically examined, together with those of other investigators, by means of Miller's abacus (A., 1925, ii, 399).

L. S. THEOBALD.

Vapour pressures in the systems ethyl phthalate with ethyl alcohol and with methyl alcohol. H. W. FOOTE and J. K. DIXON (Amer. J. Sci., 1929, [v], 17, 146-152).—The vapour pressure-composition curves for these two systems have been determined at 25° by a static method. Both show wide deviations from the ideal and to approximately the same extent. As ethyl phthalate has a vapour

pressure of approximately zero at 25° , the two systems give the partial pressures of alcohol vapour.

R. N. KERR.

Binary azeotropes. XII. M. LECAT (Ann. Soc. Sci. Bruxelles, 1928, B 48, i, 113-126; cf. A., 1928, 943).—A further list of binary organic mixtures is given containing 161 positive and 11 negative azeotropes, 27 eutectic mixtures, and a large number of euzotropes. The mixture of phenetole and isoamyl ether constitutes the first established case of azeotropy in which both the components are oxides.

O. J. WALKER.

New application of the differential ebullioscope. H. SWIENTOSLAWSKI (Compt. rend., 1929, 188, 256-258).—The author's differential ebullioscope (A., 1927, 642), in which the b. p. of the solution (T_H) and pure solvent (T_B) are obtained simultaneously at a given pressure, has been used to distinguish between pure liquids and azeotropic mixtures. The pressure-temperature curves for these coincide when $T_H = T_B$, but at other pressures may be quite divergent. Mixtures of alcohol (32.41%) and benzene were studied.

J. GRANT.

Diffusion of hydrogen in iron. E. G. MAHIN (Proc. Indiana Acad. Sci., 1927, 37, 272-276).—Experiments support the view that hydrogen liberated by "pickling" oxide-coated iron diffuses into the metal in the atomic condition and is liberated at the surface as molecular hydrogen.

CHEMICAL ABSTRACTS.

Diffusion in crystalline substances. C. TUBANDT, H. REINHOLD, and W. JOST (Z. anorg. Chem., 1928, 177, 253-285).—A new method is described for measuring diffusion processes in solid salts. The rates of diffusion of the cations in silver sulphide, chloride, bromide, and iodide, and cuprous sulphide, bromide, and iodide have been determined. For the sulphides and for silver iodide the influence of temperature T on the diffusion rate D is given by $D = Ae^{-B/T}$, where A and B are constants. For the iodides D may be calculated from the equation $D = CT\mu$, where μ is the specific conductivity and C a constant. The self diffusion D_0 may be calculated from the observed diffusion rates by use of conductivity and transport data for the pure salt and for the mixed crystals; $D_0 = D\mu_1(1-m)/\mu_2(1-n)$, where n and $1-n$ are the transport numbers and m and $1-m$ the fractional molar concentrations of the mobile ions in the mixed crystal. The self-diffusion of solid salts may be calculated approximately from the conductivity by means of the equation applicable to solutions, viz., $D = RTB/N$, where B is the mobility.

H. F. GILLBE.

Binary solutions of consolute liquids. W. D. BANCROFT and H. L. DAVIS (Proc. Nat. Acad. Sci., 1929, 15, 8-10).—A generalised form of equation for Raoult's law is proposed, and this is shown to give satisfactory results when applied to ethyl alcohol and water, and to acetone and ethyl ether. A method is described which permits of the derivation of the distribution of a substance between two miscible liquids, and this is applied to the distribution of acetone between methyl alcohol and water.

N. M. BLIGH.

System *o*-cresol-methyl alcohol-water. G. VON SZELÉNYI (Z. Elektrochem., 1929, 35, 33—37).—Measurements have been made of the mutual solubility of *o*-cresol, methyl alcohol, and water, and a series of curves is constructed for ten mixtures of methyl alcohol and water (varying from 0 to 44.3% of methyl alcohol) showing the effect of adding increasing amounts of *o*-cresol on the mutual miscibility temperatures. The binodal curves of the system are also reproduced. It is found that the solubility of *o*-cresol in methyl alcohol-water mixtures decreases with decreasing concentration of alcohol, and that the critical solution temperature rises. A mixture of pure *o*-cresol (39.5%) and water (60.5%) has a critical solution temperature of 169.7°. L. L. BIRCUMSHAW.

Influence [of alkali and alkaline-earth halides] on solubility. W. HERZ and F. HIEBENTHAL (Z. anorg. Chem., 1928, 177, 363—380).—The effect of the halides of alkali and alkaline-earth metals on the solubility of potassium chromate, potassium permanganate, phenol, mercuric oxide, potassium dichromate, iodine, and several organic acids was determined. In the case of the three potassium salts the reverse effect was also investigated. The salts were added in varying concentrations. In most cases it was possible to represent the change in solubility by a simple linear equation, but sometimes the relationship was logarithmic in form. The effect on the solubility depends to a certain extent on the at. wt. of the added cation. A. J. MEE.

Solubility of complex cobalt and chromium precipitates. I. A. BENRATH [with K. MIENES, H. STEINRATH, and K. ANDREAS (Z. anorg. Chem., 1928, 177, 286—302).—The solubilities of hexammine-, pentammine-, tetrammine-, and diethylenediamine-chromic and -cobaltic complexes in solutions containing ammonia and in acid solutions which contain a common ion at varying concentrations have been determined at 25°, and the nature of the compounds which are stable in contact with these solutions has been established. H. F. GILLBE.

Distribution of ammonia between water and chloroform at 25°. H. G. DIETRICH (J. Physical Chem., 1929, 33, 95—98).—The distribution coefficient in the system water-ammonia-chloroform has the value 35.8 ± 0.1 at 25°, when expressed as the ratio number of g.-mol. ammonia per 1000 g. of water/number of g.-mol. ammonia per 1000 g. of chloroform. The value varies with the source of the chloroform, an effect attributed to traces of impurities used to inhibit hydrolysis of this reagent. An attempt to extend the study of this system to zinc hydroxide failed on account of the length of time required to attain equilibrium and the consequent hydrolysis of the chloroform. L. S. THEOBALD.

Adsorption from solution by ash-free adsorbent charcoal. E. J. MILLER (Fifth Colloid Symposium Monograph, 1927, 55—80).—Pure sugar charcoal, and other pure charcoals, absorb acids, but not inorganic bases; only the anion of neutral salts of inorganic acids is adsorbed, whilst the absorption of salts of organic acids is partly hydrolytic and partly molecular. By the addition of certain impurities to the charcoals, adsorption anomalies as recorded in the

literature could be observed. With hydroxy- and amino-benzoic acids absorption decreases in the order *o*-, *p*-, *m*-; chloro- and dichloro-acetic acids are more strongly adsorbed than acetic, whilst glycine is not adsorbed. With butyric, valeric, and hexoic acids the *iso*-compounds are less strongly adsorbed than the *n*-compounds. Adsorption increases in the order, ammonium, trimethylammonium, triethylammonium hydroxide. Acids adsorbed on charcoal are incapable of inverting sugar. The hydroxyl ion shows negative adsorption. Pure charcoal has no isoelectric point. CHEMICAL ABSTRACTS.

Adsorption of certain vapours by charcoal at various temperatures up to and above their critical temperatures. J. N. PEARCE and C. M. KNUDSON (Proc. Iowa Acad. Sci., 1927, 34, 197—212).—The adsorption isotherms for water vapour differ from those for ethyl and methyl alcohol, ammonia, and methylamine, and indicate that retention of water is probably due merely to capillary action. Freundlich's relation applies, except near saturation, to the alcohols and ammonia, but not to water or methylamine. The applicability of other relations is investigated. CHEMICAL ABSTRACTS.

Adsorption of the fluorine ion. B. TAMAMUSHI (Kolloid-Z., 1929, 47, 58—60).—Comparison of the adsorption of fluorine ions and of chlorine ions by pure sugar charcoal from solutions of potassium fluoride and potassium chloride respectively shows that, in spite of the greater hydration of the fluorine ion, it is adsorbed more strongly than the chlorine ion. This is explained as a hydrolytic adsorption, the solution becoming faintly alkaline, and by a displacement of the equilibrium at the carbon surface, favouring complex formation in the fluoride solution. In agreement with this view, sugar charcoal adsorbs two to three times as much fluorine ions as chlorine ions from pure solutions of the corresponding acids. E. S. HEDGES.

Application of Langmuir's theory of the adsorption of gases on charcoal. M. PÓLANYI (Z. physikal. Chem., 1928, 138, 459—462).—A reply to Zeise's criticism (cf. A., 1928, 1182) of Polanyi's theory. For a number of systems to which the Langmuir adsorption isotherm is apparently applicable, further observations suggest that the agreement is fortuitous. A. J. MEE.

Adsorption of gases and vapours by different kinds of silica gels. E. BOSSHARD and E. JAAG (Helv. Chim. Acta, 1929, 12, 105—113).—Thirteen silica gels have been prepared by treatment of water-glass solutions of various concentrations with either hydrochloric or acetic acid or ferric chloride. Different methods of drying and activation have been used for the various gels. The adsorption of sulphur dioxide and bromine vapour has been measured and in both cases this is found to be dependent on the mode of preparation of the gel. Those produced from the more dilute water-glass solutions and subjected to the slowest activation have the greatest power of adsorption of sulphur dioxide. Adsorption of this gas causes a dark brown coloration of the gel. In the case of bromine vapour, adsorption is accompanied by condensation phenomena. The extent of

the latter depends on the size of the pores of the gel, which is determined by the method of activation. The size of the particles of the gel has no influence on the power of adsorption of either sulphur dioxide or bromine. The heat produced on wetting the gel with alcohol has been measured and considerable differences have been found amongst the different kinds. The swelling powers of the gels have been measured by the method of Pavlov (A., 1927, 722). The weight of finely-powdered product obtained per c.c. of gel and the resistance to pressure have also been measured.

R. N. KERR.

Siloxen as adsorbent. H. KAUTSKY and G. BLINOFF (Z. physikal. Chem., 1928, 139, 497—515).—The structure of siloxen is further discussed (cf. A., 1926, 924) and its simplicity compared with that of other adsorbents, especially carbon, is emphasised. Specific gravity determinations support this view. Siloxen is a good adsorbent for both gases and dissolved substances, although it is less active than specially-prepared carbon adsorbents. The addition of alcohols and fatty acids to siloxen during its preparation brings about, in many cases, a loosening of the structure and this effect increases with the higher members of an homologous series. It appears to be connected with adsorption of the substance by the siloxen to some extent, but it also depends on the polar nature of the substance. Acetone, which is markedly adsorbed, and ketones in general have no effect, however, on the physical structure of the siloxen. The adsorption isotherms of the first five members of the fatty acids in aqueous solution have been determined and are in good agreement with Traube's rule. Alcohols, benzoic acid, phenol, and phenylthiocarbamide also are adsorbed and certain dyes are decolorised, but this last effect may be due to reduction. Aniline hydrochloride is adsorbed only by oxidised siloxen; hydrolytic adsorption occurs, the positive ions only being fixed. Compared with other adsorbents, the simple and definite nature of the surface, which can be easily controlled, makes siloxen especially suitable for the study of adsorption phenomena.

L. S. THEOBALD.

Adsorption of carbon dioxide by ferric hydroxide. J. TILLMANS, P. HIRSCH, and K. SCHILLING (Kolloid-Z., 1929, 47, 98—101).—In connexion with the question whether the corrosion of iron is related to an adsorption of carbon dioxide by ferric hydroxide, measurements have been made of the adsorption of carbon dioxide (both in the free state and as hydrogen carbonate) by precipitated ferric hydroxide. Adsorption was found to occur. The freshly-precipitated hydroxide did not differ from a preparation 8 days old, but ferric hydroxide precipitated from a hot solution adsorbed less than the precipitate formed in the cold. When the amount of sodium hydrogen carbonate was kept constant, the amount of carbon dioxide adsorbed increased with the concentration of carbon dioxide in the solution, and when the amount of carbon dioxide was kept constant, the carbon dioxide adsorbed increased with the concentration of sodium hydrogen carbonate. The adsorption is considered to be due to the formation of a complex of the type $\text{Fe}(\text{OH})\cdot\text{CO}_3, x\text{Fe}(\text{OH})_3$.

E. S. HEDGES.

Adsorption of the alkali metals on a mercury-vacuum interface. R. S. BRADLEY (Phil. Mag., 1928, [viii], 6, 775—779).—The results of Schmidt (A., 1913, ii, 190) and Oppenheimer (A., 1928, 702) for the surface tensions of alkali metal amalgams are used in conjunction with those of Bent and Hildebrand (A., 1928, 130) for the activities of the alkali metals dissolved in mercury to calculate the Gibbs surface excess $\Gamma.d\sigma/d(\log a_2)=\text{constant}$ where σ =surface tension and a_2 =activity of the dissolved metal. The results combined with those of Bragg (A., 1920, ii, 537) for the atomic radii of the metals indicate that the surface layer is characterised by compounds of mercury with sodium and potassium, the composition of which corresponds approximately with one alkali metal atom for six mercury atoms. In caesium amalgams no such compounds are indicated.

A. E. MITCHELL.

Adsorption of potassium chromate on zinc. R. F. REED and S. C. HORNING (J. Physical Chem., 1929, 33, 136—137).—Aqueous solutions of potassium chromate react with a zinc surface, depositing on it a compound of chromium and making it less active towards methyl-violet. A 20% solution of potassium chromate yielded 0.003 mg./cm.² of adsorbed chromate on the zinc. Treatment of zinc with potassium chromate solution lessens the amount of moisture which it can adsorb.

L. S. THEOBALD.

Adsorption of iodine on calcium fluoride. J. H. DE BOER (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 906—914).—Adsorption isotherms for iodine on calcium fluoride have been determined. A theoretical explanation is offered. C. W. GIBBY.

Surface tension of solutions. I. Influence of salts on surface tension of aqueous solutions of urethane. The determinations. II. Calculation of surface tension from the drop-weight. III. Influence of salts on surface tension of aqueous solutions of urethane. Discussion of results. S. PALITZSCH (Z. physikal. Chem., 1928, 138, 379—398, 399—410, 411—431).—I. The drop-weight method was used to determine the influence of salts on the surface tension of aqueous solutions of urethane. Twenty-six salts of various kinds were used, and also hydrochloric acid. Tables are given showing the results of determinations on some four hundred solutions. The accuracy is about 1 in 500.

II. Modifications are made in the methods of Morgan and Harkins, making them simpler and more rapid. It is shown that the calculations of Iredale are not fundamentally different from those of Harkins. The radius of the dropping tube is calculated from the drop-weight of water, and the accuracy of the improved method of calculation is tested by determining the surface tension of benzene, for which a value is obtained in good agreement with that found by Sugden.

III. The results obtained in section I are re-grouped and discussed. The dependence of the influence of salts on their concentration can be investigated in two ways, first by using a solution with constant urethane concentration and variable salt concentration, and, secondly, by the reverse method of using solutions with variable urethane and constant salt concentrations. Curves are drawn for both methods. Those

which are drawn for solutions containing the same salt concentration but different urethane concentrations are very similar. They cross the curve for the surface tension of salt-free urethane solutions. The maximum lowering of the surface tension by a given quantity of a salt is in a remarkable way characteristic for that salt. Salts can be divided up into two groups according to their influence on the surface tension. In the first group are salts with bivalent acid radicals. The second contains salts with univalent acid radicals. The influence of the first class is more than double that of the second. Phosphates seem to produce a large effect, but the salt which has the greatest influence is potassium ferrocyanide. A peculiarity was noted in the fact that different preparations of potassium chloride did not give the same results although all were chemically pure. The interfacial surface tension of solutions in equilibrium with urethane solution was determined. The action of hydrochloric acid was also investigated; it differs somewhat from the action of salts. A. J. MEE.

Rate of evaporation through surface films. R. BARTLETT and T. C. POULTER (Proc. Iowa Acad. Sci., 1927, 34, 214—215).—Experiments with solutions of calcium and sodium chlorides show that the rate of evaporation is slightly influenced by the surface tension of the liquid. CHEMICAL ABSTRACTS.

Influence of adsorbed films on rates of evaporation. R. P. BELL (J. Physical Chem., 1929, 33, 99—117; cf. A., 1928, 848).—The rate of evaporation of chlorine from solution in carbon tetrachloride has been measured at 25° with varying chlorine concentrations and velocity of air current; the results are compared with various equations for the kinetics of evaporation in a current of gas. Measurements have also been made of the reduction in the rate of evaporation which is brought about by dissolving trichloroacetic acid in the carbon tetrachloride. The reduction is attributed to surface adsorption of the acid, and it would seem that a saturated surface film of the acid is formed at concentrations greater than 1.4% by weight. The surface tension of solutions of trichloroacetic acid in carbon tetrachloride has been determined by the drop-weight method; by the application of Gibbs' adsorption equation the lower limit of concentration for the formation of a saturated film is found to be 1.0—1.6% by weight, in good agreement with the value given above. The measurement of rates of evaporation is suggested as a general method for the investigation of adsorption phenomena in solutions. L. S. THEOBALD.

Osmosis of ternary liquids. General considerations. VI. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 811—822).—A theoretical discussion of the directions in which substances will diffuse through membranes. The effects have been investigated experimentally for the system sodium dithionate-barium dithionate-water, with membranes of collodion and of collodion containing copper ferrocyanide and for the system ammonium chloride-ammonium succinate-water, with membranes of collodion, pig's bladder, cellophane, collodion containing copper ferrocyanide, and parchment. C. W. GIBBY.

Mineral trees: their formation and significance. M. COPISAROW (Kolloid-Z., 1929, 47, 60—65).—A description is given of arborescent forms of several slightly soluble inorganic compounds, mainly salts of calcium, strontium, barium, and cobalt. The formation of gas bubbles is not essential for the production of these structures. An analogy is drawn between the production of tree formations on the one hand, and Liesegang rings and spiral formations on the other. E. S. HEDGES.

Liesegang rings as a periodic coagulation phenomenon. J. R. I. HEPBURN (J.C.S., 1929, 213).—The formation of Liesegang rings of basic cupric carbonate is described. The theory of Henley and Hedges (A., 1928, 1323) concerning this phenomenon is essentially the same as the earlier one of Freundlich. F. W. WILKINS.

Relation between concentration and equivalent refractive power of strong electrolytes in solution. H. KOHNER (Z. physikal. Chem., 1928, B, 1, 427—455).—In employing the mixture rule and the Lorentz-Lorenz formula to determine the variation with the concentration of the equivalent refractive power of a dissolved substance, the principal sources of error lie in the determination of the difference between the refractive index and the density of the solution and solvent. The refractive powers in aqueous solution of lithium, barium, and aluminium chlorides, sodium bromide, lithium, sodium, ammonium, and aluminium sulphates, and sodium and barium chlorates from concentrations of about 2 g.-equiv./1000 g. of water up to saturation have been measured, usually at 25°, and prove in every case to be a linear function of the concentration, increase in which causes a slight rise or slight fall in the refractive power. For a particular salt, the equivalent dispersion does not vary with the concentration. Extrapolating the refractive powers to infinite dilution, it appears that at this dilution the refractive powers of electrolytes are constituted additively of those of their ions. The variation in refractive power with concentration may be explained by supposing that with increasing concentration more and more ions with opposite charges unite without interposition of water molecules. R. CUTHILL.

Measurement of refraction of solutions. W. GEFFCKEN and H. KOHNER (Z. physikal. Chem., 1928, B, 1, 456—465).—By fitting the Pulfrich refractometer with a divided circle having finer divisions than that usually supplied, and substituting a helium tube for the sodium light and a microscope with cross-wires for the reading-lens, the accuracy of the instrument has been very considerably improved. The trough has also been modified in such a way as to permit of liquid being introduced and withdrawn rapidly and without risk of evaporation, or coming in contact with air. A new form of pycnometer capable of an accuracy of about 0.001%, when 20 c.c. of liquid are used, is described. R. CUTHILL.

Relation between specific rotation and refractive index of a solution. W. PERSCHKE (Z. Elektrochem., 1929, 35, 17—18).—Using Gumprecht's data (Physikal. Z., 1923, 24, 434) for solutions of

camphor in ethyl alcohol, camphor in benzene, and tartaric acid in water, it is shown that the relation between the specific rotatory power and refractive index of a solution may be expressed by means of the following formula, which is independent of the concentration: $\log [\alpha] = a + b \log n$, where a and b are coefficients which are approximately constant for a given optically active solute in a given solvent.

L. L. BIRCUMSHAW.

Rotatory power of tartrates of organic bases; study of strong electrolytes. E. DARMOIS (Compt. rend., 1929, 188, 388—390).—The $[\alpha]_D$ -concentration curves of ammonium tartrate and its mono-, di-, tri-, and tetra-methyl or -ethyl derivatives follow the order mentioned, the decrease in $[\alpha]_D$ being very high for tetrathylammonium tartrate, whilst for benzylamine tartrate there is a considerable increase. If it is assumed that the solutions contain only dissociated molecules, there is evidence that the decrease and increase are due respectively to dehydration and deformation of the tartrate ion.

J. GRANT.

Molecular structure in solution. IV. Densities, viscosities, and electrical conductivities of aqueous solutions of cobalt chloride and hydrochloric acid at different temperatures. O. R. HOWELL (J.C.S., 1929, 162—172).—The densities, viscosities, and electrical conductivities of two aqueous solutions, one containing 120 g. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ per litre with 4*N*-hydrochloric acid and the other hydrochloric acid alone, have been determined every 5° over the temperature range 0—80°. The difference curves are quite smooth, differing from those previously obtained (A., 1927, 1136) for solutions of cobalt chloride containing varying concentrations of hydrochloric acid. Consequently, the changes involved in the two essentially similar colour changes are fundamentally different. It is suggested that the change in the number of groups round the cobalt atom takes place by addition or subtraction of 2 molecules of water to both cation and anion on cooling and heating respectively.

F. J. WILKINS.

Chemical fogs. H. O. ASKEW (Trans. Proc. New Zealand Inst., 1928, 59, 165—207).

Unsolved problems in the molecular-kinetic behaviour of colloidal suspensions. E. O. KRAEMER (Fifth Colloid Symposium Monograph, 1927, 81—112).—A discussion of the limits of validity of the simple kinetic theory, the causes of departure from ideal relationships, and the extent to which the electric charge or volume of colloidal particles may modify their behaviour.

CHEMICAL ABSTRACTS.

Stability of submicrons. I. Crystal disruption, crystal formation, and emulsion formation. J. TRAUBE and W. VON BEHREN (Z. physikal. Chem., 1928, 138, 85—101).—Evidence is adduced for the formation of submicrons in the process of dissolution of a number of compounds among which are potassium dichromate, boric acid, aluminium citrate, mercuric chloride, and arsenic trioxide. Complex salts of nickel, iron, and cobalt are especially prone to form submicrons during the process of dissolution. Conversely, the formation of submicrons appears as an intermediate stage in the separation

from solution of many crystals, especially those of lead chloride. The stages generally recognised in the process of dissolution of a crystal are, respectively, (a) homogeneous crystal, (b) aggregate of parallel pearl-like cells, (c) scission into individual cells, and (d) scission of the single cells into submicrons. These stages occur in reverse order in the process of crystallisation. Experiments on the emulsification of chloroform by means of various peptising agents indicate that these agents are capable of forming submicrons of exceptional stability, and the number of these increases with the dispersion of the emulsion.

F. G. TRYHORN.

Colloidal gold. H. NICOL (J.S.C.I., 1928, 47, 343—344r).—Pure red sols are produced by adding hydrogen peroxide or "hyperol" in alcoholic solution to a dilute alkaline solution of a gold salt. Reduction by alcohol alone is possible, but is influenced by the nature of the container. Reduction is hastened by hydrogen peroxide, which tends to form a sol containing aurous oxide; alcohol reduces the latter to metal. The reaction proceeds in the absence of actinic light. The blue colour of gold sols is due to two causes: (a) presence of oxide, (b) presence of aggregates. The latter is unalterable if it occurs, as when sodium peroxide is used. Based on the principles studied, a method is given for preparing red sols of high sensitivity.

Tartaric acid method of preparing negatively-charged sols. II. Colloidal nature of Fehling's solution. H. DUMANSKI and A. A. CHALISEV (Kolloid-Z., 1929, 47, 121—131).—Colloid particles can always be detected in alkaline solutions of copper tartrate. In a solution containing 1 mol. of copper hydroxide to about 1.5 mols. of tartaric acid and not more than 1 mol. of sodium hydroxide, the basic salt $\text{Cu}_4\text{H}_4\text{O}_6 \cdot \text{Cu}(\text{OH})_2$ is present. This salt may also be formed by shaking copper hydroxide with an excess of copper tartrate in water; it is decomposed by more concentrated alkali solution. A colloidal basic salt, $3\text{Cu}_4\text{H}_4\text{O}_6 \cdot 5\text{Cu}(\text{OH})_2$, can be produced by mixing copper tartrate with an excess of copper hydroxide in water. When the system is gently warmed, a copper oxide sol is produced, which is negatively charged and may be purified by dialysis. Concentrated solutions of alkali cause coagulation. Copper tartrate is considered to react with sodium hydroxide in the same way as any other salt, but the copper hydroxide or basic salt remains in colloidal solution in consequence of the protective effect of organic hydroxy-compounds on negative sols. Complex tartrates of copper and the alkali metals cannot be prepared, and those the preparation of which has been claimed are said to consist of mixtures or solid sols of cupric hydroxide or basic salts in sodium tartrate crystals. Sols of cupric sulphide and of copper ferrocyanide may readily be formed from solutions of copper tartrate in sodium hydroxide. The cupric oxide sol in alkaline Fehling's solution is a strong oxidising and catalytic agent in virtue of its high degree of dispersion, and its colloidal nature is used to explain the phenomena of ageing, oxidation of sugars, formation of cuprous oxide sols, and other properties.

E. S. HEDGES.

State of copper and iron in alkaline solution in presence of hydroxylic organic substances. W. BACHMANN (Kolloid-Z., 1929, 47, 49—55).—An examination has been made of the solutions formed when sodium hydroxide is slowly added to solutions containing copper or iron salts in presence of glycol, glycerol, mannitol, dextrose, sucrose, dextrin, and starch. The investigation was made by fractional dialysis using different membranes, ultramicroscopic examination, ultra-filtration, measurement of sensitivity to electrolytes, cataphoresis, and electrolysis, and the conclusion was reached that the dissolved metal is present partly as a colloid and partly as a crystalloidal complex, the relative proportions of the two states depending on the conditions. The sensitivity of such systems to hydrolysis decreases with increasing number of hydroxyl groups in the organic substance. E. S. HEDGES.

System colloidal ferric hydroxide-hydrochloric acid-water. E. HEYMANN (Kolloid-Z., 1929, 47, 48).—A preliminary account of a study of equilibrium in aqueous ferric chloride solutions which have been allowed to age until the content of colloidal ferric hydroxide has become constant. It is shown that the quotient $[HCl]^{1/3}/[FeCl_3]$ is not constant, but undergoes a steady change with a variation of about 30%. This indicates that the active mass of the colloidal ferric hydroxide cannot be regarded as constant. The size of the particles also influences the equilibrium, and the chlorine content of the colloid particles is greater when they have been formed by hydrolysis than when the system has been prepared by adding hydrochloric acid to colloidal ferric hydroxide. E. S. HEDGES.

Micellar state of starch. M. SAMEO (Kolloid-Z., 1929, 47, 81—82).—The author summarises his views and shows that they are not completely at variance with those of Malfitano (cf. A., 1928, 1186). E. S. HEDGES.

Structures of clear sodium oleate gels and number of nuclei in these gels. R. ZSIGMONDY (Kolloid-Z., 1929, 47, 97—98).—The structures of sodium oleate gels obtained under different conditions are discussed. In those clear gels that show the presence of nuclei, the number of nuclei depends on the degree of supercooling in a similar way to the relation found with undercooled melts. E. S. HEDGES.

Theory of emulsions. WA. OSTWALD (Kolloid-Z., 1929, 47, 131—132).—The author's "phase-volume theory" of emulsions (A., 1910, ii, 194) can be applied only to the ideal case of pure, two-phase, unprotected, strictly monodisperse systems. The application of the theory to polydisperse and protected emulsions is due to a misunderstanding (cf. Bancroft, A., 1912, ii, 542). E. S. HEDGES.

Emulsions. I. Influence of soap content of both phases on the [stability of] the emulsion. J. WEICHERZ (Kolloid-Z., 1929, 47, 133—136).—With small amounts of soap as the emulsifier, oil-in-water emulsions are readily prepared, but stable water-in-oil emulsions are formed only in presence of larger amounts of soap. When such a water-in-oil emulsion is diluted with water a phase reversal occurs

at a critical phase-volume relation, with formation of an oil-in-water emulsion. This critical phase-volume relation is not connected with the phase-volume theory of Wa. Ostwald (A., 1910, ii, 194), for the critical point is a function of the soap content. E. S. HEDGES.

Absorption of light in colloid systems as a function of the layer thickness. E. GALVEZ (Kolloidchem. Beih., 1929, 28, 148—154).—Theoretical. E. S. HEDGES.

Scattering of light in colloidal solutions and gels. I. Agar sol and gel. K. KRISHNAMURTI (Proc. Roy. Soc., 1929, A, 122, 76—103).—Previous work is summarised and methods are described for measuring the relative intensity and degree of depolarisation of the light scattered by agar sols and gels over the range 10—80°. In reference to these measurements the nature of gelatinisation is discussed. Agar sols are considered as colloids having as the intermicellary liquid a molecular solution of agar. On cooling to about 35°, the hydration of the colloid particles increases appreciably and the intermicellary solution becomes supersaturated. As a result, fresh colloid particles are formed, and when these are sufficiently numerous, further supersaturation is relieved by the condensation of the dissolved agar on the particles already present in the sol. This brings about an increase in the size of the particles, and tends to make them more spherical in shape. The phenomenon of gel-formation is essentially due to the union of the hydrated particles enmeshing the intermicellary liquid, and it is particularly emphasised that the precipitation tendency is not always the main factor which is responsible for gelatinisation. A comparison of the light-scattering capacity of agar sols and gels at the same temperature shows that gels are distinctly more opalescent, and that with rise of temperature the difference between the sol and gel tends to diminish. This suggests that the micelles present in gels are bigger than those in sols at the same temperature. The intensity (I) of the scattered light increases with the concentration of the sols and gels. The regular increase with concentrations of the ratio of I in the sol and gel states indicates that the micelles in the concentrated gels are bigger and more numerous than in the dilute gels. The intensity of the light scattered by agar sols increases with time at and below 35°, until finally a constant value is reached, and the lower the temperature the more rapid is the change. The effect of sudden cooling of agar sols on the light-scattering capacity of the gel was investigated, and in all cases gel-formation was accompanied by a distinct increase in the Tyndall number. The depolarisation factor θ of the light scattered by agar sols and gels was also found to vary with temperature and concentration. With concentrated sols (2.0%) θ increases regularly as the temperature is lowered below 33°, whilst in dilute sols (0.2%) θ decreases with fall of temperature, and with 0.5% sols θ decreases at first to a minimum and then rises. The light thrown by these results on the changes in size and shape of the gel particles is discussed. L. L. BIRCHUMSHAW.

Behaviour of cellulose nitrate gels in polarised light. A. J. PHILLIPS (J. Physical Chem., 1929, 33,

118—130; cf. Tissot, B., 1926, 723).—Various commercial cellulose nitrates have been examined in polarised light. The colours exhibited by samples of varying nitrogen content depend on the degree of dispersion of the cellulose nitrate, which, in turn, is affected by the percentage of water in the nitrating bath, by the ratio of nitric to sulphuric acids, the time and temperature of nitration, viscosity, reduction processes, ultra-violet light, heat, and superheated water. The degree of dispersion effected by nitration to a definite nitrogen content is a more powerful factor in determining the colour exhibited with polarised light than is chemical constitution. The transmitted light ranges from red to blue as the degree of dispersion decreases. L. S. THEOBALD.

Silver nuclear sol and its derivatives. I. Action of light on these sols. A. GALECKI and R. SPYCHALSKI (Z. anorg. Chem., 1928, 177, 337—344).—The sensitiveness to light of a number of silver sols and derivatives has been measured in terms of the time required for complete decolorisation to be produced under irradiation by a quartz mercury arc lamp. The sensitiveness is greatest for those sols which contain the smallest particles, and dilution of the sols reduces the time needed for decolorisation. Irradiation produces a decrease of the viscosity of the sols, which, however, is less for aged sols than for those recently prepared. The viscosity of the decolorised sols, although very small, is diminished by further irradiation. After decolorisation the conductivity of the sols increases, but on further irradiation a considerable decrease of conductivity ensues; parallel changes occur in the optical properties of the sols. It thus appears that on prolonged irradiation colloidal particles are again formed. H. F. GILLBE.

Dielectric constants of silver sols when diluted with varying amounts of ethyl alcohol. G. D. ROCK and S. KLOSKY (J. Physical Chem., 1929, 33, 143—147).—The dielectric constants of silver sols prepared by heating suspensions of freshly-prepared silver oxide in water to boiling, filtering hot, cooling, and reheating to 80°, have been measured at $23 \pm 1^\circ$ in aqueous solutions containing up to 41.6% of ethyl alcohol. In agreement with Errera (A., 1923, ii, 388), the dielectric constants of the sols are substantially equal to those of the pure dispersion media. L. S. THEOBALD.

Ionic equilibrium in colloidal solutions. H. D. MURRAY (J. Physical Chem., 1929, 33, 138—142).—The stability of sols as affected by electrolytes is discussed in reference to the view that the colloidal particle first adsorbs the electrolyte, which is then free to dissociate in such a manner that the ion remaining attached to the particle is that having the same chemical nature as the particle itself. L. S. THEOBALD.

Variations of electrical charge of colloidal particles. III. The influence of non-electrolytes on the cataphoretic speed of colloidal particles and the adsorption of ions by colloidal particles as indicated by such measurements. J. MUKHERJEE, S. RAI-CHOUHURY, and A. N. RAO (J. Indian Chem. Soc., 1928, 5, 697—713; cf. A., 1928, 15).—Migration velocity measurements, at 35°,

have been made with arsenious sulphide sols in presence of methyl, ethyl, and isobutyl alcohols, carbamide, sucrose, and acetone. In all cases the rate of migration (sec. volt/cm. $\times 10^5$) decreases with added non-electrolyte, irrespective of an increase (carbamide) or decrease (sucrose) in the dielectric constant of the medium. The potential of the double layer is not determined by the change in dielectric constant alone (cf. Freundlich, "Kapillarchemie," 1922, 638), and the expression u_0/k (where u_0 —cataphoretic speed after viscosity correction and k —dielectric constant) shows a steady decrease for methyl alcohol, sucrose, and carbamide. A tentative explanation of the results is advanced depending on the change of density of the charge and the thickness of the double layer. The effect of methyl and ethyl alcohols on arsenious sulphide sols containing varying amounts of potassium chloride and hydrochloric acid has also been studied. With varying concentration of potassium chloride the values for a fixed alcohol content decrease until the electrolyte concentration is 0.02*N*, and then increase; methyl alcohol shows a corresponding minimum at about 0.005*N*, and the subsequent increase is much greater. These results indicate that neither the cataphoretic speed nor the potential of the double layer has a critical value at the coagulating concentration. It is suggested that the cataphoretic speed is proportional to the product of the surface density and the thickness of the double layer, the thickness depending on the dielectric constant. The relation between the rate of migration and the adsorption of ions is also discussed.

H. BURTON.

Variation of electrical charge of colloidal particles. IV. Effect of dilution on charge of colloidal particles in presence and absence of electrolytes. J. N. MUKHERJEE, S. P. RAI-CHAUHURI, and A. S. BHATTACHARYYA (J. Indian Chem. Soc., 1928, 5, 735—751).—A continuation of work previously described (A., 1928, 15) on the variation of the charges on arsenious sulphide sols on dilution. The rate of migration diminishes steadily on dilution with water, but in presence of potassium chloride the initial decrease is followed by an increase (in one case an increase followed by a decrease was observed). With ferric hydroxide sols the potential gradient does not remain constant during cataphoresis except when a mixture of ferric chloride and hydrochloric acid is used as the upper liquid. Five-fold dilution with water causes an increase in the rate of migration from 51.5 to 63.1, this value remaining nearly constant up to twenty-fold dilution. Coagulation of arsenious sulphide sols takes place at a much higher cataphoretic speed than that of the "pure" sol. The results previously obtained (*loc. cit.*) are ascribed to the different method of preparation, and to differences in the composition of the sol. The mechanism of coagulation and the relation between cataphoretic speed and adsorption of ions are discussed. H. BURTON.

[Electric] charge of carbon. H. R. KRUYT and G. S. DE KADT (Kolloid-Z., 1929, 47, 44).—Experiments on ash-free carbon by a cataphoretic method and by precipitation with electrolytes have shown that

the carbon particles have a negative charge in water. If the carbon is heated at 1000° in an atmosphere of carbon dioxide or in a vacuum, the product is positively charged in water. The positive carbon acquires a negative charge, however, when it is heated at 400° in a stream of oxygen. Whilst the positive carbon is not able to adsorb sodium hydroxide, the negative carbon has a high binding capacity for alkali. It is suggested that by treatment with oxygen at 400° a negative surface compound is produced, which gives carbonyl groups with water; this superficial compound may be decomposed at 1000° , leaving the carbon with a positive charge.

E. S. HEDGES.

Elastic properties of acid and alkaline silicic acid and their inner structure. M. KROGER and K. FISCHER (Kolloid-Z., 1929, 47, 10—14).—Measurements of the velocity of gelatinisation of silicic acid in relation to the nature and hydrogen-ion concentration of the reacting acid are recorded. The more rapidly gelatinisation occurs, the sooner syneresis sets in. The shrinkage due to syneresis has been measured and was found to increase with rising alkalinity of the gel; at the neutral point a discontinuity was observed. Measurements were also made of the plastic and elastic properties of the acid, neutral, and alkaline gels. For gels of the same age, the elastic properties are not very different. The plastic properties increase in passing from acid to alkaline gels. The results are discussed in relation to the inner structure of the gels.

E. S. HEDGES.

Influence of mixtures of electrolytes on the viscosity of sols of gum arabic. H. J. C. TENDELOO (Rec. trav. chim., 1929, 48, 23—26).—The influence of mixtures of potassium, barium, and pentammine cobaltic chlorides in pairs on the viscosity of sols of gum arabic has been determined at 25° . A comparison of the influence of the separate electrolytes and their mixtures at equivalent concentrations seems to indicate that there is an influence which is proportional to the total amount of the electrolytes present.

R. N. KERR.

Mol. wt. of cellulose. D. MACGILLAVRY (Rec. trav. chim., 1929, 48, 18—22).—A theoretical discussion of the theory of Hess (A., 1924, i, 142) that the rotatory power of a solution of cellulose in Schweitzer's reagent is due to a complex formed between copper and every glucose unit of the cellulose molecule. An alternative type of intermediate complex with a similar rotatory power is suggested in which only a fraction of the glucose units in the molecule combine with copper. On the assumption that each glucose unit reacts independently of the rest of the molecule a modified formula for the equilibrium is given. This formula may not be applied to determine the mol. wt. of cellulose as Hess has done. The method for calculating the equilibrium concentration of the intermediate product is described.

R. N. KERR.

Velocity function of viscosity of disperse systems. G. W. S. BLAIR (Kolloid-Z., 1929, 47, 76—81).—It is shown on theoretical grounds that a linear relation between the pressure acting on a system flowing through a capillary and the amount of liquid flowing in unit time is more probable than a

parabolic relation. Two of the examples quoted by Ostwald (A., 1925, 291) give the same mean error, no matter which form of equation is applied.

E. S. HEDGES.

Mathematical representation of the structure region of viscosity. W. OSTWALD (Kolloid-Z., 1929, 47, 176—187).—The equation given by Blair (cf. preceding abstract) is applicable only to systems showing little structure viscosity and breaks down when applied to many other cases, where structure viscosity is pronounced. At the same time, the possibility of applying Blair's equation to many practical, technical needs is recognised.

E. S. HEDGES.

Dual emulsions with examples of interest in the spraying of trees. R. M. WOODMAN (J. Physical Chem., 1929, 33, 88—94; cf. A., 1926, 676; B., 1926, 139).—Observations on dual systems at the same phase-volume ratio are recorded and discussed in relation to the preparation of spraying emulsions. Shaking 10 c.c. of light petroleum with an equal volume of 0.5% aqueous solution of potassium oleate at 25° gives an emulsion which creams upwards and is apparently of the oil-in-water type, but which actually is a water-in-oil emulsion as shown by the drop test. Re-shaking and keeping gives emulsions of both types, and finally, on further keeping inversion occurs. Experiments with aqueous solutions of potassium oleate of various concentrations and of phenol, cyclohexanol, cresol, and methylcyclohexanol show that in the case of emulsions of the type hydroxyl compound-in-soap solution an increase in the concentration of the emulsifier causes easier emulsification when the phase-volume is kept constant. When this is altered, excess of one phase tends to make it the stable one, especially when the amount of emulsifier is low (cf. *loc. cit.*), although actually no stable emulsion of the type soap-in-hydroxyl compound is obtained. In some cases where inversion occurs with a change in phase-volume ratio, a critical value of this ratio is obtained where both types of emulsion are possible according to the method of shaking employed. Since an oil-in-water emulsion is essential for spraying, these systems are unsuitable for actual practice where a concentrated emulsion is often first made and then diluted. The danger of preparing an emulsion of the wrong type may be avoided by first making the emulsion so that the phase-volume ratio of aqueous to oil media is at least $(2-4)/1$, when the emulsion of the desired type is obtained. In the system cresol-gelatin-water (A., 1926, 676) previous wetting of the containing vessel does not affect the type of emulsion formed.

L. S. THEOBALD.

Stability of emulsions, unimolecular and multimolecular films, thickness of the water film on salt solutions, and spreading of liquids. W. D. HARKINS [with J. W. MORGAN, N. BEEMAN, B. GUISBERG, and B. B. FREUD] (Fifth Colloid Symposium Monograph, 1928, 19—48).—Only di- β -naphthylamine and *s*-di- β -triphenylethyl give multimolecular films on water; other substances do so on calcium chloride solutions. Mixtures of stearic acid and phenanthrene give multimolecular films; the film strength and thickness have been investigated.

The stability of emulsions is determined from observations on the size distribution of the droplets at intervals.

CHEMICAL ABSTRACTS.

Stability of submicrons. Disintegration and formation of crystals, and formation of emulsions. J. TRAUBE (*Kolloid-Z.*, 1929, 47, 45—47).—When a drop of saturated potassium dichromate solution is allowed to crystallise on a microscope slide and a drop of water is then placed in contact with it, ultramicroscopic examination reveals the presence of numerous submicrons. These appear to be produced by disintegration of the crystals of potassium dichromate prior to their dissolution. The same phenomenon is observed with most other salts which are not too soluble, particularly with mercuric chloride, where the submicrons may have a life-period of 1 or 2 min. Complex compounds, such as potassium hexanitrocobaltate, show the effect best. The phenomenon is considered to be consistent with Smekal's theory of "lattice blocks" (*Z. techn. Phys.*, 1927, 561; *Naturwiss.*, 1922, 799), according to which crystals are built up of blocks of molecular units separated by pores or canals. The "lattice blocks" and the submicrons have the same order of magnitude, i.e., 10^{-5} mm. The precipitation of zinc ammonium phosphate and of lead chloride by mixing solutions of reagents has been followed under the ultramicroscope, and similar submicrons, exhibiting the Brownian movement, were observed. Submicrons were also observed in the emulsions formed by shaking chloroform and water with saponin or other peptising agent.

E. S. HEDGES.

Mechanical coagulation as a coagulation at the surface of contact. H. FREUNDLICH and S. LOEBMANN (*Z. physikal. Chem.*, 1928, 139, 368—374).—The coagulation by stirring of a $\text{FeO}(\text{OH})$ sol, prepared by the oxidation of iron carbonyl with hydrogen peroxide has been further investigated. This mechanical coagulation has many characteristics in common with that of the copper oxide sol previously investigated (Freundlich and Kroch, A., 1927, 18); it is independent of the concentration of the sol and of the quantity of liquid stirred, but is proportional to the square of the rate of stirring. It differs in the fact that only a definite fraction of the colloidal particles can be coagulated by stirring. Coagulation is also brought about by the passage of a current of air, and by shaking with quartz or with organic liquids such as benzene and nitrobenzene, the rate of coagulation increasing with a rise in the dielectric constant of the liquid. When coagulation is sufficiently slow, as is the case with stirring, coagula with regularly-ordered particles result. Mechanical coagulation appears to be the result of an enlargement of the surface of contact, and the present work is discussed in the light of Deutsch's (A., 1928, 1183) explanation of coagulation at an interface.

L. S. THEOBALD.

Precipitation of gelatin by inorganic colloids. R. WINTGEN and H. ENGELMANN (*Kolloid-Z.*, 1929, 47, 104—121).—The precipitation of gelatin by colloidal aluminium hydroxide has been studied on the same lines as a previous investigation by Wintgen and Lowenthal (A., 1924, ii, 739). The previous work indicated a value of about 30,000 for the equivalent

aggregate weight of gelatin when precipitated by ferric hydroxide or by chromium hydroxide, and these experiments have been repeated and the results confirmed. The value agrees with that obtained from measurements of osmotic pressure. The experiments with colloidal aluminium hydroxide give a value of only 19,700 for the equivalent aggregate weight of gelatin, but, since the intermicellar liquid was found to contain basic aluminium chloride, it is believed that the latter has a dispersing effect on some of the gelatin, thus reducing its apparent mol. wt. The equivalent aggregate weight of gelatin is greater at the isoelectric point and alters with time, undergoing a fairly sharp rise to about 220,000, followed by a slow fall to about the original value. Increasing quantities of alkali progressively diminish the equivalent aggregate weight of gelatin.

E. S. HEDGES.

Effect of electrolytes on organic isocolloid systems. L. AUER (*Kolloid-Z.*, 1929, 47, 38—43).—In an attempt to study the relation between the effect of gases on films of fatty oils and the effect of electrolytes on aqueous colloids, the influence of electrolytes on fatty oils has been investigated. The metallic salts were dissolved directly in the fatty oil (which is regarded as an isocolloid system) at temperatures between 280° and 310° . The general effect is the formation of a more viscous liquid, which when cooled produces gels of different degrees of rigidity. Examination of a large number of salts with linseed oil showed that both the cation and the anion influence the change, but the cation is predominant. Increasing concentration of the electrolyte causes greater increase in viscosity; in a few cases a lowering of viscosity is observed and then the lowering is greater for increasing concentration of the electrolyte. The nature and pressure of the atmosphere in which the experiment is conducted and the duration of heating also affect the product. The substances produced from wood oil, castor oil, linseed oil, rape oil, fish oil, sunflower oil, and olive oil are described.

E. S. HEDGES.

Unity in the theory of colloids. H. R. KRUYT (*Fifth Colloid Symposium Monograph*, 1928, 7—18).—A review.

Gel pseudomorphs. M. KROGER and K. FISCHER (*Kolloid-Z.*, 1929, 47, 5—11).—A gel of magnesium hydroxide can be prepared by adding water to a 3% solution of magnesium ethoxide in methyl alcohol. Such a gel is not very stable and rapidly undergoes syneresis, the more readily the higher is the concentration. The gel may be stabilised by the addition of glycerol, glycol, and similar substances, but the effect does not appear to be connected with the viscous nature of these substances, but appears to be a peptising effect. By using water, glycerol, and alcohol in the proportions 5 : 10 : 10, a plastic, glass-clear gel which is stable for months can be obtained. The increased stability is probably due to the fact that the gel takes some minutes to form, thus facilitating complete mixing of the solutions. Small amounts of potassium hydroxide increase the rate of formation of the gel and larger amounts cause flocculation. Mixed gels containing about

0.2*M*-magnesium hydroxide and about 0.04*M*-hydroxides of other metals have been prepared and their absorption of ultra-violet light has been studied. The gels are very transparent, the beginning of continuous absorption varying between 2200 and 3100 Å.

E. S. HEDGES.

Plastic properties of gels, their dependence on temperature, and the formation of gelatinous lenses. M. KROGER and K. FISCHER (*Kolloid-Z.*, 1929, 47, 14—19).—A method for measuring the plastic deformation of gels is described and has been applied to the study of gels of silicic acid, magnesium hydroxide, and gelatin. The plastic properties decrease with falling temperature and also with ageing. Gels may be obtained in the form of a lens by a method which is described in detail and involves the formation of a curvature by means of a mercury surface. The optical properties of some of these lenses have been investigated and good photographs may be taken by their means. E. S. HEDGES.

Consistency and gel formation. H. WAGNER (*Kolloid-Z.*, 1929, 47, 19—21).—The significance of consistency in gels is discussed and the following types of systems are defined. Sols of low viscosity are termed "liquosols" and those of high viscosity "viscosols." Similarly, gels are "liquogels" or "viscogels," according to the viscosity of the sol formed on melting the gel. Plastic or pasty substances are classified as "plastosols" and "plastogels" or "elastosols" and "elastogels," the latter being characterised by higher elasticity. E. S. HEDGES.

Definite temperatures in gelatinising systems. S. TSUDA (*Kolloid-Z.*, 1929, 47, 28—36).—At high temperatures, gelatin sols exhibit neither structure viscosity nor ageing, but both these phenomena appear at a definite temperature. For 2—8% sols the critical temperature is 33—35°, agreeing with the temperature of gelatinisation. The phenomenon is not general for colloids; for example, mercury sulphosalicylic acid has no definite setting point up to 95°. Theories of the sol-gel transformation are discussed. The effect of addition of salts and of alcohol is small, thus resembling the effect on a phenol-water mixture. Agar sol behaves in a similar manner to gelatin, and the fact that the melting temperature lies far above the setting temperature indicates that an agar sol which has been cooled and again warmed does not easily lose its structure viscosity. E. S. HEDGES.

Mechanism of the swelling of gels. K. KRISHNAMURTHI (*Nature*, 1929, 123, 242—243).—The intensity of the light scattered by gelatin at first increases and then diminishes as swelling proceeds. Imbibition of two kinds is probably concerned in the swelling: (a) the solvent is taken up inside the structure of the gel micelles; this portion, which is held firmly, probably by chemical forces, increases the volume of the micelles, and hence the light-scattering capacity of the gel; (b) the solvent remains in the intermicellar space, diluting the gel, and diminishing its light-scattering capacity. A. A. ELDRIDGE.

Electrolyte-free water-soluble proteins. VII. Hydration and sign of charge of the ions of proteins. W. PAULI (*Biochem. Z.*, 1928, 202, 337—

364).—Viscosity measurements were made on solutions of various proteins with the addition of various acid or basic substances, the hydrogen-ion concentrations being determined. A table is given showing the maximum "binding power" for positive and negative groups of egg-albumin, serum-albumin, hæmoglobin, gluten, and ψ -globulin. The first two of these are predominantly acid, the last two predominantly alkaline. Hæmoglobin, on the other hand, is an almost ideally symmetrical ampholyte. The results lead to the conclusion that at the points of maximum charge there is increase of hydration with increase of charge and greater hydration with respect to the anion under otherwise equal conditions. In many cases, however, the viscosity increase gives place to a decrease before the point of maximum "binding" power is reached, whilst in other cases it increases almost continuously until the point of maximum charge of the protein ions is practically attained. Certain anomalies in the hydration phenomena are discussed. The effect of the addition of caffeine on the viscosity of the protein solutions is also discussed and the substances investigated are grouped according to their behaviour towards caffeine. The state of combination of the nitrogen in hæmoglobin and in serum-albumin has been deduced. In the latter somewhat more than two thirds, in the former only about one third is present as diamino-nitrogen. The possible significance of these facts is noted. W. MCCARTNEY.

Difference in osmotic concentration between yolk and white of egg. J. STRAUB [with M. J. J. HOOGERDUYN] (*Rec. trav. chim.*, 1929, 48, 49—82).—The concentrations of the osmotically active components of the white and yolk have been determined analytically. Sodium, potassium, and chlorine ions are divided unequally and apparently independently between the yolk and white. The partial lowerings of the f. p. corresponding with each constituent have been calculated. If it is assumed that the skin of the live yolk is permeable to water, the difference of f. p. of the yolk and white requires, for an equilibrium state, a difference of pressure of 1.8 atm. across the skin. As the skin could not withstand such a pressure, it is concluded that the yolk and white cannot be in equilibrium. Stationary states other than equilibrium ones can be maintained only through the continual performance of work. That the maintenance of this work is dependent on the life of the egg is shown by experiments with eggs which have been (a) preserved, (b) frozen to -10° , and (c) poisoned; the difference of osmotic behaviour between the yolk and white after such treatments is much smaller than for fresh eggs. The role of the yolk skin and its permeability to water and dissolved substances in the processes performing this work are discussed. The work necessary during 24 hrs. is calculated from the gas laws to be 0.01 kg.-cal., and it is shown that this amount of energy may easily be acquired from oxidation of the dextrose in the egg by breathing. The method by which the energy of respiration may be used for the performance of work is discussed. R. N. KERR.

Reversal of charge of collodion membranes in solutions of alkaloïds. N. K. HARKEVITSCH

(Kolloid-Z., 1929, 47, 101—104).—An electro-osmotic apparatus is described. This has been applied to the measurement of the charge on membranes in alkaloid solutions. Collodion membranes have hitherto been found to be uniformly negatively charged, but a reversal of charge is obtained in solutions of salts of quinine and cocaine, the charge becoming positive in very dilute solutions. Reversal of charge of agar was not found possible in solutions of quinine, but cellulose becomes positively charged in quinine dihydrochloride solution containing about 50 millimols. per litre. Collodion membranes also show reversal of charge in dilute solutions of the hydrochlorides of quinoline, pyridine, and piperidine.

E. S. HEDGES.

Action of proteins on colloidal ferric hydroxide. H. FREUNDLICH and G. LINDAU (Biochem. Z., 1928, 202, 236).—Sensitisation and protective action are not determined by capillary-chemical factors, but are an expression of a chemical reaction similar to that suggested by Heymann and Oppenheimer for albumin-ferric chloride mixtures (cf. A., 1928, 1388).

P. W. CLUTTERBUCK.

Syneresis and hydration. Theory of syneresis. S. LIEPATOV (Kolloid-Z., 1929, 47, 21—28).—By adding various amounts of alcohol to a solution of geranin in water, it is possible to prepare a series of colloidal solutions in which the ratio of molecularly dispersed to colloiddally dispersed phase is graded. Dilute sols do not show any change of viscosity with time, but at concentrations above 0.25% of geranin a marked change of viscosity with time is observed and has been used to determine the degree of hydration of the particles. Gelatinisation of a sol is considered to take place when the particles of disperse phase come into such proximity that their mutually attractive forces come into operation. Syneresis is considered to be a continuation of this process, the particles growing together so as to squeeze out the liquid between them. The velocities of syneresis and of gelatinisation increase with the concentration of the colloid. Experiments with different concentrations of geranin gel indicate that the final stage of the gelatinisation-syneresis phenomenon is the production of a hydrate of geranin with 20.4 mols. of water. In reversible emulsoids the equilibrium between gel and solution is regulated by temperature and pressure: this fact differentiates reversible emulsoids from irreversible emulsoids and suggests a similarity between reversible emulsoids and crystal hydrates.

E. S. HEDGES.

Equilibrium between methyl alcohol, carbon monoxide, and hydrogen. D. F. SMITH and B. F. BRANTING (J. Amer. Chem. Soc., 1929, 51, 129—139).—A preliminary investigation of the above reaction at 304° and 1 atm., using a catalyst of zinc oxide, pure or promoted with chromic acid, gives a value 5.57×10^{-4} for the equilibrium constant $[\text{MeOH}]/[\text{CO}][\text{H}_2]^2$. The free energy of the reaction $\text{CO} + 2\text{H}_2 = \text{MeOH}$ is given by $\Delta F = -20857 + 41.17T - 0.01423T^2 - 54.42T$. The fugacities of the components are recorded graphically up to 400 atm. for 300°, 350°, and 400°. The results are not in accord with those of Kelley (B., 1926, 214)

but approach more closely those of Christiansen (A., 1926, 358). The yields of methyl alcohol obtained in practice at high pressure compare favourably with those calculated from the thermodynamic data here recorded.

S. K. TWEEDY.

Equilibrium constant of the esterification reaction in the gaseous phase. W. SWIENTO-SLAWSKI and S. POZNANSKI (Rocz. Chem., 1928, 8, 527—541).—See A., 1927, 204.

Modern development of the theory of solutions and its significance in biology. I. E. BENEDICENTI and G. B. BONINO (Arch. Sci. biol., 1927, 10, 76—86; Chem. Zentr., 1928, ii, 1189).—A discussion. Weak electrolytes are probably completely dissociated in solution.

A. A. ELDRIDGE.

Influence of neutral salts on acid-base equilibria. VII. Apparently anomalous behaviour of a mixture of a weak base and its salt on dilution and on the addition of a neutral salt. Dissociation constant of pyridine, pyrimidone, and *p*-phenylenediamine. I. M. KOLTHOFF and W. BOSCH (Rec. trav. chim., 1929, 48, 37—48).—The following dissociation constants at 18° have been determined by measuring the p_H of mixtures of the bases and their chlorides at different dilutions and extrapolating for infinite dilution: pyridine 1.4×10^{-9} , pyrimidone 6.9×10^{-10} , *p*-phenylenediamine 1.1×10^{-8} , 3.5×10^{-12} . Extrapolation for the first two bases is uncertain, as the dilution effect is less marked than required by the Debye-Hückel equation. The influence of adding the chlorides of potassium, sodium, and lithium and the bromide, nitrate, and iodide of potassium on the p_H of mixtures of the bases and their univalent salts and also of a mixture of the uni- and bi-valent salts of *p*-phenylenediamine has been investigated. The anion effect on the value of $\log f_1/f_0$ (f_1 and f_0 are the activity coefficients of the basic ion and the undissociated base, respectively) is approximately the same for the four anions used except with pyrimidone; the pronounced anion effect with the latter is attributed to the formation of complex or undissociated salts. Potassium chloride exerts approximately the same influence on the above expression as it does in the case of a mixture of a weak acid and its salt (A., 1928, 1325). The cation effect decreases in the order $\text{K} > \text{Na} > \text{Li}$, which is the reverse of that observed in the acid systems. In order to account for this anomalous behaviour it is suggested that sodium and lithium chlorides increase the ionic product of water.

R. N. KERR.

Behaviour of hydrogen peroxide in aqueous alkali phosphate solutions. S. HUSAIN (Z. anorg. Chem., 1928, 177, 215—226).—The partition of hydrogen peroxide between alkali phosphate solutions and amyl alcohol has been measured, and the f. p. of solutions containing phosphate and hydrogen peroxide in the ratios 1 : 2 and 1 : 4 have been determined. The results show that the tendency towards compound formation increases in the order primary, secondary, pyro-phosphate and is greater for the potassium salts than for those of sodium. Even in presence of a considerable excess of hydrogen per-

oxide the absolute quantity of compound formed is relatively small, in confirmation of the observation of previous workers that the solid complexes are largely broken down on dissolution in water.

H. F. GILLBE.

Dependence of the osmotic coefficients on the structure of the ions of the tetra-alkylammonium salts. L. EBERT and J. LANGE (Z. physikal. Chem., 1928, 139, 584—596).—F.p. data are recorded for aqueous solutions of some of the chlorides, bromides, iodides, and nitrates of the tetra-alkylammonium bases over the concentration range 0.05—1*M*. Compared with other inorganic salts, these salts show a marked individual behaviour and the curves obtained by plotting concentration against the values of $1-\phi$, where ϕ is the osmotic coefficient, do not fall into groups as do those for the halides of an alkali metal. Tetraethylammonium iodide and tetrapropylammonium iodide show the smallest lowering of the f. p., and their curves lie above that for thallium nitrate. The anomalous behaviour of the tetra-alkylammonium salts is discussed.

L. S. THEOBALD.

Entropy and vibration number of elements. W. HERZ (Z. anorg. Chem., 1928, 177, 116—118).—The variation with at. wt. of the entropies S and the vibration numbers ν of the elements in each group of the periodic table is such that for each group the quantity $S\sqrt{\nu}$ remains approximately constant.

H. F. GILLBE.

Solubility. XII. Regular solutions. J. H. HILDEBRAND (J. Amer. Chem. Soc., 1929, 51, 66—80).—A regular solution is defined as one which involves no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged. In such solutions association and chemical effects are absent. If a_1 is the activity of one component (mol. fraction N_1) of a solution, then (i) $RT \log_e a_1/N_1 = bN_1^2$, where b is a constant independent of temperature, although it often tends to diminish with rising temperature. A short discussion of this variation is given. If the system is unsymmetrical, then (ii) $RT \log_e a_2/N_2 = bN_1^2 + cN_1^3 + \dots$ (cf. Heitler, A., 1926, 1006). The constancy of b in equation (i) is demonstrated for solutions of sulphur, iodine, naphthalene, and stannic iodide. The equations are also applied to two-phase liquid systems. If T_c is the critical mixing point, then $2RT_c = b$. The equations are also confirmed by *E.M.F.* measurements on molten alloy concentration cells (Taylor, A., 1924, ii, 89). The following topics are discussed with relation to the equation: heat of dissolution, heat of mixing, volume change on mixing. A correction term is introduced in Gibbs' adsorption equation, which takes into account the deviation from the ideal solution. The solubility of stannic iodide in isooctane is 0.342 mol.-% at 25°.

S. K. TWEEDY.

Decomposition pressure of nitrides. R. LORENZ and J. WOOLCOCK (Z. anorg. Chem., 1928, 177, 380).—An addition to a previous paper (cf. this vol., 29). References are given to previous work on the formation and dissociation of zirconium nitride.

A. J. MEE.

System iron-water. G. SCHIKORR (Z. Elektrochem., 1929, 35, 62—65).—On the assumption that certain electrochemical processes alone are involved in the reaction between iron and water, it is calculated from electrochemical data that no further evolution of hydrogen should occur above a limiting pressure of (very approximately) 0.25 atm. It is found by experiment, however, that very much higher pressures than this may be reached, and it is inferred that the evolution of hydrogen is due to the decomposition of water by ferrous hydroxide (cf. Traube and Lange, A., 1926, 257). Evidence is cited in support of this contention.

L. L. BIRCUMSHAW.

Derivation of the solubility product law. W. C. VOSBURGH (Proc. Iowa Acad. Sci., 1927, 34, 213—214).—A thermodynamic derivation of the solubility product law is based on considerations of free energy and activity.

CHEMICAL ABSTRACTS.

Equilibria between metals and salts in melts. XII. Displacement of the equilibrium $\text{Cd} + \text{PbCl}_2 \rightleftharpoons \text{Pb} + \text{CdCl}_2$ by additions to the metal phase. R. LORENZ and M. HERING (Z. anorg. Chem., 1928, 177, 1—12).—Addition of either antimony or bismuth to the system $\text{Cd} + \text{PbCl}_2$ causes a displacement from right to left which increases as the content of added metal increases. Antimony forms compounds with one of the components, viz., cadmium, but bismuth does not, and the added metal is therefore considered as increasing the "nobleness" of cadmium towards lead.

H. F. GILLBE.

Ionic equilibria. III. Equilibrium between cadmium sulphide and dilute hydrochloric acid. M. AUMERAS (J. Chim. phys., 1928, 25, 727—742; cf. A., 1927, 312, 1141).—The method previously described has been applied to this system with special precautions against loss of hydrogen sulphide by evaporation and by atmospheric oxidation. On the assumption that cadmium chloride and hydrochloric acid are completely dissociated in dilute solution, an equation has been deduced from mass law considerations representing the solubility of cadmium sulphide in dilute hydrochloric acid with which the experimental results are in good agreement. The second dissociation constant of hydrogen sulphide at 16° has been calculated from the results with the addition of published data for the first dissociation constant and for the solubility product of cadmium sulphide; these give $[\text{H}^+][\text{S}^{2-}]/[\text{HS}^-] = 0.59 \times 10^{-15}$ and 0.37×10^{-15} .

R. N. KERR.

Application of the law of mass action to the double decomposition of [solutions of] salts. LEMARCHAND and (MNE.) LEMARCHAND (Compt. rend., 1929, 188, 254—256; cf. A., 1928, 1205).—The equilibrium constants for the reaction of barium sulphate with hydrochloric acid and with calcium chloride solutions at 100° have been calculated in reference to the activities of the reacting substances.

J. GRANT.

Action of silica and alumina on sodium sulphate. (MLLE.) G. MARCHAL (Compt. rend., 1929, 188, 258—260; cf. A., 1926, 924).—The decomposition of anhydrous sodium sulphate at temper-

atures up to 1300° is facilitated by the addition of powdered anhydrous silica or alumina, particularly the latter. The reaction does not proceed to completion. J. GRANT.

Gibbs' theorem applied to heterogeneous equilibria. V. POLARA (Atti R. Accad. Lincei, 1928, [vi], 8, 500—505).—Mathematical.

Saturation of sugar-lime solutions. III. A. H. W. ATEN, P. J. H. VAN GINNEKEN, and E. VERWEIJ (Rec. trav. chim., 1929, 48, 93—115).—The composition of the basic precipitates obtained by passing carbon dioxide into sugar-lime solutions (A., 1928, 21) has been determined. That of the precipitate obtained from solutions of fairly high concentration (e.g., 0.7 mol. of sugar+1.7*N*-CaO) varies between 3sugar,6CaO,CO₂ and 3sugar,6CaO,2CO₂ according to the value of *R* (the degree of saturation of the solution) and the concentration of sugar. That of the precipitate formed at lower concentrations (e.g., 0.35 mol. of sugar+1.0*N*-CaO) is 3CaO,2sugar,αCaCO₂, where α lies between 0.65 and 1.2. The solubility of calcium carbonate hexahydrate in sugar-lime solutions of varying concentrations has been determined. The effect of raising the temperature to 90° has been further investigated and the change in alkalinity on solution of the hexahydrate and on separation of the basic precipitates determined. Conductivity measurements of carbonated solutions have been carried out; a large decrease occurs after the absorption of the carbon dioxide whether a precipitate is formed or not. This decrease is much greater than can be accounted for merely on the formation of undissociated calcium carbonate. It appears that some of the free lime must be removed from the solution. This conclusion is supported by determination of the hydroxyl-ion concentration of the carbonated solutions. It is assumed therefore that complexes formed between the carbonate and hydroxide of calcium are present in solution. The approximate composition of these complexes has been calculated from the conductivity of the solutions during the transformation of the basic precipitate into the hexahydrate. It varies between 2CaCO₃,Ca(OH)₂ and CaCO₃,2Ca(OH)₂. The presence of such complexes is confirmed by ultrafiltration experiments on freshly-carbonated solutions and also by periodic examination of the solutions under the ultramicroscope. R. N. KERR.

Systems KCl-FeCl₃-H₂O and AlCl₃-FeCl₃-H₂O between 0 and 60°. G. MALQUORI (Gazzetta, 1928, 58, 891—898; cf. A., 1928, 20).—The isotherms for the system KCl-FeCl₃-H₂O at 0°, 25°, 35°, and 60° show that the double chloride FeCl₃,2KCl,H₂O is stable at all temperatures and separates only from solutions which are rich in ferric chloride. Data for the system AlCl₃-FeCl₃-H₂O at 0° show that the two solids AlCl₃,6H₂O and FeCl₃,6H₂O may be present in the solid phase, but at 40° and 60° there is no ferric salt in the solid phase even when the co-existing solution contains 45% of ferric chloride. O. J. WALKER.

Reciprocal salt pair MgSO₄-2NaNO₃-H₂O. II. W. SCHRODER (Z. anorg. Chem., 1928, 177, 71—85).—Isotherms of the system MgSO₄-Na₂SO₄-H₂O

show that at 75° astrakanite alone is present. In the system Mg(NO₃)₂-MgSO₄-H₂O, at high nitrate concentrations, the transition from hexahydrate to monohydrate invariably takes place through an intermediate series of hydrates; at nitrate concentrations lower than about 50% no monohydrate is formed, but a series of metastable hydrates, of relatively high stability, is produced. The influence of temperature on the system MgSO₄-2NaNO₃-H₂O is described. The space boundaries of the various phases in this system have been calculated, and the influence of temperature is described.

H. F. GILLBE.

Equilibria between water and the nitrates and sulphates of sodium [and potassium] at 50—90°. E. CORNEC and H. KROMBACH (Caliche, 1928, 10, 396—401).—In contradiction to Hamid's results (A., 1926, 245, 246), potassium nitrate and sodium sulphate are capable of co-existence in contact with the saturated solution at 90°. On the addition of a solution of glaserite to a sodium nitrate solution the reaction Na₂SO₄,3K₂SO₄+6NaNO₃ → 4Na₂SO₄+6KNO₃ takes place, the reaction products being partly precipitated; the resulting solution, saturated with sodium and potassium nitrates and sodium sulphate, has *d* 1.761. On further addition of glaserite a point is reached at which the double salt co-exists with a solution, *d* 1.724, saturated with sodium sulphate, potassium nitrate, and glaserite. At 50° darapskite and potassium nitrate can co-exist, but this is not possible for sodium nitrate and sodium sulphate; the reverse obtains at 66.5°. At temperatures in the neighbourhood of 60° two types of solution exist, one saturated with sodium nitrate, sodium sulphate, and potassium nitrate, and the other with sodium and potassium nitrates and darapskite; above 60° the first is stable and the second labile, whilst below 60° these conditions are reversed. H. F. GILLBE.

Thallous double halides. A. BENRATH and G. AMMER (Z. anorg. Chem., 1928, 177, 129—136).—Heterogeneous equilibria at 25° have been determined for three-component systems containing thallous chloride and water, together with cadmium, mercuric, zinc, magnesium, calcium, strontium, or barium chloride. The following double chlorides have been found to exist: CdCl₂,TlCl, HgCl₂,TlCl, ZnCl₂,2TlCl, ZnCl₂,3TlCl, and MgCl₂,3TlCl; the alkaline-earth metal chlorides do not form double salts with thallous chloride. The salts CdBr₂,TlBr, ZnBr₂,2TlBr, and ZnI₂,3TlI also exist.

H. F. GILLBE.

Elimination of systematic errors occurring in the earlier thermochemical data. W. SWIEN-TOSLAWSKI (Rec. trav. chim., 1929, 48, 1—6).—Polemical. A reply to the criticism by Verkade and Coops (A., 1928, 845) of the author's previous work (A., 1920, ii, 470). R. N. KERR.

Calorimetric researches. II. Heat of combustion of a proposed secondary calorimetric standard: salicylic acid. L. J. P. KEFFLER (J. Physical Chem., 1929, 33, 37—51; cf. A., 1927, 193).—Details are given of the determination of the heat of combustion of salicylic acid which, as a mean of nineteen combustions carried out adiabatically

under varied conditions with eight different samples obtained by recrystallisation from three different preparations of the acid, has the value 5234.8 g.-cal.¹⁵/g. (in a vacuum). This value holds for an isothermal reaction at 20° approximately, and may be compared with 6319 g.-cal.¹⁵/g. for benzoic acid as standard. From an examination of the results of recent investigators, the value 5235 ± 1 g.-cal.¹⁵/g. (in a vacuum) is finally suggested.

L. S. THEOBALD.

Heat of formation of double chlorides of cadmium and potassium. P. AGOSTINI (Atti R. Accad. Lincei, 1928, [vi], 8, 393—394).—From measurements of the heat of precipitation of cadmium hydroxide by potassium hydroxide from solutions of the double salts KCl.CdCl₂ and 4KCl.CdCl₂ and from solutions of cadmium chloride, the heats of formation of the two double salts were calculated as 3.65 and 0.989 kg.-cal., respectively.

F. G. TRYHORN.

Thermochemical study in the furan series. P. LANDRIEU, F. BAYLOCC, and J. R. JOHNSON (Bull. Soc. chim., 1929, [iv], 45, 36—49).—Measurements of the heats of combustion of furan, ethylenefuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, furfuraldehyde, furoic acid, and furylacrylic acid and of the corresponding benzene compounds are recorded. The molecular heats of formation have been calculated; those for the furan compounds are lower than those of the corresponding benzene compounds by a nearly constant amount of 26.4 g.-cal. The molecular heats of combustion at constant pressure of the furan compounds are likewise lower than those of the corresponding benzene compounds by a mean value of 284 g.-cal. per mol., the maximum variation being 0.5%. The only exception occurs with the hydrogenated alcohols, but if allowance be made for the additional hydrogen atoms present in the benzene compound the corrected value is in good agreement with the above mean.

R. N. KERR.

Calculation of the integral and differential heats of solution and dilution of potassium chloride and of the molecular heat of potassium chloride solutions at great dilution. E. LANGE and J. MONHEIM (Z. Elektrochem., 1929, 35, 29—33).—The experimental values obtained by Lange and Leighton (A., 1928, 1329) for the heats of dilution of dilute solutions of potassium chloride have been used to calculate the integral and differential heats of solution and dilution of potassium chloride at 12.5° and 25°, for concentrations ranging from 0.0007 to 0.9028 mols./100 mols. of water. The mean temperature coefficients of these quantities have also been calculated for the temperature range 12.5—25°, together with the specific and molecular heats of the solution over the whole concentration range. At great dilution, the specific heat is not a linear function of the concentration.

L. L. BIRCUMSHAW.

Transport numbers of lithium chloride and bromide, and sodium iodide dissolved in acetone and alcohol. W. BIRKENSTOCK (Z. physikal. Chem., 1928, 138, 432—446).—It has been shown by Bruns and Thonnessen that the conductivity of concentrated aqueous solutions of cadmium iodide

and alcoholic solutions of cadmium iodide, potassium iodide, etc. is increased by the addition of iodine. If a slowly moving I₃ ion is formed, the dissociation must have increased in order to account for this increase of conductivity. In order to find out whether complex aggregates exist in the solutions, the transport numbers of lithium chloride and bromide and sodium iodide in acetone and in mixtures of acetone and methyl alcohol were determined. Lithium chloride and bromide show strong association in acetone solution. The complexity is greatest with lithium chloride and decreases through lithium bromide to sodium iodide, which is not, or, at least, only a little, associated. The type of aggregate formed, i.e., whether it is Li₂Cl₂, Li₃Cl₂, etc., cannot be determined by the experiments described. It is very probable that the acetone solution of lithium chloride contains very large aggregates of the form Li_nCl_n, on the one hand because of the low conductivity, and on the other because the great influence of dilution on the conductivity of this solution can be explained only in this way. The aggregates were in each case destroyed by the addition of methyl alcohol.

A. J. MEE.

Effect of addition of iodine on the conductivity of solutions of halogen salts of sodium, lithium, and potassium in mixtures of alcohol and acetone. F. NIES (Z. physikal. Chem., 1928, 138, 447—458).—The addition of iodine to a solution of sodium iodide in acetone, or in a mixture of acetone and methyl alcohol, increases the conductivity. The effect diminishes as the proportion of methyl alcohol is increased. The conductivity of a solution of lithium bromide in acetone is also increased by the addition of iodine. For methyl alcohol solutions of lithium chloride and potassium iodide the increase in conductivity is confined to the more concentrated solutions. In acetone and in acetone-methyl alcohol mixtures, lithium chloride behaves like sodium iodide; the equivalent conductivity is increased on adding iodine, the increase being very much greater than for sodium iodide. The iodine not only affects the complex, but also the simple molecules, and also forms complex ions with the other halogens. The results of the experiments are not compatible with the theory of complete dissociation.

A. J. MEE.

Effect of diffusion at a moving boundary between two solutions of electrolytes. D. A. MACINNES and I. A. COWPERTHWAIT (Proc. Nat. Acad. Sci., 1929, 15, 18—21).—Since the method of moving boundaries affords an accurate means for determining the transference number of an electrolyte, experiments have been made to determine whether the movement of the boundary is affected by the diffusion of one electrolyte into the solution of the other. It was found that the diffuse zone between the two solutions moves at the same rate as the fully-formed boundary, and that the latter regains its original sharpness shortly after restarting the current. The probable action of the mechanism involved is outlined.

N. M. BLOCH.

Calculation of the [electrode] potentials of potassium and sodium. P. DROSSBACH (Z. Elektrochem., 1929, 35, 95—96).—The values pre-

viously obtained for the electrode potentials of sodium and potassium (A., 1928, 481) are higher than the experimental values. It is now found that the influence of concentration is considerably greater than had been supposed, and on allowing for this and re-calculating, the values $\epsilon_{Na} = -2.72$ volts and $\epsilon_K = -2.97$ or -2.96 volts are obtained, in good agreement with the experimental values -2.72 and -2.92 volts, respectively. L. L. BIRCUMSHAW.

Concentration cells in ethyl alcohol : sodium and potassium iodides. G. F. ISAACS and J. R. PARTINGTON (Trans. Faraday Soc., 1929, 25, 53—59).—The *E.M.F.* of the cells— $Ag[AgI, NaI(c_1)] NaI(c_2), AgI[Ag, Ag[AgI, KI(c_1)] KI(c_2), AgI[Ag]$ with ethyl alcohol as the solvent have been measured between 0.001*N* and 0.5*N*. Satisfactory results are not obtained at higher or lower concentrations, but within this range the *E.M.F.* are adequately represented by Nernst's equation in the form $E = 2(1 - n_a)RT/F \log_e \lambda_1 c_1 / \lambda_2 c_2$, where n_a is the anion transport number and λ_2 are the conductances at c_1, c_2 , respectively. The values of n_a are constant except at the higher concentrations. Measurements of the *E.M.F.* at 25° agreed closely with those calculated from readings at the ordinary temperature on the assumption that the *E.M.F.* is proportional to the absolute temperature. F. G. TRYHORN.

Oxide cells of cadmium, copper, tin, and lead. C. G. MAIER (J. Amer. Chem. Soc., 1929, 51, 194—207).—From potential measurements of oxide electrodes containing barium hydroxide as electrolyte against standard electrodes (Maier, Parks, and Anderson, A., 1926, 1210) the molar free energies (g.-cal.) at 25° are calculated for cadmium monoxide (−55,064), cadmium hydroxide (−112,178), cuprous oxide (−34,672), cupric oxide (−30,800), stannous oxide (−61,332), and stannic oxide (−123,000). The heats of formation also are tabulated. Those calculated from the cell coefficients differ somewhat from those calculated from the free energy and entropy. Oxide electrodes are highly polarisable and very sensitive to traces of electro-negative impurities. It is not possible to obtain permanently stable cells with such electrodes.

S. K. TWEEDY.

Studies on the periodic system. I. Ionic potential as a periodic function. II. Ionic potential and related properties. G. H. CARTLEDGE (J. Amer. Chem. Soc., 1928, 50, 2855—2863, 2863—2872).—I. A periodic classification is put forward, based on the conception of an "ionic potential" (=charge/radius). Hydrogen occurs twice in the system, as an alkali-like ion and a halogen-like ion, respectively, although the former resemblance stops short with the valency. The triads of group eight fall logically into the scheme, as also do the rare earths, and all the valencies of multivalent elements are satisfactorily provided for. The ions fall into families which are characterised by the degree of completeness of their outer electron shells.

II. The relations between ionic potential, ϕ , and certain ionic properties are discussed. In aqueous solution, cations are basic, amphoteric, or acidic, according as $\sqrt{\phi}$ is less than 2.2, between 2.2 and

3.2, or greater than 3.2. Cations for which $\sqrt{\phi}$ exceeds 2.2 form volatile chlorides which, in the liquid state, are non-conductors. Binary crystals increase in hardness as the ϕ values of their constituents increase. The heat of hydration of gaseous ions increases with the ϕ value and the heat of solution of salts with a common anion increases with the ϕ -value of the cation, except in the case of fluorides, when the reverse holds. S. K. TWEEDY.

Determination of the activity of one substance from that of another by a cell with a liquid junction. R. F. NIELSEN and H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1929, 51, 223—224).—It is contended that Schuhmann's experiments, instead of proving that the activity coefficients of hydrochloric and perchloric acids are the same at all concentrations, show that the hydrogen-ion activity in hydrochloric acid solutions is the same as that in perchloric acid solutions of the same molality. The method used by Schuhmann (cf. A., 1924, ii, 152) does not afford evidence for equal mean activity coefficients in equimolar solutions of two electrolytes with a common ion. S. K. TWEEDY.

Study of complex formation by the polarographic method. (MME.) N. DEMASSIEUX and J. HEYROVSKY (Bull. Soc. chim., 1929, [iv], 45, 30—35; cf. A., 1927, 1159).—Study of complex formation by an electrolytic method which makes use of the dropping mercury cathode has been extended to the salts of platinum, mercury, and copper. Experiments with potassium hexachloro- and hexabromo-platinates and tetrachloro- and tetrabromoplatinates show that the complexes in each case are dissociated in solution. Dissociation of the tetracyanoplatinite ion, on the other hand, cannot be detected. The metal can likewise not be deposited from the complex cyanides of iron, zinc, and copper, but with those of silver, gold, and cadmium the metal is deposited easily and reversibly at the cathode. The behaviour of mercuric cyanide to which potassium cyanide has been added is peculiar; a sharp-pointed maximum is obtained on the polarisation curve and this is attributed to adsorption of ions on the drops of mercury. The cyano-, tartrato-, oxalato-, and hyposulphito-complexes of copper have been examined. The cyano-complex is not dissociated at all in freshly-prepared solutions, but becomes so partly on keeping or on dilution of the solution; the other three complexes are all partly dissociated. The constant for the oxalato-complex has been determined, $K = [Cu(C_2O_4)_2^{2-}] / [Cu^{2+}] \times [C_2O_4^{2-}]^2 = 0.25 \times 10^{13}$. R. N. KERR.

Current density-potential curves in the region of residual currents of various metals. W. J. MÜLLER and K. KONOPICKY (Z. Elektrochem., 1928, 34, 840—849).—The current densities at increasing potentials have been measured for copper, platinum, lead, iron, nickel, and aluminium in 0.02*N*-sulphuric acid, without and with the passage of hydrogen through the electrolyte, using zinc as the reference electrode. In the case of copper, the agitation of the electrolyte by the hydrogen was accompanied by an increase in the residual current from 2×10^{-5} to 13×10^{-5} amp. In the case of all the metals investig-

ated, the residual current is strongly influenced by the gas content of the electrolyte. When oxygen is completely removed by hydrogen the residual current changes little and has a value less than 10^{-3} amp. in an undisturbed electrolyte, but when the electrolyte is saturated with oxygen the residual current reaches a constant value about ten times as large. Air produces a similar effect. The overvoltage, determined by breaks in the current-potential curves, is practically independent of the oxygen content of the electrolyte with copper, lead, aluminium, and nickel, but with platinum and iron it is changed by 0.14 and 0.1 volt, respectively. The apparent specific potentials of the electrodes, defined as the potential at which the current density-potential curve cuts the axis of zero current, are markedly influenced by the presence of oxygen in the electrolyte. The respective displacements towards the positive side are for copper and iron 0.05 volt, lead about 0.08 volt, aluminium 0.15 volt, and about 0.25 volt for nickel. They cannot be interpreted as passivity effects, for these are essentially associated with higher current densities. The hydrogen-overvoltage curves can be represented by a formula of the type established by Tafel and modified by Glasstone (A., 1925, ii, 133). For the metals, a formula of similar type holds.

L. S. THEOBALD.

Periodic phenomena at the anode. W. J. MÜLLER (Z. Elektrochem., 1928, 34, 850—852).—Polemical. The explanation of the periodic passivity of chromium and other electrodes in terms of the oxygen-film theory of passivity advanced by Strauss and Hinnüber (A., 1928, 1098) is adversely criticised. Previous observations of the author and his co-workers (A., 1928, 713, 1319) render it untenable, and further, it is pointed out that the observations of Strauss and Hinnüber can be explained in terms of the metal transformation theory of passivity.

L. S. THEOBALD.

Periodic phenomena at the anode. J. HINNÜBER (Z. Elektrochem., 1928, 34, 852—853).—A reply to Müller's criticism (preceding abstract).

L. S. THEOBALD.

Experimental foundations of the passivity theory. W. J. MÜLLER (Z. Elektrochem., 1929, 35, 93—94).—Examination of the current density-potential curves for anodes exhibiting active and passive states, given in a previous paper (cf. A., 1928, 135, 713), shows that, although the oxygen content has a pronounced influence on the magnitude of the cathodic residual current, the presence of dissolved oxygen has no effect on the anodic part of the curve in the residual current region. On this evidence, Hinnüber's theory of the passivating action of oxygen dissolved in the electrolyte on the metal (A., 1928, 1098), which was advanced to explain the phenomenon of periodic passivity of chromium and chromium alloys, cannot be accepted. Various theories of passivity are discussed, and it is claimed that the phenomenon of anodic passivity is always due, primarily, to the formation of a non-conducting film (salt or basic salt), and secondarily, in the case of metals exhibiting true (chemical) passivity, to a change in the atoms of the metal caused by the

high effective current density resulting from the deposition.

L. L. BIRCUMSHAW.

Experimental foundations of the passivity theory. J. HINNÜBER (Z. Elektrochem., 1929, 35, 95).—In reply to Müller (cf. preceding abstract), it is emphasised that the author's investigations have been concerned only with those cases where no visible protective layer is formed on the passive metal (i.e., chromium and chromium alloys). Reference is made to the fact, observed by Eggert (A., 1927, 423), that chromium remains active in dry hydrogen or nitrogen, but becomes passive on introduction of oxygen or exposure to the atmosphere.

L. L. BIRCUMSHAW.

Corrosion, residual current, and passivity. III. F. TÖDT (Z. Elektrochem., 1928, 34, 853—857; cf. this vol., 145).—Measurements of the residual currents between iron and platinum, combined with observations on the corrosion of the iron, have been made in various solutions, and it is shown that the current strength between a noble and a non-noble metal immersed in the same solution is a measure of the corrosion of the latter. The corrosive properties of solutions and the corrosion of metals can thus be directly indicated by a method which is quicker and simpler than the classic method of analysis. Corrosion and passivity are discussed in relation to these residual currents.

L. S. THEOBALD.

Electrical behaviour of surfaces of corroding iron. A. L. MCAULAY and S. H. BASTOW (J.C.S., 1929, 85—92).—A study has been made of the change of potential with time when iron is introduced into 0.5*N*-potassium sulphate solution. It is found that iron, when corroding, is in a stable and reproducible state, and, provided that the electrodes are first aged by prolonged immersion in an electrolyte and the condition of aeration of the electrolyte is standardised, reproducible results can be obtained. Mild steel and cast iron give results similar to electrolytic iron, but stainless steel shows a completely different behaviour. The time-potential curves show that the film present on iron after exposure to air increases its resistance to destruction by the electrolyte with increasing time of exposure up to about 2 hrs. Anodic oxidation in alkali gives films more resistant to destruction than exposure to air. In all cases, however, prolonged immersion in the electrolyte produces the same final state.

F. J. WILKINS.

Passivity of metals. II. Breakdown of the protective film and the origin of corrosion currents. U. R. EVANS (J.C.S., 1929, 92—110).—An attempt has been made to decide whether corrosion is due to the presence of invisible cavities in a metal, the interiors of which, being less accessible to dissolved oxygen, become anodic towards the area outside, or to breaks in a protective film where the exposed metal becomes anodic towards the surrounding film-covered surface. Breakdown of the protective film on iron, steel, or aluminium tends to occur where the surface has been bent or cut, or where rolling or casting defects occur at the surface. The phenomena can be explained satisfactorily only by assuming that the places of attack represent weak points in the invisible oxide film. Sometimes

(as with zinc) corrosion starts at the site of pre-existing cavities.

Differential aeration currents are due to differences of potential existing between (1) the places where the film is kept in good repair by a supply of oxygen, and (2) those where it is not kept in repair. An *E.M.F.* of nearly 0.5 volt can be set up merely by differences in oxygen accessibility. The *E.M.F.* falls when a corrosion-current flows. The extension of breakdown, or the repair of the film, can be followed by changes in *P.D.* F. J. WILKINS.

Mechanism of corrosion. U. R. EVANS (J.C.S., 1929, 111—129).—The corrosion of half-immersed specimens of zinc, aluminium, iron, steel, and copper in salt solutions commences at a limited number of weak points, mainly along the bottom and cut edges, but sometimes at defects occurring in the centre, or, in special circumstances, at the water line. The insoluble corrosion products are of four different types which depend on the way in which the anodic and cathodic products come together.

Under conditions of differential aeration, electrolytic iron is attacked nearly as fast as steel, whilst potassium sulphate and potassium chloride cause similar rates of corrosion, although the shapes of the corroding areas are different. In magnesium sulphate the rate of attack is slower. Zinc is attacked more quickly than iron, and aluminium much more slowly. The replacement of air by oxygen not only increases the rate of corrosion, but also restricts the corroded area to strips running along the bottom portion and the two edges. Doubling the breadth of half-immersed specimens nearly doubles the amount of corrosion, but increase of the length of the specimens has much less effect. The rate of corrosion is almost the same in 0.05*M.*- and 0.1*M.*-potassium chloride.

In the interpretation of the results it is suggested that the *E.M.F.* of the metal-oxygen cell, which determines the magnitude of the corrosion current and the rate of corrosion, is dependent on three factors: (a) anodic polarisation, (b) cathodic polarisation, and (c) the fall of potential across the liquid. For aluminium (a) is the important factor, but for zinc, iron, and steel (b) controls the rate of corrosion.

F. J. WILKINS.

Ignition temperature of combustible gaseous mixtures. M. PRETTE and P. LAFFITTE (Compt. rend., 1929, 188, 397—399; cf. this vol., 33).—The ignition temperatures of mixtures of hydrogen and air, or hydrogen, oxygen, and carbon dioxide, are raised considerably in the presence of small quantities of the residual gases from a previous combustion, to an extent which increases with the initial pressure (10⁻⁴—20 mm. of mercury) and with the hydrogen content. The presence of air has an analogous but less marked effect. The results explain the apparent divergence in the results of various workers.

J. GRANT.

Effect of compression on the explosive properties of explosive gas mixtures. A. HAID and A. SCHMIDT.—See B., 1929, 113.

Ignition of mixtures of air with natural gas and with methane by induction coil sparks. E. G. MEITER.—See B., 1929, 83.

Flame movement in gaseous explosive mixtures. O. C. DE C. ELLIS.—See B., 1929, 82.

Experiments with carefully dried substances. D. McINTOSH (Proc. Nova Scotian Inst. Sci., 1928, 17, 142—148).—A mixture of carbon monoxide (2 mols.) and oxygen (1 mol.), kept for 15 hrs. in a glass vessel, the lower part of which was immersed in carbon dioxide and ether in a Dewar flask, failed to explode when sparked. Even immersion for 5 hrs. in the low-temperature mixture usually prevented an explosion. At -50° to -60°, when 1 mol. of water is present to 40,000 mols. of gas, explosion can take place.

Sodium sulphate, carefully dried in air, or by connexion with a tube containing liquid air or phosphorus pentoxide, still caused immediate precipitation when introduced in minute fragments into a supersaturated solution of the same salt. No precipitation occurred, however, when the salt had previously been heated at 45° for 1 hr., indicating that crystallisation was due to the decahydrate.

Chlorine failed to react with mercury at -180° after both had been dried by suitable means, using liquid air. Below -65°, however, reaction took place. Freshly-distilled ammonia and hydrogen bromide, carefully dried by means of low temperatures, reacted at once when brought into contact. The vapour pressure of water must thus be reduced below 0.001 mm. to prevent their interaction.

Ether, twice re-distilled at -80°, boiled at its normal temperature. An unsuccessful attempt was made to dry ether in a special apparatus of Pyrex glass by distillation at low temperature followed by slow distillation through phosphorus pentoxide.

B. W. ANDERSON.

Kinetics of the decomposition of solutions of sodium hypochlorite. F. GIORDANI and E. MATTHIAS (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], 34, 137—141).—To confirm that the decomposition of sodium hypochlorite solutions involves two simultaneous reactions, $\text{NaOCl} + 2\text{HClO} \rightarrow \text{NaClO}_3 + 2\text{HCl}$, $2\text{NaOCl} \rightarrow 2\text{NaCl} + \text{O}_2$, measurements have been made of the temperature coefficient of the velocity of decomposition of hypochlorite solutions. If the decomposition proceeds according to the first equation alone the velocity coefficient should be proportional, not only to the coefficient for this reaction, but also to the square of the hydrolytic constant of the reaction giving rise to the hypochlorous acid, and thus should be abnormally high. On the other hand, the temperature coefficient of the second reaction should be normal. The velocity of decomposition of a solution containing 0.3 g.-mol./litre of sodium hypochlorite was increased 6.96 times by a temperature rise of 15° (31—46°), and that of a solution containing 0.381 g.-mol./litre 11.96 times by the same temperature rise. At 31° the influence of the alkalinity of the solution predominated, but at 46° this effect was negligible. F. G. TRYHORN.

Influence of non-electrolytes on the velocity of ionic reactions. A. VON KISS and (FRL.) L. HATZ (Rec. trav. chim., 1929, 48, 7—17).—The study of the reaction between iodine and persulphate ions (A., 1928, 1332) has been extended to the influence of

added non-electrolytes. Addition of methyl or ethyl alcohol or glycerol lowers the speed of the reaction, whilst that of sucrose or carbamide increases it. No simple relation was found between the velocity and the concentration of non-electrolyte; $\log k$ is not linearly proportional to the concentration, as was the case for the addition of electrolytes. Neutral salt action in solutions to which non-electrolytes have been added has also been studied. Addition of potassium nitrate or sulphate, ammonium nitrate, and hydrochloric acid increases the rate in an aqueous ethyl alcohol solution to a greater extent than in a pure aqueous solution, but with the sulphates of aluminium and magnesium and lithium chloride the reverse is the case. The effect of varying the concentration of salt in alcoholic solution has been determined for lithium chloride and ammonium nitrate; the curves correlating velocity and salt concentration follow the same course as in aqueous solution, but deviate more markedly from the latter as the concentration of salt increases. Variation of the concentration of the reacting components causes a more marked effect for solutions to which ethyl and methyl alcohol have been added than for pure aqueous solutions; this effect increases with the concentration of non-electrolyte. Increase of the iodide-ion concentration, that of the persulphate ion being kept constant, increases the rate of the reaction. The connexion between the reaction rate and the physico-chemical properties of the solvent, particularly the dielectric constant, is briefly discussed but no simple relation is found.

R. N. KERR.

Periodic law. P. PETRENKO-KRITSCHENKO (J. pr. Chem., 1929, [ii], 120, 225—237).—Comparative reaction velocity measurements for the interactions of potassium hydroxide, tetramethyl- and tetraethyl-ammonium hydroxides, barium hydroxide, thallium hydroxide, sodium ethoxide, metallic silver, ammonia, piperidine, water, ethyl alcohol, silver nitrate, potassium acetate, and potassium thiocyanate with halogeno- and halogenonitro-derivatives of methane and ethane, the chlorotoluenes, and halogenoacetic acids have revealed that the strengths of the linkings which, in each case, join the methane carbon atom to the first-removed halogen atom vary periodically from the mono-, through di-, to the tetra-halogeno-methanes.

R. J. W. LE FÈVRE.

Mutarotation of galactose. T. M. LOWRY and G. F. SMITH (J. Physical Chem., 1929, 33, 9—21; cf. Worley and Andrews, A., 1928, 374).—Data relating to the mutarotation of galactose in water at 20° and at 0.8° are recorded, and a simplified, graphical method of analysing the complex mutarotation curves of α - and β -galactose is described. Assuming that only α -, β -, and μ -sugars are present in the equilibrium mixture, the percentage of α -galactose is found to be approximately 30% at 20° and at 0°. Solubility measurements of α -galactose in water at 0° confirm this to a certain extent by giving an uncorrected proportion of 37% of the α -sugar in the equilibrium mixture as against the value 6.6% found by Riiber and Minsaas (A., 1926, 1228).

L. S. THEOBALD.

Velocities of nitration. F. H. COHEN (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 692—700).—

The velocity of nitration of benzene in acetic anhydride and in glacial acetic acid has been investigated at 0°, 18°, 25°, and 40°. Good bimolecular velocity coefficients were not obtained at the highest and lowest temperatures. Nitrous acid catalyses the reaction. The possibility of nitric acid reacting with the solvent is discussed. In the presence of concentrated sulphuric acid nitric acid reacts vigorously with acetic anhydride to give tetranitromethane. This reaction is greatly retarded by carbamide. No nitration takes place in glacial acetic acid.

C. W. GIBBY.

Stability maxima of some organic substances. II. I. BOLIN (Z. anorg. Chem., 1928, 177, 227—252; cf. A., 1925, ii, 411).—The following values of the p_H of maximum stability at 25° have been determined: ethyl butyrate 5.65, methyl benzoate (80°) 4.0, ethyl benzoate (80°) 4.15, phenyl acetate 4.1, benzyl acetate 4.3, ethyl phenylacetate 4.9, ethyl acetoacetate 4.4, ethyl α -chloropropionate 4.0, ethyl hippurate 4.4, and methylacetanilide 6.0. Substances which are hydrolysed by both acids and alkalis may be classified in two groups; the members of the first group have their maximum stability at p_H less than 5, whilst those of the second group, consisting of secondary amines etc., are of maximum stability in the neighbourhood of the neutral point. For esters of the fatty acids the optimum p_H is for a weak acid lower than for a strong acid; for methyl esters the optimum p_H is somewhat less than for the corresponding ethyl esters. Introduction of a phenyl group lowers the optimum p_H and increases the velocity of decomposition of the ester.

H. F. GILLBE.

Analogies between physiological rhythms and the rhythmical reactions in inorganic systems. R. S. LILLIE (Science, 1928, 67, 593—598).—The conditions controlling a rhythmic reaction between iron and nitric acid are discussed. The rate of the rhythm depends on the extent of the active area, concentration of acid, temperature, polarisation, and length of the wire. Biological analogies are considered.

A. A. ELDRIDGE.

Kinetics of the combustion of carbon monoxide. W. FINKELSTEIN and W. MASCHOWETZ (Z. physikal. Chem., 1928, 138, 369—378).—The kinetics of the combustion of carbon monoxide in the presence of glass is studied. The glass loses its catalytic activity in the presence of carbon dioxide. The combustion is a third order reaction. The mechanism of the reaction is explained in terms of adsorption. It would seem that reaction takes place between activated oxygen molecules adsorbed on the glass and carbon monoxide molecules. Two molecules of carbon monoxide must collide with each molecule of oxygen. Hence the reaction must be of the third order. The adsorption of oxygen on the glass must be small, as the catalytic effect is so low, and is physical in nature. On the other hand, since in glass a weak acid (silica) is combined with strong bases (sodium and calcium oxides) carbon dioxide will be attracted to the surface by chemical forces. The adsorption of carbon dioxide on the glass must therefore be of a chemical nature and practically irreversible. The poisoning of the glass surface by carbon dioxide therefore depends on

the stability of the adsorbed carbon dioxide layer in comparison with that of the layers of carbon monoxide and oxygen.

A. J. MEE.

Corrosion and rusting of alloyed and plain cast iron. P. KOTZSCHKE and E. PIVOVARSKI.—See B., 1929, 97.

Corrosion phenomena. XIII. Dissolution of metals with evolution of hydrogen, "catalytic" effect of foreign metals, and its connexion with the overvoltage series. A. THIEL and J. ECKELL (Korrosion u. Metallschutz, 1928, 4, 121—133, 145—151; Chem. Zentr., 1928, ii, 1146).—See A., 1927, 1034.

Activator, promoter, or accelerator? A. MITTASCH (Z. Elektrochem., 1929, 35, 96—97).—A question of nomenclature. L. L. BIRCUMSHAW.

Acid catalysis in hydrolytic reactions. J. N. BRONSTED and W. F. K. WYNNE-JONES (Trans. Faraday Soc., 1929, 25, 59—76).—The conception of an acid or base as a substance with a tendency to dissociate or associate protons leads to the extended theory of acid and basic catalysis, which ascribes catalytic activity to acid or basic molecules in general and not solely to hydrogen and hydroxyl ions. It is shown that there is no *a priori* reason for excluding hydrolytic reactions from the scope of this theory, although there is a possibility of the effects escaping detection. From an analysis of the conditions obtaining in such reactions it is shown that if in a reaction catalysed by hydrogen or hydroxyl ions there is a detectable but not too large "spontaneous" reaction, then the conditions are favourable for the detection of effects of acids and bases in general. To verify this effect measurements were made by the dilatometric method of the acid catalysis of the hydrolysis of ethyl orthoformate, ethyl orthoacetate, ethyl orthopropionate, ethyl orthocarbonate, acetal, and ketal. These substances were chosen as being themselves neutral and giving hydrolysis products which also are neutral. Catalysis by acids other than the hydrogen ions was undetectable in the hydrolysis of acetal and ethyl orthoformate, a circumstance which renders these reactions suitable for the determination of hydrogen-ion concentration and for the investigation of salt effects. Catalytic effects due to water molecules, *m*- and *p*-nitrophenol, cacodylic and acetic acids, as well as to hydrogen ions were observed in the hydrolysis of the other substances investigated. The activities of these catalysts were found to be dependent on their strengths as acids. The "spontaneous" hydrolysis of the different substances employed was measured, and found in each case to be of small velocity (k_0^0 of the order of 10^{-7}). Values are given for the dissociation constants of formic, acetic, and cacodylic acids, and for *m*- and *p*-nitrophenol, calculated from the data for the various reactions in different buffer solutions. The results afford definite evidence of the catalytic effects of uncharged acid molecules, and taken in conjunction with previous work on the decomposition of nitramide and the mutarotation of dextrose, support strongly the extended acid and basic theory of catalysis.

F. G. TRYHORN.

Inhibitive action of alcohols on the oxidation of sodium sulphite. H. N. ALYEA and H. L. J. BACKSTROM (J. Amer. Chem. Soc., 1929, 51, 90—109; cf. A., 1927, 737).—The thermal (21°) and also the photochemical oxidation of sodium sulphite solutions in presence of *isopropyl*, *sec*-butyl, and benzyl alcohols was investigated. The oxidation of the sulphite induces an oxidation of the alcohol to an extent which increases with increasing alcohol concentration when the latter is low, but is independent of the concentration when the latter is high. When two alcohols are present, the same net amount of alcohol is oxidised, each one being oxidised in proportion to its inhibitory power. The chain length of the thermal reaction is equal to the photochemical quantum efficiency, or the induced oxidation obeys the Einstein photochemical equivalence law; in the process of breaking the reaction chain two molecules of alcohol seem to be oxidised instead of one (compare Cremer, A., 1927, 947). Copper sulphate accelerates the thermal reaction, but does not alter the ratio of oxidised sulphite to oxidised alcohol. Quinol exhibits anomalous behaviour as an inhibitor, possibly because it is directly oxidised and then reacts with the sulphite. Delicate colorimetric methods of determining traces (0.00005 mol./litre) of acetone, methyl ethyl ketone, and benzaldehyde are recorded. Minute traces of ketones may be removed from lower-boiling alcohols by refluxing the latter for several hours with a very small amount of *p*-nitrophenylhydrazine, nitrogen being simultaneously bubbled through the solution.

S. K. TWEEDY.

Use of iodine and iron as a chlorine carrier. H. E. FIERZ-DAVID (Naturwiss., 1929, 17, 13).—In the chlorination of benzene derivatives iodine together with iron is an extraordinarily active catalyst. By the use of 1% of iron and 0.1% of iodine, chlorinations which could be effected in the ordinary way only slowly and at high temperatures were carried out more rapidly and at lower temperatures. The chlorine derivatives obtained by this method are purer than those prepared with the use of iron or other carriers alone. Other combinations were tried, including iodine together with nickel, antimony, cobalt, bismuth, tin, phosphorus, and zinc, but these gave no satisfactory results. The catalyst goes into solution rapidly, producing a deep brown colour.

A. J. MEE.

Decomposition of ammonia by iron. A. MITTASCH, E. KUSS, and O. EMERT (Z. Elektrochem., 1928, 34, 829—840; cf. A., 1928, 605).—The decomposition of ammonia by iron containing 0.035% of carbon and by iron containing before reduction potassium or aluminium oxide has been studied over the range 100—450° by a dynamic method. The catalysts were reduced in specially purified hydrogen at 400—480°. With the freshly-reduced iron, decomposition of the ammonia could be detected at 200°, with the formation of a nitride and the evolution of hydrogen. At 350°, appreciable amounts of nitrogen appear, and finally, at about 450°, a mixture of hydrogen and nitrogen in stoichiometrical proportions is formed. In the case of iron activated by the addition of the oxides, the formation of nitrogen occurs first at a lower temperature, viz., 100°, as well as that of the stoichiometric

mixture. The velocity of the ammonia decomposition is determined by that of the formation of the nitrogen from the intermediate nitride which is produced, and the decomposition is shown to take place in the stages (i) iron+ammonia=iron nitride+hydrogen, and (ii) iron nitride=iron+nitrogen. The second stage is dependent on the temperature and on the addition of activators and it is generally the slower reaction, but under certain conditions it may become faster than (i). Decomposition, however, takes place exclusively at the metal independently of the individual effects of the added substances. At 360° and in the range 15–600 mm. pressure, the velocity of decomposition of the ammonia is independent of the total pressure and of the rate of passage of the gas over the metal.

Iron carbide, and mixtures of iron with other substances, especially the finely-divided carbide obtainable by reduction of the cyanide (*loc. cit.*), have also been investigated as catalysts. In all cases, the effective portion of an iron-containing catalyst is the metal itself. The carbide, both fine and coarse-grained, is not a catalyst for the synthesis or decomposition of ammonia. A method by which the effective portion of an iron-containing catalyst for ammonia can be determined is described together with a new gasometer for storage and exact analysis; the gasometer is especially suitable for use with highly-purified gases.

L. S. THEOBALD.

Copper catalysts prepared from precipitated hydroxide. I. Activity as a function of the temperature of precipitation. P. K. FROLICH, M. R. FENSKE, and D. QUIGGLE (J. Amer. Chem. Soc., 1929, 51, 61–65).—The catalytic activity of copper catalysts prepared by reduction at 200° of the hydroxide obtained on precipitating copper nitrate solution with ammonia varies with the temperature of precipitation. The reaction studied was the catalytic decomposition of methyl alcohol vapour at 360° (cf. A., 1928, 1112); formaldehyde and methyl formate are produced simultaneously. A maximum activity occurs when the hydroxide is precipitated at 22°. X-Ray examination indicates that a small particle size of the dry hydroxide gel is associated with the more active catalysts. A minimum particle size at 22° may be produced as the result of two opposing factors, viz., the tendency for the initial particle size to decrease with falling temperature of precipitation, and the tendency for the initially formed particles to grow while the hydroxide is drying at 110°.

S. K. TWEEDY.

Copper catalysts prepared from precipitated hydroxide. II. Comparison of sodium hydroxide and ammonia as a precipitating agent. P. K. FROLICH, M. R. FENSKE, L. R. PERRY, and N. L. HURD (J. Amer. Chem. Soc., 1929, 51, 187–193).—When sodium hydroxide is the precipitating agent (cf. preceding abstract) the catalysts are much more active, due to promoter action of occluded sodium salts. Below 313° the activity of such catalysts is independent of time; at 380° the catalytic power is immediately destroyed. Thus fused occluded sodium salts appear to cover the active patches of the catalysts. Copper catalysts prepared by precipitating copper chloride or sulphate with sodium hydroxide

are practically inactive. The promoted catalysts favour the formation of methyl formate in the thermal decomposition of methyl alcohol rather than that of formaldehyde. The conclusions are confirmed by experiments with catalysts containing known amounts of sodium nitrate. The results may explain some of the discordant observations recorded in the literature.

S. K. TWEEDY.

Synthesis of water with a silver catalyst. II. Energy of activation and mechanism. A. F. BENTON and J. C. ELGIN (J. Amer. Chem. Soc., 1929, 51, 7–18).—The synthesis of water in presence of a silver catalyst was investigated, the adsorption by the catalyst of oxygen and of water vapour (in presence of oxygen) being measured also. The oxygen adsorption is nearly independent of temperature and pressure (cf. A., 1927, 118). Water vapour is adsorbed much more strongly by a silver surface covered with adsorbed oxygen than by a bare surface. The reaction rate is independent of the oxygen pressure, but proportional to the hydrogen pressure and to the fraction of catalyst surface free from adsorbed water. The calculated energy of activation is 16,000 g.-cal. It is concluded that reaction occurs at every collision of hydrogen with "dry" adsorbed oxygen in which the energy available on collision exceeds the energy of activation. The results are probably not in disagreement with Taylor's theory of catalyst surfaces.

S. K. TWEEDY.

[Catalytic] synthesis of methane from carbon dioxide and hydrogen. M. RANDALL and F. W. GERARD.—See B., 1929, 82.

[Catalytic] synthesis of higher hydrocarbons from water-gas [at atmospheric pressure]. II. D. F. SMITH, C. O. HAWK, and D. A. REYNOLDS.—See B., 1929, 82.

Catalytic oxidation of naphthalene. T. KUSAMA.—See B., 1929, 88.

Effect of inhibitors on the acid dissolution of copper and copper alloys. H. O. FORREST, J. K. ROBERTS, and B. E. ROETHELI.—See B., 1929, 98.

Theory of chemical action in electrical discharge. S. C. LIND (Science, 1928, 67, 565–569).—An address to the American Electrochemical Society, April 26, 1928.

Formation of ozone in the electrical discharge at pressures below 3 mm. J. K. HUNT (J. Amer. Chem. Soc., 1929, 51, 30–38).—During the first half minute the quantity of ozone formed is approximately proportional to the input of electricity, but equilibrium is soon reached. The yield increases with increasing pressure, but at a decreasing rate; it is independent of the electrode material (small electrodes were used; aluminium gives abnormally high results) and increases with increasing cathode area. The number of ion pairs and of ozone molecules produced are both of the same order of magnitude. The following mechanism is suggested: $O_2 = O^+ + O^-$; $O^+ + O_2 = O_3^+$; $O^- + O_2 = O_3^-$; $O_3^+ + O_3^- = 2O_3$ or $O_3^+ + O^- = 2O_2$ and $O_3^- + O^+ = 2O_2$.

S. K. TWEEDY.

Electrolytic preparation of hydroxylamine. J. G. STSCHERBAKOV and D. M. LIBINA (Z. Elektrochem., 1929, 35, 70–83).—Different methods of

determination of the hydroxylamine produced by the electrolytic reduction of nitric acid in sulphuric acid solution using a mercury cathode yield distinctly different results, and it is concluded that, besides hydroxylamine, considerable quantities of a second reducing agent are formed by the electrolysis. This is proved to be a compound of hydroxylamine-*iso*-monosulphonic acid with sulphuric acid, $(\text{NH}_2 \cdot \text{O} \cdot \text{SO}_3\text{H})_2 \cdot \text{H}_2\text{SO}_4$. A low nitric acid concentration favours the formation of the *iso*-compound, which liberates iodine from potassium iodide, is oxidised to nitric acid by titration with permanganate in the cold, and is hydrolysed by heating to hydroxylamine. The combined sulphuric acid may be determined by titration with alkali, using phenolphthalein. An electrolyte containing the two compounds remains stable at the ordinary temperature for an indefinite period of time. An increase in the sulphuric and nitric acid concentrations up to certain limits (15–16*N*-sulphuric acid and *N*-nitric acid) causes an increase in the current yield of hydroxylamine, whilst below 3–4*N*-sulphuric acid a pronounced decrease takes place. For nitric acid concentrations above *N*, considerable quantities of oxides of nitrogen are formed. The most favourable acid concentrations, current densities, and temperatures are given, with which a mean current yield of 60–70% of hydroxylamine is obtainable. Under certain conditions (*e.g.*, the presence of foreign metals in the electrolyte, dissolved from the electrodes), the nitric acid is not reduced at the mercury cathode, but a hydrogen evolution of almost 100% takes place. At higher nitric acid concentrations, oxides of nitrogen are formed. In these circumstances, the cathode is found to be covered with a thin, scarcely visible film, which acts as a diaphragm and prevents reduction. The presence of the film increases the current yield of the *iso*-compound. At the end of the electrolysis, the free nitric acid may conveniently be removed by electrolysis with a copper cathode, since by this means the nitric acid is reduced to ammonia, whilst the hydroxylamine and *iso*-compound are unaffected.

L. L. BIRCUMSHAW.

Influence of current density in the electrolytic preparation of sodium perborate. F. GIORDANI and R. INTONTI (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], 34, 30–36).—The yields of sodium perborate, obtained by electrolysis of solutions of borax and sodium carbonate under conditions in which the current passing through the electrolyte was 10, 5, and 2.5 amp./litre, respectively, have been determined. Assuming that the perborate is formed according to the schemes $\text{Na}_2\text{CO}_3 \rightarrow \text{NaCO}_3' + \text{Na}$, $2\text{NaCO}_3' + 2F \rightarrow \text{Na}_2\text{C}_2\text{O}_6$, $\text{Na}_2\text{C}_2\text{O}_6 + \text{NaBO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 + \text{NaBO}_2 \cdot \text{H}_2\text{O}_2$, $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaOH} \rightarrow 4\text{NaBO}_2 + \text{H}_2\text{O}$, it is shown that the effective instantaneous yield of perborate is given by $\rho = 2F(V/I)k(\text{Na}_2\text{C}_2\text{O}_6)(\text{NaBO}_2)/\rho_1$, where ρ_1 is the current efficiency in the formation of sodium percarbonate, V the volume of the solution, and I the current intensity.

F. G. TRYHORN.

Electrolytic precipitation of metals. K. ARNDT (Ber., 1929, 62, [B], 80–84).—Study of the distribution of a metal on a cathodic surface frequently

gives wave-like curves with distinct maxima and minima. Interposition of a non-conducting screen of mica or celluloid, pierced with a fine hole in the centre, between cathode and anode in the electrolysis of Öttel's solution (150 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 50 g. H_2SO_4 , and 50 g. of alcohol per litre) causes the metal to be deposited in concentric rings which are more or less sharply defined. All the crystals have approximately the same size (5 μ). It is considered that the current initially causes an approximately uniform distribution of crystal nuclei and that subsequently the particles in unfavourable positions pass into solution whilst metal is deposited at the favourable positions. Study has also been made of the deposition of copper on a silvered cathode without a shield with a current density so small that the individual crystals can be measured and counted, Öttel's solution being used. Increased current density, cooling, or dilution increases the number of copper crystals, which is lessened by warming or decrease in current density. At the ordinary temperature with 8 milliamp. the size is about 1.5 μ , with 40 milliamp. about 0.5 μ . At 0° the size is also approximately 0.5 μ , whereas at 35° the few particles may attain 5 μ . From the warm bath crystals are obtained as much as 5 μ long. Addition of 0.1% of gelatin to the acid copper bath renders the copper particles so small that they cannot be distinguished under the microscope. A uniform copper deposit is also obtained from a copper bath containing potassium cyanide.

H. WREN.

Theory of electro-deposition of chromium from aqueous solutions of chromic acid. E. MÜLLER and P. EKWALL (Z. Elektrochem., 1929, 35, 84–89; cf. Schischkin and Gernet, A., 1928, 489).—A microscopical examination has been made of the deposits obtained under various conditions when 30% aqueous solutions of chromic acid are electrolysed, using smooth platinum electrodes. Photomicrographs are reproduced, showing the results with very carefully purified chromic acid, free from all traces of sulphate, with chromic acid 0.001, 0.01, 0.05, and 0.1*N* with respect to sulphuric acid, and chromic acid free from sulphate but containing trivalent chromium. The last-named solution was prepared by boiling chromic acid with hydrogen peroxide and contained about 0.13 g. of trivalent chromium to 1 g. of hexavalent chromium. The results confirm Müller's previous view (cf. A., 1926, 913), that a non-conducting diaphragm of chromic chromate is formed at the cathode, which hinders access of chromium ions but is permeable to hydrogen ions. At potentials lower than –1.1 volt, deposition of metallic chromium begins to take place, the first layer of metal deposited forming an alloy with the platinum. In the presence of sulphate ions, the chromic chromate diaphragm is considered to be mechanically imperfect and may be removed by the gaseous hydrogen evolved. For this reason, the presence of sulphates promotes deposition of chromium in a bright coherent form. Similar results are obtained if sulphate-free chromic acid containing trivalent chromium is used. A study was made of the cataphoretic behaviour of solid chromic chromate in the colloidal state, prepared by adding excess of alcohol to a concentrated solution

of pure chromic acid, dissolving the brown gel, which formed after some time, in water, and dialysing the resulting solution. The chromic chromate migrates to the cathode, and is believed to be a basic compound with the composition $\text{Cr}_2(\text{OH})_4\text{CrO}_4$.

L. L. BIRCUMSHAW.

Electrolytic oxidation of methyl alcohol in alkaline solution. S. TANAKA (*Z. Elektrochem.*, 1929, 35, 38—42).—An investigation has been made of the relations between anode potential and current density in the electrolytic oxidation of methyl alcohol mixed with an equal volume of 8*N*-sodium hydroxide, using as anode material smooth and spongy platinum, palladium, and rhodium, smooth gold, and silver. The current-potential curves for the smooth metals are all similar in form, but differ from those for the spongy metals, which resemble those obtained in the electrolytic oxidation of formaldehyde in alkaline solution (cf. Müller and Takegami, A., 1928, 1338). A current rise is observed in the low potential region, followed by a sudden fall, after which a second current rise occurs in the high potential region. In no case was any evolution of gas observed on the first rise, and with the smooth metals, the current rise at low potentials was absent. With rising temperature, the first rise becomes steeper and leads to higher current densities. The anolyte was analysed for formaldehyde and formic acid. No aldehyde appears to be produced, and it is considered that the reaction occurring in the low potential region may be represented by $\text{CH}_3\text{O}' + \text{OH}' \rightarrow 4 \text{ faradays} = \text{H}\cdot\text{CO}_2\text{H} + 2\text{H}'$ or $\text{CH}_3\text{O}' + 3\text{OH}' \rightarrow 4 \text{ faradays} = \text{H}\cdot\text{CO}_2\text{H} + 2\text{H}_2\text{O}$. A theory developed to explain the observed phenomena is based on the supposed adsorption of the alcohol anions on the electrode surface.

L. L. BIRCUMSHAW.

Regularity of the physical and chemical action of X-rays. R. GLOCKER (*Z. tech. Phys.*, 1928, 9, 201—207; *Chem. Zentr.*, 1928, ii, 1063).—The law of photochemical equivalence is not applicable to X-rays, since the number of electrons liberated as a secondary process far exceeds that of the electrons primarily liberated by the absorption of the radiation. In photochemical reactions in solution, electrons liberated from all the molecules present, and not merely those of the solute, are active in the chemical change.

A. A. ELDRIDGE.

Photo-expansion of chlorine. W. H. MARTIN, A. F. W. COLE, and E. E. LENT (*J. Physical Chem.*, 1929, 33, 148—153).—Contrary to the observation of Shenstone (*J.C.S.*, 1897, 71, 471), purified and dried chlorine still shows expansion when exposed to light. Chlorine fractionated by means of liquid air over purified phosphorus pentoxide showed practically no decrease in expansion, as compared with the undried chlorine, when insulated by the light from a carbon arc. Baking-out the expansion bulb at 425° under a pressure of less than 0.0001 mm. of mercury for 4 days before admission of the dried chlorine had no effect on the photo-expansion. The present experiments together with those previously reported (A., 1926, 559) show that dried chlorine at 1 atm. and at lower pressures exhibits no abnormal scattering nor any fluorescence which can be detected visually or

photographically. The assumption that dry chlorine does not expand on insolation but re-radiates adsorbed energy is unwarranted.

L. S. THEOBALD.

Photochemical union of hydrogen and chlorine. A. J. ALLMAND and E. BEESLEY (*Nature*, 1929, 123, 164).—The results of a study of the effect of the intensity of monochromatic light are in agreement with those of (Mrs.) Chapman, Kornfeld and Steiner, and Marshall. The effect of wave-length (Å.) on the quantum efficiency is as follows: 2600, 0.10; 3130, 0.49; 3650, 0.53; 4050, 1.00; 4360, 0.67; 5460, 0.22. The sensitivity of the gas used corresponded with a yield of the order of 2×10^5 mols. of hydrogen chloride per quantum of blue light absorbed; the mixture showed no induction period, but gave a marked Draper effect during the first instants of insolation. The relative temperature coefficients (between 19.7° and 25°) of the quantum efficiency increase slowly with wave-length between 3130 and 4360 Å. When acting simultaneously, two monochromatic beams gave a velocity equal to the sum of their separate effects.

A. A. ELDRIDGE.

Budde effect in bromine. E. MATTHEWS (*Trans. Faraday Soc.*, 1929, 25, 41—43).—A slight expansion on illumination by a 100-c.p. lamp was recorded for mixtures of dried bromine vapour and air at temperatures between 20° and 95°; a smaller expansion was shown by dry bromine vapour in the absence of air, and a somewhat greater one in the case of a mixture of bromine vapour and air which had not been dried over phosphorus pentoxide.

F. G. TRYHORN.

Further test of the radiation hypothesis. L. S. KASSEL (*J. Amer. Chem. Soc.*, 1929, 51, 54—61).—The decomposition rate of nitrogen pentoxide, even at very low pressure, is not increased by radiation of wave-length less than 5 μ; not more than 3% of the total thermal reaction can be caused exclusively by radiation of wave-length less than 5 μ. The region between 5 and 10 μ may be all-important if the radiation theory is the true explanation (which is improbable) of the anomalous nitrogen pentoxide decomposition. If the diameter for intrinsic energy transfer of the nitrogen pentoxide molecule is approximately independent of the energy, and if it is larger than the kinetic theory diameter (which would supply an explanation of the anomalous decomposition rate), then the thermal conductivity of the gas should be abnormally large.

S. K. TWEEDY.

Mechanism of the photochemical decomposition of nitrogen pentoxide. W. P. BAXTER and R. C. DICKINSON (*J. Amer. Chem. Soc.*, 1929, 51, 109—116).—From measurements of the relative rates of decomposition of nitrogen pentoxide at 0° by radiations of wave-lengths 4350, 4050, and 3660 Å., and comparison with the rates of decomposition of nitrogen dioxide, it is concluded that the mechanism of the pentoxide decomposition is essentially that suggested by Norrish (A., 1927, 119, 528).

S. K. TWEEDY.

Herschel effect. LUPPO-CRAMER (*Z. wiss. Phot.*, 1928, 26, 249—259).

Spectral distribution of the inner photo-effect in the silver halides. E. A. KIRILLOV (Z.

wiss. Phot., 1928, 26, 235—248).—The photo-electric conductivity of granular layers of silver halides has been investigated. New maxima in the longer waves have been found. In the case of silver bromide, the conductivity was less in the presence of light.

W. E. DOWNEY.

Photolysis of silver bromide. E. MUTTER (Z. wiss. Phot., 1928, 26, 193—234).—The bromine liberated by the photolysis of silver bromide in the presence of water exists as ions. Nitric acid dissolves the photolytic silver in small degree, the degree of regression being a function of the time and of the concentration of the solution. As a result of secondary reactions, hydrogen ions and free oxygen also appear. This behaviour is explained by the hypothesis that the hydroxyl ion behaves as an acceptor. The nitrite ion behaves similarly. The quantum yield in the presence of the nitrite ion is approximately 1. For equivalent substances the yield is only about 0.1 owing to the strong regression. Thus, the same amount of silver causes a much stronger blackening in the presence of nitrite than in that of equivalent substances.

W. E. DOWNEY.

Photolysis of silver halides in the light of the quantum theory and the photo-electric effect. H. KIESER (Z. wiss. Phot., 1928, 26, 275—287).—Theoretical. Cf. Mutter (preceding abstract).

W. E. DOWNEY.

Sensitometry of desensitised films. H. ARENS and J. EGGERT (Z. wiss. Phot., 1928, 26, 111—126).—Three-dimensional models have been prepared showing the relationships between the darkening D and $\log i$ and $\log t$ for the Agfa "extra rapid" plate and for the same plate when desensitised before exposure by immersion in 1/2000 phenosafranine solution containing 2% of potassium bromide. The forms of surface obtained differ in both position and form. For the desensitised plate a section parallel to the $\log t$ axis exhibits maxima, which decrease as i decreases; at low values of i no darkening is produced. The intensity plane, parallel to the $\log i$ axis, is of the normal form, which, however, remains unaltered at high values of t . Although the desensitised plate has a rather steeper intensity curve, there is no typical difference in the time curves. The Schwarzschild exponent n assumes anomalous values for the desensitised plate; over a wide range $n=0$ and in the region of reversal $n=-2.3$. No simple numerical expression can be obtained for the degree of desensitisation.

H. F. GILLBE.

Relation between the photo-electric and the photographic effect in silver bromide. L. W. BUTLER (Proc. Iowa Acad. Sci., 1927, 34, 277).—The results obtained by Toy, Edgerton, and Vick (A., 1927, 293) are confirmed. CHEMICAL ABSTRACTS.

Photometric and spectrophotometric studies.
I. Reflexion spectroscopy. K. SCHAUM (Z. wiss. Phot., 1928, 26, 97—110).—A method is described for the measurement of reflexion spectra, especially of opaque substances. The reflexion spectra of a number of aromatic azo-compounds have been determined, and in general the curves obtained resemble those of the absorption spectra. The influence of irradiation on films of a number of dyes has been

investigated; the number of large particles increases, whilst the reflexion, and to a smaller extent the absorption, spectra are altered; this effect is dependent on the presence of oxygen, since it is at a maximum in pure oxygen but is not produced in a vacuum or in an atmosphere of hydrogen, and is probably partly photochemical and partly physical in nature. Analogous effects on the spectra are produced in some cases by treatment of the film with hydrogen peroxide, whilst coagulation of certain dye solutions by electrolytes results in similar effects.

H. F. GILLBE.

Influence of metallic magnesium on the formation of formaldehyde and sugars by the action of ultra-violet rays on calcium hydrogen carbonate solutions. G. MEZZADROLI and E. VARETON (Atti R. Accad. Lincei, 1928, [vi], 8, 511—515).—The power to reduce iodine solution acquired by calcium hydrogen carbonate solutions on exposure to ultra-violet rays (cf. Mezzadrolì and Gardano, A., 1928, 255) rises to a maximum after 30 min. when open basins, or after 1 hr. when closed transparent vessels, are used to contain the liquid, the reducing power being the higher in the latter case. The total amount of reducing substances formed is increased by the presence in the solutions of metallic magnesium, which also results in the formation of sugars which reduce Fehling's solution and form an osazone.

T. H. POPE.

Induction period and after-effect in photochemical reactions. R. M. PURAKAYASTHA (J. Indian Chem. Soc., 1928, 5, 721—732).—The induction period in the photo-bromination of cinnamic acid and stilbene (A., 1926, 366; 1928, 172) is diminished by any factor (*e.g.*, temperature, intensity of light) causing an increase in the velocity of the reaction. During the oxidation of tartaric acid by bromine (A., 1925, ii, 1179) the induction period increases with increased concentrations of tartaric acid, and to a certain point with bromine. Above this concentration of bromine a decrease is manifested owing to reaction being due to free bromine molecules. α -Hydroxy- β -phenylpropionic and mandelic acids are oxidised by bromine in the dark, the latter only slowly. The reactions are markedly accelerated by light, and then show both induction periods and after-effects. When potassium bromide is added to any of the above oxidation reactions in a concentration eight to ten times as great as that of the bromine the induction period either disappears or is reduced considerably. The period of gradually increasing velocity observed in these oxidations is not explained satisfactorily by Ghosh and Basu (A., 1928, 970), and it is assumed that the bromine molecules are hydrated. Whilst such molecules are active in the dark, on exposure to light they become activated, and this period of activation is, presumably, the induction period. In presence of bromide ions only a small percentage of the hydrated molecules exist as such owing to the change $\text{Br}^+ + \text{Br}_2 \rightleftharpoons \text{Br}_3^+$, and reaction proceeds normally. The after-effect is probably due to the existence of chain-reactions. H. BURTON.

Photochemical studies. VIII. Photochemical decomposition of malonic acid both in the

presence and absence of uranyl sulphate. W. C. PIERCE, A. LEVITON, and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1929, 51, 80—89).—The early stages of the decomposition lead almost exclusively to the formation of carbon dioxide and acetic acid, both in the presence and in the absence of the catalyst. The quantum efficiency of the catalysed reaction is smaller than that of the uncatalysed reaction and is not markedly influenced by the wave-length. In presence of radiation from a mercury arc lamp the decomposition rate increases with addition of uranyl sulphate and approaches a practically constant value, whereas with constant catalyst concentration the rate of decomposition of malonic acid is approximately proportional to the cube root of the acid concentration. The degree of ionisation of the acid seems to be without influence on the rate, since the addition of sulphuric acid is without effect. There is no evidence for the formation of a light-sensitive complex molecule, but the possible existence of such a complex is not eliminated. The results seem to indicate that there are two independent reactions, due to the light absorbed by the catalyst and by the malonic acid, respectively; it is possible, also, that with constant malonic acid concentration the rate of the catalysed reaction is proportional to the intensity of the light absorbed by the catalyst. The mechanism may involve the deactivation of uranyl sulphate molecules by collision with other uranyl sulphate molecules or with malonic acid molecules. Below 0.01*M*, uranyl sulphate behaves towards phenolphthalein as though it were an equivalent amount of sulphuric acid.

S. K. TWEEDY.

Zinc oxide and chlorophyll as optical sensitizers. J. BOHR (Helv. Chim. Acta, 1929, 12, 121—153).—An experimental investigation based on the theoretical views of Baur (A., 1928, 1338). The sensitizing action of zinc oxide on the reduction of Prussian blue and of copper salts with and without the addition of anodic depolarisers (dextrose and glycerol) has been examined. Even in the presence of dextrose the reduction of Prussian blue by light reaches an equilibrium value of only 36%. On the other hand, if an anodic depolariser be present cupric salts are reduced by light to the cuprous state and finally to the metallic state and the amount of reduced copper obtained is linearly proportional to the duration of exposure to light. Without an anodic depolariser only cupric oxide is obtained, a fact which is attributed to oxidation of cuprous oxide formed at first. By the action of light on electrolytic gas in the presence of moist zinc oxide, water and hydrogen peroxide have been obtained.

Reduction of a large number of azo-dyes takes place by exposure to light in the presence of chlorophyll in methyl-alcoholic solution. The chlorophyll itself is destroyed, but this can be prevented by adding one of the following anodic depolarisers: oil of turpentine, piperidine, phenylhydrazine. Addition of the last-named was found to produce the most rapid photolysis. Some other vat, azine, and triphenylmethane dyes have also been studied. No reduction is obtained by exposure to light in the presence of chlorophyll alone, but by addition of phenylhydrazine reduction takes place. Experiments

have also been carried out on systems in which the chlorophyll is in one liquid layer, *i.e.*, a solution in benzene or carbon tetrachloride, and the dye is in another aqueous layer; the sensitising action of chlorophyll in these systems is reduced.

R. N. KERR.

Action of light on anthracene. E. HIBBERT.—See B., 1929, 88.

Chain reactions. M. BODENSTEIN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1928, 490—497).

Ignition of detonating gas by hydrogen atoms. F. HABER and H. D. VON SCHWEINITZ (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1928, 499—506).—According to Bonhoeffer and Haber (*cf.* this vol., 11) the mechanism of the burning of detonating gas is a chain reaction of the form (a) $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$, (b) $2\text{H} + \text{O}_2 = 2\text{OH}$, so that the addition of a sufficient quantity of hydrogen atoms or hydroxyl radicals should bring about explosion at the ordinary temperature. This has been accomplished for hydrogen atoms. A stream of hydrogen was fed into an arc, a small concentration of hydrogen atoms being thereby produced, and their recombination prevented by rapid cooling. The stream of molecular and atomic (about 0.1%) hydrogen was then brought into contact with oxygen. A definite lag, varying in duration according to the strength of the arc current, was observed between switching on the arc and the commencement of the explosion. That the explosion was due to decomposition products of hydrogen was established by the fact that no explosion occurred when hydrogen was replaced by argon.

In other experiments arranged, *e.g.*, to eliminate the possibility that the explosion could be due to direct heating by the arc, similar results were obtained.

The explosion cannot be due to the heat developed by such reactions as $2\text{H} + 0.5\text{O}_2 = \text{H}_2\text{O} + 157 \text{ kg.-cal.}$, for this would require a 5% concentration of hydrogen atoms in order to produce the ignition temperature of 600°, as against the measured concentration of 0.1%.

S. J. GREGG.

Compounds of alkali phosphates with hydrogen peroxide. H. MENZEL and C. GABLER (Z. anorg. Chem., 1928, 177, 187—214).—The solubilities have been determined of the salts $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, KH_2PO_4 , and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in water from about -3° to $+25^\circ$ and in aqueous hydrogen peroxide solutions of various concentrations at 0° . The formation of compounds between hydrogen peroxide and the phosphates is indicated by the rapid increase of solubility as the hydrogen peroxide concentration increases. Cryoscopic measurements with phosphate in hydrogen peroxide solution, and determination of the partition coefficients of hydrogen peroxide between these solutions and amyl alcohol, also indicate some combination between the hydrogen peroxide and the dissolved phosphate. By evaporation of the solutions at the ordinary temperature in a current of dry air the compounds $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}_2$, $\text{K}_2\text{HPO}_4 \cdot 2.5\text{H}_2\text{O}_2$, and $\text{KH}_2\text{PO}_4 \cdot 1-1.25\text{H}_2\text{O}_2$ have been isolated; the sodium compound, although hygroscopic, is stable in dry air, and may be differentiated both microscopically and by its X-ray diagram from $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$; the

compound $K_2HPO_4 \cdot 2.5H_2O_2$ is similar to the sodium salt. The monopotassium compound is considerably less stable, whilst the analogous sodium salt has not been prepared. By precipitation with alcohol an oily substance is obtained, of approximate composition $Na_2HPO_4 \cdot 2H_2O_2 \cdot 10H_2O$, which, however, on evaporation yields only $Na_2HPO_4 \cdot 2H_2O_2$. The formulæ ascribed to these substances are supported by the observations that ether extracts hydrogen peroxide from the salts, and that at 130° in a vacuum hydrogen peroxide is evolved, leaving the anhydrous salts. These compounds are thus to be distinguished from the true perphosphates obtained electrolytically.

H. F. GILLBE.

Constitution of double salts. XV. Ammine iodides. G. SPACU and O. VOICU (Bul. Soc. Stiinte Cluj, 1928, 4, 42—56; Chem. Zentr., 1928, ii, 1196).—The following compounds are described: $(NH_4)_2[ZnI_4(C_6H_5N)_2]$, from zinc ammonium iodide and pyridine in benzene, yellow, decomposed by light and air, and hydrolysed by water; $Na_2[ZnI_4(C_6H_5NH_2)_2]$, stable in air; $K[PbI_3(NH_3)_3]$; $[CdI_4][Ba(H_2O)_2(C_6H_5NH_2)_2]$; $[HgI_3][Cu(C_6H_5N)_4]$; $[HgI_3][Cu(C_6H_5N)_5]$.

A. A. ELDRIDGE.

Dehydration of $3CdSO_4 \cdot 8H_2O$. L. CONIGLIO (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], 34, 119—122).—The hydrate $3CdSO_4 \cdot 5H_2O$, formed from $3CdSO_4 \cdot 8H_2O$ at 41.5° (cf. Carpenter and Jette, A., 1923, ii, 292), exists over a range of more than 70° . At about 120° the hydrate $3CdSO_4 \cdot 2H_2O$ is obtained, and at about 138° the hydrate $3CdSO_4 \cdot H_2O$. This last is converted into the anhydrous salt at 150° . The continued existence of the termolecular complex $3CdSO_4$ in the above hydrates is noteworthy.

E. W. WIGNALL.

Reaction of fusible and infusible white precipitates of mercury [mercuriammonium chlorides]. P. RAY and P. BANERJI (J. Indian Chem. Soc., 1928, 5, 715—719).—Ammoniacal hydrogen peroxide converts both the infusible (I) and fusible (II) white precipitates of mercury, $HgCl \cdot NH_2$ and $HgCl_2 \cdot 2NH_3$, respectively (cf. Franklin, A., 1905, ii, 581; 1907, ii, 264), into mercury and ammonium chloride. Mercuric oxide also gives mercury under the same conditions and is probably an intermediate product. Ethyl mercaptan reacts with I in alcoholic solution, yielding mainly mercuric mercaptide and smaller amounts of ethylthiolmercuric chloride, ammonium chloride, and ammonia. Under similar conditions II furnishes approximately equal amounts of the above mercaptides, indicating that dissociation of II occurs thus: $[Hg(NH_3)_2Cl_2] \rightleftharpoons HgCl_2 + 2NH_3$ or $[HgNH_2]Cl + NH_4Cl$. When I or II is treated with thiocarbamide in aqueous or alcoholic solution, ammonia is evolved and mercuric sulphide and the double compound of mercuric chloride and thiocarbamide are precipitated. The soluble residue contains ammonium chloride and gives on treatment with ammoniacal silver nitrate silver cyanamide. Thiocarbanilide and I give mercuric sulphide and diphenylguanidine hydrochloride, also formed together with ammonium chloride from II. It is concluded that I reacts as the equilibrium mixture $HgCl \cdot NH_2 \rightleftharpoons [Hg \cdot NH_2]Cl$.

H. BURTON.

Boron hydrides. XII. $B_{10}H_{14}$. A. STOCK and E. POHLAND (Ber., 1929, 62, [B], 90—99; cf. A., 1926, 1217).—The initial material consisted of residues of boron hydrides remaining after heating B_4H_{10} and from which B_5H_9 and unchanged B_4H_{10} had been removed. The product after 4 years in a vacuum contained nothing volatile except $B_{10}H_{14}$, a little hydrogen, and some B_5H_9 ; the less stable B_5H_9 had become decomposed. The non-volatile residue in the tubes consisted of the colourless hydride containing 12 atoms of boron, and the yellow hydride ($B:H$ —about 5:4) insoluble in carbon disulphide. The hydride B_5H_9 combines with ammonia, giving the compound $B_5H_9 \cdot 4NH_3$, which passes at 200° into hydrogen and $B_3N_3H_6$. The hydride $B_{10}H_{14}$ is separated from the small amounts of accompanying volatile hydrides by fractional condensation. The pure material has m. p. 99.6 — 99.7° . The vapour tensions between 55° and 156° are recorded and from these the b. p./760 mm. is calculated to be about 213° . The values d^{20}_m , temp. 0.94 , $d^{99.0}_m$ 0.92 , and d^{100}_m 0.78 (molten) are given. The hydride is stable at the ordinary temperature, but decomposes slowly at 200° , extensively at 250° , giving hydrogen and a non-volatile, yellow material. Air and oxygen in the absence of moisture do not affect it at 50 — 60° . It is insoluble in water, by which it is quantitatively hydrolysed at 200° to boric acid and hydrogen; the action occurs moderately rapidly at 100° , but very slowly at the atmospheric temperature. Incomplete hydrolysis with an excess of water does not appear to yield any other hydride, but a boron compound with about the same volatility as water appears to be produced when the hydride is in excess. Sodium hydroxide dissolves $B_{10}H_{14}$ and the solution continuously evolves hydrogen; very stable, partly oxidised boron compounds appear to be produced. At low temperatures, $B_{10}H_{14}$ combines loosely with about $6NH_3$, which is evolved at the atmospheric temperature. When it is heated with ammonia a complex change occurs accompanied by evolution of hydrogen but without production of $B_3N_3H_6$. Electrolysis of solution of $B_{10}H_{14}$ in liquid ammonia follows a complicated course, but the electrolyte character of the additive compound is established. Hydrogen chloride does not react with $B_{10}H_{14}$ in presence of aluminium chloride at 100° . Apparently, the treatment of $B_{10}H_{14}$ with an excess of iodine leads to two groups of products, one of which is soluble in carbon disulphide and contains mainly the di-iodo-compound $B_{10}H_{12}I_2$, whereas the other is insoluble in carbon disulphide and contains 10—12 atoms of iodine in the molecule. The intermediate iodides are obviously unstable. Boron tri-iodide is not produced. $B_{10}H_{14}$ forms rhombic crystals, $a:b:c = 0.6935:1:0.2728$. Röntgenographic investigation affords little evidence of the structure of the molecule.

H. WREN.

Heterotri-salts. V. Heterotri-borates and their isomorphism with other heterotri-series. G. CANNARI (Gazzetta, 1928, 58, 840—844; cf. A., 1927, 220).—Since the radius of the boron atom is presumably not much different from those of silicon and phosphorus, it seemed likely that boron might be able to replace these two elements as the central

atom in the complex anions of silico- and phosphotungstovanadates of the types
 $R_8[Si(W_2O_7)_x(V_2O_6)_y]_n \cdot nH_2O$ and
 $R_7[P(W_2O_7)_x(V_2O_6)_y]_n \cdot nH_2O$, respectively, where $x+y=6$. By allowing solutions containing commercial boric acid and alkali tungstates and vanadates to crystallise at the ordinary temperature small quantities of alkali polyborate separate at first. From the reddish-brown liquor which finally remains, small amounts of large brown crystals separate, which show the same crystallographic characteristics as the above-mentioned silico- and phospho-tri-salts. They are mixed crystals containing silicon and phosphorus, which were originally present as impurities in the boric acid, and they are not formed if the latter is purified by recrystallisation before use. Borotungstovanadates could not be obtained in the pure state, showing that boron is apparently incapable of co-ordinating the W_2O_7 and V_2O_6 groups simultaneously.

O. J. WALKER.

Hydrated aluminium silicates. I. Rehydration of metakaolin and synthesis of kaolin. C. J. VAN NIEUWENBURG and H. A. J. PIETERS (Rec. trav. chim., 1929, 48, 27—36).—Metakaolin (dehydrated kaolin) when treated with steam under a pressure of about 100 atm. for 2—6 days takes up water. This reaction is never wholly complete, the maximum amount of water present after rehydration being 14.5% (theory 15%). The amount taken up is dependent on the temperature of ignition of the original kaolin. If this is above 850°, the faculty of rehydration is gradually lost. Alumina takes up water when treated in a similar way: the amount taken up corresponds with the formula $Al_2O_3 \cdot H_2O$, but the product obtained is not identical with diaspore. The water taken up in this case also depends on the temperature of ignition of the alumina; if this be above 1000° a sharp break in the percentage of water taken up occurs. Under the same conditions amorphous silica takes up a quantity of water not exceeding 5.3%. It is shown that metakaolin cannot be simply a mixture of alumina and silica, since an artificial mixture of the two oxides in the correct ratio takes up only 11% of water. A product resembling kaolin has been synthesised by precipitating alumina and silica together in the correct proportions and treating the dried precipitate with steam for 12 days under a pressure of 200—260 atm. The water content is low, 9.1% (theor. 14.0%), but the solubility in dilute hydrochloric acid is of the right order and the physical properties are in good agreement with those of kaolin.

R. N. KERR.

Action of aluminium, ferrous and ferric iron, and manganese in base-exchange reactions. O. C. MAGISTAD.—See B., 1929, 93.

Higher oxides of some rare-earth elements. H. A. PAGEL and P. H. M.-P. BRINTON (J. Amer. Chem. Soc., 1929, 51, 42—54).—The composition of air-ignited praseodymium oxide varies with the conditions of ignition and especially of cooling, but with any specific set of conditions reasonably concordant compositions are obtained. By heating lower oxides at 370° for 11.5 hrs. in pure oxygen under a pressure of 215 lb. per sq. in., praseodymium dioxide

of 99.2% purity is obtained. Higher purity could never be attained. The presence of ceria produces an abnormally high degree of oxidation of praseodymium only when the oxygen is under pressure. The oxide Pr_6O_{11} dissociates above 700°, but re-oxidises on cooling below 400° (cf. Prandtl and Huttner, A., 1926, 137). Lanthanum, neodymium, samarium, gadolinium, erbium, and ytterbium formed no higher oxides, and it is questioned whether these elements should occupy other than the third group of the periodic table. A method of adapting a balance for weighing hygroscopic substances is described, as well as a furnace applicable for the study of oxidation under pressure.

S. K. TWEEDY.

Silicic acids. W. DILTNEY and E. HOLTERHOFF (Ber., 1929, 62, [B], 24—31).—The difficulty of differentiating between combined and adsorbed water in silica gels has led the authors to attempt the union of the hydroxyl group with the silicon atom without the presence of water. For this purpose, silicon tetrachloride is allowed to react with about 4.5 mols. of triphenylcarbinol in anhydrous ether at the atmospheric temperature. The separated silicic acid is washed with anhydrous ether until the solvent is free from triphenylmethyl chloride as judged by the absence of halochromism on addition of concentrated sulphuric acid and exposed to the air for not more than $\frac{1}{2}$ hr. The product then contains 29.6—26.2% of water and hence cannot consist of orthosilicic acid ($H_2O=37.5\%$). Variation in the temperature of the reaction between 2° and 35° shows the proportion of water to diminish somewhat with rising temperature, the extreme values being 28.1% and 26.6%, with a mean value of about 27.5%. If the proportion of triphenylcarbinol is reduced to 3 mols., hydrogen chloride is evolved and a chlorine-free silicic acid is produced containing only a slightly smaller percentage of water, which, in the most favourable case, is 1% greater than that required by metasilicic acid.

The silicic acids thus obtained continuously lose water on exposure to air. Products dried until the water content is about 17% and then allowed to re-absorb moisture become constant in weight when 25% of the latter is present. Subsequent dehydration in a vacuum proceeds rapidly and rehydration of a product containing 13% of water leads to a material containing 25%. This amount is 1% in excess of that required for metasilicic acid, but 2% below that of the original material. The water in the hydrates is therefore regarded as constitutional, but so relatively loosely combined that a distinction cannot be made between adsorbed or united water by desiccation in air or in a vacuum.

Replacement of ether as solvent by carbon disulphide, chloroform, carbon tetrachloride, and benzene with consequent possibility of operating at a higher temperature shows that the proportion of water in the hydrates diminishes as the temperature rises and is also reduced by the use of 3 mols. instead of 4.5 mols. of triphenylcarbinol. The rules are not, however, without exception, since the nature of the solvent is not without influence.

H. WREN.

Silicic acids. V. R. SCHWARZ and H. RICHTER (Ber., 1929, 62, [B], 31—36; cf. A., 1927, 634).—

Silicic acid gels are obtained by the hydrolysis of silicon tetrachloride by water at 0°; the product is poured into much water and repeatedly washed with water until free from chlorine. It is subsequently dried by means of acetone, methyl or ethyl alcohol, or liquid ammonia, the temperature not being allowed to exceed 2° during the whole process. The products obtained with the three drying agents just named contain approximately 23% of water, corresponding thus with a polymetasilicic acid, $[\text{SiO}_2 \cdot \text{H}_2\text{O}]_x$. The probability that the material is a definite hydrate is established, not only by the stoichiometric relationship, but also by its non-identity with the compound derived by subjecting gels from silicate solutions to a precisely similar treatment. Hydrolysis of titanium tetrachloride at 0° followed by desiccation of the product with acetone yields a product containing 32.4% of water, thus corresponding closely with the hydrate $\text{TiO}_2 \cdot 2\text{H}_2\text{O}$.

Dehydration of silicic acid gels by liquid ammonia yields results not greatly dissimilar from those of Biltz and Rahlfs (cf. A., 1928, 854), the observed ratio being $\text{SiO}_2 : \text{H}_2\text{O} : \text{NH}_3 = 6 : 2.95-3.5 : 1.7-2.14$. Since the gels originally contain polymerised metasilicic acid, it appears that the ammonia causes a secondary change, the effect of which is a dehydration to the di-acid stage.

Hydrates poorer in water are obtained if the temperature is allowed to rise during hydrolysis of silicon tetrachloride; at 100°, the product formed has the composition $3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. It is remarkable that almost identical substances result from the ammonia and acetone processes and that the amount of adsorbed ammonia is unusually small.

H. WREN.

Constitution of double salts. XVI, XVII. Ammine bromides. G. SPACU and J. DICK (Bul. Soc. Stiinte Cluj, 1928, 4, 84-103, 110-124; Chem. Zentr., 1928, ii, 1196-1197).—The following hexamethylenetetramine (H), pyridine, and piperazine (P), compounds have been prepared:

$[\text{MnH}_6][\text{SnBr}_6]$ (also $+2\text{H}_2\text{O}$); $[\text{NiH}_6][\text{SnBr}_6]$ (also $+2\text{H}_2\text{O}$); $[\text{CoH}_6][\text{SnBr}_6]$ (also $+4\text{H}_2\text{O}$); $[\text{MnH}_5 \cdot \text{H}_2\text{O}][\text{SnBr}_5\text{OH}] \cdot 4\text{H}_2\text{O}$; $[\text{Mn}(\text{C}_5\text{H}_5\text{N})_6][\text{SnBr}_6]$; $[\text{Co}(\text{C}_5\text{H}_5\text{N})_6][\text{SnBr}_6]$; $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_6][\text{SnBr}_5\text{OH}]$; $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_6][\text{SnBr}_4(\text{OH})_2]$; $[\text{MnP}_3][\text{SnBr}_6] \cdot 6\text{H}_2\text{O}$; $[\text{NiP}_3][\text{SnBr}_6] \cdot 8\text{H}_2\text{O}$; $[\text{CoP}_3][\text{SnBr}_6] \cdot 8\text{H}_2\text{O}$; $[\text{MnP}_4][\text{SnBr}_6] \cdot 6\text{H}_2\text{O}$; $[\text{NiP}_4][\text{SnBr}_6] \cdot 8\text{H}_2\text{O}$; $[\text{CoP}_4][\text{SnBr}_6] \cdot 8\text{H}_2\text{O}$; $[\text{MnP}_6][\text{SnBr}_6] \cdot 6\text{H}_2\text{O}$; $[\text{NiP}_6][\text{SnBr}_6] \cdot 8\text{H}_2\text{O}$; $[\text{CoP}_6][\text{SnBr}_6] \cdot 8\text{H}_2\text{O}$.

A. A. ELDRIDGE.

Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. VII. Effect on aqueous solutions of stannates of change of hydrogen-ion concentration by addition of hydrochloric acid. G. JANDER, F. BUSCH, and T. ADEN (Z. anorg. Chem., 1928, 177, 345-362).—Two methods are used to investigate the changes in solutions of alkali stannates on increasing the hydrogen-ion concentration. The first makes use of the fact that a knowledge of the diffusion coefficient of the stannate radical will give an approximate value for its mol. wt. The diffusion coefficient was determined for solutions of varying p_{H} , and a graph of the coefficient against the p_{H} was drawn. In

strongly alkaline solutions the diffusion coefficient of the stannate radical is 0.44. With increasing p_{H} it decreases and reaches 0.36 at p_{H} 11.6. By applying the usual diffusion relationship $D_1\sqrt{M_1} = D_2\sqrt{M_2}$, where D_1 , D_2 are the diffusion coefficients, M_1 , M_2 are the mol. wts. of the radicals, to this case, it is found that the mol. wt. of the stannic acid radical in the least strongly alkaline solution (p_{H} 11.6) must be 1.5 times as great as that in the most strongly alkaline solution. The second method of investigation used was the absorption of visible and ultra-violet light. It has been shown that if with increasing hydrogen-ion concentration there is an association, then a displacement of the absorption band towards the longer waves will occur. On investigating solutions of alkali stannates of which the hydrogen-ion concentration was varied by addition of sodium hydroxide or hydrochloric acid, it was found that solutions which were made alkaline or were already alkaline by hydrolysis gave no appreciable absorption. On the other hand, addition of acid caused at a definite concentration a strong absorption in the ultra-violet, at a wave-length of about 300μ . Further addition of acid caused no change in the characteristic absorption, but merely made it more intense. It is concluded that the change on acidifying a solution of an alkali stannate can scarcely be represented as the change of a normal into an acid stannate: $\text{Na}_2[\text{Sn}(\text{OH})_6] + \text{HCl} = \text{NaH}[\text{Sn}(\text{OH})_6] + \text{NaCl}$, but probably as $2[\text{Sn}(\text{OH})_6]'' + 2\text{H}^+ = [\text{Sn}_2(\text{OH})_{10}]'' + 2\text{H}_2\text{O}$. This reaction is comparable with the conversion of a chromate into a dichromate. An attempt was made to prepare salts of the second stannic acid, $\text{H}_2\text{Sn}_2(\text{OH})_{10}$, but by the methods used only salts of the lower acid were obtained. This is not in contradiction to the physical results.

A. J. MEE.

Thermal decomposition of ammonia, with particular reference to the existence of active and inactive phases of ammonia. W. H. STRINGFELLOW (J.C.S., 1929, 1-8).—An attempt has been made to substantiate the evidence brought forward by Baly and Duncan (*ibid.*, 1922, 121, 1008) to demonstrate the existence of active and inactive phases of ammonia. Both synthetic and gas-works liquid ammonia have been used, but in no case has any indication of the phenomenon been obtained.

F. J. WILKINS.

Reaction between nitric oxide and hydrogen sulphide. J. PIERCE (J. Physical Chem., 1929, 33, 22-36).—Hydrogen sulphide and nitric oxide interact to form water, sulphur, and nitrogen, and the conditions of the reaction have been investigated between 28° and 100° in a modified Klemene manometer. The effect of the addition of silica gel, alone and impregnated with 1% of ferric oxide, and of glass wool is to accelerate the reaction. No ammonium sulphide or nitrous oxide could be detected in the products of the reaction (cf. Thomson, Gmelin-Kraut's "Handbuch"), which is more complex than is represented by the equation $2\text{NO} + 2\text{H}_2\text{S} = 2\text{H}_2\text{O} + 2\text{S} + \text{N}_2$. The mechanism proposed is that 2 mols. of nitric oxide condense to 1 mol. of N_2O_2 , which is adsorbed and reacts with hydrogen sulphide to form sulphur, nitrogen, and water. Finally, hydrogen

sulphide is adsorbed by the colloidal sulphur on the reacting surface and oriented so that its hydrogen ion extends outwards. The negative temperature coefficient found is attributed to decreased association of the nitric oxide to N_2O_2 molecules at higher temperatures. Sulphur, by forming a mechanically-coated surface, is the cause of the inhibitory effect observed.

L. S. THEOBALD.

Monochloroamine and hydrazine. II. M. BODENSTEIN (Z. physikal. Chem., 1928, **139**, 397—415; cf. A., 1928, 34).—The formation of hydrazine from aqueous solutions of ammonia and monochloroamine and the subsequent decomposition with evolution of nitrogen have been studied. Purification of the water used has an effect similar to the addition of gelatin in favouring increased yields of hydrazine, which increase with increasing purification of the water. The addition of very small amounts of cupric, ferrous, and cobaltous ions decreases the amount of hydrazine formed in the order given, copper having the greatest effect. Mannitol and gelatin increase the yields of hydrazine by counteracting the catalytic effects of the metallic ions; this is attributed to adsorption of these ions by the gelatin or mannitol.

[With TITSCHACK.]—Kinetic measurements show that the reaction between ammonia and monochloroamine to form hydrazine is proportional to the concentration of the reactants, that it has a high temperature coefficient, and that it is only slightly catalysed by the copper ion. Hydrazine is always the first product of the reaction between these two substances; the more or less extensive decomposition which follows is a dependent reaction, and it is this second reaction which is influenced by the various catalysts. The process is represented by the equations (i) $NH_2Cl + NH_3 = NH_2 \cdot NH_2 + HCl$, and (ii) $NH_2 \cdot NH_2 + 2NH_2Cl = N_2 + 2NH_4Cl$.

L. S. THEOBALD.

Concentrating hydrazine hydrate solutions. C. D. HURD and C. W. BENNETT (J. Amer. Chem. Soc., 1929, **51**, 265—269).—A solution containing a maximum concentration of 95—96% of hydrazine hydrate (12% of the original amount) remains when a 40—45% solution (5 parts) is heated with xylene (13 parts) until the latter has completely distilled. Larger yields of less concentrated solution are obtained by using less xylene. Most of the remaining hydrazine may be recovered from the distillate. Toluene has a smaller dehydrating effect and benzene practically none. Attempts to liberate hydrazine from its hydrochloride by means of sodamide, calcium carbide, or aluminium carbide were unsuccessful.

H. E. F. NOTTON.

Action of hydrogen sulphide on chromates. I. H. B. DUNNICLIFF and C. I. SONI (J. Physical Chem., 1929, **33**, 81—87).—The action of hydrogen sulphide on aqueous solutions of potassium chromate at the ordinary temperature and at 85° has been investigated. Chromium hydroxide contaminated by sulphur is precipitated, leaving a yellow, alkaline filtrate containing potassium sulphide, polysulphide, and thio-sulphate and colloidal sulphur. At the ordinary temperature with a 2% solution the reaction is slow and is exothermic. The yellow crystals obtained by evaporation under reduced pressure from the filtrate

resulting from the action of hydrogen sulphide at 85° on 2—15% solutions gave, on analysis, a polysulphide content corresponding with the formulæ $K_2S_{4.67}$ — $K_2S_{6.61}$. The mechanism of the reaction, which may be conventionally represented by the equation $2H_2CrO_4 + 3H_2S = 2Cr(OH)_3 + 2H_2O + 3S$, is discussed.

L. S. THEOBALD.

Preparation of sulphuryl chloride. E. TERLINCK.—See B., 1929, 128.

Two ammonium molybdotellurates. V. W. MELOCHE and W. WOODSTOCK (J. Amer. Chem. Soc., 1929, **51**, 171—174).—*Ammonium mono- and dimolybdotellurates*, $3(NH_4)_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 7H_2O$ and $3(NH_4)_2O \cdot 2TeO_3 \cdot 6MoO_3 \cdot 10H_2O$, respectively, are obtained as clear white crystals by the interaction in suitable proportions of telluric acid, molybdic acid, and ammonia in aqueous solution. The crystals decompose at 550°, leaving a residue of tellurium dioxide admixed with a little molybdic oxide. Excess of ammonia converts the di-salt into the mono-compound. The compounds are unsuitable for the colorimetric determination of small quantities of tellurium.

S. K. TWEEDY.

Oxidation with fluorine. XI. Action of fluorine on solutions of the salts of thallium, manganese, copper, and lead. F. FICHTER and E. BRUNNER (Helv. Chim. Acta, 1929, **12**, 214—221; cf. A., 1927, 741).—Oxidation of thallous sulphate in neutral solution by fluorine is only partial on account of the simultaneous formation of hydrogen peroxide, but in moderately concentrated sulphuric acid solution it is almost complete. From these solutions crystals of the composition $TlH(SO_4)_2 \cdot 4H_2O$ have been obtained. Oxidation of thallous nitrate even in acid solution is only partial, again due to the reducing action of hydrogen peroxide formed by the action of fluorine on nitric acid. By passing fluorine through a solution of manganous carbonate in orthophosphoric acid which is shown by analysis to contain $Mn(H_2PO_4)_2$, oxidation takes place to an extent not exceeding 66%. The incomplete oxidation is again attributed to the formation of hydrogen peroxide. As permonophosphoric acid has been shown previously to be formed by the action of fluorine on orthophosphoric acid, this oxidation may be explained on the theory that the oxidising agent is a peroxide or peracid derived from the anion such as sulphur tetroxide in the case of sulphates. It was not found possible to oxidise copper or lead salts by means of fluorine.

R. N. KERR.

Univalent iron, cobalt, and nickel. L. CAMBI (Atti R. Accad. Lincei, 1928, [vi], **8**, 535—536).—A reply to Manchot (A., 1928, 1344).

Reactivity of iron vapour with molecular nitrogen. A. MITTASCH and W. FRANKENBURGER (Z. physikal. Chem., 1928, **139**, 386—396).—Thin wires of electrolytic iron, previously melted and drawn out in a vacuum, were vaporised at 1240—1355° Abs. by electrical heating in an atmosphere of nitrogen at pressures of the order of 0.1 mm. No union of the iron and the nitrogen could be detected manometrically, the gas pressure at a given temperature remaining practically constant for several hours.

L. S. THEOBALD.

Reaction between ferric sulphate solution and cuprous sulphide. L. WHITBY (J.C.S., 1929, 60—61).—The reaction between cuprous sulphide and ferric sulphate solution consists of two stages. The first may be represented: $\text{Cu}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuS} + \text{CuSO}_4 + 2\text{FeSO}_4$. The second consists of a slower reaction between cupric sulphide formed in the first stage and more ferric sulphate, $\text{CuS} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 2\text{FeSO}_4 + \text{S}$. At the ordinary temperature the first reaction predominates, the second being negligible except at higher temperatures.

F. J. WILKINS.

Reactions between iron, its hydroxides, and water. A. SCHIKORR (Z. Elektrochem., 1929, 35, 65—70; cf. this vol., 266).—A detailed investigation has been made of the action of air-free water and ferric oxide (or meta-ferric hydroxide) on iron filings, whereby hydrogen is evolved and the oxide is blackened. The black oxide is shown to be mainly triferrous tetroxide, formed by reduction of the hydroxide, whilst the evolution of hydrogen is due to the decomposition of water by dissolved ferrous hydroxide. Metallic iron and the solid hydroxide act as catalysts for the latter process. A series of experiments is described which indicates that the rate of hydrogen evolution (a) increases to a maximum value with increase in the amount of ferric hydroxide sol present; (b) is almost doubled by raising the temperature from 25° to 35°; and (c) is inversely proportional, at atmospheric pressure, to the cube root of the hydrogen pressure. The action of air-free water on compact rusted iron causes blackening of the iron, but no, or only an extremely slow, evolution of hydrogen.

L. L. BIRCUMSHAW.

Oxidation of cobaltous sulphate and potassium cobaltous oxalate with ozone. E. BRUNNER (Helv. Chim. Acta, 1929, 12, 208—213).—By passing ozonised oxygen into a well-cooled solution of cobaltous sulphate in sulphuric acid, crystals of $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ have been obtained. This is not a practicable method for the preparation of this salt, however, as only small quantities may be used in each experiment and it is necessary to pass the gas for long periods. On the other hand, oxidation of potassium cobaltous oxalate proceeds smoothly by this means and the method is suggested as practicable for the preparation of potassium cobaltoxalate.

R. N. KERR.

Cobaltic monoammine. C. DUVAL (Compt. rend., 1929, 188, 176).—Sodium aminocobaltiborate, $\text{Na}_2[\text{Co}(\text{BO}_2)_5\text{NH}_2]$, has been prepared as a slightly water-soluble, violet-grey precipitate by heating 10 g. of triamminecobaltic nitrate, $[\text{Co}(\text{NO}_3)_3 \cdot (\text{NH}_3)_3]$, with 1.5 g. of sodium metaborate and 50 c.c. of water at 45° for 15 min. The solution is then cooled.

J. GRANT.

Ruthenium hydroxytrichloride, ruthenium tetrachloride, and ruthenium trichloride. H. REMY and A. LUERS (Ber., 1929, 62, [B], 200—209; cf. A., 1928, 722).—Fresh solutions of ruthenium tetroxide in concentrated hydrochloric acid contain ruthenium tetrachloride or the corresponding acid, $\text{H}_2[\text{RuCl}_6]$ as shown by the preparation of the alkali salts (Krauss, A., 1921, ii, 514). When the solutions are heated, the tetrachloride becomes hydrolysed to

the compound $\text{Ru}(\text{OH})\text{Cl}_3$, the change proceeding slowly even in solutions saturated with hydrogen chloride. In moderately dilute solution, the process is arrested when one chlorine atom is replaced by hydroxyl and proceeds beyond this stage only in solutions containing much less hydrochloric acid. In addition, reduction of ruthenium with evolution of chlorine, $\text{RuCl}_4 = \text{RuCl}_3 + \text{Cl}$, can occur, but, contrary to previous observers, this action is hindered rather than accelerated by rise in temperature unless a current of indifferent gas is passed through the solution. If carbon dioxide is passed until chlorine is no longer evolved, a partial reduction to tervalent ruthenium is observed unless the conditions for hydrolysis have been provided before driving out the chlorine. Solutions of ruthenium hydroxytrichloride do not evolve chlorine when treated with carbon dioxide and the valency of the metal does not alter. Solutions of ruthenium trichloride prepared according to Krauss and Kükenthal (A., 1924, ii, 196, 770) contain quadrivalent as well as tervalent ruthenium, the former frequently preponderating considerably. Quadrivalent ruthenium is also present in solutions prepared according to Gall and Lehmann (A., 1927, 123; 1928, 975). Evaporation to a syrupy consistency with concentrated hydrochloric acid has little influence on the valency of ruthenium unless repeated very frequently. A more marked effect is produced when the solutions are evaporated to dryness, but, in every case, the process comes to a conclusion when about half of the metal has passed into the tervalent state. Further reduction could not be effected by repeated evaporation to dryness extending over more than a week. It appears therefore impossible to obtain the pure trichloride by simply evaporating with hydrochloric acid a product containing large amounts of quadrivalent ruthenium. Ruthenium tetroxide reacts initially with concentrated hydrochloric acid, yielding the product RuO_2Cl_2 , which is rapidly reduced further by excess of acid to ruthenium tetrachloride. This compound is unstable in solution, decomposing either into the trichloride or into the hydroxytrichloride. Pure solutions of the latter substance can be prepared readily and from them the "hydrated pentachlororuthenates" now recognised as hydroxypentachlororuthenates.

H. WREN.

Detection of active hydrogen atoms with zinc ethyl. F. HAUROWITZ (Mikrochem., 1929, 7, 88—93).—Zinc ethyl dissolves readily in pyridine with the evolution of heat and the formation of a yellow liquid which fumes only slightly in contact with air. This solution forms a delicate test for the presence of active hydrogen in organic compounds in place of magnesium methyl iodide as recommended by Zerevitinov (A., 1907, ii, 509), but the test is not quantitative, as only 60—95% of the active hydrogen forms ethane. With benzoic acid about 66% of the theoretical yield of ethane is obtained, the remainder of the benzoic acid forming apparently a complex compound with zinc benzoate which is unaffected by excess of the zinc ethyl.

A. R. POWELL.

Potentiometric micro-titrations. F. L. HAHN (Z. anal. Chem., 1929, 76, 146—149).—An ampli-

fication of the work of Zintl and Betz (A., 1928, 977). H. F. GILLBE.

p_{H} measurement with the glass electrode and vacuum tube potentiometer. L. W. ELDER, jun., and W. H. WRIGHT (Proc. Nat. Acad. Sci., 1928, 14, 936—939).—The utility of the glass electrode for p_{H} measurements has been limited by difficulties attendant on the necessity of employing a quadrant electrometer. A method is described of using instead a vacuum tube potentiometer. The preparation of a special glass, which was used blown into small bulbs to form the electrodes, is described. In preliminary experiments the apparatus appeared to give satisfactory results. N. M. BLIGH.

Amidosulphonic acid as primary standard in volumetric analysis. K. MISUTSCH (Pharm. J. [Russia], 1928, 310—313; Chem. Zentr., 1928, ii, 1129).—Amidosulphonic acid, $\text{NH}_2\cdot\text{SO}_3\cdot\text{OH}$, and hydrochloric acid give identical results when titrated with sodium hydroxide, carbonate, or borate.

A. A. ELDRIDGE.

Precipitation of group II acids (chloride group) in the presence of other acid radicals. L. J. CURTMAN and W. W. PLECHNER (Chem. News, 1929, 138, 65—67).—The neutral solution is diluted to 50 c.c. and 1 c.c. of 0.25*N*-silver nitrate added. After addition of 5 c.c. of concentrated nitric acid the solution is warmed and stirred. A precipitate indicates the presence of one or more of the following: chloride, bromide, iodide, cyanide, thiocyanate, ferriyanide, ferrocyanide, sulphide. J. S. CARTER.

Effect of sunlight on the determination of chlorine [in water] by the *o*-tolidine method. F. R. McCURMB and W. R. KENNY.—See B., 1929, 114.

Qualitative microanalysis. III. [Detection of thiocyanate, fluoride, and copper, two methods of distinguishing between tap water and distilled water, detection of alkali in water, and a drop reaction for ammonia.] F. FEIGL [with G. HIRSCH and I. TAMCHYNA] (Mikrochem., 1929, 7, 10—20).—Addition of thiocyanate to a 0.1*N*-iodine solution containing 1.3 g./100 c.c. of sodium azide catalyses the reaction $2\text{NaN}_3 + \text{I}_2 = 2\text{NaI} + 3\text{N}_2$ and the solution becomes decolorised with evolution of nitrogen; as little as 0.03 mg. of thiocyanate is readily detected in the presence of most inorganic oxyacids and the common organic acids by this test, but sulphides and thio-sulphates interfere and must be previously removed by mercuric chloride. For the detection of fluoride in insoluble substances the substance is treated with a hydrochloric acid solution of the violet zirconium alizarin compound (de Boer, A., 1924, ii, 705), which becomes yellow if fluorine is present. Traces of copper in solution may be detected by adding a few drops of dilute zinc nitrate solution followed by a solution of 8 g. of mercuric chloride and 9 g. of ammonium thiocyanate in 100 c.c. of water; with 0.00075 mg. of copper per c.c. a violet, crystalline precipitate is obtained. Tap water may be distinguished from distilled water by the reddish-violet colour it gives on the addition of a few drops of a blue ammoniacal solution of 2:3-dihydroxyanthraquinone or by the

red, crystalline precipitate it produces with a solution of the sodium salt of 2:4:5:7-tetranitro-1:8-dihydroxyanthraquinone; both these reactions are due to the presence of calcium and magnesium in tap water. Addition of a solution of the compound $\text{Hg}(\text{CN})_2\cdot\text{AgNO}_3$ to water containing free alkali produces a turbidity due to the formation of silver cyanide. To detect ammonia in a neutral or slightly acid solution 1 drop of the liquid is mixed with 1 drop of a dilute solution of *p*-nitrodiazobenzene in hydrochloric acid on a small watch-glass and a small piece of quicklime is dropped into the mixture; if ammonia is present a red ring appears round the lime. A. R. POWELL.

Detection of sulphurous acid with Bettendorf's reagent. S. DUNAJEVA (Pharm. J. [Russia], 1928, 379; Chem. Zentr., 1928, ii, 1129).—When Bettendorf's reagent is covered with a solution containing sulphite, reduction to sulphide produces a yellowish-brown ring of tin sulphides; 0.06% of sulphite can be detected. A. A. ELDRIDGE.

Electrolytic analysis of nitrates. Apparatus for reduction with nascent hydrogen in presence of catalysts. M. RABINOVITSCH and A. S. FOKIN (Z. Elektrochem., 1929, 35, 18—20).—The nitrate, in alkaline solution, is reduced to ammonia by means of nascent hydrogen, formed by the decomposition of sodium amalgam. Details are given of the apparatus, consisting of a small electrolytic cell with a mercury cathode. The presence of a catalyst (tungsten, vanadyl sulphate, or chloroplatinic acid) is recommended to accelerate the decomposition of the alloy, which is continuously produced during the electrolysis. The values obtained for a series of analyses of potassium nitrate are in satisfactory agreement with those found by Devarda's method.

L. L. BIRCUMSHAW.

Conductometric titration of phosphoric acid with sodium hydroxide. (MISS) J. C. LANZING and L. J. VAN DER WOLK (Rec. trav. chim., 1929, 48, 83—92).—The neutralisation of phosphoric acid by sodium hydroxide has been investigated conductometrically at eight dilutions between 0.3 and 0.005*N*. Comparison with the theoretical curve for the titration of a tribasic acid shows that the first break at all dilutions agrees well with the theoretical, the second is displaced to the right, and the third is not found except for the two highest concentrations. The first branch of the curve shows a minimum with 0.3*N*-solution, but becomes straight at lower concentrations. The determination of phosphoric acid conductometrically should be restricted to the first end-point and the concentration of acid should not be above 0.1*N*. R. N. KERR.

Standards for Gutzeit test [for arsenic]. A. T. HENLEY.—See B., 1929, 94.

Detection of the presence of reducing radicals in the systematic analysis for the acids. L. J. CURTMAN and W. W. PLECHNER (Chem. News, 1929, 138, 50—51).—To 5 c.c. of solution are added 0.5 c.c. of 3*N*-sulphuric acid and 2 drops of 0.1*N*-permanganate. If no bleaching occurs the amount of arsenite, thiosulphate, sulphite, sulphide, iodide, bromide, thiocyanate, ferrocyanide, or nitrite present does not

exceed 1 mg. and the amount of tartrate or oxalate present does not exceed 10 mg. If no bleaching occurs on warming, oxalate and tartrate may be assumed to be absent and the amount of cyanide present does not exceed 10 mg.

J. S. CARTER.

Determination of arsenic in presence of organic substances, halogens, and heavy metals. E. SCHULEK and P. VON VILLECZ (*Z. anal. Chem.*, 1929, 76, 81—103).—The substance is treated with 30% hydrogen peroxide solution in presence of concentrated sulphuric acid. After reduction of the quinquevalent arsenic to the trivalent state by hydrazine sulphate, excess of which is destroyed by the hot sulphuric acid present, potassium bromide is added and the solution is titrated with 0.1N- or 0.01N-potassium bromate solution.

H. F. GILLBE.

Determination of arsenic. E. G. MAHIN and A. F. DOYLE (*Proc. Indiana Acad. Sci.*, 1929, 37, 269—272).—In the reduction of arsenic to the trivalent condition by means of potassium iodide, loss of arsenic as the tri-iodide is to be avoided. Limitation of the amount of potassium iodide employed is desirable.

CHEMICAL ABSTRACTS.

Apparatus for the determination of carbon dioxide. R. C. WILEY (*J. Amer. Chem. Soc.*, 1929, 51, 222—223).—A simple apparatus designed to minimise contamination with atmospheric carbon dioxide is described.

S. K. TWEEDY.

Microchemical separation of barium and calcium. R. STREBINGER (*Mikrochem.*, 1929, 7, 100—105).—The microchemical determination of barium by precipitation with ammonium dichromate in ammonium acetate solution followed by collection of the precipitate in a filter tube and weighing after drying at 140° yields slightly high results, but good results are obtained if the precipitate is dissolved in dilute nitric acid, the chromic acid reduced with alcohol, and the barium precipitated with ammonium sulphate. Calcium is determined in the filtrate from the barium chromate by precipitation with ammonium oxalate and weighing as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ after drying at 110°.

A. R. POWELL.

Rapid determination of total hardness [of water] by separate determination of lime and magnesia hardness. K. V. LUCK and H. J. MEYER. —See B., 1929, 114.

Separation of beryllium from aluminium, iron, and copper by 8-hydroxyquinoline. M. NIESSNER (*Z. anal. Chem.*, 1929, 76, 135—145).—Since beryllium does not form a compound with 8-hydroxyquinoline, this reagent may be employed to obtain a rapid and complete separation of beryllium from iron, aluminium, and copper.

H. F. GILLBE.

Determination of beryllium as pyrophosphate and as anhydrous sulphate. V. CUPR (*Z. anal. Chem.*, 1929, 76, 173—191).—Direct precipitation of beryllium ammonium phosphate and subsequent ignition to pyrophosphate yields untrustworthy results. Beryllium should be precipitated from solutions containing ammonium salts with ammonia as hydroxide, or, if the solution contains phosphate, as the voluminous phosphate. If salts of the alkali

metals are present beryllium should be reprecipitated. Ammonium phosphate is added and the solution made faintly acid (methyl-red). The solution is then diluted and made just alkaline with ammonia. Washing is effected with a 1%, faintly ammoniacal solution of ammonium nitrate. The resulting pyrophosphate is a white powder.

Beryllium sulphate is completely dehydrated at 400°, and if the period of heating does not exceed 2—3 hrs. there is no further decomposition.

J. S. CARTER.

Precipitation of zinc as sulphide from faintly acid solutions. J. MAJDEL (*Z. anal. Chem.*, 1929, 76, 204—212).—Under the conditions described previously (A., 1928, 859) quantitative separation from iron, aluminium, chromium, nickel, cobalt, and manganese is effected. If metals of the copper and arsenic groups are present 5—7 c.c. of 1:1-sulphuric acid are added, and the solution is evaporated until fumes of sulphur trioxide are evolved. After dilution to 50 c.c., the hot solution is treated with hydrogen sulphide and the precipitated sulphides are washed with a solution containing 5 c.c. of concentrated sulphuric acid per 100 c.c., saturated with hydrogen sulphide. The filtrate and washings are boiled to expel hydrogen sulphide and zinc is determined as described. The precipitated zinc sulphide should be washed with a 1% solution of ammonium sulphate saturated with hydrogen sulphide.

J. S. CARTER.

Detection of zinc in presence of manganese, nickel, and cobalt. R. RIPAN (*Bul. Soc. Stiinte Cluj*, 1928, 4, 80—83; *Chem. Zentr.*, 1928, ii, 1239).—(a) In the absence of acids, e.g., thiocyanic, which give a precipitate with pyridine, the solution is treated with 16% potassium iodide solution and excess of pyridine; the compound $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2]\text{I}_2$ is precipitated quantitatively, whilst cobalt, nickel, and manganese do not react. (b) Precipitation with 10% sodium bromide solution and 0.5—1 c.c. of pyridine affords the corresponding bromide; 0.01 mg. of zinc can be detected.

A. A. ELDRIDGE.

Determination of cadmium in the metallic state in organic and inorganic compounds. H. TER MEULEN and (MLLE.) H. J. RAVENSWAAY (*Rec. trav. chim.*, 1929, 48, 198—200).—A method for the determination of cadmium similar to that for mercury and arsenic (A., 1926, 490, 492) is described. The compound is heated in a current of hydrogen and the cadmium formed by reduction is distilled into a quartz tube and weighed. If sulphur or halogens are present in the compound it must be mixed with calcium carbonate before heating and it is also advisable to add to the current of hydrogen a little ammonia. Good results have been obtained with both organic and inorganic compounds, the error not exceeding 0.1% in any case. An attempt has been made to apply the same method to the determination of zinc, but the results obtained are always too high, owing to a thin layer of oxide covering the metal.

R. N. KERR.

Reduction bead test as a simple preliminary test. H. BRINTZINGER (*Z. anal. Chem.*, 1929, 76, 149—150).—The substance is mixed with about three times its weight of a reducing flux, such as 2 parts of

sodium oxalate, 2 parts of potassium oxalate, and 1—1.5 parts of borax, and heated on magnesia in the reducing flame. Characteristic metallic beads are produced in many cases. H. F. GILLBE.

Gravimetric determination of lead. I. Soluble salts. P. N. DAS-GUPTA, G. C. ROY, and K. M. SIL (J. Indian Chem. Soc., 1928, 5, 657—660).—The precipitation of the complex $Pb_3O_7 \cdot 3H_2O$ (Brauner, J.C.S., 1894, 65, 394) by the action of alkaline hydrogen peroxide on lead nitrate and acetate is quantitative when the alkali used is ammonia. The complex is unaffected by heating at 180°. It is insoluble in ammonia, but soluble in alkali hydroxides and ammonium salts. Hydrogen peroxide in excess converts it into lead hydroxide. In presence of ammonium acetate, ammonium nitrate, sodium acetate, and potassium nitrate precipitation of the complex is quantitative provided the concentrations of the salts do not exceed 1, 4, 8, and 16 g. per 100 c.c. of solution, respectively. The method appears to be most trustworthy in the determination of relatively large amounts of lead. H. BURTON.

Electrolytic determination of small quantities of lead. A. SEISER, A. NECKE, and H. MÜLLER (Z. angew. Chem., 1929, 42, 96—98).—Lead is deposited on a platinum gauze anode as dioxide. The blue coloration obtained on placing the washed anode in a solution of tetramethyldiaminodiphenylmethane in glacial acetic acid is made the basis of the colorimetric determination. The electrolyte should contain about 1% of nitric acid and about 10 mg. of copper. Iron does not interfere, but the amount of manganese or bismuth present should not exceed 0.2—0.5 mg. The method is primarily intended for the determination of small amounts (0.01—0.1 mg.) of lead in blood etc. Directions are given for the pre-treatment of the blood samples (cf. Arch. Hyg., 1928, 99, 158). J. S. CARTER.

Hexamethylenetetramine as a microchemical reagent. I. M. KORENMAN (Pharm. Zentr., 1929, 70, 1—3).—Microchemical reactions with salts of silver, lead, mercury, cadmium, bismuth, tin, and antimony, and the appearances of the precipitates obtained, are described. S. I. LEVY.

Rapid electrolytic determination and separation of some metals without mechanical agitation of the electrolyte. N. VENSOVITCH (Bull. Soc. chim. Belg., 1928, 37, 353—376).—Results are given of numerous experiments on the determination and separation of metals by Sand's method, using electrodes of the Fischer type. The following determinations and separations are quantitatively possible by this method: copper from acid and ammoniacal solutions, silver, cadmium; copper from zinc, copper from zinc and tin, copper from tin, copper from nickel, zinc, and iron, copper from nickel and zinc, silver from copper; the simultaneous separation and determination of copper and silver.

F. G. TRYHORN.

Detection and identification of specific cations with sodium alizarinsulphonate. F. G. GERMUTH and C. MITCHELL (Amer. J. Pharm., 1929, 101, 46—52).—The reactions of sodium alizarin-

sulphonate with solutions of 36 different metallic salts are described. Characteristic precipitates are obtained with solutions of aluminium, titanous, chromic, ferric, uranium, cupric, platinum, bismuth, mercuric, and thallos salts. The formation of the precipitate is accelerated and made more sensitive by the previous addition of a small amount of ammonia. The degree of sensitivity of the reactions is in the above order, aluminium being the most sensitive, and detection of the metals was easily effected in aqueous solutions of concentration 1 in 10^4 .

E. H. SHARPLES.

Electrometric titration of manganese by the Volhard method. B. F. BRANN and M. H. CLAPP (J. Amer. Chem. Soc., 1929, 51, 39—41).—The Volhard method of titrating manganese may be satisfactorily carried out electrometrically at 90° by a modified "dead stop end-point" method (Foulk and Bawden, A., 1926, 927), a platinum cathode and silver anode being used. The latter is permanently depolarised by adding a trace of chloride ion to the solution. S. K. TWEEDY.

Iodometric determination of iron. E. C. GREY (J.C.S., 1929, 35—39).—The causes of error in the iodometric titration of iron have been traced to the presence of copper, or of iron as oxide or colloidal hydroxide, and conditions affording accurate results are defined. The occurrence of iron in these forms can be prevented by carrying out the titration in a solution containing a suitable excess of acid. The copper is removed by dissolving out with ammonia solution. In the absence of colloidal ferric hydroxide the amount of copper present can be determined with fair accuracy by the rate of return of the blue colour after thiosulphate titration. By means of this effect it is possible to detect 1—2 parts of copper in 2,000,000 parts of water. F. J. WILKINS.

Determination and separation of metals using 8-hydroxyquinoline. VII. Determination of iron, manganese, nickel, and cobalt. Separation of iron from aluminium, manganese, and alkaline-earth metals. Separation of manganese from nickel, zinc, and alkaline-earth metals. R. BERG (Z. anal. Chem., 1929, 76, 191—204).—Iron and nickel are precipitated from solutions containing acetate in presence of 10—20%, and 5—10% of acetic acid, respectively, whereas manganese and cobalt are precipitated from neutral or faintly acid solutions only. This dependence of solubility on acidity is made the basis of the separation of iron from manganese and metals of the alkaline-earth series, and the separation of manganese from nickel and zinc, which is precipitated from solutions containing about 6% of acetic acid. Manganese can be separated from alkaline-earth metals, which are not precipitated from faintly acid media. The separation of iron and aluminium is based on the fact that in presence of tartaric or malonic acid aluminium gives no precipitate with 8-hydroxyquinoline. The precipitates are most conveniently evaluated bromometrically. With iron the bromination etc. is effected in presence of phosphoric acid. J. S. CARTER.

Diphenylamine as indicator in the titration of iron with dichromate. F. J. WATSON (Chem.

Eng. Min. Rev., 1928, 20, 355—357).—Diphenylamine may be employed satisfactorily as an internal indicator provided that as the end-point is approached time be allowed for the colour changes to develop, and that not more than 1 c.c. of saturated mercuric chloride solution has been added to oxidise the excess of stannous chloride used for the reduction. Since the indicator change is reversible, the end-point, if overstepped, may be obtained by adding 1 c.c. of standard ferrous ammonium sulphate solution and re-titrating. It is not necessary to make an allowance for the quantity of dichromate used to oxidise the indicator if the first appearance of the purple colour be taken as the end-point. H. F. GILLBE.

Microchemical mineral analysis. [Detection of nickel, cobalt, copper, zinc, and cadmium.] A. MARTINI (Mikrochem., 1929, 7, 30—32).—Addition of ammonium thiocyanate and pyridine to a neutral cobalt solution produces a rose-coloured precipitate which becomes sky-blue and crystalline on addition of nitric acid. An ammoniacal copper solution to which ammonium thiocyanate has been added yields with pyridine green crystals of the compound

$3(C_5H_5N, HSCN), Cu(NH_3)_4(SCN)_2$, and with quinoline sulphate green monoclinic crystals of the compound $3(C_5H_5N, HSCN), Cu(NH_3)_4(SCN)_2$. Zinc sulphate yields with a dilute acid solution of aniline hydrochloride colourless triclinic crystals of zinc aniline chloride, $C_6H_5 \cdot NH_2 \cdot HCl, ZnCl_2$. Ammoniacal solutions of copper, nickel, and cadmium salts yield with ammonium thiocyanate and aniline characteristic crystalline compounds of the type

$(C_6H_5 \cdot NH_2, HSCN), M(NH_3)_4(SCN)_2$; the copper compound separates in green, triclinic rosettes, the nickel compound in pale green, highly refracting, triclinic prisms, and the cadmium compound in monoclinic colourless prisms. Cobalt solutions give a rose-coloured crystalline precipitate with ammonium thiocyanate and aniline. A. R. POWELL.

Ceric sulphate as a volumetric oxidising agent.

"III. Determination of chromium in presence of manganese, iron, and vanadium. IX. Preparation and stability of solutions. H. H. WILLARD and P. YOUNG (J. Amer. Chem. Soc., 1929, 51, 139—149, 149—152).—VIII. The chromic salt is oxidised by excess of ceric sulphate solution, and then (i) the excess is titrated in presence of chromic acid with sodium nitrite or sodium oxalate; (ii) small excess of sodium nitrite is added, followed by carbamide, after which the chromic acid is titrated with standard ferrous sulphate; or (iii) sodium azide is added, followed by titration with standard ferrous sulphate. Iron and large amounts of manganese may be present; if vanadium is present, the method gives the sum of the chromium and vanadium, although the vanadium may be subsequently determined with the same solution. The titrations are carried out electrometrically, but in method (ii) an internal indicator, e.g., diphenylamine, may be used.

IX. Ceric sulphate solution prepared from commercial hydrated oxide usually suffices for volumetric work. Ceric sulphate solutions are cheap, and when containing sulphuric acid exhibit a constant normality over a considerable period and are insensitive to the

influence of light or air. The normality of solutions containing sulphuric acid remains unchanged after boiling for an hour or so, even if a little nitric or perchloric acid is present, although in presence of large quantities of the latter acids oxygen is lost.

S. K. TWEEDY.

Determination of vanadium in steel. K. SWOBODA.—See B., 1928, 131.

Micro-titration of bismuth. J. STRAUB (Z. anal. Chem., 1929, 76, 108—111).—A convenient volume of solution containing 0.1—1.0 mg. of bismuth is diluted to 5 c.c. and treated with small crystals of potassium iodide until it becomes faintly yellow. The whole of the bismuth is then precipitated as basic iodide by addition of 5 c.c. of water and heating on the water-bath. The precipitate, after collection and washing with alcohol and with water, is decomposed by 5% potassium hydroxide solution, and the resulting solution, containing all the iodine as potassium iodide, is rendered slightly acid with hydrogen chloride solution and treated with an excess of bromine water. After decolorisation by 5% phenol solution 0.1 g. of potassium iodide is added and the liberated iodine is titrated with 0.005*N*-sodium thiosulphate solution in presence of starch. At the end-point the colour of the solution changes from green to a faint yellow; a pure blue is not produced at any stage. H. F. GILLBE.

Fusion of rare metal ores. III. Determination of tantalum and niobium. G. W. SEARS (J. Amer. Chem. Soc., 1929, 51, 122—129; cf. B., 1926, 282).—Tantalum and niobic acids are insoluble in hot 3*N*-hydrochloric acid; if the pyrosulphate fusion has been carried out at about 650° the iron and titanium are completely soluble in this acid. If the fusion is carried out for 10—15 min. at 835—850°, only the niobium is rendered soluble in fuming sulphuric acid and it is not reprecipitated when the cold acid solution is poured into water which is kept cooled. Methods based on these results are given for the determination and separation of niobium and tantalum. Asbestos is not wholly resistant to the action of hot fuming sulphuric acid. S. K. TWEEDY.

Potentiometric determination of octavalent osmium. W. R. CROWELL and H. D. KIRSCHMAN (J. Amer. Chem. Soc., 1929, 51, 175—179).—Hydrazine reduces octavalent osmium to the quadrivalent state in acid solution, and the reaction can be followed potentiometrically. Hydrobromic acid is preferably used, the reaction probably being $N_2H_4 \cdot H_2SO_4 + H_2OsO_5 + 6HBr = N_2 + H_2SO_4 + H_2OsBr_6 + 5H_2O$. The bulk of the reaction is carried out in sealed tubes kept at 100° for 30 min., the end-point being determined by subsequent potentiometric titration at 70°. The method, which serves to determine 10^{-5} g.-mol. of tetroxide, is accurate to about 0.2—0.3%.

S. K. TWEEDY.

Automatic pipette. M. HYMAN (J.S.C.I., 1928, 47, 368r).—A modification of an ordinary pipette which is filled by suction as usual, but in which the level of the liquid is brought automatically to the graduation mark, is described and figured.

Pneumatic regulator for manipulation of burettes without taps. E. SCHILOV (Z. anal. Chem.,

1929, 76, 212—216).—The upper portion of the burette is connected to the air-space between an elastic membrane and a plate, the volume of which can be varied by means of a screw. J. S. CARTER.

Precision valve for gases and liquids, especially liquid burettes, and a "tapless" burette. P. FUCHS (Z. anal. Chem., 1929, 76, 166—173).—The arrangement is essentially a narrow glass tube terminating in a hook, over which a piece of rubber tubing is pushed, so that the open end of the hook is sealed by the rubber. Contact is broken by pressing the rubber immediately above the hook. The device may conveniently replace the usual burette tap. J. S. CARTER.

Vacuum tube potentiometer for rapid *E.M.F.* measurements. H. M. PARTRIDGE (J. Amer. Chem. Soc., 1929, 51, 1—7).—The Wheatstone bridge is replaced by an amplifier employing in conjunction a tetrode and a triode valve. A very stable balance is obtained. Calibration of the valves is obviated. Only one adjustment is required; the device, which virtually operates electrostatically, is direct reading and may be used with cells containing glass electrodes. p_H values, reproducible to 0.02 unit, may be rapidly determined with the apparatus. S. K. TWEEDY.

Tantalum as a constructional material for chemical apparatus. F. HEINRICH and F. PETZOLD.—See B., 1929, 99.

Steam drying oven with detachable base. H. J. S. SAND (J.C.S., 1929, 214).

F. J. WILKINS.

Evaporation at low temperatures. E. JANTZEN and H. SCHMALFUSS.—See B., 1929, 77.

[Apparatus for determining] heat of adsorption on charcoal of certain organic vapours. L. MCKINLEY and J. N. PEARCE (Proc. Iowa Acad. Sci., 1927, 34, 216).—Experiments were performed with an apparatus comprising a sensitive thermo-couple in a calorimeter system consisting of a known weight of oil of low specific heat in a Dewar flask.

CHEMICAL ABSTRACTS.

Nephelometric and colorimetric measurements with a photo-electric current. E. CUBONI (Boll. Inst. Sieroterap. Milan., 1927, No. 6, 3 pp.; Chem. Zentr., 1928, ii, 919).—The observations are made by means of a photo-electric cell.

A. A. ELDRIDGE.

[Apparatus for] experimental structure analysis. A. GELLER (Schweiz. Min. Petr. Mitt., 1927, 7, 219 Chem. Zentr., 1928, ii, 964).

Chemical reaction in the interferometer U-gauge. C. BARUS (Proc. Nat. Acad. Sci., 1928, 14, 939—943).—To determine how far the course of a chemical process would be reproduced by the apparatus, the absorption of atmospheric oxygen by phosphorus was tested. Pressure and temperature changes in enclosed volumes of air connected with the U-gauge, one limb containing the phosphorus, are plotted against time, and the results obtained are discussed.

N. M. BLIGH.

Nomography. V. IX—XII. O. LIESCHE.—See B., 1929, 115.

Geochemistry.

Ratios of zirconium to hafnium and niobium to tantalum in minerals. G. VON HEVESY and K. WURSTLIN (Z. physikal. Chem., 1928, 139, 605—614).—The ratio zirconium : hafnium in 16 minerals has been investigated and found to have the mean value 50 : 1. The ratio niobium : tantalum has the value 1 : 1 approximately. These values, together with the non-existence of a hafnium mineral or of a mineral in which the hafnium content exceeds that of zirconium, are discussed and an explanation is advanced. L. S. THEOBALD.

Chemical composition of the tectites, and in particular of those of Cambodia. A. LACROIX (Compt. rend., 1929, 188, 284—288; cf. *ibid.*, 117).—Chemical analyses and a number of physical and morphological properties of tectites have been collected, and a relation has been shown to exist between density and refractive index. Cambodia glass melts at 750—1200°. In general, tectites are rich in silica (particularly free silica), and free alumina, and contain alkali metals, of which the potassium is always in excess over the sodium. The lime, magnesia, and iron contents are relatively high, but phosphoric acid is absent, whilst traces of manganese and titanium are sometimes found. Three chemico-mineralogical types are distinguished: (1) Darwin glass (queenstownite), which is exceptional in that it

contains little lime or alkali metals. (2) Moldavites. (3) Australites, billitonites, and Cambodia tectites. Explosive properties of tectites may be due to bubbles of occluded hydrogen, nitrogen, or oxides of carbon, and these serve to distinguish them from the obsidians, which may contain hydrogen chloride, sulphur dioxide, and sometimes chlorine. J. GRANT.

Chemical composition of liparite. G. CAROBBI (Gazzetta, 1928, 58, 801—808).—An investigation of the green mineral which along with malachite is found in lava incrustations in the Lipari Islands. It is suggested that the name "liparite" should be reserved for this mineral, which is a hydrated silicate of copper with the copper partly replaced by calcium and magnesium. The composition is SiO_2 33.08, Fe_2O_3 1.79, Al_2O_3 1.19, CaO 0.81, MgO 2.07, CuO 35.10, H_2O (loss on drying over calcium chloride) 9.32, H_2O (further loss on heating to a high temperature) 16.98, CO_2 traces (total 100.54). The mineral is birefringent (mean n 1.51) and has d^{25} 2.080. The crystal structure is undetermined. Liparite appears to be identical with chrysocolla, and the nearest formula is $\text{H}_2\text{CuSiO}_4 \cdot 2\text{H}_2\text{O}$. O. J. WALKER.

Microscopical study of the complex cupro-argentiferous minerals of Colquijirca (Peru). J. ORCEL and G. R. PLAZA (Compt. rend., 1929, 188, 181—183).—Two types of mineral of different

origin are distinguished: (1) Hypogenic minerals, formed at a depth, consisting essentially of chalcopyrites, pyrrargyrite, blonde, galena, pyrites, enargite, panabaso, and orubescite. (2) Supergenic minerals from the cementation zone, formed from the above minerals by metasomatic replacement, and containing native silver, stromeyerite, and pyrrargyrite. The silver content is high in the cupro-argentiferous minerals, less when associated with lead and copper, and variable when zinc also is present. J. GRANT.

Presence of atacamite in the incrustation of the Vesuvian lava of [the eruption of] 1631. G. CAROBBI (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], 34, 78—83).—The green portion of the incrustation on this lava consists essentially of atacamite, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$, as was suggested by Scacchi (Mem. Soc. Ital. Sci., 1882, [iii], 4, No. 8).

E. W. WIGNALL.

Klockmannite. P. RAMDOHR (Zentr. Min. Geol., 1928, A, 225—232; Chem. Zentr., 1928, ii, 868).—Klockmann's so-called umangite is a new mineral, klockmannite, CuSe .

A. A. ELDRIDGE.

[Rhomboclase, szomolnokite, and berthierite.] J. KRENNER (Zentr. Min. Geol., 1928, A, 265—271; Chem. Zentr., 1928, ii, 1198).—Rhomboclase from Szomolnok, Hungary, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, has H 2. Szomolnokite, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, has d 3.035, $a:b:c=0.9544:1:0.8999$, β $86^\circ 39' 54''$. Berthierite has d 4.622.

A. A. ELDRIDGE.

Tikhvinite. J. M. ANSHELES and N. J. VLODAVETZ (Mem. Soc. Russe Min., 1927, 56, 53—60; Chem. Zentr., 1928, ii, 976).—A new mineral, tikhvinite, from the bauxite deposits in the Tikhvin district contains SiO_2 0.56, TiO_2 0.16, Al_2O_3 31.14, Fe_2O_3 2.25, SrO 24.43, P_2O_5 18.05, SO_4 8.47, H_2O 12.54, corresponding with the formula $2\text{SrO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{SO}_3 \cdot 6$ or $7\text{H}_2\text{O}$; it has d 3.32, H 4½, n 1.62.

A. A. ELDRIDGE.

Iron ores of South Africa. E. KRENKEL (Naturwiss., 1929, 17, 57—63).—A résumé of the Geological Survey Memoir (1928, 26, 1—264) by P. A. Wagner. Some of the chemical analyses of the ores are quoted.

L. J. SPENCER.

Relations between refractivity, density, and chemical composition in the granite group. H. VON PHILIPSBORN (Ber. Sachs. Ges. Wiss. nat.-phys. Kl., 1928, 40, No. 3, 1—42; Chem. Zentr., 1928, ii,

1197).—The above relations are discussed. Accurate refractivity and dispersion data were ascertained.

A. A. ELDRIDGE.

Origin of Mediterranean red earths (*Terra rossa*). A. REIFENBERG (Kolloidchem. Beih., 1929, 28, 55—147).—The Mediterranean red earths are a product of the alternating rainy winter and dry summer characteristic of the Mediterranean climate. They are produced only in presence of limestone and have an alkaline reaction; they are rich in soluble salts, poor in humus, and have a high iron content. The humus is coagulated by the electrolytes present and is therefore incapable of protecting the iron, and the most important constituents from the colloidal-chemical point of view are silicic acid, ferric oxide, and alumina. Experiments have been carried out on the inter-relations of these three colloids. Colloidal silicic acid peptises ignited ferric oxide, ferric hydroxide, and also ferrous oxide. The light green sol produced in the last case oxidises gradually in air and immediately on addition of hydrogen peroxide to a yellow ferric hydroxide-silicic acid sol. The three ferric hydroxide-silicic acid sols formed by these means are essentially different in optical, mechanical, and electrical properties and behave differently towards coagulation by electrolytes; they are regarded as artificial systems representing the factors involved in the formation of clays. It is considered that in the weathering of the earths the colloidal silicic acid formed by hydrolysis protects the iron and aluminium oxides, probably by replacement of part of the alkali in the colloidal micelle by molecules of the sesquioxides. This would explain the alkaline reaction of the earths. The protected ferric oxide sols are relatively more stable and are coagulated only by high concentrations of electrolytes.

E. S. HEDGES.

Geology and mineralogy of soils. I. Study of a region characterised by diverse rocks and partly covered with glacial drift. R. HART (J. Agric. Sci., 1929, 19, 90—105).—Mineralogical details of the soils are recorded. The mineral contents of the glacial soils and alluvium are very similar and contain fresh ferrosilicates in considerable quantity. Soils on the screes and hillwash are characterised by their content of rock fragments and iron oxides. Drift soils contain potash, phosphate, and lime-bearing minerals.

A. G. POLLARD.

Organic Chemistry.

Oxidation of methane with nitrogen peroxide. P. K. FROLICH, P. J. HARRINGTON, and A. H. WAITT (J. Amer. Chem. Soc., 1928, 50, 3216—3221).—The oxidation commences at 430° , but the temperature rises after the reaction starts. Methyl alcohol could not be detected in the oxidation products, but it is probably formed and immediately decomposed into carbon monoxide and hydrogen. Large amounts of formaldehyde are produced; its formation is favoured by a low peroxide concentration, a slow rate of flow of the reactants, and absence of reacting surfaces. Liquid nitrogen peroxide seems capable of oxidising higher hydrocarbons to acetic acid.

S. K. TWEEDY.

Intermediate products of the combustion of methane. E. H. RIESENKELD and D. GURIAN (Z. physikal. Chem., 1928, 139, 169—197).—The combustion of methane in oxygen and of oxygen in excess of methane at various concentrations at the orifices of quartz capillaries has been investigated. The intermediate products detected were formaldehyde, carbon monoxide, hydrogen peroxide, and, in the first case, ozone. In the combustion of methane in oxygen the yields of hydrogen peroxide and formaldehyde decrease with an increase in the amount of excess oxygen, whilst that of ozone increases. When oxygen burns in methane, the yield of hydrogen

peroxide again diminishes, whilst that of formaldehyde rises continually with an increasing excess of methane, but ozone is not formed. Maximal quantities are formed for (i) formaldehyde, with large excess of methane and the strongest cooling possible, (ii) hydrogen peroxide, at equivalent quantities of methane and oxygen (1:2 mols.) with strongest cooling, and (iii) ozone, with large excess of oxygen and slower cooling. Hydrogen peroxide does not arise, as has been previously assumed, from formaldehyde; the formation of these two products is independent. When equivalent quantities of methane and oxygen are used, the cone of the oxygen flame is more than double as high as that of the methane flame, which, however, is the hotter. The mechanisms are also different in the two cases. Other conditions being equal, substitution of the quartz capillaries by those of copper or silver is without influence on the quantities of the intermediate products formed. The mechanism of the formation of these products is concluded to be first the decomposition of methane into CH_2 and atomic hydrogen, which forms mainly molecular hydrogen and some hydrogen peroxide. The CH_2 then burns partly to carbon monoxide and partly to formaldehyde. The atomic oxygen arising from the decomposition of hydrogen peroxide forms ozone, which, on slow cooling, again decomposes. Finally, carbon dioxide and water result from the further oxidation of these products.

L. S. THEOBALD.

Action of aluminium chloride on olefinic hydrocarbons. A. SZAYNA.—See B., 1929, 117.

Ozonisation of gaseous unsaturated hydrocarbons. I. Ethylene. II. Propylene and a "cracking gas." E. BRINER and P. SCHNORF (Helv. Chim. Acta, 1929, 12, 154—181, 181—186).—I. An apparatus is described for the ozonisation of a gas either in absence or in presence of water or water vapour. The liquid ozonide from ethylene is stable at 0° , becomes a vitreous mass at -80° , and at the ordinary temperature evolves hydrogen. The values of d and n_D vary slightly with the ratio of ethylene to ozone used. Mol.-wt. determinations on the ozonide in acetic acid or water give values which are too high, but diminish after some time, owing to decomposition. The ozonide is soluble in water in all proportions and such solutions decompose slowly at the ordinary temperature and more rapidly at 65° . In each case more formic acid than formaldehyde is produced and hydrogen is always evolved. This is due to the presence in the ozonide of formaldehyde peroxide, shown to be identical with dihydroxymethyl peroxide (Wieland and Winkler, A., 1923, i, 650). The production of this is formulated $\text{CH}_2\text{:CH}_2 + \text{O}_3 + \text{H}_2\text{O} \rightarrow [\text{OH}\cdot\text{CH}_2\cdot\text{O}]_2$, the water either being present because of incomplete drying or formed by oxidation of some ethylene. Decomposition of the peroxide occurs: $[\text{OH}\cdot\text{CH}_2\cdot\text{O}] \rightarrow 2\text{CH}_2\text{O}_2 + \text{H}_2$, and explains the preponderance of formic acid. The ozonide contains only traces of hydrogen peroxide; the peroxide cannot be formed by the action of hydrogen peroxide on formaldehyde (cf. Wieland and Winkler, loc. cit.). The free ozonide is isolated by vacuum distillation as a highly explosive liquid, b. p. $20^\circ/16$ —

17 mm. Ozonisation in presence of water gives similar results, but if the ozonide is decomposed by sodium hydrogen sulphite formaldehyde is the chief decomposition product, and is isolated as the additive compound. Addition of an ammoniacal solution of the ozonide to ammonium chloride solution gives hexamethylenetetramine, a small amount of ammonium formate, and oxygen.

II. Ozonisation of propylene proceeds in much the same manner as of ethylene. The stable products are formaldehyde, acetaldehyde, and formic and acetic acids. The evolution of hydrogen is not so marked as in the case of ethylene, although peroxides are again produced. Ozonisation of a "cracking gas" containing ethylene (15%), propylene (12%), butylene (8%), and other hydrocarbons proceeded similarly to the above examples. H. BURTON.

Electron displacement in carbon compounds.

V. Addition of hydrogen chloride to γ -ethyl- Δ^2 -pentene. H. J. LUCAS (J. Amer. Chem. Soc., 1929, 51, 248—253).— γ -Ethyl- Δ^2 -pentene (cf. Brooks and Humphrey, A., 1918, i, 286) and hydrogen chloride in glacial acetic acid yield almost quantitatively γ -chloro- γ -ethylpentane. This is in accordance with the hypothesis of electron displacement (cf. A., 1926, 943), but contrary to that of alternating polarity. γ -Ethylpentan- β -ol, obtained together with a little δ - ϵ -dimethyl- γ -diethyloctane- δ -diol, m. p. 100.7 — 101.2° , from γ -ethylpentan- β -one and sodium in alcohol, is converted by concentrated hydrochloric acid in presence of zinc chloride at the ordinary temperature into β -chloro- γ -ethylpentane, b. p. 62.0 — $62.5^\circ/50$ mm., d_4^{25} 0.8911, n_D^{25} 1.4295. γ -Ethylpentan- γ -ol is similarly converted into γ -chloro- γ -ethylpentane, b. p. 83 — $83.5^\circ/100$ mm., n_D^{25} 1.4311. The product from γ -ethyl- Δ^2 -pentene and hydrogen chloride had b. p. 78 — $79^\circ/90$ mm., d_4^{25} 0.8951, 1.4311. H. E. F. NOTTON.

Action of acetylene on selenium. F. P. MAZZA and L. SOLAZZO (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 33, 236—239).—The action of acetylene on selenium at 250 — 300° yields selenophen, b. p. 207 — 209° (cf. Foa, A., 1910, i, 187), and the selenium analogue of thionaphthene, selenonaphthene, $\text{C}_8\text{H}_4\text{Se}$, m. p. 53 — 54° , which gives a sparingly soluble picrate. T. H. POPE.

[Conjugated] diacetylenic hydrocarbons. V. GRIGNARD and TCHOUFAKI (Compt. rend., 1929, 188, 357—361).—The interaction of reagents, CR_2CMgX (2 mols.), and iodine (2 atoms) yields diacetylenic hydrocarbons through the probable intermediate formation of the α -iodoacetylene (1 mol.; cf. Grignard and Perrichon, A., 1926, 381). In this way the following are prepared: Δ^2 -decadi-inene, b. p. $88^\circ/12$ mm.; Δ^2 -dodecadi-inene, b. p. $103^\circ/8$ mm.; Δ^2 -tetradecadi-inene, b. p. 118 — $119^\circ/4$ mm.; $\alpha\delta$ -diphenyl- Δ^2 -butadi-inene, m. p. 86.5 — 87° ; $\alpha\delta$ -di-2:4-dimethylphenyl- Δ^2 -butadi-inene, m. p. 145.5 — 146° ; $\alpha\zeta$ -diphenyl- Δ^2 -hexadi-inene, m. p. 101° ; $\alpha\theta$ -diphenyl- Δ^2 -octadi-inene, m. p. 118° ; iodoacetylene, b. p. 32° ; α -iodo- Δ^2 -hexatri-inene, m. p. 52° ; di-iododiacetylene, m. p. 101 — 105° ; Δ^2 -butadi-inene, b. p. 8.5 — 9° ; and phenyltriacyetylene, b. p. $52^\circ/18$ mm., d_4^{25} 0.9708, n_D^{25} 1.534. Hydrolysis of the product of the reaction of

iodine (1.5 mol.) and the dimagnesium derivative of acetylene yields a dark-coloured powder part of which sinks in ethyl iodide but does not scratch glass. This last-named product contains 98% of carbon and no hydrogen; it may be a condensed form of carbon (C_6).

G. A. C. GOUGH.

Action of sulphuric acid in preparing alkyl halides. R. McCULLOUGH and F. CORTESE (J. Amer. Chem. Soc., 1929, 51, 225—228).—Sulphuric acid acts both on alcohols and on alkyl halides, particularly isopropyl, *sec.*-butyl, isobutyl, and isoamyl bromides, forming unsaturated products, the polymerides of which form unstable coloured additive products with acids. Accordingly, when alcohols are both distilled and washed with hydrobromic acid alone (cf. Michael and others, A., 1916, i, 361; Norris, *ibid.*, 461), the products are of greater purity and deteriorate much less rapidly on keeping than when sulphuric acid is used, although the yields are smaller. Stable samples of allyl halides are prepared by treating allyl alcohol (1 vol.) for several days at the ordinary temperature with hydrochloric acid (*d* 1.19; 8 vols.), hydrobromic acid (*d* 1.4; 7 vols.), or hydriodic acid (*d* 1.7; 6 vols.) and washing the product with alkali before distillation.

H. E. F. NOTTON.

Action of alkyl chlorides in the Wurtz reaction. H. F. LEWIS (Proc. Iowa Acad. Sci., 1927, 34, 222).—The replacement of butyl bromide by chloride in the preparation of octane gives yields up to 20% (based on the chloride), but the reaction is difficult to control, and a highly inflammable by-product is produced.

CHEMICAL ABSTRACTS.

Manufacture of $\alpha\beta$ -trichloroethane. I. G. FARBERIND. A.-G.—See B., 1929, 122.

Molecular compounds of organic iodides with sulphur. H. RHEINBOLDT and K. SCHNEIDER (J. pr. Chem., 1929, [ii], 120, 238—248).—A study of the phase-diagrams of the binary systems organic iodide-sulphur has been made. Iodoform gave two eutectics (42% and 69% S) at 85° and 91°. Tetraiodoethylene gave two eutectics (54% and 68% S) at 95.5° and 101°. The following mixtures gave eutectics: $\alpha\beta$ -di-iodoethane-sulphur, 28% S at 65°; di-iodoethylene-sulphur, 29% S at 54°; tri-iodo-nitroethylene-sulphur, 35% S at 80°; di-iodoacetylene-sulphur, 29% S at 48°; *p*-di-iodobenzene-sulphur, 53.5% S at 91°; iodoform-antimony tribromide, 63% SbBr₃ at 62°; tetrabromoethylene-sulphur, 13% S at 44°; diphenyliodonium tri-iodide-sulphur, 94% S at 117°. The following gave neither maxima nor minima: methylene iodide-sulphur; bromoform-sulphur. The compounds of sulphur with iodoform and tetraiodoethylene (Anger, A., 1908, i, 241) were isolated.

R. J. W. LE FEVRE.

Relationship of constitution of alkyl halides to the formation of nitroparaffins and alkyl nitrites. R. B. REYNOLDS and H. ADKINS (J. Amer. Chem. Soc., 1929, 51, 279—287; cf. Meyer and Stuber, A., 1872, 692, 804; Neogi and others, J.C.S., 1906, 89, 1905; 1916, 109, 701).—Alkyl halides are treated with silver nitrite, first in the cold and then under reflux, until the halogen-free distillate gives correct analyses for a mixture of alkyl nitrite and nitroparaffin. The proportion of the latter is determined by hydrolysing a

weighed sample with alcoholic sodium hydroxide and analysing the residue, after removal of alcohol, for carbon by a wet combustion method. This method is not applicable to *tert.*-alkyl derivatives. *n*-Butyl chloride does not react with silver nitrite under these conditions, whilst isoamyl chloride, *tert.*-butyl and cyclohexyl iodides, and benzyl and phenylethyl bromides do not give a simple mixture of isomerides. The percentage yield and the percentage of nitroparaffin in the products from the following bromides are allyl: 74.9, 79.8; *n*-propyl: 86.1, 77.4; *iso*-propyl: 78.5, 40.3; *n*-butyl: 88.2, 77.9; *isobutyl*: 77.2, 57.8; *sec.*-butyl: 68.3, 30.0; *tert.*-butyl: 60.0, 48.3; *isoamyl*: 78.2, 67.5; *n*-heptyl: 94.3, 71.0, and *sec.*-octyl: 82.1, 34.3; and from the following iodides: *n*-propyl: 85.9, 66.9; *isopropyl*: 71.7, 31.8; *n*-butyl: 85.1, 60.7; *isobutyl*: 74.9, 40.0, and *sec.*-butyl: 70.0, 31.9. The results show that, except with *sec.*-butyl bromide, a larger yield and a larger proportion of nitroparaffin are obtained from an alkyl bromide than from the corresponding chloride or iodide. Among isomeric derivatives, *n*-alkyl halides give a larger yield and a larger proportion of nitroparaffin than do *isoalkyl*, and *tert.*- give more than *sec.*-alkyl halides. The proportion of nitroparaffin formed is not greatly affected by the size or unsaturation of the alkyl radical. The reactivity of the alkyl halides increases in the order: allyl, *tert.*-butyl, *sec.*-alkyl, *isoalkyl*, *n*-alkyl- and the iodides are more reactive than the bromides.

H. E. F. NOTTON.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. II. Synthesis of methyl alcohol with catalysts composed of copper and zinc. P. K. FROLICH and others.—See this vol., 153.

Determination of the configuration of polyalcohols by means of boric acid. J. BOESEKEN (Bull. Soc. chim. Belg., 1928, 37, 385—402).—A lecture.

J. W. BAKER.

Cyclic acetals. J. D. VAN ROON (Rec. trav. chim., 1929, 48, 173—190; cf. Hill, Hibbert, and others, A., 1928, 1114, 1213).—The separation of the two isomeric ethylideneglycerols from the mixture obtained by Hill and Hibbert's method (A., 1924, i, 133) or by the action of acetaldehyde or paracetaldehyde on glycerol, is not possible by careful fractional distillation. Benzoylation of the mixture in quinoline (Fischer, Bergmann, and Barwind, A., 1920, i, 805) gives $\alpha\gamma$ -ethylideneglyceryl β -benzoate, b. p. 183°/20 mm., m. p. 85°, monoclinic, also obtained by the action of paracetaldehyde and hydrogen bromide or chloride on β -benzoylglycerol $\alpha\gamma$ -ditriphenylmethyl ether (Helferich and Sieber, A., 1928, 44), and $\alpha\beta$ -ethylideneglyceryl γ -benzoate, b. p. 173°/20 mm., d_4^{20} 1.1663, n_D^{20} 1.5100, also prepared from paracetaldehyde and glyceryl α -benzoate in presence of 1% of dry hydrogen chloride. Both ethylideneglyceryl benzoates yield glyceryl α -benzoate when hydrolysed with 0.5*N*-hydrochloric acid in acetone solution (cf. Fischer, A., 1920, i, 808). $\alpha\gamma$ -Ethylideneglycerol (phenylcarbamide derivative, m. p. 134°) and $\alpha\beta$ -ethylideneglycerol (phenylcarbamide derivative, m. p. 129°) have b. p. 176° and 187°, respectively. Small amounts of dry hydrogen chloride have an equilibration action on

mixtures of the ethyleneglycerols, and subsequent benzoylation of mixtures equilibrated by 1% of dry hydrogen chloride at 0—180° shows that the $\alpha\beta$ -form predominates at all temperatures, and increases with rise of temperature.

Paraformaldehyde and glycerol react in presence of 1% of dry hydrogen chloride at 130°, yielding a product (50%), b. p. 193—194°, which when benzoylated in quinoline affords $\alpha\gamma$ -methyleneglyceryl β -benzoate, b. p. 181°/20 mm., m. p. 74.6°, and $\alpha\beta$ -methyleneglyceryl γ -benzoate, b. p. 173°/20 mm., d_4^{25} 1.2011, n_D^{25} 1.5184, obtained also from glyceryl α -benzoate or $\alpha\beta$ -isopropylideneglyceryl γ -benzoate and formaldehyde. Hydrolysis of these esters with 4*N*-sodium hydroxide solution gives $\alpha\gamma$ -methyleneglycerol, b. p. 193.8°, 94°/20 mm., d_4^{25} 1.220, n_D^{25} 1.4527 (phenylcarbamide derivative, m. p. 133°), and $\alpha\beta$ -methyleneglycerol, b. p. 192.5°, 93°/20 mm., d_4^{25} 1.2008, n_D^{25} 1.4469 (phenylcarbamide derivative, m. p. 72°). These ethers are also affected by small amounts of dry hydrogen chloride, but appreciable amounts of undistillable condensation products are formed.

H. BURTON.

Partial esterification of polyhydric alcohols.
VII. Unreliability of proofs of the structure of disubstituted glycerols. A. FAIRBOURNE and G. W. COWDREY (J.C.S., 1929, 129—135; cf. Fairbourn and Foster, A., 1927, 131).—The " $\alpha\beta$ "-diphthalimidoglycerol of Philippi and Seka (A., 1923, i, 1185) is identical with the " $\alpha\gamma$ "-isomeride of Godeckmeyer (A., 1888, 1294) and Gabriel (A., 1889, 486). The corresponding " $\alpha\beta$ " and " $\alpha\gamma$ "-diphthalimido-acetates and -benzoates have been synthesised and are also identical. It is considered that the only absolute proof of $\alpha\beta$ -structure is resolution, and that this cannot be extended to derivatives. *Diphthalimidoacetoxyp propane* was synthesised by three methods: (a) $\text{OH}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br} \xrightarrow{\text{KX}} \text{OAc}\cdot\text{CH}_2\cdot\text{CHX}\cdot\text{CH}_2\text{X}$ (X = phthalimido-group); (b) $\text{CH(OH)(CH}_2\text{Cl)}_2 \xrightarrow{\text{KX}} \text{CH(OAc)(CH}_2\text{X)}_2$; (c) $\text{CH(OH)(CH}_2\text{X)}_2 \xrightarrow{\text{AcCl}} \text{CH(OAc)(CH}_2\text{X)}_2$, all of which yielded the same product, m. p. 194°. Specimens of *diphthalimidobenzoyloxypropane* similarly synthesised by methods (a) and (c) were identical, m. p. 194—195°. $\alpha\beta$ -Dibromohydrin palmitate, m. p. 34°, was prepared by method (a), using palmityl chloride and also by dibromination of *allyl palmitate*, m. p. 20—25°. $\alpha\gamma$ -Dibromohydrin palmitate, m. p. 35.5°, was similarly obtained, using method (a), and depressed the m. p. of the $\alpha\beta$ -isomeride to 28°. *Monopalmitin di-p-nitrobenzoate*, m. p. 102°, was prepared by heating silver *p*-nitrobenzoate and either $\alpha\beta$ - or $\alpha\gamma$ -dibromohydrin palmitate. $\alpha\gamma$ -Dichlorohydrin β -triphenylmethyl ether, m. p. 108—109°, obtained from $\alpha\gamma$ -dichlorohydrin and triphenylmethyl chloride in pyridine solution is also described.
 C. W. SHOPPEE.

Additive compounds of hydrogen chloride with ethyl ether and acetone. D. McINTOSH (Proc. Nova Scotian Inst. Sci., 1928, 17, 112—113).—The existence of the three ether-hydrogen chloride compounds $\text{Et}_2\text{O}\cdot\text{HCl}$, $\text{Et}_2\text{O}\cdot 2\text{HCl}$, and $\text{Et}_2\text{O}\cdot 5\text{HCl}$ found by Maass and McIntosh (A., 1913, i, 584), two of which

Hirai (A., 1926, 908) was unable to obtain, was confirmed by the method of thermal analysis. Crystallisation of the first two compounds was induced by inoculation; the last-named compound separated only after cooling and prolonged stirring. The existence of the acetone-hydrogen chloride compounds, $\text{COMe}_2\cdot\text{HCl}$ (Hirai, *loc. cit.*) and $2\text{COMe}_2\cdot 5\text{HCl}$ (Archibald and McIntosh, J.C.S., 1904, 85, 919), was also confirmed.

B. W. ANDERSON.

Isomorphism in oxonium compounds. D. McINTOSH (Proc. Nova Scotian Inst. Sci., 1928, 17, 116—117).—Relationships between the chemical constitutions of various oxonium compounds were investigated by determining which compounds formed an isomorphous series, the method being to inoculate supercooled solutions of the various compounds with compounds of supposedly similar nature. Systems examined were: ethyl ether with hydrogen chloride, bromide, and iodide; ethyl alcohol, acetone, and ethyl acetate with hydrogen bromide; ethyl ether, ethyl alcohol, ethyl acetate, and acetone with chlorine and bromine; and methyl ether with hydrogen bromide and iodide. Supercooled ethyl ether-hydrogen chloride is precipitated at once by its own crystals and by the corresponding hydrobromide, and, more slowly, by the hydriodide, but not by the corresponding salts of methyl ether, by acetone-hydrobromide, or by ether-chlorine. The compound $\text{Et}_2\text{O}\cdot 2\text{HCl}$ is precipitated by its own crystals and by $\text{Et}_2\text{O}\cdot 2\text{HBr}$, but not by ether-hydriodide, whilst $\text{Et}_2\text{O}\cdot 5\text{HCl}$ is unaffected by any oxonium compound. The oxonium-chloride compounds are precipitated by the corresponding bromides, not by other halogen compounds. Thus compounds of each class made with the same organic substances are isomorphous, whilst corresponding compounds with closely related organic substances are not.
 B. W. ANDERSON.

Carbohydrates and polysaccharides. XX. β -Methyl glyceryl ether. H. HIBBERT, M. S. WHELEN, and N. M. CARTER (J. Amer. Chem. Soc., 1929, 51, 302—306).—The α - and β -methyl glyceryl ethers, important for the identification of glycerides, are most conveniently characterised as the *p*-nitrobenzylidene acetals (cf. this vol., 47, 170). α -Methyl glyceryl ether also gives a *di-p*-nitrobenzoate, m. p. 108°, and a *diphenylurethane*, m. p. 118—119°, and β -methyl glyceryl ether a *di-p*-nitrobenzoate, m. p. 155°, and a *diphenylurethane*, m. p. 102°.

H. E. F. NOTTON.

Alkyl peroxides. II. Methyl ethyl peroxide and refractometric investigations on alkyl peroxides. A. RIECHE [with F. HRTZ] (Ber., 1929, 62, [B], 218—225; cf. A., 1928, 734).—Methyl ethyl peroxide is obtained only in traces by the action of diazomethane on ethyl hydroperoxide, readily by means of methyl sulphate. It has b. p. 40°/740 mm., d_4^{25} 0.8337, n_D^{25} 1.35987; the vapour density is normal. Like the other alkyl peroxides, it is only a feeble oxidising agent, liberating iodine from acidified potassium iodide only slowly and in traces. There is therefore a fundamental difference between the alkyl peroxides and hydrogen peroxide or ethyl hydroperoxide, which liberate iodine quantitatively. The peroxidic oxygen can be determined by titanium tri-

chloride. In stability and other properties methyl ethyl peroxide is intermediate between the dimethyl and diethyl compounds. For dimethyl peroxide the constants d_4^{20} 0.868, f. p. -100° to -105° , are recorded. Diethyl peroxide, d_4^{27} 0.8266, m. p. about -70° , from hydrogen peroxide, ethyl sulphate, and potassium hydroxide, has b. p. $64^\circ/740$ mm.; fractions collected close to the true b. p. contain considerable quantities of ether. Refractometric determinations on dimethyl, methyl ethyl, and diethyl peroxides show that the peroxidic oxygen cannot be present in purely ether-like linking. The refractions and dispersions of the compounds differ by definite amounts from the values calculated for ethereal oxygen. The formulation $R\cdot O\cdot O\cdot R$ expresses badly the union of peroxidic oxygen in alkyl peroxides and the structure $RO\cdot OR$ is preferred. Decomposition into radicals with univalent oxygen is excluded, since all alkyl peroxides have normal vapour densities. H. WREN.

isoPropyl and n-propyl sulphates. R. LEVAILLANT (Compt. rend., 1929, 188, 261—263).—Anhydrous isopropyl alcohol is added slowly to sulphuryl chloride in carbon tetrachloride at 0° , the whole is washed with ice-water, and the lower layer is distilled in a vacuum below 90° , giving in 34% yield isopropyl sulphate, b. p. $78-80^\circ/3.7$ mm., d_4^{20} 1.118, n_D^{20} 1.409. The preparation of phenyl isopropyl ether, b. p. $63-65^\circ/11$ mm., d_4^{20} 0.959, n_D^{20} 1.4983, and of phenyl n-propyl ether, b. p. $81^\circ/17$ mm., d_4^{20} 0.969, n_D^{20} 1.503, is described. n-Propyl sulphite, b. p. $82^\circ/15$ mm., d_4^{20} 1.042, n_D^{20} 1.426, is oxidised to the sulphate by permanganate. C. HOLLINS.

β -Hydroxyethyl allyl sulphide and its derivatives. S. M. SCHEBLIN and V. V. VASILEVSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 1629—1632).—Treatment of allyl mercaptide with ethylene chlorohydrin yields β -hydroxyethyl allyl sulphide, b. p. $90-92^\circ/12$ mm., d_4^{20} 1.0325, which with phosphorus trichloride gives β -chloroethyl allyl sulphide, b. p. $68^\circ/12$ mm., d_4^{20} 1.0768, and with acetic anhydride the corresponding acetate, b. p. $95^\circ/12$ mm., d_4^{20} 1.0469.

M. ZVEGINTZOV.

Stereoisomerism of disulphoxides and related substances. IV. Di- and tri-sulphoxides of trimethylene trisulphide. E. V. BELL and G. M. BENNETT (J.C.S., 1929, 15—19).—Hydrogen peroxide in acetone yields trimethylene trisulphide monoxide, m. p. 187° , converted by further treatment with hydrogen peroxide in glacial acetic acid into a mixture of α -trimethylene trisulphide dioxide, decomp. $220-280^\circ$ (labile form, square plates, extinction angle 16° ; stable form, monoclinic prisms, extinction angle 35°), and β -trimethylene trisulphide dioxide, decomp. $200-215^\circ$, pointed needles, extinction angle 32° (cf. Hinsberg, A., 1913, i, 818). The α -dioxide when further oxidised yields a single α -trimethylene trisulphoxide, decomp. $230-280^\circ$ (cf. Hinsberg, A., 1912, i, 546; 1914, i, 797), and the β -dioxide similarly yields this α -trioxide together with β -trimethylene trisulphoxide, decomp. $220-260^\circ$, extinction angle 32° . The above oxides all yield trimethylene trisulphide when gently reduced, and the solubilities of the stable α -dioxide, the β -dioxide, and the isomeric trioxides in water at 25° are recorded.

The isomeric form of trimethylene trisulphide reported by Hinsberg has been examined; trimethylene trisulphide was heated with hydriodic acid (d 1.7) at 100° , and a substance, m. p. 247° (decomp.), isolated. It is reconverted into the ordinary trisulphide, m. p. 216° , by crystallisation, and its composition differs slightly from that of $[CH_2S]_3$. C. W. SHOPPÉE.

Oxidation of unsaturated compounds. I. Oxidation of crotonic and isocrotonic acids, of γ -isocrotonolactone, and of maleic anhydride. G. BRAUN (J. Amer. Chem. Soc., 1929, 51, 228—248).—Crotonic and isocrotonic acids are oxidised by perbenzoic acid in chloroform in presence of water, yielding 63% of the theoretical of *dl*-erythro- (I), m. p. 81.5° , and *dl*-threo- (II), m. p. $74-75^\circ$, α - β -dihydroxybutyric acids, respectively (cf. Melikoff, A., 1888, 1056; Milas and Terry, A., 1925, i, 780). The same products are formed in aqueous solution. Crotonic acid is oxidised by potassium and barium chlorates in presence of osmic acid to II (80% and 38% yields, respectively) together with about 20% of a chlorohydroxybutyric acid, m. p. 76° . The formation of the latter indicates that, contrary to the statement of Hofmann (A., 1913, ii, 609), hypochlorous acid is formed during chlorate oxidations. Addition of hypochlorous acid also occurs when barium crotonate is oxidised with chlorate in neutral solution, but it is reduced to a minimum when crotonic and isocrotonic acids are oxidised by adding silver chlorate during some weeks to an aqueous solution at 0° (82% yields of II and I, respectively). The prefixes assigned to the acids I and II indicate their relationship to erythronic and threonic acids, assuming the usually accepted structure for crotonic acid and the occurrence of *cis*-addition in chlorate oxidations (cf. Glattfeld and Woodruff, A., 1927, 1054). Oxidations of γ -isocrotonolactone (Lespiau, A., 1905, i, 566) with silver, barium, or alkali chlorates give good yields of erythronolactone, but no chloro-derivative. Maleic anhydride is also oxidised without chlorination by barium chlorate to 90% and by silver chlorate to 70% of mesotartaric acid. H. E. F. NOTTON.

Determination of higher unsaturated fatty acids. H. H. ESCHER (Helv. Chim. Acta, 1929, 12, 27—49).—Saturated, unsaturated, and brominated fatty acids are converted by an excess of thionyl chloride into the corresponding acid chlorides and then treated with excess of *p*-aminoazobenzene in an indifferent solvent. After removal of solvent and excess of base by washing with aqueous-alcoholic hydrochloric acid, the resulting anilide is dried. The yields are from 87.5 to 98%. For full details of the method the original must be consulted. A scheme for the analysis of a fat is appended which gives the usual constants from the same specimen.

Condensation products of *p*-aminoazobenzene with the following acids are described: *palmitic*, m. p. $121.5-122.5^\circ$; *stearic*, m. p. $123-124^\circ$; *oleic*, m. p. $93-94^\circ$; *elaidic*, m. p. $111.5-112.5^\circ$; *oleic acid dibromide*, m. p. $90-91.5^\circ$; *elaidic acid dibromide*, m. p. $131-132^\circ$; *linoleic acid tetrabromide*, m. p. $137-138^\circ$, and *linolenic acid hexabromide*, m. p. $193-194^\circ$. The compound from oleic acid dibromide and aminoazo-*p*-xylene has m. p. 155° . H. BURTON.

Attempt to remove hydrogen from higher fatty acids. T. SUZUKI and T. KURITA (Suppl. Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 5—6).—Attempts to dehydrogenate palmitic, stearic, and oleic acids and their esters under diminished pressure (10—0.1 mm.) and at temperatures ranging from atmospheric to 300°, in the presence of various catalysts, were unsuccessful.

A. I. VOGEL.

Pityrol. VI. Distillation of palmitic acid. S. SHOYAMA (Mem. Coll. Sci. Kyoto, 1928, 11, 533—542).—Dry sodium palmitate was distilled from a Fischer retort at 380—540°, and yielded tar 70%, coke 24%, and gas 6%. The gas contained carbon monoxide 11.8%, carbon dioxide 12.2%, ethylene 1.7%, paraffins and hydrogen 27.4%. Fractionation of the part of the tar volatile with steam revealed the presence of the paraffins from C_9H_{20} to $C_{13}H_{28}$, confirmed by their physical constants and analysis. Olefinic hydrocarbons in the same portion of the tar were separated by means of liquid sulphur dioxide, and fractionated; the series from C_7H_{14} to $C_{13}H_{26}$ were identified. From the non-volatile portion of the tar, consisting mainly of unsaturated hydrocarbons C_{15} , C_{19} , C_{20} , C_{30} , palmitone was isolated; $C_{14}H_{30}$, $C_{18}H_{38}$, and $C_{20}H_{42}$ were also identified in this portion.

B. W. ANDERSON.

Conversion of higher fatty acids into barium salts. H. H. ESCHER (Helv. Chim. Acta, 1929, 12, 103—105).—Solutions of higher fatty acids in methyl or ethyl alcohol, ether, chloroform, carbon tetrachloride, or dichloroethane can be conveniently titrated with a solution (about 2N) of barium hydroxide in methyl alcohol. The resulting barium salt is usually precipitated in a pure condition.

H. BURTON.

Distillation of higher unsaturated fatty acids. H. H. ESCHER (Helv. Chim. Acta, 1929, 12, 99—102).—Oleic and similar acids are much more sensitive to heat (up to 150°) than is usually supposed. This sensitivity is more apparent in the oleic than in the elaidic series. Distillation of the acids is best carried out in a high vacuum and even then only an apparent purification occurs. Even with one distillation through a glass column partial rearrangement is unavoidable.

H. BURTON.

Pityrol. VII. Distillation of oleic acid. H. OGATA (Mem. Coll. Sci. Kyoto, 1928, 11, 543—547).—Sodium oleate, when distilled from a Fischer retort at 390—550°, yielded tar 65%, coke 17%, and gas 18%. More than 80% of the tar consisted of unsaturated hydrocarbons. By repeated distillation the part of the tar volatile with steam was divided into 18 fractions, examination of which showed the presence of a series of olefines from C_7H_{14} to $C_{16}H_{32}$. Similarly the non-volatile portion, after separation of 10% of unchanged sodium oleate, was found to contain the olefines from $C_{14}H_{28}$ to $C_{18}H_{36}$. B. W. ANDERSON.

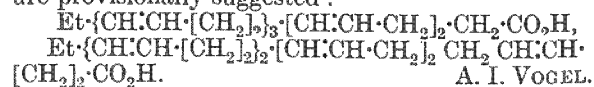
So-called "arachidic acid" and other acids of high mol. wt. from arachis oil. D. HOLDE, W. BLEYBERG, and I. RABINOWITSCH (Ber., 1929, 62, [B], 177—183; cf. Ehrenstein and Stuewer, A., 1923, i, 1057; Cohen, B., 1926, 98).—The technical fatty acids from arachis oil were worked up by a combination

of distillation in a high vacuum, crystallisation of the acids and their esters, and fractional precipitation of the lithium salts (cf. Holde and Godbole, A., 1926, 268, 498). The presence of *n*-docosoic acid, $C_{22}H_{44}O_2$, doubted by Cohen (*loc. cit.*), is placed beyond doubt. The acid is shown by the mixed m. p. method to be *n*- instead of *iso*-behenic acid (cf. Ehrenstein and Stuewer, *loc. cit.*). In addition, small quantities of an acid, $C_{26}H_{52}O_2$, m. p. 69—70°, mol. wt. 323—324, were separated which appears homogeneous, since the m. p. remains constant after lithium precipitation and repeated crystallisation; further characterisation appears, however, to be required, since the m. p. is considerably lower than that recorded by Levene and Taylor (A., 1924, i, 827) for the synthetic acid. *n*-Eicosoic acid, detected by Cohen in arachis oil, was absent or present only in traces in the "crude arachidic acid" of m. p. 73°, but is probably contained in the separated lower acids. The acid $C_{26}H_{52}O_2$, m. p. 79°, isolated by Holde and Godbole (*loc. cit.*) from Indian arachis oil, was isolated from the fraction of highest mol. wt. The m. p., 78—78.8°, agrees closely with that recorded previously, but the mol. wt., 381—384, corresponds more closely with $C_{25}H_{50}O_2$ than with $C_{26}H_{52}O_2$. Although fractional precipitation with lithium acetate did not lead to recognisable separation, cautious distillation in a high vacuum gave a residue which, after crystallisation from acetone, had m. p. 81—82.4°, mol. wt. 390. It appears therefore that the lithium method alone does not afford certain evidence of homogeneity with very sparingly soluble fatty acids of high mol. wt.

Tetracosic acid, m. p. 83—84° (presumably the *n*-acid), has been isolated from the portions of lowest b. p. of the free acids of beeswax.

H. WREN.

Constitution of clupanodonic acid. M. TSUJIMOTO (Bull. Chem. Soc. Japan, 1928, 3, 299—307).—Clupanodonic acid, $C_{22}H_{34}O_2$, was isolated from Japanese sardine oil by the author's lithium-salt-acetone method (cf. Armstrong and Hilditch, A., 1925, i, 778; McGregor and Beal, A., 1927, 145) and had d_4^{25} 0.9410, n_D^{25} 1.5057, neutralisation value 170.7, iodine value 388.5. Ozonolysis of the acid followed by decomposition of the ozonide with water afforded acetaldehyde, propaldehyde, carbon dioxide, and a comparatively large amount of succinic acid, but no azelaic acid (cf. Armstrong and Hilditch), whereas *amyl clupanodonate* (saponification value 139.5) similarly treated furnished a product insoluble in water which gave a 49% yield of succinic acid on hydrolysis. The latter fact is regarded as evidence for the first ethylenic linking being situated between the fourth and fifth carbon atoms; acetaldehyde and carbon dioxide are considered to be secondary decomposition products of malon-aldehyde or -semialdehyde. The absence of glyoxal or glyoxylic acid and of oxalic acid from the decomposition products together with the constancy of the iodine value after reduction with sodium and alcohol point to the absence of conjugated double linkings. The following two formulæ for the acid are provisionally suggested:



A. I. VOGEL.

Oxidation of lignoceric acid. F. A. TAYLOR and P. A. LEVENE (J. Biol. Chem., 1928, 80, 609—613).—Repetition of the work of Meyer and others (A., 1913, i, 1151) and of Levene and Taylor (A., 1922, i, 714) has given α -bromolignoceric acid, m. p. 69.5—70.5°, α -hydroxylignoceric acid, m. p. 94—95°, and *isotricosic* acid, m. p. 76.5—77.5°.

C. R. HARRINGTON.

Sodium salts of ω -hydroxy-butyric, -valeric, and -hexoic acids. C. S. MARVEL and E. R. BIRKHEIMER (J. Amer. Chem. Soc., 1929, 51, 260—262).—Details are given of the conversion of γ -phenoxybutyronitrile into γ -phenoxybutyric acid, γ -bromobutyric acid, γ -butyrolactone, and sodium γ -hydroxybutyrate, of δ -valerolactone into sodium δ -hydroxyvalerate, and of ϵ -bromohexoic acid into a mixture of ϵ -hexolactone and a polymeric product, both of which are hydrolysed by alkali to sodium ϵ -hydroxyhexoate.

H. E. F. NOTTON.

Formation of methyl sodiochloromalonate and its reaction with iodine. Stability of halogenoethanes. A. ECCLES (Proc. Leeds Phil. Soc., 1929, 1, 356—359).—The lability of halogen atoms in halogenoethanes is discussed on the basis of the relative displacability of the unshared electrons in the four halogen atoms (I > Br > Cl > F; cf. Ingold and others, A., 1928, 164, 402). In the hexahalogenoethane molecule two opposing factors are in operation: (1) the intrinsic tendency of the halogen atom to assume anionic condition, and (2) the cationising effect of the halogen atoms on each other. On heating, the amplitude of the oscillations of the shared electrons increases with resulting extremes of negative and positive polarisation, so that in molecules above a certain critical energy separation of negative and positive ions occurs with thermal decomposition into the corresponding tetrahalogenoethylene and free halogen. Attachment of a powerful electron sink such as the carbomethoxy-group (Cooper and Ingold, A., 1927, 558) to a carbon atom bearing an atom of strong anionic tendency (halogens) will cause an increase in the amplitude of oscillation of the carbon-halogen shared electrons and a correspondingly increased tendency towards elimination of halogen. In agreement with this view the action of iodine on *methyl chlorosodiomalonate* yields only methyl ethylenetetracarboxylate (identical with a specimen prepared by the action of iodine on methyl disodioethanetetracarboxylate), the intermediate methyl $\alpha\beta$ -dichloroethanetetracarboxylate produced momentarily eliminating chlorine with the formation of the unsaturated compound (cf. Bischoff and Rach, A., 1885, 244).

J. W. BAKER.

Reaction of alkali molybdates with malic and tartaric esters. E. DARMOIS (Bull. Soc. chim., 1928, [iv], 43, 1214—1229; cf. A., 1926, 457).—Further evidence is adduced in support of the two-stage hydrolysis of ethyl malate. Although molybdotartrates have not been actually isolated, measurements of the mutarotation of mixtures of tartaric esters and molybdates indicate that such substances exist and that hydrolysis of the esters occurs in two stages.

J. S. CARTER.

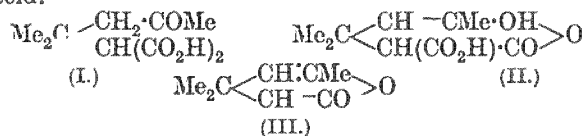
Influence of the solvent on the optical rotation of ethyl tartrate. T. J. HEBERT and J. N. PEARCE

(Proc. Iowa Acad. Sci., 1927, 34, 218—219).—Values of $[\alpha]$ depend on the composition of the solvent (ethyl alcohol, methyl alcohol, benzene, and toluene, and binary mixtures thereof), on the concentration of ester, and on the temperature. CHEMICAL ABSTRACTS.

Replacement of hydroxyl group in hydroxy-acid esters by chlorine with phosphoryl chloride and pyridine. (Steric course of substitution.) T. WAGNER-JAUREGG (Helv. Chim. Acta, 1929, 12, 61—63).—Methyl *l*(-)-malate is converted by treatment with phosphoryl chloride in cold pyridine into methyl *d*(+)-chlorosuccinate, b. p. 106—107°/10—11 mm., $[\alpha]_D^{20} +36.6^\circ$. Similarly, methyl (+)-mandelate gives methyl (-)-phenylchloroacetate, b. p. 130—131°(corr.)/15.5—16 mm., $[\alpha]_D^{18} -62.2^\circ$. Methyl *r*-phenylchloroacetate has b. p. 129—130°(corr.)/13—15 mm. Partial racemisation occurs during the formation of methyl (-)-phenylchloroacetate. Substitution is of the same order as with phosphorus pentachloride (cf. A., 1928, 506).

H. BURTON.

Keto-lactol tautomerism. I. Ring-chain tautomerism in α -carboxy- γ -acetyl- $\beta\beta$ -dimethylbutyric acid and a synthesis of γ -acetyl- $\beta\beta$ -dimethylbutyric acid. M. QUDRAT-I-KHODA (J.C.S., 1929, 201—209).—Evidence is adduced to show that both the forms I and II are necessary to explain all reactions of α -carboxy- γ -acetyl- $\beta\beta$ -dimethylbutyric acid.



Condensation of mesityl oxide and cyanoacetamide with sodium ethoxide yields 6-hydroxy-2-keto-3-cyano-4:4:6-trimethylpiperidine, m. p. 272° (decomp.), also obtained by synthesis from mesityl oxide and ethyl cyanoacetate, which condense to give ethyl α -cyano- γ -acetyl- $\beta\beta$ -dimethylbutyrate, b. p. 160°/16 mm., $d_4^{20} 1.03705$, $n_D^{20} 1.44652$ (semicarbazone, m. p. 166.5°), yielding with aqueous ammonia δ -amino- δ -hydroxy- α -cyano- $\beta\beta$ -dimethylhexoamide [trihydrate, m. p. 87° (decomp.)], which is converted by alcoholic sodium ethoxide into the above trimethylpiperidine. It is dehydrated by phosphoryl chloride to 2-keto-3-cyano-4:4:6-trimethyl-2:3:4:5-tetrahydropyridine, m. p. 253°, but is unaffected by dilute sodium hydroxide; hydrolysis with concentrated potassium hydroxide yields only α -carboxy- γ -acetyl- $\beta\beta$ -dimethylbutyric acid, m. p. 95° (semicarbazone, m. p. 177°); the ethyl ester, b. p. 153°/12 mm., $d_4^{20} 1.03921$, $n_D^{20} 1.4413$ (semicarbazone, m. p. 76°), is converted by alcoholic sodium ethoxide into ethyl 5:5-dimethyl-5:6-dihydroresorcinol-4-carboxylate. When hydrolysed with concentrated hydrochloric acid, the above trimethylpiperidine yields the dilactone of α -carboxy- γ -acetyl- $\beta\beta$ -dimethylbutyric acid, m. p. 137°, also obtained by hydrolysis with concentrated hydrochloric acid of ethyl α -cyano- γ -acetyl- $\beta\beta$ -dimethylbutyrate or of the tetrahydropyridine described above (cf. Vorländer and Gartner, A., 1899, i, 259). The dilactone is converted by hot dilute sodium hydroxide into α -carboxy- γ -acetyl- $\beta\beta$ -dimethylbutyric acid; at 200° it loses carbon dioxide, giving the unsaturated lactone (III).

Oxidation of α -carboxy- γ -acetyl- $\beta\beta$ -dimethylbutyric acid with sodium hypobromite gives α -carboxy- $\beta\beta$ -dimethylglutaric acid, m. p. 173° (decomp.) (cf. lit.), which passes into $\beta\beta$ -dimethylglutaric acid when heated. It decomposes at 130–140°, yielding a mixture of the dilactone and γ -acetyl- $\beta\beta$ -dimethylbutyric acid (cf. Bredt, A., 1898, i, 264), b. p. 162°/25 mm., d_4^{20} 1.03646, n_D^{20} 1.44652 [semicarbazone, m. p. 172° (decomp.): cf. Vorländer and Gartner, *loc. cit.*], in relative quantities which suggest that the parent acid is a mixture of the forms I and II in the ratio of about 3:1. Ethyl γ -acetyl- $\beta\beta$ -dimethylbutyrate, b. p. 112°/17 mm., d_4^{20} 0.96248, n_D^{20} 1.43047 (semicarbazone, m. p. 114°), is obtained directly from the acid and has also been synthesised as follows: $\beta\beta$ -dimethylglutaric anhydride is converted by absolute alcohol into *ethyl hydrogen $\beta\beta$ -dimethylglutarate*, b. p. 164°/16 mm., d_4^{20} 1.05774, 1.4403, which with thionyl chloride yields the corresponding *chloride*, b. p. 117°/16 mm.; this with zinc methyl iodide in benzene yields the ester, which, after purification through the semicarbazone, m. p. 114°, has b. p. 113°/18 mm., d_4^{20} 0.96323, n_D^{20} 1.43067. The synthetic ester is completely converted by alcoholic sodium ethoxide into dimethyldihydroresorcinol and is hydrolysed to the γ -acetyl- $\beta\beta$ -dimethylbutyric acid, b. p. 162°/25 mm. [semicarbazone, m. p. 172° (decomp.)], described above. Thus the free acid appears to possess the normal ketonic structure I. On the other hand, the acid reacts with acetyl chloride at the ordinary temperature in the lactonic form (II), yielding the lactone (III), b. p. 82°/10 mm., d_4^{20} 0.98658, n_D^{20} 1.45573 (cf. Bredt, *loc. cit.*), which is re-converted into the keto-acid by alcoholic potassium hydroxide. Reduction of γ -acetyl- $\beta\beta$ -dimethylbutyric acid with sodium and alcohol yields $\beta\beta$ -trimethylvalerolactone, b. p. 120°/18 mm., d_4^{20} 0.98039, n_D^{20} 1.47743. C. W. SHOPPEE.

Dimethyldihydroresorcinol as reagent for aldehyde, and carbon assimilation. D. VORLÄNDER (Z. angew. Chem., 1929, 42, 46–47. P. MAYER (*ibid.*, 48). C. NEUBERG (*ibid.*, 48).—A question of priority. C. HOLLINS.

Condensation products of formaldehyde and urea. POLLOPAS, LTD., E. C. C. BALY, and E. J. BALY.—See B., 1929, 138.

Oxygen-compound formation with acetaldehyde at low temperature. D. LEB. COOPER (Proc. Nova Scotian Inst. Sci., 1928, 17, 140–141).—When oxygen was bubbled through a mixture of acetaldehyde and manganese acetate at the low temperature of a carbon dioxide-ether bath, the solution became dark pink, possibly owing to the formation of some complex, but no peroxide stable at the ordinary temperature was formed. Absorption reached a maximum after a few hours, which probably represented the solubility of oxygen in the mixture. By warming to the ordinary temperature, some oxidation of the acetaldehyde to acetic acid occurs. B. W. ANDERSON.

Preparation of aldehydes and ketones by degradation of quaternary ammonium bases. J. VON BRAUN and W. TEUFFERT [and, in part, G. MANZ] (Ber., 1929, 62, [B], 235–241; cf. von Braun

and Heymons, this vol., 62).—Dihydrocitronellol, d_4^{20} 0.835, $[\alpha]_D^{20}$ +3.85°, prepared by hydrogenation of *d*-citronellol in the presence of platinum, is converted into $\beta\gamma$ -dimethyloctyl bromide, which, with trimethylamine in benzene at 100°, affords the quaternary bromide, $C_{10}H_{12}\cdot NMe_3Br$, m. p. 255°. Treatment of this with silver oxide followed by addition of potassium hydroxide to the concentrated solution and distillation under atmospheric pressure yields *dimethyl- $\gamma\gamma$ -dimethyloctylamine*, $CHMe_2\cdot[CH_2]_5\cdot CHMe\cdot[CH_2]_2\cdot NMe_3$, b. p. 95–98°/13 mm., d_4^{20} 0.7757, n_D^{20} 1.4302, $[\alpha]_D^{20}$ –4.79° (*methiodide*, m. p. 243°), and *$\gamma\gamma$ -dimethyl- Δ^8 -octene*, b. p. 45–46°/13 mm., 154°/atm., d_4^{20} 0.7321, n_D^{20} 1.4176, $[\alpha]_D^{20}$ –12.38°. The hydrocarbon is converted by ozonisation in chloroform and subsequent decomposition of the ozonide into *isononanaldehyde*, $CHMe_2\cdot[CH_2]_3\cdot CHMe\cdot CHO$, b. p. 72–74°/15 mm., 185–186°/752 mm., d_4^{20} 0.819, n_D^{20} 1.4203, $[\alpha]_D^{20}$ –9.1°, which reacts very slowly with hydroxylamine and semicarbazide, but is very easily oxidised to *α -dimethylheptic acid*, b. p. 127–130°/13 mm., d_4^{20} 0.8975, n_D^{20} 1.4287, $[\alpha]_D^{20}$ –14.1°.

Ethyl ethylmalonate is transformed by sodium and *n*-octyl bromide in presence of ether into *ethyl ethyl- n -octylmalonate*, b. p. 171–180°/13 mm. The corresponding *acid*, m. p. 72°, loses carbon dioxide with formation of *ethyloctylacetic acid*, b. p. 186°/12 mm. *Ethyl ethyloctylacetate*, b. p. 135–137°/12 mm., is reduced by sodium and alcohol to β -ethyl- β -octylethyl alcohol, b. p. 135–137°/12 mm., which is converted successively into β -ethyl- β -octylethyl bromide, b. p. 135–137°/12 mm., and the quaternary bromide, $C_8H_{17}\cdot CHEt\cdot CH_2\cdot NMe_3Br$, m. p. 225–227°. The salt is transformed in the usual manner into a mixture of *dimethyl- β -ethyl- β -octylethylamine*, $C_8H_{17}\cdot CHEt\cdot CH_2\cdot NMe_2$, b. p. 124°/13 mm., d_4^{20} 0.7913 (*picrate*), and *as-ethyloctylethylene*, b. p. 91–93°/11 mm., d_4^{20} 0.7703. The hydrocarbon is converted through its ozonide into ethyl octyl ketone, which, after purification through its semicarbazone, m. p. 91–92°, has b. p. 112°/12 mm., m. p. 12.5°. Its odour is considerably less pronounced than that of methyl nonyl ketone. The non-crystalline *oxime* has b. p. about 146°/13 mm.

Ethyl sodiomalonate and γ -phenylpropyl bromide afford ethyl γ -phenylpropylmalonate, b. p. 202°/11 mm., and small amounts of *ethyl di- γ -phenylpropylmalonate*, b. p. about 230°/1 mm. With β -phenylethyl bromide, ethyl γ -phenylpropylmalonate gives *ethyl β -phenylethyl- γ -phenylpropylmalonate*, b. p. 215–217°/1 mm. The corresponding *acid*, m. p. 124°, decomposes into β -phenylethyl- γ -phenylpropylacetic acid, b. p. 263–265°/18 mm., the *ethyl ester*, b. p. about 253–255°/18 mm., of which is reduced by sodium and alcohol to *β -phenylethyl- β - γ -phenylpropylethyl alcohol*, b. p. 242–245°/13 mm. The corresponding *bromide*, which has almost exactly the same b. p., is transformed into the extremely hygroscopic quaternary bromide (I), which yields *di- $CH_2Ph\cdot CH_2\cdot CH_2\cdot CH(CH_2\cdot CH_2Ph)\cdot CH_2\cdot NMe_3Br$* , (I), *methyl- β - β -phenylethyl- β - γ -phenylpropylethylamine*, b. p. about 200°/0.7 mm. (*picrate*, m. p. 109°), and *as- β -phenylethyl- γ -phenylpropylethylene*, b. p. 199–200°/14 mm., d_4^{20} 0.915, n_D^{20} 1.5517. Ozonisation of the

hydrocarbon followed by treatment of the product with zinc dust gives β -phenylethyl γ -phenylpropyl ketone, b. p. 213—215°/11 mm., m. p. 31° after softening at 30° (non-crystalline semicarbazone).

H. WREN.

Catalytic reduction of geraniol and citronellal by means of nickel. K. SUZUKI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 3—4).—The first molecule of hydrogen was attached much more rapidly to citronellal than to geraniol. At this stage the product was, in both cases, citronellol with some dihydro-citronellol. The second molecule of hydrogen was introduced much more slowly in each case.

B. W. ANDERSON.

α -Bromo- and α -hydroxy-aldehydes. II. Bromination of valeraldehyde. R. DWORZAK and A. ENENKEL (Monatsh., 1928, 50, 449—458).—Catalytic dehydrogenation of a sample of amyl alcohol, $[\alpha]_D -2.47^\circ$ (whence 42% of α -methylbutyl alcohol), with a brass catalyst (details to be published later) gives a mixture of valeraldehydes, b. p. 90—92°, $[\alpha]_D +0.35^\circ$. This is polymerised by treatment with concentrated sulphuric acid into paravalerdehede, b. p. 122—124°/10 mm., which on bromination at -10 to -5° and subsequent treatment with alcohol (cf. A., 1927, 1055) affords α -bromo- α -methylbutaldehyde ethylacetal, b. p. 83°/10 mm., $d_{20}^{25} 1.29$, $[\alpha]_D +0.12^\circ$, and $\alpha\alpha$ -dibromo- β -methylbutaldehyde ethylacetal, b. p. 121°/10 mm., $d_{20}^{25} 1.37^\circ$. The former acetal is hydrolysed by boiling with water to the corresponding hydroxy-aldehyde, b. p. about 120°/high vacuum, which with *p*-nitrophenylhydrazine gives a homogeneous, dark red precipitate.

H. BURTON.

α -Bromo- and α -hydroxy-aldehydes. III. Crystalline lactaldehyde and its behaviour towards dilute aqueous alkalis. R. DWORZAK and W. PRODINGER (Monatsh., 1928, 50, 459—475).—Crystalline, dimeric α -hydroxypropaldehyde (I) [*p*-nitrophenylhydrazone, m. p. 126.5° (corr.)], has been obtained in 35% yield by the hydrolysis of α -bromopropaldehyde ethylacetal, b. p. 69°/9 mm. (A., 1927, 1055), with water and prolonged extraction with ether of the resulting solution after neutralisation and saturation with sodium sulphate. The residue from this is distilled in a vacuum, when a mixture of I and unimolecular lactaldehyde is obtained. Cryoscopic determinations of I in aqueous solution show that after keeping for 24 hrs. the solution contains the unimolecular aldehyde only. When I is treated with 1% sodium hydroxide solution during several days oxidation occurs: this is minimised by working in an atmosphere of nitrogen. With 4% sodium hydroxide solution for 5 days a chloroform-soluble syrup is obtained which appears to be a condensation product of 3 mols. of lactaldehyde with loss of 1 mol. of water. The product reduces Fehling's solution slightly in the cold. Lactaldehyde is oxidised by aqueous copper acetate to pyruvaldehyde.

H. BURTON.

Inosinic acid. IV. Ribophosphoric acid. P. A. LEVENTE and T. MORY (J. Biol. Chem., 1929, 81, 215—219).—Ribophosphoric acid undergoes lactone formation slowly, indicating the formation of an $\alpha\delta$ -lactone and the attachment of the phosphoric acid

residue in the ϵ -position; the suggestion of Robinson (A., 1927, 960, 1225) is therefore not accepted.

C. R. HARRINGTON.

Precipitation of carbohydrates and glucosides by alkaloid precipitants. L. ROSENTHALER (Pharm. Acta Helv., 1928, 3, 93—96; Chem. Zentr., 1928, ii, 374).—Under the conditions employed, potato, wheat, maize, rice, barley, arrowroot, and sago starches gave with bromine and hydrobromic acid, silicotungstic acid, and phosphomolybdic acid more or less precipitate, and with tannin a turbidity. Aloin, convallamarin, digitalin, gitalin, and strophanthin gave a positive test with silicotungstic and phosphomolybdic acids; *Gypsophila* saponin reacted similarly, but was not precipitated by tannin or by bromine and hydrobromic acid. Thus precipitation of carbohydrates and glucosides can occur if the basicity due to the bridge oxygen atom is not too much weakened by hydroxyl or other acid groups.

A. A. ELDRIDGE.

Influence of sugars on the stability of hydrogen sulphite solutions. E. HÄGGLUND (Ber., 1929, 62, [B], 84—90).—The action of dextrose on the stability of sodium hydrogen sulphite solutions at 135° has been investigated. About 4—5 hrs. after the maximal temperature has been attained, the sulphur dioxide content suddenly diminishes and the amount of sulphuric acid increases rapidly. At this period, a rapid increase in the amount of "loosely combined" sulphurous acid is observed but this subsequently diminishes greatly. At this stage, considerable amounts of dithionic and, possibly, polythionic acids are present which are transition products in the conversion of sulphurous into sulphuric acid. Under similar conditions in the absence of dextrose the sulphur dioxide content diminishes at a slower rate and the amount of sulphuric acid increases very slowly. The sugar content, as judged by the behaviour towards Fehling's solution, diminishes considerably, probably owing to oxidation. Instability of the hydrogen sulphite solutions increases with increasing sulphite concentration exactly as would be expected with solutions free from sugar. The catalytic effect of mannose, xylose, and arabinose is approximately the same as that of dextrose, whereas laevulose is less, but distinctly, effective. The acceleration of the decomposition of sulphite by sugars depends on the reactive carbonyl group of the latter. It is certain that the production of sulphuric acid is not due to reduction of the sugar by sulphur dioxide. The catalytic effect is due in the main to the facilitated formation of such intermediate products of the sulphite reaction, particularly thiosulphate ions, which cause and accelerate the decomposition.

H. WREN.

Oxidative decomposition of sugar. I. Action of "chloramine-T" on dextrose. K. BERNHAUER and K. SCHÖN (Biochem. Z., 1928, 202, 159—163).—The oxidation of dextrose (1 mol.) using sodium *p*-toluenesulphonchloroamide by eight equivalents of oxygen giving rise to 2 mols of acetic acid and 2 mols. of carbon dioxide (Bleyer and Braun, A., 1927, 341) could not be quantitatively confirmed. Acetic acid cannot be detected and considerable amounts of formic acid are obtained. Gluconic acid is not

formed initially, since this substance is not attacked by "chloramine-T."

P. W. CLUTTERBUCK.

Oxidation of dextrose in alkaline solution with formation of carbon monoxide. M. NICLOUX (Compt. rend. Soc. Biol., 1928, 99, 226—228; Chem. Zentr., 1928, ii, 1077).—The consumption of oxygen and the yield of carbon monoxide are maximal at 85°. Lævulose, lactose, galactose, and maltose, but not sucrose until inverted, are similarly attacked. The effect of various salts is examined.

A. A. ELDRIDGE.

Colorimetric determination of dextrose. A. B. SCHACHKELDIAN (J. Russ. Phys. Chem. Soc., 1928, 60, 1517—1520).—The method is based on the red coloration, due to the formation of picramic acid, which is developed when a solution of dextrose is treated with picric acid in the presence of alkali. The intensity of the colour depends on the concentration of dextrose, and can be compared with a standard scale. Disaccharides do not give the reaction, whilst lævo-hexoses produce a more intense colour. If chlorine ions are present, the coloration is fainter, and a special solution containing chlorides must be used as a standard of comparison.

M. ZVEGINZOV.

Hexosediphosphate. P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1928, 80, 633—638).—Hydrolysis of the methylglucoside of hexosediphosphate (cf. Morgan, A., 1927, 749) at 100° with 0.1N-hydrochloric acid consisted of initial rapid rupture of the glucosidic linking followed by much slower liberation of 1 mol. of phosphoric acid; the hexosediphosphate is therefore a γ -derivative, and the stable monophosphate of Neuberg (A., 1913, i, 423) is ζ -lævulosephosphate.

C. R. HARRINGTON.

Pityrol. VIII. Distillation of sucrose. Y. HIDAKA (Mem. Coll. Sci. Kyoto, 1928, 11, 549—551).—Pure sucrose when distilled from an iron retort at 240—610° gave a distillate consisting of water 75%, neutral portion 4.5%, acidic substance 1.5%, and humus 8.5%. Furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde were identified as the neutral constituents, and formic and lævulic acids in the acidic portion.

B. W. ANDERSON.

Constitution of daphnin. F. WESSELY and K. STURM (Ber., 1929, 62, [B], 115—119).—The glucodaphnetin obtained by Leone (A., 1925, i, 1283) from β -acetobromoglucose and 7 : 8-dihydroxycoumarin is considered to have the glucose residue substituted in the 8- rather than in the 7-hydroxyl group of 7 : 8-dihydroxycoumarin. Until direct comparison can be made, the identity of this synthetic with the natural glucoside is not regarded as established and the present work refers to the synthetic material. Tetra-acetyldaphnin, m. p. 217°, $[\alpha]_D^{25}$ -31.64° in methyl alcohol, and daphnin, m. p. 216—217°, $[\alpha]_D^{25}$ $+29.36^\circ$ in methyl alcohol, are prepared by Leone's method. Treatment of tetra-acetyldaphnin with diazomethane followed by hydrolysis of the product affords 8-hydroxy-7-methoxycoumarin, m. p. 175° (corr.) after slight previous softening, which is similarly prepared from daphnin. 8-Hydroxy-7-ethoxycoumarin, m. p. 145 (corr.) after slight softening, is obtained

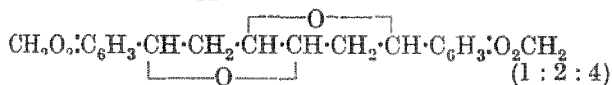
analogously. Treatment of 8-hydroxy-7-methoxycoumarin with diazoethane in absolute alcohol gives an 80—90% yield of 7-methoxy-8-ethoxycoumarin, m. p. 85.5° (corr.) [8-methoxy-7-ethoxycoumarin has m. p. 80.5° (corr.)], which is converted by successive treatment with sodium methoxide and ethyl alcohol and with ethyl iodide into 4-methoxy-2 : 3-diethoxycinnamic ester, hydrolysed to 4-methoxy-2 : 3-diethoxycinnamic acid, m. p. 157—158°. Oxidation of the acid by permanganate yields 4-methoxy-2 : 3-diethoxybenzoic acid, identical with the acid, m. p. 75° (corr.) after softening, obtained by treatment of methyl 4-methylpyrogallolcarboxylate with ethereal diazoethane and hydrolysis of the product. H. WREN.

Constitution and properties of fraxin. F. WESSELY and E. DEMMER (Ber., 1929, 62, [B], 120—126).—Fraxin, obtained by extraction of the young bark of *Fraxinus excelsior* with boiling water, precipitation of the extract with lead acetate, decomposition of the precipitate by hydrogen sulphide, and crystallisation of the glucoside from alcohol, forms pale yellow, hydrated crystals, m. p. 205° (corr.) when slowly heated. It is readily hydrolysed by hot, dilute sulphuric acid to fraxetin and dextrose and belongs to the β -series, since it is attacked by emulsin. Since the constitution of fraxetin has been elucidated (Wessely and Demmer, A., 1928, 893) the possible positions of the glucose residue and the methyl group in the 6 : 7 : 8-trihydroxycoumarin structure of fraxin are 8 : 6 or 7 : 6; the decision in favour of the former is reached as follows. Fraxin is converted by successive treatment with ethereal diazomethane and hydrolysis into 8-hydroxy-6 : 7-dimethoxycoumarin, m. p. 195° (corr.; decomp.), which with diazoethane affords 6 : 7-dimethoxy-8-ethoxycoumarin, m. p. 108.5° (corr.). By a similar series of changes fraxin is converted into 8-hydroxy-6-methoxy-7-ethoxycoumarin, m. p. 153—154° (corr.; decomp.), and 6 : 8-dimethoxy-7-ethoxycoumarin, m. p. 82° (corr.). Dimethyldaphnetin is oxidised by potassium persulphate in alkaline solution in the presence of ferrous sulphate to a hydroxydimethoxycoumarin (cf. Bargellini, A., 1916, i, 490) which must be 6-hydroxy-7 : 8-dimethoxycoumarin, since it is methylated by diazomethane to 6 : 7 : 8-trimethoxycoumarin, m. p. 103—104° (corr.), identical with dimethylfraxetin. Diethyldaphnetin, b. p. 160°/0.2 mm., m. p. 67—78° (corr.), prepared by treating daphnetin with diazoethane, is oxidised to 6-hydroxy-7 : 8-diethoxycoumarin, b. p. 170°/0.2—0.4 mm., m. p. 149—150° (corr.), which is methylated to 6-methoxy-7 : 8-diethoxycoumarin, m. p. 80—81° (corr.), identical with diethylfraxetin (A., 1928, 893). Oxidation of 7-methoxy-8-ethoxycoumarin affords 6-hydroxy-7-methoxy-8-ethoxycoumarin, m. p. 156—157° (corr.), methylated to 6 : 7-dimethoxy-8-ethoxycoumarin, m. p. 108.5° (corr.), identical with the compound obtained from fraxin. H. WREN.

Sesamin. J. BOESEKEN and W. D. COHEN (Biochem. Z., 1928, 201, 454—463).—Sesamin, m. p. 122.5°, $[\alpha]_D^{25}$ $+68.6^\circ$ in chloroform, is shown to have the composition $C_{20}H_{18}O_6$. It is not reduced at 250°/100 atm. by hydrogen, and on oxidation no intermediate stages could be detected. The six oxygen atoms are held in ether linkings, and it contains the methylene-

dioxy-group attached to a benzene nucleus. Nitration with a mixture of nitric and acetic acids yields *dinitrosesamin*, $C_{20}H_{16}O_{10}N_2$, m. p. 235–245° (tin salt of reduction product, $C_{20}H_{22}O_6N_2Cl_6Sn$, has $[\alpha]_D^{25} +60.0^\circ$), 4-nitro-1:2-methylenedioxybenzene, and a little nitropiperonal (cf. Salway, J.C.S., 1909, 95, 1163).

The action of magnesium ethyl iodide on sesamin gives a product with two ethyl groups, showing that sesamin has two methylenedioxy-groups. Alcoholic hydrogen chloride produces an *isomeride*, m. p. 95—98° [α]_D¹⁸ +86.6° (in chloroform), probably by a kind of Walden inversion. Acetic acid in presence of sulphuric acid at 60° gives a third *isomeride* of sesamin, m. p. 118—120°, [α]_D¹⁸ +73.3°. The following constitution is suggested :



J. H. BIRKINSHAW.

Solanine. G. ODDO (Ber., 1929, 62, [B], 267—271; cf. Oddo and others, A., 1905, i, 455; 1906, i, 527, 980; 1911, i, 671; Colombano, A., 1908, i, 99; 1912, i, 798).—In their criticisms of the work of Oddo and co-workers, Zemplén and Gerecs (this vol., 51) have overlooked the established difference between the glucosides extracted from *Solanum sodomæum* (with which Oddo has worked) and *S. tuberosum* (investigated by Colombano). Zemplén has used a technical variety of solanine of unknown origin, but usually derived from *S. tuberosum*. H. WREN.

Methyl salicylate glucoside of *Gaultheria procumbens*, L., identical with monotropin. M. BRIDEL and (MLE.) S. GRILLON (Bull. Soc. Chim. biol., 1928, 10, 1326—1335).—See A., 1928, 1224.

Formulæ of *Digitalis* glucosides. II. A. WINDAUS (Nachr. Ges. Wiss. Gottingen, 1927, 422—426; Chem. Zentr., 1928, ii, 669—670).—The formula $C_{23}H_{32}O_3$ previously ascribed to digitaligenin is replaced by the formula $C_{23}H_{30}O_3$, which is supported by the fact that oxidation of hexahydrodigitaligenin affords a dicarboxylic acid, $C_{23}H_{34}O_8$, m. p. 286—287° (dimethyl ester, m. p. 174°), but this conclusion is rendered uncertain by the observation that pure digitaligenin on oxidation yields no toxigenone, but a product, $C_{23}H_{28}O_3$, m. p. 197°. A. A. ELDRIDGE.

Carbohydrates. VII. Starch acetate. P. BRIGL and R. SCHINLE (Ber., 1929, 62, [B], 99—103).—Rice starch, swollen with hot water, precipitated by alcohol, and dried with alcohol and ether, is heated with pyridine and acetic anhydride at 80° until a transparent jelly is produced which yields starch triacetate, $[\alpha]_D^{20} +162.40^\circ$ in chloroform. The product is soluble in chloroform, *s*-tetrachloroethane, and glacial acetic acid, giving solutions which are very viscous even when dilute. Hydrolysis with alcoholic potassium hydroxide yields starch which appears more freely soluble in water than the original material, but gives the blue coloration with iodine and normal hydrolysis by diastase. The acetate has a high mol. wt., since it does not appreciably increase the b. p. of chloroform. The constant cannot be determined by Rast's method. In glacial acetic acid the acetate

does not suffer dialysis under conditions whereby the acetates of dextrose, sucrose, and maltose readily pass through the membrane.

Repetition of the work of Friese and Smith (A., 1928, 1925) on rice and potato starch affords a starch acetate which, contrary to these authors, is soluble in chloroform or glacial acetic acid, yielding colloidal solutions which slowly pass through a Jena glass filter, size ≤ 7 . Intensive desiccation appears to render the acetate less soluble.

Many of the conclusions of Peiser (A., 1927, 753) with regard to the composition of starch acetate and the constitution of starch are invalid, since acetylation by acetic anhydride in presence of sulphuric acid yields a partly changed product in which free reducing groups are present. H. WREN.

Disruption of the corn [maize] starch granule and its relation to the constituent amyloses. T. C. TAYLOR and C. O. BECKMANN (J. Amer. Chem. Soc., 1929, 51, 294—302).—The discrepancies in the values obtained by previous workers for the proportions of α - and β -amylose in starch (cf. Sherman and Baker, A., 1916, i, 767; Ling and Nanji, J.C.S., 1923, 123, 2666) are due to the fact that starch pastes prepared with boiling water at 1 or 2 atm. pressure contain, even after passage through a ball mill or homogeniser, a large proportion of swollen but unruptured granules. The high viscosity of the paste is mainly due to the presence of these gelatinised particles. When dry maize starch is ground in a quartz ball mill the viscosity and apparent α -amylose content of 1% pastes prepared from it gradually decrease until, when unbroken granules can no longer be detected microscopically, these values are identical with those previously obtained for a 1% paste in which the granules had been ruptured by chemical means (cf. B., 1926, 717). This proves that the latter treatment does not alter the relative proportions of α - and β -amylose in the product. The viscosity of a paste from untreated starch is approximately equal to that of a β -amylose solution of ten times the concentration.

H. E. F. NOTTON.

Allylcellulose. I. SAKURADA (J. Soc. Chem. Ind. Japan, 1928, 31, 638—642).—By treating tissue paper with 40—50% sodium hydroxide solution and allyl bromide, the higher cellulose allyl ethers (tri- and di-ether of C_6 unit) were directly obtained. The halogen-absorbing power of the resulting ether was concordant with the result of elementary analysis, and the double linking remained intact by etherification. The tetrabromide of cellulose diallyl ether was isolated almost pure. The higher allyl ether is partly soluble in alcohol, benzene, and carbon tetrachloride, but its solubility is not so great as expected.

Y. TOMODA.

Manufacture of mixed acid esters of cellulose or esters of cellulose ethers. I. G. FARBENIND. A.-G.—See B., 1929, 126.

Action of fatty acids on cellulose. C. J. MALM and H. T. CLARKE (J. Amer. Chem. Soc., 1929, 51, 274-278).—Prolonged refluxing of native cellulose with acetic acid effects esterification up to a limit (6-7% Ac) which is independent of the source and

molecular complexity (cuprammonium viscosity) of the fibre, and corresponds with the formula $C_{24}H_{39}O_{20}Ac$. The same product is obtained more rapidly at higher temperatures. The corresponding *propionate* and *butyrate* are obtained similarly. Cellulose which has been mercerised or regenerated from its nitrate, from viscose, from cuprammonium solution, or from a solution of its acetate yields on similar treatment *acetates* of the limiting composition $C_6H_7O_5Ac$ (21—22% Ac). These differ from cellulose in their capacity to retain basic dyes. Cellulose regenerated from cellulose acetate which has retained its original fibrous structure is esterified to a much smaller extent (about 10.8% Ac). These results are regarded as evidence that native cellulose has the unit molecule $C_{24}H_{40}O_{20}$. H. E. F. NOTTON

Cellulose xanthamides. T. NAKASHIMA (J. Soc. Chem. Ind. Japan, 1928, 31, 629—633).—Cellulose xanthamides were obtained by the interaction of sodium cellulose xanthoacetic acid and ammonia or amines. Y. TOMODA.

Influence of poles and polar linkings on tautomerism in the simple three-carbon system. I. Prototropy and anionotropy in trialkylpropenylammonium derivatives. C. K. INGOLD and E. ROTHSTEIN (J.C.S., 1929, 8—14).—Prototropic and anionotropic changes are recorded in the system C-C-C, the facilitating group being the trialkylammonium ion. *Diethyl-γ-chloroallylamine*, b. p. 55°/9 mm. (*hydrochloride*, m. p. 221°; *picrate*, m. p. 78°), obtained in 57% yield from *γ-chloroallyl chloride* and diethylamine, when treated with ozone yields *hydrochloric acid*, carbon monoxide, and probably *diethylaminoacetaldehyde*; with ethyl iodide it yields *triethyl-γ-chloroallylammonium iodide*, m. p. 210° (*picrate*, m. p. 125°), also prepared directly from *γ-chloroallyl chloride* and triethylamine through the quaternary hydroxide. These salts do not react with triethylamine at 100°. When triethyl-*γ-chloroallylammonium chloride* or *iodide* is warmed with alcoholic sodium ethoxide and the product treated with *picric acid triethyl-α-ethoxyallylammonium picrate*, m. p. 122—123°, is obtained; the corresponding acetate when treated with ozone and then with *picric acid* yields formaldehyde and *triethylethoxyaldehydomethylammonium picrate*, m. p. 110—111°, hydrolysed by *hydrochloric acid* to *triethylhydroxyaldehydomethylammonium picrate*, m. p. 195—196°; triethyl-*α-ethoxyallylammonium chloride* when warmed with concentrated *hydrochloric acid* yields *triethyl-α-hydroxyallylammonium chloride*, oily (*picrate*, m. p. 145°; *chloroplatinate*), and the corresponding acetate when treated with ozone and then with *picric acid* gives the preceding *hydroxyaldehydo-picrate*, m. p. 195—196°.

γ-Chloroallyl chloride with alcoholic trimethylamine yields *trimethyl-γ-chloroallylammonium chloride*, m. p. 193° (*picrate*, m. p. 141°), which with ozone gives *hydrochloric acid*, carbon monoxide, and betaine; neither the chloride nor the *picrate* reacts with diethyl- or triethyl-amine at 100°. The chloride is converted into *trimethyl-α-ethoxyallylammonium picrate*, m. p. 111—112°, and the acetate of this base yields formaldehyde and *trimethylethoxyaldehydo-*

methylammonium picrate, m. p. 168°, hydrolysed to *tri-methylhydroxyaldehydomethylammonium picrate*, m. p. 182—184°. Trimethyl-*α-ethoxyallylammonium chloride* when treated with warm *hydrochloric acid* yields non-crystalline *trimethyl-α-hydroxyallylammonium chloride (picrate)*, m. p. 149°, and the acetate of the latter base gives the preceding *hydroxyaldehydo-picrate*, m. p. 182—184°.

The ease of hydrolysis by acids of the ethoxy-compounds described above (which resemble esters rather than ethers) suggests that this effect, as also failure to replace the ethoxy-group by bromine, is due to the electron-affinity of the $\cdot NR_3^+$ group.

C. W. SHOPPEE.

Diaminobutanes. E. STRACK and H. FANSELOW (Z. physiol. Chem., 1929, 180, 153—160).—Various diaminobutanes have been prepared and characterised by the preparation of their *m-nitrobenzoyl* derivatives. Putrescine (*αδ-diaminobutane*) yields a *m-nitrobenzoyl* derivative, m. p. 240°; *βγ-diaminobutane* yields two *m-nitrobenzoyl* derivatives, (m. p. 238° (soluble in methyl alcohol) and 320° (insoluble); *αγ-diaminobutane m-nitrobenzoyl* derivative, m. p. 199°. *αβ-Diaminobutane (m-nitrobenzoyl* derivative, m. p. 197°) could not be obtained by Demjanoff's method (A., 1907, i, 174) and is best prepared by the action of saturated alcoholic ammonia on propaldehyde cyanohydrin for 3 hrs. at 100° and reduction of the aminonitrile with sodium and alcohol, or, in small yield, by the action of saturated methyl-alcoholic ammonia for 24 hrs. at 100° on *αβ-dibromobutane*. *αγ-Diamino-β-methylpropane* (Johnson and Joyce, A., 1916, i, 755) (*m-nitrobenzoyl* derivative, m. p. 182°) is obtained by similar reduction of methylmalononitrile. *αβ-Diamino-β-methylpropane* (not obtained by Sidorenko's method, A., 1907, i, 270) is prepared by reduction of *α-aminoisobutyronitrile* and yields two *m-nitrobenzoyl* derivatives, m. p. 145° and 174°, the former being converted into the latter by heating with alcohol. J. W. BAKER.

Reaction between carbon disulphide and some diamines and guanidines. E. STRACK (Z. physiol. Chem., 1929, 180, 198—211).—When an alcoholic solution of tetramethylenediamine is treated with carbon disulphide *δ-aminobutyldithiocarbamic acid*, $NH_2[CH_2]_3\cdot NH\cdot CS_2H$, m. p. 173° (all m. p. are uncorr.; decomp.), is obtained (cf. von Braun and Lemke, A., 1923, i, 6). When an alcoholic suspension of this is heated at 100° hydrogen sulphide is eliminated and *tetramethylenethiocarbamide*, $NH[CH_2]_3\cdot NH$, m. p. 177°, results.

Pentamethylenediamine and carbon disulphide afford *ε-aminoamylidithiocarbamic acid* (cadmium, barium, and silver salts).

Ethyl-*δ*-thiocarbamide hydrobromide reacts with tri-, tetra-, and penta-methylenediamines in alcoholic solution, forming *α-amino-γ-guanidinopropane hydrobromide*, m. p. 116° (*sulphate*, m. p. 265°), and *αγ-diguanidinopropane*, m. p. 135° (*hydrobromide*, m. p. 218°; *sulphate*, m. p. 270° after sintering at 260°); *αδ-diguanidinobutane hydrobromide*, m. p. 212°, after sintering at 205° [*sulphate*, m. p. 297° (lit. 291°)] (cf. Kiesel, A., 1922, i, 531); *α-amino-ε-guanidinopentane hydrobromide*, m. p. 105° (*sulphate*, m. p. 284°),

and *α*-diguandinopentane, m. p. 173° (decomp.; hydrobromide, m. p. 217° after sintering at 212°; sulphate, m. p. 317°), respectively. Guanidine reacts with carbon disulphide in alcoholic solution at 100° yielding *guanidine trithiocarbonate*, $\text{CS}[\text{SH}, \text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{NH}_2]_2$, m. p. 133—135° after sintering at 125°, also obtained from guanidine sulphate and sodium trithiocarbonate. The production of this salt demonstrates the following changes: $\text{CS}_2 + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2\text{S}$; $\text{CS}_2 + \text{H}_2\text{S} = \text{CS}(\text{SH})_2$. The above trithiocarbonate is decomposed by dilute acids, including carbonic acid, into hydrogen sulphide, and when it is treated with aqueous lead acetate lead trithiocarbonate is obtained. The *trithiocarbonates* obtained from methyl- and ethyl-guanidines, *α*-diguandinopropane, *αδ*-diguandinobutane, and *αε*-diguandinopentane have m. p. 153°, 165°, 95° (decomp.), 193° (decomp.), and 190° (decomp.), respectively. *α*-Amino-*δ*-guanidinobutane (agmatine) and *α*-amino-*ε*-guanidinopentane react with carbon disulphide forming the corresponding *dithiocarbamates*, m. p. 210° (decomp.) after sintering at 200° and 201°, respectively. These compounds are postulated as internal salts $\text{CS} \cdot \text{NH} \cdot [\text{CH}_2]_n \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2 \cdot \text{HS}$.

The compound previously abstracted as $\text{C}_{12}\text{H}_{22}\text{N}_4\text{S}_3$ (Wrede, Strack, and Hettche, A., 1928, 511), and the compound $\text{C}_{14}\text{H}_{30}\text{N}_8\text{S}_4$ (*loc. cit.*) are postulated as $[\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CS}]_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{SH}$, respectively.

H. BURTON.

Glutaric series. C. RAVENNA and R. NUCCORINI (Gazzetta, 1928, 58, 853—864).—The formation of a dipeptide of aspartic acid from asparagine (A., 1920, i, 150) has no analogy in the glutaric series. Beetroot glutamine, m. p. 178—186°, according to conditions of preparation, when boiled with water for 10 days lost ammonia, but yielded glutamic acid, with pyrrolidonecarboxylic acid, which substances also formed some labile compounds of undefined character. *Ammonium hydroxyglutamate* was prepared by precipitation from an ethereal solution of the acid. It was converted when heated into the *diamide*, m. p. 181—182° (decomp.), of glutamic acid, which on further heating at its m. p. lost a molecule of water, furnishing the unimolecular *lactone amide*,



E. W. WIGNALL.

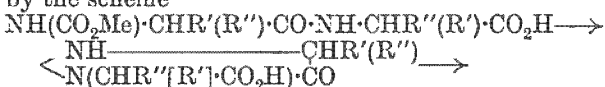
Ammonium creatinine picrate. I. GREENWALD (J. Biol. Chem., 1929, 81, 73—75).—Addition of excess of picric acid to a concentrated ammoniacal solution of creatinine yields *ammonium creatinine picrate*, m. p. 241°, which, on successive recrystallisations from water, dissociates, yielding eventually creatinine picrate; the ammonium creatinine picrate may be utilised for the recovery of creatinine from ammoniacal mother-liquors containing the latter.

C. R. HARRINGTON.

Structure and rate of hydrolysis of peptides. P. A. LEVENE, L. W. BASS, and R. E. STEIGER (J. Biol. Chem., 1929, 84, 221—230).—The hydrolysis of

dipeptides by erepsin followed the course of a unimolecular reaction, the reaction constant being of the same order of magnitude with all those peptides which were attacked by the enzyme except the alanyl peptides, which gave anomalous results. The hydrolysis of glycylglycine was retarded by the presence of free glycine; the action of the enzyme was confined to peptides containing the naturally occurring optical modification of the amino-acids; glycyl-*D*-isovaline was not attacked. *Chloroacetyl-L-valine* had m. p. 112—113°, $[\alpha]_D^{25} -15^\circ$ in alcohol, and yielded *glycyl-L-valine*, $[\alpha]_D^{25} +20.3^\circ$ in water. C. R. HARRINGTON.

Polypeptide N-carboxylic acids. F. WESSELY, E. KEMM, and J. MAYER (Z. physiol. Chem., 1929, 180, 64—74).—Hydrolysis of either methyl (or ethyl) alanyl-glycine-*N*-carboxylate or methyl glycylalanine-*N*-carboxylate yields the same product, *carbonyl-glycinealanine* (I; $\text{R}'=\text{H}$, $\text{R}''=\text{Me}$), m. p. 182° (methyl ester, m. p. 106°). Similarly, a repetition of Leuchs and Sander's work (A., 1925, i, 1248) shows that the product of hydrolysis of (unpurified) ethyl carbomethoxyglycyl-*β*-aminobutyrate or of carbomethoxy-*β*-aminobutyrylglycine ethyl ester is not an *N*-carboxylic acid, but is the *diethyl* ester, m. p. 103—104°, of carbonylglycine-*β*-aminobutyric acid (I; $\text{R}'=\text{H}$, $\text{CHR}''=\text{CHMe} \cdot \text{CH}_2$). These changes are explained by the scheme



(I), and support the view (A., 1928, 623) that the dibasic acids obtained by hydrolysis of the carbalkoxy-peptides are not peptide-*N*-carboxylic acids but carbonylbisamino-acids. Similarly, hydrolysis of the *carbomethoxy*-derivative, m. p. 179.5°, of phenylalaninephenylalanine yields two acids, m. p. 203° and 176°, respectively, both of which yield *ethyl* esters, m. p. 142—143° and 138°, which are identical with the corresponding esters of carbonylbisphenylalanine (m. p. 145° and 141.5°), identification being complicated in this case by optical isomerism.

J. W. BAKER.

Aminoacetals and aminoaldehydes containing three carbon atoms. R. VOET (Bull. Soc. chim., 1929, [iv], 45, 61—69).—*γ*-Chloropropaldehyde dimethylacetal (A., 1927, 1172) reacts readily with amines at 100°, affording with 1 mol. of tertiary amines the hydrochloride of the aminoacetal, and with primary and secondary amines (2 mols.) the free aminoacetal and the amine hydrochloride and some tertiary amide $\text{NR}[\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OMe})_2]_2$. Concentrated hydrochloric acid converts the aminoacetals into the corresponding aminoaldehydes, obtained in crystalline monomeric and non-crystalline polymeric forms, the latter possessing no reducing properties and reacting slowly to give the same semicarbazonones as the crystalline form. The aminoaldehydes are non-toxic and possess no physiological activity. The following are described: *γ*-methylaminopropaldehyde dimethylacetal, b. p. 164.5°/760 mm. (yield 80%) (hydrochloride), and *γ*-methyliminodipropaldehyde tetramethylacetal, b. p. 130°/20 mm., $d_{20}^{20} 0.9759$; *γ*-ethylaminopropaldehyde dimethylacetal

(yield 70%), b. p. 177.3°/760 mm., d^{20}_D 0.9095 (hydrochloride), and γ -ethyliminodipropaldehyde tetramethylacetal (yield 10%), b. p. 133°/20 mm., d^{20}_D 0.9608. γ -Propylaminopropaldehyde dimethylacetal (yield 60%), b. p. 195.5°/760 mm., d^{20}_D 0.9002 (hydrochloride), and γ -propyliminodipropaldehyde tetramethylacetal (yield 9%), b. p. 140°/20 mm., d^{20}_D 0.9483; γ -diethylaminopropaldehyde dimethylacetal (yield 95%), b. p. 194.2°/760 mm., d^{20}_D 0.8846 (hydrochloride); γ -dipropylaminopropaldehyde dimethylacetal (yield 82%), b. p. 223.4°/760 mm., d^{20}_D 0.8715 (hydrochloride); γ -methylaminopropaldehyde hydrochloride (acetosemicarbazone, $C_7H_{16}O_3N_4$, m. p. 300°); γ -ethylaminopropaldehyde hydrochloride (semicarbazone, $C_8H_{18}O_3N_4$, m. p. 301.5°) (cf. Wohl and Losanitsch, A., 1906, i, 107); γ -propylaminopropaldehyde hydrochloride (semicarbazone, $C_9H_{20}O_3N_4$, m. p. 303°), and γ -diethylaminopropaldehyde hydrochloride (semicarbazone, $C_{10}H_{22}O_3N_4$, m. p. 309.5°, chloroaurate, decomp. at 100°). R. BRIGHMAN.

Reaction for carbamide. F. PISANI (Annali Chim. Appl., 1928, 18, 555—556).—This reaction depends on the conversion of carbamide into hydrazine by hypochlorite or hypobromite in alkaline solution. The hypobromite solution is added dropwise to an alkaline carbamide solution, total oxidation of the carbamide being avoided; 1 drop of hypobromite solution suffices for 0.002—0.003 g. of carbamide. Slight excess of 5% mercuric chloride solution is then added and the liquid filtered. On addition to the filtrate of 4 c.c. of 50% potassium hydroxide solution, reduction of the mercury compound to mercury soon occurs and may be accelerated by heating. The reaction is not given by ammonium salts, ureines, or ureides. T. H. POPE.

Iodometric determination of thiosemicarbazide. A. GAFFRE (J. Pharm. Chim., 1929, [viii], 9, 19—23).—In presence of sodium hydrogen carbonate, iodine and thiosemicarbazide require contact for 8 hrs. for complete reaction to occur. After acidification, which decomposes the cyanogen iodide formed, 10 atoms of iodine are found to react with 1 mol. of thiosemicarbazide. In presence of sodium hydroxide, only 30 min. contact is necessary and 12 atoms of iodine are absorbed by 1 mol. of thiosemicarbazide. E. H. SHARPLES.

Pseudohalogens. III. The pseudohalogen tricyanomethyl and the mixed halogen tricyanomethyl bromide. L. BIRCKENBACH and K. HUTTNER (Ber., 1929, 62, [B], 153—163; cf. A., 1926, 30).—The validity of the previous hypothesis that the halogen character of an atonic complex is attributable to the presence of an outer ring of seven electrons is further established by experiments with the tricyanomethyl group. With regard to the nomenclature of compounds such as $Br \cdot C(CN)_3$, $K \cdot C(CN)_3$, the terminology bromotricyanomethane is considered unsatisfactory, since the union of the two parts is not aliphatic as in bromomethane and the terms "tricyanomethyl bromide," "potassium tricyanomethylide," etc. are adopted.

Malononitrile and cyanogen bromide are added successively to a solution of sodium ethoxide in absolute alcohol and the sodium tricyanomethylide is transformed into the corresponding silver salt, the

yield being about 90%. Treatment of a suspension of an excess of silver tricyanomethylide in anhydrous ether with bromine at -10° gives tricyanomethyl bromide, colourless rhombic crystals, m. p. 72° (decomp.) after becoming yellowish-red at 68°. The compound is very sensitive to moisture. A crystal first reddens and then bleaches moist blue litmus paper. Iodine is liberated from alcoholic ammonium iodide and aqueous potassium iodide, $Br \cdot C(CN)_3 + 2KI = K \cdot C(CN)_3 + KBr + I_2$, reaction in the latter case proceeding more rapidly than hydrolysis and being quantitative. With aqueous potassium bromide bromine is liberated. Aqueous sulphurous acid dissolves tricyanomethyl bromide with reduction to $CH(CN)_3$ and hydrogen bromide; the bromide ion can be titrated potentiometrically with 0.1N-silver nitrate, thus giving a ready method of determining bromine in the compound. Tricyanomethyl bromide and aqueous potassium cyanide afford potassium tricyanomethylide and cyanogen bromide; evidence of the production of tetracyanomethane is not produced. Water slowly dissolves tricyanomethyl bromide, the solution becoming first yellow, then colourless, and again yellow; hypobromite is initially produced, followed by cyanogen bromide. Aqueous alkali hydroxide rapidly dissolves tricyanomethyl bromide, 1 mol. of which neutralises 2 mols. of alkali; the oxidising power of the solution diminishes rapidly. Almost the whole of the bromine is transformed into bromide, the hypobromite being consumed. From silver iodide suspended in ether or benzene tricyanomethyl bromide liberates iodine, a complex equilibrium being established. Silver selenocyanide in benzene liberates bromine. Dry ethylene appears to react with tricyanomethyl bromide in the molar ratio 1:1, giving a red, presumably polymerised, compound of unknown structure. The decomposition tension of potassium tricyanomethylide in 0.1N-solution is 2.08 volts, whereas for bromine under similar conditions the value is 1.68 volts. In absolute alcoholic solution the value is 1.38 volts. Tricyanomethyl is therefore more electronegative than bromine and is placed next to chlorine in the affinity series of the halogens.

Treatment of iodine chloride with potassium cyanide gives potassium chloride and cyanogen iodide; occasionally iodine is liberated in small amount. H. WREN.

Formation of cyanogen by oxidation of hydrocyanic acid. B. RICCA and F. PIRONE (Annali Chim. Appl., 1928, 18, 550—555).—Experiments with hydrocyanic acid, potassium cyanide, and ferro- and ferri-cyanides show that, in a medium rendered acid with sulphuric acid, hydrocyanic acid is oxidised, in nearly all cases, to cyanogen by sodium persulphate, hydrogen peroxide, potassium permanganate, potassium dichromate, and manganese, lead, and tin dioxides; the proportions of the latter vary widely with the experimental conditions and with the nature of the oxidising agent (cf. Bellucci and Ricca, A., 1924, ii, 672, 791; A., 1926, 489). T. H. POPE.

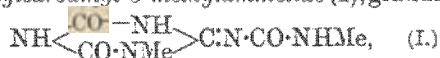
Carbimides. VI. Condensations of methylcarbimide with cyanamide under the influence of triethylphosphine. K. H. SLOTTA and R. TSCH-

SCHE (Ber., 1929, 62, [B], 137—145; cf. A., 1927, 346, 548, 578).—Cyanamide reacts with methylcarbamide in anhydrous ether in the presence of triethylphosphine, giving *dimethylcarbamylcyanamide*, $(\text{NHMe}\cdot\text{CO})_2\text{N}\cdot\text{CN}$, decomp. 124° , in 80% yield. The compound is decomposed by ethereal diazomethane with production of *N-cyano-NN'-dimethylcarbamide*, m. p. 114° , in small amount. In methyl-alcoholic suspension, it is converted by hydrogen sulphide at the atmospheric temperature into *N-cyano-N'-methylcarbamide*, decomp. 122° (silver salt), whereas if the solution is subsequently boiled and the passage of hydrogen sulphide is continued *N-methylthiohuret*, $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, decomp. 198° , is produced. Dimethylcarbamylcyanamide is transformed by ammonia into *N'-guanyl-N-methylcarbamide*, decomp. 165° (silver salt), and by sodium azide and dilute acetic acid into 4-*N-methylureido-1:2:3:5-tetrazole*, $\begin{array}{c} \text{N}=\text{N} \\ | \quad | \\ \text{NH}-\text{N} \end{array} \text{C}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$, decomp. above 300°

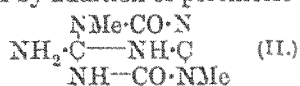
after softening at 265° , converted by boiling water into methylcarbamide and *C-aminotetrazole*, m. p. 203° . In all these changes the primary action is decomposition into cyanomethylcarbamide (which undergoes further change) and methylcarbamide. The latter compound is identified in the action of hydrazine hydrate on dimethylcarbamylcyanamide, whereby *NN'-dimethylcarbamylhydrazine*, decomp. 270° , is produced. When dimethylcarbamylcyanamide is treated with boiling ethyl acetate, it decomposes into methylcarbamide and *N-cyano-N'-methylcarbamide*, which polymerises normally to *NN'-dimethylcarbamyl-N-cyanoguanidine*, $\text{NHMe}\cdot\text{CO}\cdot\text{N}(\text{CN})\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$, m. p. 280 — 285° (decomp.) after softening at 190° . The last substance is transformed by boiling water into *N-methylcarbamyl-N'-cyanoguanidine*, decomp. 320 — 325° , and by boiling hydrochloric acid or sodium hydroxide into *N-methylammelins*,

$\text{NMe}\cdot\begin{array}{c} \text{CO}-\text{NH} \\ | \quad | \\ \text{C}(\text{NH})\cdot\text{NH} \end{array}\text{C}\cdot\text{NH}$, decomp. 242 — 245° . If, however, dimethylcarbamylcyanamide is boiled with ethyl acetate containing a little triethylphosphine, abnormal polymerisation of cyanomethylcarbamide occurs with production of 6-methylcarbamyl-5-methylammelins, $\text{NH}\cdot\begin{array}{c} \text{C}(\text{NH})\cdot\text{NH} \\ | \quad | \\ \text{CO}-\text{NMe} \end{array}\text{C}\cdot\text{N}\cdot\text{CO}\cdot\text{NHMe}$, decomp.

290° (diacetyl derivative, m. p. 214°). The compound is transformed by boiling 30% potassium hydroxide into *N-methylcyanuric acid*, m. p. 288° , and by short treatment with 2*N*-sodium hydroxide into ammonia and 6-methylcarbamyl-5-methylammelide (I), gradual de-



comp. above 300° . Treatment of 6-methylcarbamyl-5-methylammelins with concentrated sulphuric acid at 80 — 100° followed by addition of perchloric acid to the



diluted solution yields a substance, decomp. 250° , from which boiling sodium carbonate solution liberates the dicyclic isomeride of 6-methylcarbamyl-5-methylammelins (II), decomp. 320° . H. WREN.

Σ

Tertiary phosphines containing the *n*-butyl radical. W. C. DAVIES and W. J. JONES (J.C.S., 1929, 33—35).—By the action of magnesium *n*-butyl bromide on phosphorus trichloride, phenyldichlorophosphine, and *p*-tolylidichlorophosphine, the corresponding tertiary phosphines are obtained. They are colourless liquids, unimolecular in freezing benzene and stable in air. The following are described: *tri-n-butylphosphine*, b. p. $149.5^\circ/50$ mm., d_4^{25} 0.8118 (carbon disulphide additive compound, m. p. 65.5°); *methyltri-n-butylphosphonium iodide*, m. p. 133.5° ; *ethyltri-n-butylphosphonium iodide*, m. p. 153° ; *phenyldi-n-butylphosphine*, b. p. 184.5 — $185.5^\circ/50$ mm., d_4^{25} 0.9115 (mercuric chloride compound, m. p. 160.5°); *phenylmethyl-di-n-butylphosphonium iodide*, m. p. 168° ; *phenylethyl-di-n-butylphosphonium iodide*, m. p. 147° ; *p-tolyldi-n-butylphosphine*, b. p. $197^\circ/50$ mm., d_4^{25} 0.9076 (mercuric chloride compound, m. p. 112°); *p-tolylmethyl-di-n-butylphosphonium iodide*, m. p. 130.5° .

Tri-n-butylphosphine oxide, b. p. 300° , is prepared by the action of magnesium *n*-butyl bromide on phosphoryl chloride, or by boiling tri-*n*-butylphosphine in a current of air, and by oxidising it with warm 40% nitric acid. C. W. SHOPPE.

Tetraethylphosphonium nitrite. P. C. RAY and N. RAY (J. Indian Chem. Soc., 1928, 5, 733—734).—When tetraethylphosphonium iodide is treated with silver nitrite a poor yield of *tetraethylphosphonium nitrite* is obtained owing to the formation of an insoluble double salt of silver iodide and the original iodide. The most convenient method of preparation is to treat tetraethylphosphonium sulphate with barium nitrite and evaporate the resulting aqueous solution in a vacuum over sulphuric acid. H. BURTON.

β -Substituted alkylarsinic acids and their derivatives. I. S. M. SCHERLIN and G. J. EPSTEIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1487—1492).—See A., 1928, 1231.

Factors affecting starting of Grignard reagents. H. GILMAN and R. J. VANDERWAL (Rec. trav. chim., 1929, 48, 160—162).—A study has been made of the effect of (a) moisture, (b) addition of rubber, powdered glass, mercury, small amounts of decomposed Grignard reagents, and magnesium bromide etherate, (c) presence of dry nitrogen, carbon dioxide, hydrogen chloride, carbon dioxide-free air, and oxygen, (d) solvents, and (e) temperature on the time necessary for a mixture of magnesium (0.5 g.), butyl bromide (2 c.c.), and dry ether (5 c.c.) to give the positive colour test previously described (A., 1925, ii, 1011; 1928, 160). Magnesium bromide etherate is a positive catalyst; water, oxygen, carbon dioxide, hydrogen chloride, benzene, light petroleum, and the outside surface of new rubber stoppers are all negative catalysts; at low temperatures the action is delayed. The other substances have no appreciable action. H. BURTON.

Qualitative colour test for reactive organo-metallic compounds. H. GILMAN and L. L. HECK (Rec. trav. chim., 1929, 48, 193—197).—The colour test previously described (A., 1925, ii, 1011; 1928, 160) is more sensitive when a hot, saturated solution of Michler's ketone in benzene is used. Positive

results can be obtained for low concentrations of the Grignard reagent by using 5–10 c.c. The minimal concentration for a positive test varies from 0.01 to 0.05*M* for 14 typical Grignard reagents.

H. BURTON.

Preparation of magnesium allyl bromide. H. GILMAN and J. H. McGLUMPHY (Bull. Soc. chim., 1928, [iv], 43, 1322–1328).—Yields of 90–95% of magnesium allyl bromide are obtained by Gilman and McCracken's method (A., 1924, i, 23; 1927, 865), using 0.5 mol. of allyl bromide, 3 atoms of finely-divided magnesium (cf. Gilman and Zoellner, A., 1928, 401, 875), and 7.5 mols. of ether. By filtering off the excess of magnesium yields of 90.5% of δ -phenyl- Δ^2 -butene are obtained by treatment with benzyl chloride; in presence of excess of magnesium the yield is reduced by formation of magnesium benzyl chloride and subsequent decomposition to dibenzyl. Benzophenone similarly affords 74.9% of diphenylallylcarbinol, and acetophenone 80.2% of phenylmethylallylcarbinol. Carbon dioxide, however, gives only 21.7% of vinyl-acetic acid, oily non-acid products being formed in considerable amount.

R. BRIGHTMAN.

Reaction between organomagnesium halides and some salts. H. GILMAN and J. E. KIRBY (Rec. trav. chim., 1929, 48, 155–159).—The action of cuprous cyanide on magnesium phenyl bromide in ether, benzene, and toluene gives 6.5, 64, and 100% of diphenyl, respectively. Silver and nickel cyanides, silver cyanate, cuprous and silver thiocyanates, silver carbonate, chromate, phosphate, and citrate afford varying amounts (traces to 90%) of diphenyl. Mercuric cyanide produces mercuric phenyl bromide. Silver cyanide converts magnesium benzyl chloride into dibenzyl, whilst mercuric acetate gives 49% of mercuric benzyl chloride. No addition of the Grignard reagent to any group attached to a metal takes place.

H. BURTON.

Preparation of mercury diisobutyl by the reaction of Frankland and Duppa. H. F. LEWIS and E. CHAMBERLIN (J. Amer. Chem. Soc., 1929, 51, 291–294; cf. J.C.S., 1863, 16, 415).—The following optimum procedure has been developed for this reaction: sodium (2 mols.) in the form of 0.25% amalgam is added to a mixture of isobutyl iodide (1 mol.) and ethyl acetate (0.5 mol.) or acetone (1 mol.), which is kept at 0–5°. Water is then added and the product extracted with ether and distilled (yield, 0.282 mol.). Other carbonyl compounds such as isovaleraldehyde and acetic anhydride also act as catalysts. isobutyl bromide yields only traces of mercury diisobutyl when substituted for the iodide. The by-products consist mainly of diisobutyl.

H. E. F. NOTTON.

Organic mercury bases and their salts. K. H. SLOTTA and K. R. JACOBI (J. pr. Chem., 1929, [ii], 120, 249–300).—Interaction of ethereal solutions of the appropriate magnesium alkyl bromide with mercuric bromide gave the mercuric alkyl bromides: methyl, m. p. 172°; ethyl, m. p. 198° (lit. 193.5°), *n*-propyl, m. p. 140°, *n*-butyl, m. p. 136°, *n*-amyl, m. p. 127°, *n*-hexyl, m. p. 127.5°, *n*-heptyl, m. p. 118.5°, and *n*-cetyl, m. p. 101.5°. Treatment of the foregoing compounds with methyl-alcoholic potassium

hydroxide followed by the corresponding halogen acid gave: mercuric methyl chloride, m. p. 167°, and iodide, m. p. 152° (lit. 145°), mercuric ethyl chloride, m. p. 192°, and iodide, m. p. 186°, mercuric *n*-propyl chloride, m. p. 147°, and iodide, m. p. 113°, mercuric *n*-butyl chloride, m. p. 130°, and iodide, m. p. 117°, mercuric *n*-amyl chloride, m. p. 110°, and iodide, m. p. 110°, mercuric *n*-hexyl chloride, m. p. 125°, and iodide, m. p. 110°, mercuric *n*-heptyl chloride, m. p. 119.5°, and iodide, m. p. 103°, mercuric *n*-cetyl chloride, m. p. 102°, and iodide, m. p. 82°.

The following mercuric alkyl hydroxides were obtained from the corresponding bromides: methyl, m. p. 137°; ethyl, m. p. 37°; *n*-propyl, m. p. 78°; *n*-butyl, m. p. 68°; *n*-amyl, m. p. 50°; *n*-hexyl, m. p. 54.5°; *n*-heptyl, m. p. 54°; *n*-cetyl, m. p. 78°; phenyl, sinters at 195°, froths at 200° (chloride, m. p. 271°; bromide, m. p. 280°; iodide, m. p. 269°); α -naphthyl, sinters at 228° (chloride, m. p. 193°; bromide, m. p. 201°; iodide, m. p. 219°).

Neutralisation of these mercuric *n*-alkyl hydroxides in methyl-alcoholic solution with anhydrous hydrocyanic acid followed by absorption of the water and methyl alcohol by calcium chloride under reduced pressure gave the mercuric alkyl cyanides: methyl, m. p. 93°; ethyl, m. p. 77°; *n*-propyl, m. p. 28°; *n*-butyl, m. p. 42°; *n*-amyl, m. p. 39°; *n*-hexyl, m. p. 38°; and *n*-heptyl, m. p. 53°.

In a similar manner acetic acid gave mercuric alkyl acetates: methyl, m. p. 101°; ethyl, m. p. 54°; *n*-propyl, m. p. 57°; *n*-butyl, m. p. 56°; *n*-amyl, m. p. 52°; *n*-hexyl, m. p. 50°; and *n*-heptyl, m. p. 45°; nitric acid gave the mercuric alkyl nitrates: methyl, decomp. 168° after softening at 100°, becoming green at 135°; ethyl; *n*-propyl, m. p. 75°; *n*-butyl, m. p. 75°; *n*-amyl, m. p. 78°; *n*-hexyl, m. p. 75°; and *n*-heptyl, m. p. 66°; whilst analogous use of sulphuric acid led to the mercuric alkyl sulphate: methyl, decomp. 255°; ethyl, decomp. 199°; *n*-propyl, decomp. 196°; *n*-butyl, m. p. 181°, decomp. 183°; *n*-amyl, decomp. 188°; *n*-hexyl, m. p. 173°, decomp. 174°, and *n*-heptyl, m. p. 180° (decomp.).

Tables and curves are included to show (1) solubilities of mercuric *n*-alkyl halides in ethyl alcohol at 18° and 78°, in chloroform at 18°, and in water at 100°, (2) m. p. of mercuric *n*-alkyl halides, (3) changes in molecular conductivity of mercury *n*-alkyl bases with increase of alkyl radical, and (4) m. p. of mercuric *n*-alkyl cyanides.

R. J. W. LE FEVRE.

Properties of conjugated compounds. VI. Dibromination products of cyclic butadienes. E. H. FARMER and W. D. SCOTT (J.C.S., 1929, 172–180).— $\Delta^{1,3}$ -cyclohexadiene, b. p. 80°, d_4^{20} 0.8421, n_D^{20} 1.4760, on bromination in chloroform, or preferably *n*-hexane, below –15°, and immediate removal of the solvent in a vacuum yields: (a) 1:2-dibromo- Δ^3 -cyclohexene, m. p. 68°, easily oxidised by neutral potassium permanganate in aqueous acetone at 0° to 1:2-dibromo-3:4-dihydroxycyclohexane, m. p. 96–98°, which yields succinic acid on further oxidation; (b) a stereoisomeric 1:2-dibromo- Δ^3 -cyclohexene, liquid, yielding an isomeric 1:2-dibromo-3:4-dihydroxycyclohexane, oily, and succinic acid. Both these 1:2-dibromides pass readily into 1:4-di-

bromo- Δ^2 -cyclohexene, b. p. 110—120°/2 mm., m. p. 108° (cf. Crossley and Haas, J.C.S., 1903, 83, 498; 1904, 85, 1403; Zelinski and Gorsky, A., 1908, i, 619), which is converted into succinic acid by hot aqueous chromic acid. This 1 : 4-dibromide is the sole product of bromination if there is prolonged delay in working up the reaction mixture, or if heat is used in the removal of the solvent. The possibility of reversing the 1 : 2 \rightarrow 1 : 4-change could not be gauged owing to the decomposition of the 1 : 4-dibromide when maintained at 100°. The proportion in which the original bromides appear varies little with the nature of the solvent or the degree of dilution.

cyclopentadiene, b. p. 42°, was prepared from the dimide, some specimens of which had m. p. 19° and others m. p. 32° (cf. Staudinger and Rheiner, A., 1924, i, 274; Wieland and Bergel, A., 1926, 56); both modifications have the same b. p., 56°/13 mm., and yield cyclopentadiene on depolymerisation. On bromination with a slight deficiency of bromine in *n*-hexane at -15°, it yields: (a) *trans*-1 : 4-dibromo- Δ^2 -cyclopentene, m. p. 45—46° (cf. Thiele, A., 1901, i, 181), oxidised by neutral permanganate in aqueous acetone to *trans*-1 : 4-dibromo-2 : 3-dihydroxycyclopentane, m. p. 75° (yield 52%), further oxidised by cold aqueous chromic acid to *r- $\alpha\alpha'$* -dibromoglutaric acid, m. p. 142° (yield 85%; cf. Thiele, *loc. cit.*); (b) *cis*-1 : 4-dibromo- Δ^2 -cyclopentene, b. p. 72°/5 mm., 82°/15 mm., d^{20}_D 1.9198 (cf. Thiele, *loc. cit.*), in small quantity, converted by neutral permanganate into *cis*-1 : 4-dibromo-2 : 3-dihydroxycyclopentane, m. p. 76° (mixed m. p. with *trans*-glycol about 45°), yielding *meso- $\alpha\alpha'$* -dibromoglutaric acid, m. p. 170° (cf. Thiele, *loc. cit.*), by further oxidation with cold aqueous chromic acid; (c) 1 : 2-dibromo- Δ^3 -cyclopentene, d^{20}_D 1.8867, yielding with neutral permanganate a syrupy dibromoglycol from which none of the isomeric 1 : 4-dibromoglycols could be separated, and this on oxidation with aqueous chromic acid gave a syrupy dibromo-acid together with a trace of *meso- $\alpha\alpha'$* -dibromoglutaric acid. The syrupy acid on treatment with zinc and acetic acid yields glutacetic acid; both the $\alpha\alpha'$ -dibromoglutaric acids yield glutaric acid on debromination with zinc and acetic acid (cf. Thiele, *loc. cit.*). The 1 : 2-dibromide is converted (with decomposition) by distillation into the solid 1 : 4-form to a small extent, but mainly yields the liquid 1 : 4-form. In hexane solution, with increasing dilution the proportion of solid 1 : 4-dibromide formed falls steadily; the effect of substituting chloroform for hexane is to reduce largely the proportion of solid 1 : 4-form, and to increase the total proportion of 1 : 4-dibromide in the product.

C. W. SHOPPEE.

Manufacture of *o*- and *p*-xylenes. I. G. FAR-
BENIND. A.-G.—See B., 1929, 123.

Alkyl esters of aromatic sulphonic acids as alkylating agents. W. M. RODIONOV [with ROMANOV and (MLLES.) VVEDENSKAJA, VIASKOV, FEDER-
NIKOV, FEDEROV, and TOURKOWSKAJA] (Bull. Soc. chim., 1929, [iv], 45, 109—121).—The action of ammonia on the arylsulphonyl esters previously described (A., 1926, 532) gives alkylamines in low yields, especially of ethylamine, methyl *p*-toluenesulphonate giving 30% of methylamine. Hydroxy-

aldehydes are readily alkylated with these reagents, monohydroxy-aldehydes giving higher yields than the dihydroxy-aldehydes. Phenyltrimethylammonium *p*-toluenesulphonate in methyl alcohol with sodium methoxide, after removal of sodium *p*-toluenesulphonate, when heated at 120° with vanillin, yields 88% of veratraldehyde, and with protocatechualdehyde 58.3%. Salicylaldehyde yields 72% of anisaldehyde, the *m*- and *p*-methoxyaldehydes being similarly obtained in 88% and 70% yields, respectively. Aliphatic alcohols did not react (cf. Schopf, A., 1927, 472) and with hydrazine, methyl *p*-toluenesulphonate reacts violently. Hydrastine benzenemethylsulphonate, m. p. 218° (yield quantitative), is converted quantitatively into methylhydrastine with 1% sodium hydroxide. Narceine and methyl *p*-toluenesulphonate when treated successively with potassium iodide and hydroxide yield *narceonic acid*, m. p. 207—208°. Allyl *p*-toluenesulphonate and aqueous potassium thiocyanate give about 40—43% of allylthiocarbimide.

Methyl β -naphthalenesulphonate, m. p. 56° (yield 82%), and methyl α -naphthalenesulphonate, m. p. 72—73° (yield 68—70%), are readily converted by dimethylaniline into the compounds, C₁₉H₂₂O₃NS, β - and α -naphthylphenyltrimethylammonium sulphonate, m. p. 206—208° and 161°, respectively. The corresponding ethyl α - and β -naphthalenesulphonates (yield 65—66%) and their compounds with dimethylaniline are oils. 1-Phenyl-3-methyl-5-pyrazolone and methyl naphthalenesulphonate give a similar oily additive product. All four sulphonates are effective alkylating agents. The compound derived from ethyl α -naphthalenesulphonate and dimethylaniline converts phenol into phenetole (88%), but not anisole. Morphine yields 75% of codeine. Naphthalene-1 : 5-disulphonyl chloride with methyl alcohol and sodium hydroxide is converted into methyl 1 : 5-naphthalenedisulphonate, m. p. 205°, which with dimethylaniline gives the additive compound, m. p. 262° (yield 70%), which converts morphine into codeine in 73—74% yield. Phenylbenzyltrimethylammonium chloride, analogous to these ammonium sulphonates, acts exclusively as a benzylating agent, converting morphine into peronine (yield 50%). The alkyl *p*-toluenesulphonates cannot be used as alkylating agents and give no quaternary compounds with tertiary bases. R. BRIGHTMAN.

Highly polymerised compounds. XIV. Polystyrene, a model of caoutchouc. H. STAUDINGER, M. BRUNNER, K. FREY, P. GARBSCH, R. SIGNER, and S. WEHRLI (Ber., 1929, 62, [B], 241—263; cf. this vol., 51).—Caoutchouc and polystyrene (formerly "metastyrene") must possess a similar structure, since both hydrocarbons yield very viscous, colloidal solutions in organic media. Investigation of the former compound is rendered difficult by its ready auto-oxidation, the uncertainty of the removal of impurities from the natural material without alteration of the structure of the product, and the incomplete identity of natural and synthetic caoutchoucs. Polystyrene represents a pure hydrocarbon in which the colloidal character cannot depend on impurities. The large molecules can be formed only by the linking of individual molecules to long chains; since the chains

are saturated, their union by normal valencies to three-dimensional molecules is excluded. The union occurs symmetrically, $\cdots \text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdots$. The molecules are not auto-oxidisable. Contrary to the views of Stobbe (A., 1910, i, 235; 1915, i, 660), the polystyrenes are mixtures of molecules of similar structure but varying length of chain. Styrene polymerises very slowly in the cold, increasingly rapidly as the temperature rises to 250° ; above 300° , depolymerisation occurs. The product obtained without the aid of heat is a very viscous, glassy mass which can scarcely be pulverised. It swells with organic solvents in which it dissolves very slowly. Its solubility is small, 2% solutions being very viscous. Polystyrenes prepared at higher temperatures are glasses which increase in brittleness with rise of temperature of preparation. At 240° , a readily powdered product is obtained. The solubility increases with rise of temperature of preparation, the easily-powdered products dissolving freely in ether without previous swelling. Cryoscopic determinations in benzene show that the mean mol. wt. of polystyrene mixtures diminishes with rise of temperature of preparation. The values 8000—10,000 have an accuracy of about 15%, whereas higher values are estimated and those above 15,000 cannot be determined. The relatively simpler products which do not exhibit characteristic colloidal properties are termed "hemicolloids," whereas those which swell and yield highly viscous solutions are designated "eucolloids." Hemicolloids similar to the mixtures obtained at 240° are also prepared by the polymerisation of styrene in dilute solution under the influence of tin tetrachloride and other halides. The product, mean mol. wt. 3000—4000, can be separated by suitable treatment with solvents into fractions, the most soluble of which have the lowest mol. wt. and temperature of liquefaction and give the least viscous solutions. In comparison with the paraffins, the free solubility of polystyrenes, mol. wt. 3000—10,000, in benzene or chloroform is very striking, but is attributed to their amorphous nature. Polymerisation of styrene at atmospheric temperature leads to very large molecules of estimated mean mol. wt. 10,000—200,000. It is assumed that these "macromolecules" are identical with the primary, colloidal particles. The large intermolecular forces of such macromolecules explain the sparing solubility, swelling power, and high viscosity in solution of the eucolloidal polystyrenes. When heated at temperatures up to 240° in an atmosphere of carbon dioxide, the complex polystyrenes are transformed into products giving solutions in benzene which have greatly diminished viscosity (η 370—1.8). Solutions of eucolloidal polystyrene diminish in viscosity as the temperature is raised: since the process is irreversible, a degradation of the molecules must be assumed. The less viscous solutions of hemicolloidal polystyrenes do not show any change in viscosity, since their molecules are relatively stable. The viscosity increases proportionally with the concentration, showing the single molecules to be mobile in solution. With polystyrenes of mean mol. wt. 10,000 and more the increase of viscosity is more than proportional to the concentration. With increase in mol. wt., solubility in the polystyrenes gradually gives place to swelling,

showing that there is probably no essential difference between the two processes. In the former, the smaller molecules become detached, solvatised, and dissolved. In the latter, the solvent first penetrates between the molecules and the single molecules only pass into solution when the process of solvatisation is complete. Swelling is therefore an intermolecular, not an intermicellar phenomenon (except with regard to substances like cellulose). Since polystyrenes which swell have a mean mol. wt. of about 100,000, it must be assumed that other complex compounds such as caoutchouc, albumin, cellulose derivatives, and starch, which also show this property, have very large molecules; substances of mol. wt. 3000—15,000 do not swell. The tenacity of hemicolloidal polystyrenes, mol. wt. 3000—10,000, is very slight, but increases with increasing mol. wt. The marked tenacity of eucolloidal polystyrenes must therefore be connected with the presence of very long molecules which are irregularly oriented, since the effect is the same in all directions. Polymerisation of styrene cannot occur in such a manner as to leave two terminal trivalent carbon atoms, for indications of their presence are not obtained in the relatively simple hemicolloids and the intermediate production of derivatives of α -methylstyrene is improbable, since it is less readily polymerised than styrene. The additive products formed under the influence of stannic chloride are formulated $\text{CHPh}\cdot\text{CH}_2\cdot[\text{CHPh}\cdot\text{CH}_2]_x\cdot\text{CHPh}\cdot\text{CH}_2$ ($x = 30\text{--}100$)

SnCl_4

and may be expected to be decomposed by water giving products with two terminal hydroxy-groups, the presence of which would not be easily detected in such large molecules. If, however, decomposition is effected by hydrogen chloride, methyl alcohol, or acetic acid, the presence of the readily characterised residues cannot be established. The terminal valencies, therefore, probably satisfy one another with production of many-membered rings. This accounts for their lack of ability to crystallise, since the molecules cannot arrange themselves in a lattice. As eucolloidal polystyrene is the terminal member of a polymeric-homologous series, so is caoutchouc the ultimate product of a polymeric-homologous series of polyrenes with a very high mean mol. wt. Pummerer's view that it is formed by association of a basal molecule, $(\text{C}_5\text{H}_8)_8$, is improbable. Meyer's view that caoutchouc is composed of micelles formed by the union of main valency chains of 50—100 isoprene groups is untenable in this form, since polystyrene chains of 50—100 units form hemicolloidal substances. Eucolloidal polystyrenes probably consist of about 1000 basal molecules united in a long chain by normal co-valencies, and the molecules of caoutchouc are of a similar order of magnitude. The macromolecules are identical with the primary colloidal particles. The size of the latter in benzene solution has been shown to be about 200,000 and this is regarded as a determination of mean mol. wt.

H. WREN.

Highly polymerised compounds. XV. Reduction of polystyrene. H. STAUDINGER, E. GEIGER, and E. HUBER (Ber., 1929, 62, [B], 263—267; cf. preceding abstract).—Polystyrene is reduced in the presence of nickel at 270° (under the same conditions

as caoutchouc) to *hexahydropolystyrene*. The primary action is a degradation of the larger to smaller molecules which are sufficiently active to permit reduction. At the ordinary temperature polystyrene is not reduced in presence of platinum, whereas styrene affords ethylcyclohexane. Hexahydropolystyrene is a colourless powder which is not attacked by concentrated sulphuric acid and does not give a coloration with tetranitromethane. It decomposes at 350–400°, giving a little hexahydrostyrene, but mainly di-, tri-, and tetra-meric hydrocarbons, whereas polystyrene at 300° gives styrene with a little distyrene. Cracking of hexahydropolystyrene is analogous to that of hydrocaoutchouc. Determinations in benzene show hexahydropolystyrene to be a hemicolloid of mean mol. wt. 3000–4000. It can be separated into more and less soluble portions distinguished by mol. wt. and viscosity. The reduction of polystyrene to hexahydropolystyrene is considered to place beyond doubt that in polystyrene the individual molecules are united in a long chain by normal co-valencies.

H. WREN.

Compounds of antimony trichloride and stannic chloride with unsaturated hydrocarbons. H. VON EULER and H. HELLSTROM (Svensk Kem. Tidskr., 1929, 41, 11–15; cf. A., 1928, 1405).—Mainly a discussion of the colour reactions of compounds of the carotin type with metallic chlorides. The coloured solution obtained by mixing 1 c.c. of a 20% chloroform solution of stilbene with 0.1 c.c. of a 20% stannic chloride solution shows an absorption band at 535–495 μ (max. 515 μ) and at 405 μ . The 95% alcoholic extract of cod-liver oil (lipoid fraction) gives the colour reaction with antimony trichloride twice as intensely as the original oil, the latter showing correspondingly diminished absorption. Dierygosteryl phosphate gives a characteristic colour with antimony chloride (A., 1928, 1406) and with stannic chloride, the latter being intensely red with a green fluorescence, with an absorption band at 434 μ . On dilution the colour changes to violet and then green (band at 620–640 μ) and finally a new band at 505–485 μ appears.

J. W. BAKER.

Diphenyl and its derivatives. III. Stereoisomerism of monophenylnaphthalene and dinaphthyl derivatives. IV. Considerations on the great number of optical antipodes without asymmetric atoms which can be derived [from diphenyl]. L. MASCARELLI (Gazzetta, 1928, 58, 791–800, 865–869; cf. this vol., 181).—Theoretical. Assuming that α - and β -phenylnaphthalenes may be regarded respectively as 2:3- and 3:4-disubstituted diphenyls, the nature of the further substitution necessary to impede free rotation of the phenyl group and thus give rise to stereoisomerism is discussed, together with the similar conditions for stereoisomerism in $\alpha\alpha$ -, $\beta\beta$ -, and $\alpha\beta$ -dinaphthyls.

E. W. WIGNALL.

Symmetry of naphthalene. K. LONSDALE (Proc. Leeds Phil. Soc., 1929, 1, 346–348).—A naphthalene molecule which, in agreement with X-ray investigations (Bragg, A., 1922, ii, 128), has a centre of symmetry only and accounts satisfactorily for the observed differences in the absorption spectra

of the ten dichloronaphthalenes (de Laszlo, A., 1928, 514) can be built up on the author's assumption (A., 1928, 1079) of an anisotropic carbon atom having two A and two B valencies. Such a molecule may have either a double linking in the 9:10-position, or a centric configuration. In this molecule all the four α -positions are identical, $\beta_2 = \beta_6$, $\beta_3 = \beta_7$, but $\beta_2 \neq \beta_3$.

J. W. BAKER.

Hydrogenation of fluorene under pressure with nickel or osmium as catalysts, together with traces of cerium and thorium oxides. V. S. SADIKOV and A. K. MICHAÏLOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1567–1573).—See A., 1928, 1235.

Pyrogenic dissociation of condensed ring systems. N. A. ORLOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1447–1458).—Tetrahydrophenanthrene when treated with hydrogen at 450–470°/70–170 atm. with an iron oxide catalyst gave a mixture of phenanthrene, tetrahydronaphthalene and its homologues, and benzene and its homologues. Similar products, together with free carbon, were obtained by heating tetrahydrophenanthrene with aluminium chloride at atmospheric pressure. Berginisation of retene gave small quantities of benzene hydrocarbons, naphthalene and its homologues, and methylphenanthrene. Coal-tar oil, under the same conditions, yielded a mixture of benzene and naphthalene hydrocarbons, together with some phenanthrene derivatives. Anthracene and aluminium chloride gave free carbon, hydrogenated products of anthracene, naphthalene, and its homologues. Fluorene, on berginisation, yielded much benzene, toluene, and higher homologues, together with unchanged fluorene and its hydrogenated products. It is concluded that the condensed nuclei hydrocarbons are first hydrogenated to the tetrahydro-derivatives, which are thus broken by the further action of hydrogen to alkyl derivatives of naphthalene and benzene. The presence of a catalyst, such as aluminium chloride, causes the reactions to take place at atmospheric pressure, the hydrogen being formed by the complete dehydrogenation of part of the hydrocarbons, with separation of free carbon. It is suggested that the formation of naphthalene and its derivatives in high-temperature coal tar is due to the cracking in the presence of hydrogen of the primary tars formed, which always contain the tetrahydro-derivatives of the condensed nuclei hydrocarbons. M. ZVEGINTZOV.

Benzopolymethylene compounds. XV. Composition, constitution, and synthesis of fluoranthene. J. VON BRAUN and E. ANTON (Ber., 1929, 62, [B], 145–151; cf. A., 1926, 1139; 1927, 666).—The conception of fluoranthene as a derivative of indene is not in harmony with the authors' experiments on the stability of ring systems. Since, however, the presence of an additional carbon atom to the molecule of fluoranthene or its quinone makes little difference in the analytical results, the possibility is suggested that it is actually a naphthalene derivative (I); this is shown to be the case by direct synthesis.



[With H. WAGNER.]—Ethyl dibenzofulvenecarb-

oxylate, from fluorenone, zinc, and ethyl bromoacetate, is very readily hydrogenated in the presence of nickel under pressure at 230° to ethyl 9-fluorenylacetate, b. p. 193—194°/12 mm., from which 9-fluorenylacetic acid, b. p. 218—220°/11 mm., is derived. 9-Fluorenylacetyl chloride, b. p. 194—196°/13 mm., from the acid and thionyl chloride, does not react with aluminium chloride in light petroleum at 60°. Ethyl fluorenylacetate is reduced by Ladenburg's method to fluorene and β -9-fluorenyl ethyl alcohol, b. p. 190—195°/13 mm., but the conversion of the alcohol through the corresponding bromide and cyanide into fluorenylpropionic acid does not occur readily. The sodio-derivative of ethyl 9-fluorene-carboxylate is smoothly converted by ethyl β -chloropropionate into the ester, $C_{12}H_9 > C(CO_2Et) \cdot CH_2 \cdot CH_2 \cdot CO_2Et$, b. p. 247°/14 mm., which is almost quantitatively hydrolysed and decarboxylated to β -9-fluorenylpropionic acid. The acid is transformed by thionyl chloride into the corresponding chloride, b. p. 180—185°/0.8 mm., m. p. 58—59°, which, when heated with aluminium chloride in light petroleum, affords 4-keto-1:2:3:4-tetrahydrofluoranthene, m. p. 98° (semicarbazone, m. p. 250—251°; oxime, m. p. 170—171°). Reduction of the ketone by Clemmensen's method yields 1:2:3:4-tetrahydrofluoranthene, b. p. 155°/0.7 mm., m. p. 69°, dehydrogenated by lead oxide to fluoranthene (9:10-benzoacene-phthene), m. p. 110°. H. WREN.

Preparation of perylene. C. MARSCHALK (Bull. Soc. chim., 1928, [iv], 43, 1388—1402).—When 2:2'-dinaphthol is heated with zinc, zinc chloride, or a mixture of these or with ferric chloride or aluminium chloride, yields of 2—12% of perylene are obtained, β -dinaphthylene oxide being the main product. With phosphoryl chloride and zinc at 100—200° some phosphine is evolved and an intermediate product is obtained which is insoluble in toluene, contains no chlorine, and is decomposed by potassium hydroxide into 2:2'-dinaphthol and phosphate. On distillation in presence of a little lime it affords perylene in yields up to 46.5%. The action of 1 mol. of phosphoryl chloride on 1 mol. of 2:2'-dinaphthol yields 2:2'-dinaphthol chlorophosphate, $(C_{20}H_{12}O_2) \cdot POCl_2$, 2 mols. of hydrogen chloride being evolved, from which the corresponding sodium phosphate and hydrogen phosphate, $(C_{20}H_{12}O_2) \cdot PO \cdot OH$, are obtained by hydrolysis with dilute sodium carbonate: the cyclic structure of these products is indicated by their stability towards boiling sodium hydroxide solution. When heated alone the dinaphthol chlorophosphate yields 12% of perylene, but on distilling with zinc and zinc chloride after previous heating at 270° for 14—2 hrs., yields of 46—55% of perylene are obtained. Similarly, when heated with zinc and zinc chloride the hydrogen phosphate gives 21% of perylene, only traces being formed on heating alone. With aluminium chloride in carbon tetrachloride, but not in nitrobenzene (cf. Scholl, A., 1922, i, 336) at the ordinary temperature or when heated at 100° in absence of solvent, the sodium dinaphthol phosphate yields 1:12-dihydroxyperylene phosphate (cf. Zincke and Dengg, A., 1922, i, 1013), converted by alkaline fusion into 1:12-dihydroxyperylene. With phosphorus trichloride 2:2'-dinaphthol gives a similar condensation product,

$C_{20}H_{12}O_2 \cdot PCl_3$, which is converted by sodium carbonate into a chlorine-free phosphate, and with zinc and zinc chloride affords 33% of perylene.

R. BRIGHTMAN.

Relationship between constitution and taste among some derivatives of carbamide. H. THATE (Rec. trav. chim., 1929, 48, 116—120).—The following substituted carbamides are obtained by the action of potassium cyanate on the requisite aniline hydrochloride: phenyl-, α -phenyl- α -methyl-, *v*-tolyl-, m. p. 176° (lit. 158° and 180°), α -*p*-tolyl- α -methyl-, m. p. 103°. α -Phenyl- α -methyl-, m. p. 156°, and α -*p*-tolyl- α -methyl-biurets, m. p. 167°, are formed as by-products with the corresponding carbamides. Whilst phenyl-carbamide is bitter, the remainder are sweet, showing that substitution of the imido-hydrogen atom by a methyl group has a sweetening influence (cf. Lorang, A., 1928, 285). H. BURTON.

Existence of dihydro- and octahydro-*p*-indole. E. FERBER (Ber., 1929, 62, [B], 183—195).—Repetition of the work of von Braun and Gavrilov (A., 1912, i, 497) fails to confirm the production of dihydro-*p*-indole. β -Phenylethyl chloride, b. p. 96°/23 mm., conveniently prepared by heating β -phenylethyl alcohol saturated with hydrogen chloride in sealed tubes at 140—160°, is converted by nitric acid (*d* 1.5) at -15° into a mixture of β -*p*-nitrophenylethyl chloride, m. p. 48—49°, β -*o*-nitrophenylethyl chloride, and small amounts of β -2:4-dinitrophenylethyl chloride, m. p. 136°. The *p*-nitro-compound is reduced by stannous chloride and hydrochloric acid to β -*p*-aminophenylethyl chloride hydrochloride, m. p. 209—210°, decomp. about 212° (corresponding chlorostannate and chloroplatinate, m. p. 192—193° after blackening). Contrary to von Braun (*loc. cit.*), the slow distillation of an ethereal solution of the base leaves the compound almost quantitatively unchanged, as does protracted treatment with boiling ethyl alcohol. When heated at 100—115°, the base affords products of high mol. wt. formed by external condensation. The liquid products obtained by nitration of β -phenylethyl chloride and consisting largely of the *o*-nitro-compound (see above) are reduced to β -*o*-aminophenylethyl chloride hydrochloride, m. p. 205°; the corresponding free base passes when its ethereal solution is distilled (more simply when the base is distilled with steam) into *o*-dihydroindole, b. p. 228—230° [nitroso-derivative, m. p. 81—82°; picrate, m. p. 172°; hydrochloride, m. p. 219° (subl.)]; benzenesulphonyl compound, m. p. 130—132°].

β -Phenylethyl acetate is converted by treatment with nitric acid (*d* 1.5) at -15° to -12° and subsequent hydrolysis of the product with methyl-alcoholic hydrogen chloride into β -*p*-nitrophenylethyl alcohol, m. p. 60—61° (benzoate, m. p. 105.5°), the constitution of which is confirmed by its formation from β -*p*-nitrophenylethyl chloride. The alcohol is reduced by zinc dust in presence of calcium chloride to β -*p*-aminophenylethyl alcohol, m. p. 108° (dibenzoyl derivative, $C_6H_5ONBz_2$, m. p. 136°; hydrochloride, m. p. 163°), converted by nitrous acid in presence of aqueous copper sulphate at 90° into β -*p*-hydroxyphenylethyl alcohol, m. p. 92—93° (dibenzoyl derivative, m. p. 111°), in 65% yield. The phytochemical conversion

of *p*-aminophenylethyl alcohol into the corresponding phenol could not be effected.

Hydrogenation of *p*-amino- or *p*-nitro-phenylethyl chloride by Skita's method in strongly acid solution affords β -*p*-aminocyclohexylethyl chloride, b. p. about 136° , d_4^{25} 1.0332, n_D^{25} 1.5036 [non-crystalline hydrochloride and picrate; chloroplatinate, m. p. 231° (decomp.)], with small amounts of α , δ -di-*p*-aminocyclohexyl-*n*-butane, b. p. about $312^\circ/720$ mm. (decomp.), d_4^{25} 0.9774, n_D^{25} 1.5077 (hydrochloride, m. p. 207°), and tertiary base. Intramolecular condensation to a perhydro-*p*-indole could not be effected. At 180 – 200° the compound is converted into a substance, $C_{24}H_{45}N_3$ [picrate, m. p. (indef.) 143° ; *p*-toluenesulphonyl derivative, m. p. 143° (indef., decomp.)], which appears to be a secondary amine. Hydrogenation of β -*p*-aminophenylethyl alcohol hydrochloride affords β -*p*-aminocyclohexylethyl alcohol, m. p. 77 – 85° , probably a mixture of *cis*- and *trans*-isomerides; the non-crystalline picrate and hydrochloride are described. H. WREN.

Sulphonic acids of 6-chloro-*o*-toluidine. I. G. FARBERIND. A.-G.—See B., 1929, 123.

Compounds of the higher oxy-acids of the halogens with benzidine. A. E. KRETOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1427–1433).—Chloric acid and benzidine in alcoholic solution give two compounds with 1 and 2 mols. of the acid to 1 mol. of benzidine, respectively. Bromic acid yields only one compound, with 2 mols. of the acid. Both the benzidine chlorate and the bromate can be titrated quantitatively with phenolphthalein as indicator, and explode on rapid heating. The iodate can be obtained by treating iodic acid with benzidine in acetic or hydrochloric acid solutions, and the reaction can be employed for the quantitative precipitation of iodic acid. All the salts are colourless, but darken on keeping. Perchloric acid and benzidine in equimolecular proportions in alcoholic solution give a blue salt, whilst if an excess of perchloric acid is present, a white salt is obtained. M. ZVEGINZOV.

Bis-semidine inversion in aromatic dihydrazo-compounds. B. C. GUHA and H. K. BANERJEE (J. Indian Inst. Sci., 1928, 11 A, 231–239).—The semidine inversion of several aromatic dihydrazo-compounds has been studied and the resulting diamines have been diazotised and coupled with various amines and phenols. *s*-Diphenylthiocarbohydrazide, prepared in greatly improved yield by heating phenylhydrazine phenyldithiocarbazine at 80° for 3–4 hrs., is converted by 3% hydrochloric acid at 60 – 65° into diaminodiphenylthiocarbamide (which could not be isolated either as the free base or its hydrochloride), giving a bisdiazo-compound which couples with the appropriate second component to yield thiocarbamidobisbenzeneazo- β -naphthol (sodium salt), m. p. 131 – 132° , dimethylaniline, m. p. 164 – 166° , resorcinol, m. p. 158° (explosively), and reacts with phenylthiocarbimide, phenylcarbimide, and formaldehyde to yield, respectively, diphenylthiocarbamidodiphenylthiocarbamide, $CS(NH\cdot C_6H_4\cdot NH\cdot CS\cdot NHPh)_2$, m. p. 182 – 183° , diphenylcarbamidodiphenylthiocarbamide, m. p. 238 – 240° , and dimethyleneaminodiphenylthiocarbamide, not melting below 300° . Similarly, inversion of diphenyl-

carbohydrazide (Skinner and Ruhrmann, A., 1888, 274) yields diaminodiphenylcarbamide (unstable) which is not identical with the *pp'*- or (stable) *oo'*-diamino-compound, since it diazotises and couples to yield carbamidobisbenzeneazo- β -naphthol (sodium salt, m. p. 131 – 132°), dimethylaniline, m. p. 160 – 161° , resorcinol, m. p. 157° (decomp.); and yields diphenylcarbamidodiphenylcarbamide, m. p. 236 – 238° , and dimethyleneaminodiphenylcarbamide, not melting at 300° , whilst the *pp'*-diaminodiphenylcarbamide couples with β -naphthol to give an azo dye, m. p. 263° , and reacts with phenylthiocarbimide to yield a diphenylthiocarbamidodiphenylcarbamide, different from those obtained from the inversion compound. Reduction of *pp'*-dinitrodiphenylthiocarbamide does not yield the corresponding *pp'*-diamino-derivative, since this seems to lose 1 mol. of hydrogen sulphide, the product being *p*-aminophenyl-*p*-phenyleneguanidine, $C_6H_4\langle\begin{smallmatrix} NH \\ NH \end{smallmatrix}\rangle C:N\cdot C_6H_4\cdot NH_2$, m. p. 295° (decomp.)

(isolated as its hydrochloride), identical with the product obtained by the loss of ammonia from the base obtained by hydrolysis of *pp'*-diacetamidodiphenylthiocarbamide (obtained by heating acetyl-*p*-phenylenediamine with carbon disulphide). By the usual methods it is converted into the sodium salt of *p*-phenyleneguanidinobenzeneazo- β -naphthol and phenylthiocarbamidophenyl-*p*-phenyleneguanidine, both m. p. above 300° . J. W. BAKER.

Azo-triarylmethane and azo-pyrone dye-stuffs (meta series). R. N. SEN and B. GHOSH.—See B., 1929, 89.

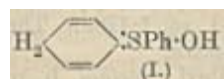
Formals and mixed carbonic esters. S. SABETAY and P. SCHVING (Bull. Soc. chim., 1928, [iv], 43, 1341–1345).—Chloromethyl ethers, obtained by saturating an alcoholic suspension of trioxymethylene with hydrogen chloride, with sodium derivatives of alcohols or phenols in ether, alcohol, or in benzene afford mixed formals. In some cases, e.g., benzyl alcohol and β -phenylethyl chloromethyl ether, heating without sodium or solvent is sufficient. β -Phenylethyl chloromethyl ether has b. p. 119 – $121.5^\circ/16$ mm., n_D^{25} 1.5227; β -phenylethyl cyanomethyl ether, b. p. 96 – $98^\circ/15$ mm., n_D^{25} 1.5416, d_4^{25} 1.067; benzyl chloromethyl ether, b. p. 102 – $102.5^\circ/14.5$ mm., d_4^{25} 1.5270 (cf. Hill and Keach, A., 1926, 271), and dicyclohexylformal, b. p. 139 – $140^\circ/14$ mm., d_4^{25} 0.9741, n_D^{25} 1.4702. The following β -phenylethyl methylene ethers, $CH_2Ph\cdot CH_2\cdot O\cdot CH_2\cdot OR$, are described; methyl, b. p. 102 – $103^\circ/13$ mm., n_D^{25} 1.4951, d_4^{25} 1.002; ethyl, b. p. 113 – $113.5^\circ/14$ mm., n_D^{25} 1.4846, d_4^{25} 0.9757; acetyl, b. p. 136 – $137^\circ/13$ mm., n_D^{25} 1.4950; isobutyl, b. p. 131 – $132^\circ/14$ mm., n_D^{25} 1.4793, d_4^{25} 0.9504; phenyl, b. p. 181 – $182^\circ/14$ mm., d_4^{25} 1.074, n_D^{25} 1.5501; *o*-tolyl, b. p. $190^\circ/14$ mm., n_D^{25} 1.5472, d_4^{25} 1.061, *m*-4-xylyl, b. p. 203 – $204^\circ/17$ mm., d_4^{25} 1.045; α -naphthyl, b. p. 213 – $215^\circ/2$ mm.; benzyl, b. p. 192 – $194^\circ/14$ mm., d_4^{25} 1.012, n_D^{25} 1.5436; guaiacyl, b. p. $207^\circ/12$ mm., n_D^{25} 1.5562; linolyl, b. p. 198 – $199^\circ/15$ mm., n_D^{25} 1.5120. Phenyl- γ -phenylpropyl methylene ether has b. p. $166^\circ/2$ mm., d_4^{25} 1.059, n_D^{25} 1.5451; phenyl benzyl methylene ether, b. p. $172^\circ/14$ mm., d_4^{25} 1.090, n_D^{25} 1.5560; benzyl methyl methylene ether, b. p. 95 – $97^\circ/16$ mm., n_D^{25} 1.4941, d_4^{25} 1.013. β -Phenylethyl chloroformate and

phenol in chloroform in presence of pyridine afford *phenyl β-phenylethyl carbonate*, m. p. 89°, b. p. 203°/15 mm. *α-Phenylpropyl ethyl carbonate*, b. p. 131—133°/14 mm., n_D^{20} 1.4858, is similarly prepared from *α-phenyl-*n*-propyl alcohol*. *β-Phenylethyl bromide*, phenol, and potassium hydroxide in presence of copper at 160° yield *phenyl β-phenylethyl ether*, b. p. 162—163°/14 mm., d_4^{20} 1.054, n_D^{20} 1.5706 (cf. Schorigin, A., 1925, i, 1404). R. BRIGHTMAN.

Nitration of methane- and ethane-sulphon-*p*-phenetidides. F. REVERDIN (Helv. Chim. Acta, 1929, 12, 113—121).—Methanesulphonyl chloride reacts with an aqueous suspension of *p*-phenetidine in presence of sodium carbonate, forming *methane-sulphon-*p*-phenetide*, m. p. 127° (*acetyl derivative*, m. p. 112°), which is nitrated in hot alcoholic solution by nitric acid (d 1.185) to *3-nitro-4-methanesulphonamidophenetole*, m. p. 100°. This is hydrolysed by cold concentrated sulphuric acid to *2-nitro-*p*-phenetidine*. Similar nitration with nitric acid, d 1.4, gives *3:5-dinitro-4-methanesulphonamidophenetole*, m. p. 176—177°. When nitration is effected by cold nitric acid (d 1.52) alone a small amount of *2:3:5-trinitro-4-methanesulphonamidophenetole*, m. p. 235° (not sharp, crystallographic data given), is obtained. Corresponding nitrations of *4-ethanesulphonamidophenetole*, m. p. 83° (*acetyl derivative*, m. p. 81°), yield *3-nitro-*, m. p. 91—92°, *3:5-dinitro-*, m. p. 182°, and *2:3:5-trinitro-4-ethanesulphonamidophenetole*, m. p. 229°, respectively. *2:5-Dinitro-4-ethanesulphonamidophenetole*, m. p. 166—167°, is obtained by the action of nitric acid (d 1.52) at -5° to 2° .

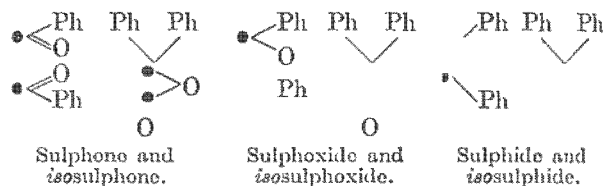
H. BURTON.

***iso*Phenyl sulphide and its derivatives.** O. HINSBERG (Ber., 1929, 62, [B], 127—135).—Phenyl sulphide reacts moderately violently with hot 70% perchloric acid containing a little glacial acetic acid, yielding the basic *perchlorate* of *isodiphenylsulphonium hydroxide*, $(C_{12}H_{10}S)_2.HClO_4.H_2O$, which usually contains a small proportion of more highly oxygenated and chlorinated compounds. It is converted by potassium iodide in presence of methyl alcohol into the basic *hydriodide*, $(C_{12}H_{10}S)_2.I.H_2O$; the *chloroplatinate*, $C_{48}H_{46}O_2S_4Cl_2Pt$, is described. The basic perchlorate is converted by methyl-alcoholic potassium hydroxide into the amor-



phous *isodiphenylsulphonium hydroxide* (I), which is unusually stable towards reducing agents. The base decomposes when heated at 280—350°, giving a yellow oil oxidised by hydrogen peroxide to a substance, m. p. 225° (see later), mainly diphenyl sulphone, m. p. 127°, and *isophenyl sulphone*; it consists therefore mainly of diphenyl sulphide. Distillation of the basic hydriodide proceeds similarly. The sulphonium base is converted by potassium hydroxide in boiling methyl alcohol into *isophenyl sulphide*, b. p. 300—340°/atmos. pressure (partial decomp.), which is isomerised to diphenyl sulphide when repeatedly distilled and transformed, apparently smoothly, by perchloric acid into *isodiphenylsulphonium perchlorate*. The *isosulphide* is transformed by an excess of hydrogen peroxide into the corresponding *sulphone*, $Ph.SO_2.Ph.0.5H_2O$, m. p. 81° [also (?)

+0.25MeOH, m. p. 83°], and by moderated oxidation into the non-crystalline *sulphoxide*, $C_{12}H_{10}OS$. The compound, m. p. 225°, is regarded as (?) *isophenoxthin sulphone*, $C_{12}H_8O_3S.0.5H_2O$. Since the usual structural and spatial formulae are inadequate for the full explanation of the observed isomerism, recourse is had to the atomic formulae of sulphur containing two valency centres, thus leading to the following expressions:



H. WREN.

Halogen derivatives of β-naphthol unsubstituted in position 1. C. MARSHALK (Bull. Soc. chim., 1928, [iv], 43, 1361—1367).—Halogen derivatives of β-naphthol with the 1-position unsubstituted are obtained by elimination of the *α*-amino-group from 1-amino-2-naphthol derivatives. Thus, *3-bromo-1-nitroso-β-naphthol* (Bromme, A., 1888, 490) is converted by sodium hyposulphite at 30—35° into *3-bromo-1-amino-β-naphthol*, which yields an insoluble *diazo-oxide*, reduced by sodium stannite to *3-bromo-β-naphthol*, m. p. 84—85°. *3-Chloro-1-nitroso-β-naphthol* (Zincke and Schmunck, A., 1890, 1146), obtained by the action of sulphuryl chloride on nitroso-β-naphthol in tetrachloroethane, and *3:4-dichloro-1-nitroso-β-naphthol* similarly yield *3-chloro-1-amino-β-naphthol*, *3-chloronaphthalene-1:2-diazo-oxide*, *3-chloro-β-naphthol*, *3:4-dichloro-1-amino-β-naphthol*, *3:4-dichloronaphthalene-1:2-diazo-oxide*, and *3:4-dichloro-β-naphthol* (cf. B., 1926, 869). The last-named is reconverted into *3:4-dichloro-1-nitroso-β-naphthol* by nitrous acid.

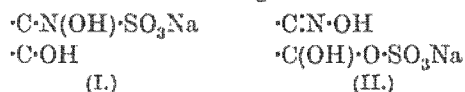
R. BRIGHTMAN.

Naphthalene series. I. Mechanism of the reaction of naphthalene derivatives with hydrogen sulphite. N. N. VOROSHOV [with A. G. KASSATIN] (Ber., 1929, 62, [B], 57—68).—Previous investigations of the interaction of hydrogen sulphites with phenols have usually involved such drastic treatment that no guarantee is afforded of the isolation of primary products (cf. Bucherer, A., 1904, i, 309; 1905, i, 48; Fuchs and Pirak, A., 1927, 53; Voroshev, A., 1917, i, 300). An instance of reaction under mild conditions is now recorded. β-Naphthol is treated with sulphuric acid (d 1.84) at a temperature which is finally raised to 42—45° and the product is diluted with ice and neutralised by chalk. The solution of calcium salts is saturated with sodium chloride, which causes an immediate separation of a mixture of sodium β-naphthol-1- and -6-sulphonates, whereas the -8-sulphonate separates more slowly. The mixed salts are treated with boiling 96% alcohol in which the -6-sulphonate is insoluble, whereas the -1-sulphonate dissolves. Addition of 50% sodium hydroxide to the alcoholic solution causes the precipitation of the *disodium* salt of β-naphthol-1-sulphonic acid. Saturation of a cold, aqueous solution of the salt with sulphur dioxide causes the precipitation of the

additive compound, $C_{10}H_8O \cdot S_2Na$, for which the sulphurous ester formula suggested by Bucherer for analogous cases is shown to be untenable. The hydrogen sulphite compound decomposes into its components in aqueous solution in a degree which increases with increasing dilution. Decomposition increases rapidly under the influence of hydroxyl ions even in the presence of alkalis as weak as sodium hydrogen carbonate. Addition of hydrogen ions increases the stability of the hydrogen sulphite compound in aqueous solution, even minimal quantities of acid retarding the decomposition. The graphs representing the equilibria of the hydrogen sulphite compound under the influence of dilution and on addition of hydroxyl and hydrogen ions are closely analogous to those of the similarly constituted compounds from benzene-azo- β -naphthol. Since, further, a series of analogies in chemical character between the hydrogen sulphite compounds of azonaphthol dyes and the colourless naphthol derivatives has been established (Voroshcov, *loc. cit.*) it appears that in both cases the reactive hydroxyl group is particularly important for the production of hydrogen sulphite compounds. Treatment of saturated solutions of the hydrogen sulphite compound of the sodium salt of β -naphthol-1-sulphonic acid with the chlorides of barium, copper, zinc, or mercury gives crystalline precipitates of new salts; in dilute solution, the sulphites of the heavy metals are precipitated. The barium, $C_{10}H_8O \cdot S_2Ba$, and the corresponding copper salt have been analysed.

H. WREN.

Naphthalene series. II. Action of sodium hydrogen sulphite on nitrosonaphthols. N. N. VOROSHOV and S. W. BOGDANOV (Ber., 1929, 62, [B], 68—80).—1-Nitroso- β -naphthol unites with sodium hydrogen sulphite giving the additive compound, $C_{10}H_8O \cdot NSNa$, thus excluding Bucherer's ester formula and indicating the structure I or II.



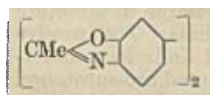
The properties of the compound agree with those recorded in the literature except that it does not appear to be decomposed into its components by acid, but converted into a brown compound soluble in alkali (cf. G.P. 82097). Since the action of sodium hydrogen sulphite on the methyl ether of 1-nitroso- β -naphthol, $O \cdot C_{10}H_7 \cdot N \cdot OMe$, gives an additive product, $C_{11}H_{10}O_5NSNa$, which is closely analogous in properties to that derived from 1-nitroso- β -naphthol, it may be assumed that the last compound reacts in the quinoneoxime form. Addition of sodium hydrogen sulphite to a solution of sodium 1-nitroso- β -naphthol-6-sulphonate followed by sodium hydroxide gives the pale green disodium salt of nitrosonaphtholsulphonic acid; the isolation of the hydrogen sulphite compound is difficult on account of its ready solubility, but its additive nature is placed beyond doubt by examination of the corresponding barium compound. Treatment of the mixture of 4- and 2-nitroso- α -naphthols with sodium hydrogen sulphite shows that only the 4-nitroso-compound is able to form an unstable hydrogen sulphite compound which has not been obtained homogeneous. A ready

means of separating these nitrosonaphthols from one another is thus afforded. Isolation of the 4-derivative from its hydrogen sulphite compound, after separation of the insoluble 2-nitroso- α -naphthol, is effected by addition of alkali hydroxide and subsequently of acid. Only those nitrosonaphthols react with hydrogen sulphite which resemble in structure the similarly active azo-compounds. The passive behaviour of 2-nitroso- α -naphthol finds its counterpart in that of the similarly constituted azo-substance. Ability to add hydrogen sulphite is found in those azo-, nitroso-, and sulphonic acid derivatives of naphthols in which these groups occupy the position 1, whilst the hydroxyl group is in the position 2 or 4. Naphthol derivatives in which the azo-, nitroso-, or sulphonic acid groups are in position 2 and the hydroxyl group in position 1 do not add hydrogen sulphite. The hydrogen sulphite compounds of the azo-compounds must therefore possess the same structure as those of the nitroso-derivatives and, since the ketone hydrogen sulphite formula has been established for the former, it must also be applied to the latter. The hydrogen sulphite compound of 1-nitroso- β -naphthol, therefore, has the constitution II.

H. WREN.

Nitroarylsulphuric acids and their reduction products. G. N. BURKHARDT and H. WOOD (J.C.S., 1929, 141—152).—The preparation of arylsulphuric acids from *o*-, *m*-, and *p*-nitrophenols and 1:4- and 1:2-nitronaphthols is described (cf. Burkhardt and Lapworth, A., 1926, 511). The arylsulphuric acids are prepared by addition of the appropriate phenol to a mixture of chlorosulphonic acid and dimethylaniline; the following potassium salts were prepared: potassium *o*-nitrophenyl sulphate, *p*-nitrophenyl sulphate, 1-nitro-2-naphthyl sulphate, and 4-nitro-1-naphthyl sulphate. Reduction of these by warm ferrous sulphate solution in the presence of precipitated calcium carbonate or barium carbonate gives the corresponding amino-compounds. The following are described: potassium *o*-aminophenyl sulphate, potassium *p*-aminophenyl sulphate (acids precipitate from aqueous solution the corresponding hydrogen *p*-aminophenyl sulphate), potassium *p*-benzylideneaminophenyl sulphate, $C_{13}H_{10}O_4NSK \cdot 0.5H_2O$, potassium *p*-acetamidophenyl sulphate, potassium 1-amino-2-naphthyl sulphate, $C_{10}H_8O_4NSK \cdot 0.5H_2O$; potassium 4-amino-1-naphthyl sulphate; hydrogen 4-amino-1-naphthyl sulphate. The potassium amino-aryl sulphates are all hydrolysed less readily by mineral acid than is potassium phenyl sulphate itself. By diazotisation and coupling are obtained: from hydrogen *p*-aminophenyl sulphate and resorcinol, potassium dihydroxybenzeneazophenyl sulphate, $C_{12}H_9O_6N_2SK \cdot 1.5H_2O$; from the same base and potassium β -naphthoxide potassium 2-hydroxynaphthaleneazophenyl sulphate, $C_{16}H_{11}O_5N_2SK \cdot 0.5H_2O$; from potassium *o*-aminophenylsulphate and potassium β -naphthoxide *o*-hydroxybenzeneazo- β -naphthol. Alkaline reduction of potassium *o*-nitrophenyl sulphate (either zinc dust and potassium hydroxide solution or sodium amalgam and water) gives potassium azobenzene 2:2'-disulphate, $(KO \cdot SO_2 \cdot O \cdot C_6H_4 \cdot N)_2 \cdot 0.5H_2O$ and potassium hydrazo-

benzene 2:2'-disulphate. The last-named compound, by treatment with hydrogen chloride, yields 4:4'-diaminodiphenylene dihydrogen 3:3'-disulphate, $C_{12}H_{10}N_2(SO_3H)_2 \cdot 2.5H_2O$ (potassium salt), which, by hydrolysis gives 3:3'-dihydroxybenzidine identical with the demethylation product of dianisidine.



Diacetyl-3:3'-dihydroxybenzidine, m. p. 292° (decomp.), is dehydrated by heating at 300°, giving the *dianhydro*-derivative (annexed formula), m. p. 164—165°. 4-Hydroxynaphthaleneazo- β -naphthol has m. p. 236° (lit. 228—229°).

R. J. W. LE FEVRE.

Synthesis of meso-alkyl and meso-aryl anthracene derivatives. V. E. DE B. BARNETT and N. F. GOODWAY (J.C.S., 1929, 20—23).—1:5-Dichloro-9-benzhydrylanthrone, m. p. 191° (prepared by boiling 1:5-dichloroanthrone with benzhydryl chloride and aqueous potassium hydroxide), gave, by reduction with either zinc dust and alcoholic potassium hydroxide or zinc dust and hydrogen chloride in acetic acid, 1:5-dichloroanthracene. Interaction, in ethereal solutions, with Grignard compounds gave (in low yield) the corresponding crystalline dihydroanthranols in the cases where halides of Et, Prⁿ, Prⁱ, Bu, *iso*-Bu, and *iso*amyl were employed. Higher yields were obtained from magnesium methyl, benzyl, and phenyl halides. These dihydroanthranols undergo facile transannular loss of benzhydryl rather than water with resultant formation of the corresponding 1:5-dichloro-9-alkylantracene.

The following m. p. of 10-substituted 1:5-dichloro-9-benzhydryldihydroanthranols are given: 10-methyl, 160°; ethyl, 140°; propyl, 185°; isopropyl, 170°; *n*-butyl, 182°; isobutyl, 212°; *iso*amyl, 193°; benzyl, 206°; phenyl, 259°. The last compound underwent change in boiling xylene solution to an isomeric compound, m. p. 271°; both isomerides lose benzhydryl with formation of 1:5-dichloro-9-phenylantracene. The isomerism may be due to a non-coplanar arrangement of the anthracene ring system such as suggested by Schlenk (A., 1928, 1031).

R. J. W. LE FEVRE.

Cholesterol. V. E. MONTIGNIE (Bull. Soc. chim., 1928, [iv], 43, 1403—1405).—When treated with an acetic acid solution of mercuric oxide, cholesterol yields α -hydroxycholestenol, m. p. 180° (Mauthner and Suida, A., 1896, i, 425), and resinous products. Only the acetate is obtained when cholesterol is heated with 10 mols. of acetic anhydride at 150°; with 1 mol. of camphoric acid at 190—200°, *cholesteryl camphorate*, $C_{30}H_{48}(CO_2C_{10}H_{16})_2$, m. p. 133—134°, is obtained. Perchloric acid at 100° acts as a dehydrating agent, giving β -cholesterylene, m. p. 193°, and α -cholesterylene, m. p. 79—80° (cf. A., 1927, 556, 969).

R. BRIGHTMAN.

Specific colour reaction for ergosterol and its transformation products. E. P. HAUSSLER and E. BRÄUCHLI (Helv. Chim. Acta, 1929, 12, 187—193).—The Tortelli and Jaffe colour reaction (A., 1914, ii, 822) appears to be specific for ergosterol and its derivatives. A positive reaction can be obtained with 1—1.5 mg. even in presence of cholesterol or phyto-sterol. Zymosterol (Maclea, A., 1928, 329) after

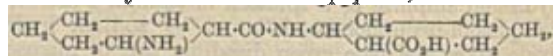
further purification from ether, or removal of admixed ergosterol by irradiation, has m. p. 105—107°, $[\alpha]_D^{25} +44.0^\circ$ in chloroform. It also gives the above colour reaction, but not so strongly as ergosterol, indicating that it might be an isomeride or a rearrangement product. Definite positive reactions are given by *iso*ergosteryl acetate, dehydroergosterol, and dehydroergosteryl acetate. From one attempt to prepare *iso*ergosteryl acetate a substance, m. p. 132—134°, $[\alpha]_D^{25} -170.9^\circ$ in chloroform, was obtained. This depresses the m. p. (133—135°) of *iso*ergosteryl acetate, and gives a positive colour reaction. Irradiation of a solution of ergosterol in olive oil for 3.5 hrs. causes a 50% diminution in the intensity of the colour; the decrease in colour of an irradiated benzene solution is of the same order after 4 hrs., but after 16 hrs. the original intensity is almost reached. Positive reactions were also given by the lipid from calf's bone-marrow, two specimens of linseed oil, poppy-seed and chaulmoogra oils, and the ether extract from *Meconium*.

The reaction is not given by cholesterol from various sources, or its derivatives, phytosterol, plant and animal lipoids, olive, cotton-seed, sesamé, nut, walnut, peach, sweet almond, soya-bean, castor, croton, hydnocarpus, and rapeseed oils, the sterols from gallstones, cholic, glycocholic, and taurocholic acids, and the bile acids from ox, pig, and human bile.

H. BURTON.

Norcarane. F. EBEL, R. BRUNNER, and P. MANGELLI (Helv. Chim. Acta, 1929, 12, 19—26).—When cyclohexene is treated at 88° with ethyl diazoacetate in presence of copper bronze 53% of ethyl *norcaranecarboxylate*, $C_4H_8 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{Et}$, b. p. 109—110°/18 mm., is obtained. This is hydrolysed by alcoholic potassium hydroxide to *norcaranecarboxylic acid*, m. p. 97°, the barium salt of which when distilled with barium and zinc oxides yields a mixture, b. p. 111—112°, of *norcarane*, b. p. 110°, and an unsaturated hydrocarbon (about 35%), separable by treatment with benzoyl peroxide. H. BURTON.

Products of the auto-condensation of ethyl hexahydroanthranilate and ethyl Δ^4 -tetrahydroanthranilate. F. P. MAZZA [with M. FERRAJOLO] (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 33, 229—236).—Gradual auto-condensation of ethyl hexahydroanthranilate yields *hexahydroanthranilic dipeptide anhydride*, $\text{CH}_2\text{CH}_2\text{CH}(\text{CO} \cdot \text{NH} \cdot \text{CH} \cdot \text{CH}_2\text{CH}_2) \text{CH}_2\text{CH}_2\text{CH}(\text{CO} \cdot \text{NH} \cdot \text{CH} \cdot \text{CH}_2\text{CH}_2) \text{CH}_2\text{CH}_2$, m. p. 300—305° (decomp.), which forms a *diacetyl* derivative, m. p. 210—211°, and is hydrolysed by aqueous potassium hydroxide to the *dipeptide*,



decomp. about 250°; this gives a *copper salt* (+2H₂O) and an *ethyl ester*, m. p. 102°. Δ^4 -Tetrahydroanthranilic dipeptide anhydride, m. p. about 280°, the *dipeptide*, m. p. 270°, and its *ethyl ester*, m. p. 106—108°, were also prepared.

T. H. POPE.

Salts of aromatic nitriles. II. Potassio-phenylacetoneitrile. M. M. RISING, I. E. MUSKAT, and E. W. LOWE (J. Amer. Chem. Soc., 1929, 51, 262—265; cf. A., 1928, 881).—Sodiophenylaceto-

nitrile has been previously described (Upson and Thompson, A., 1922, i, 343). Potassium powder and phenylacetonitrile in dry ether in an atmosphere of nitrogen yield yellow *potassiophenylacetonitrile*, which, like the sodio-derivative, reacts in tautomeric forms.

H. E. F. NOTTON.

Action of phthalic anhydride on triaminoresorcinol. M. COVELLO [with P. L. SCATOLOA] (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 33, 240—243).—*Triphthalylstyphnamine*,

$\left[\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{N} \right]_3 \text{C}_6\text{H}(\text{OH})_2 [1:3], \text{ m. p. above } 300^\circ$, prepared by heating triaminoresorcinol hydrochloride with phthalic anhydride in an atmosphere of carbon dioxide, gives, when treated with aqueous potassium hydroxide, *styphnaminotriphthalic acid*, $(\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH})_3\text{C}_6\text{H}(\text{OH})_2$, m. p. 235° , which forms a silver salt, an acetyl derivative, m. p. above 300° , and a benzoyl derivative, m. p. 275° , and yields phthalimide when oxidised by nitric acid.

T. H. POPE.

Resolution of *dl*-thyroxine. C. R. HARRINGTON (Biochem. J., 1928, 22, 1429—1435).—*Formyl-3:5-di-iodothyronine* (the term thyronine is used for de-iodothyronine), m. p. 207° , is prepared by treating the racemic di-iodothyronine with formic acid. The racemic formyl derivative was boiled with *l*-phenylethylamine and on cooling an optically impure salt separated, but the mother-liquor yielded fairly pure *formyl-1:3:5-di-iodothyronine*, $\text{C}_{24}\text{H}_{21}\text{O}_5\text{N}_2\text{I}_2$, m. p. 214° (decomp.), $[\alpha]_{\text{D}}^{25} +27.8^\circ$. This was converted by hydrobromic acid into *1:3:5-di-iodothyronine*, m. p. 256° (decomp.), $[\alpha]_{\text{D}}^{25} -1.3^\circ$, from which *l*-thyroxine, m. p. $235\text{—}236^\circ$, $[\alpha]_{\text{D}}^{25} -3.2^\circ$, was obtained by iodination (cf. Harrington and Barger, A., 1927, 358). The preparation of *d*-thyroxine, m. p. 237° (decomp.), $[\alpha]_{\text{D}}^{25} +2.97^\circ$, was carried out on similar lines. The *d*- α -phenylethylamine salt of the racemic formyl derivative of di-iodothyronine, m. p. $187\text{—}188^\circ$, $[\alpha]_{\text{D}}^{25} -21.9^\circ$, was converted into *formyl-d-3:5-di-iodothyronine*, m. p. 210° , $[\alpha]_{\text{D}}^{25} -26.9^\circ$, from which *d-3:5-di-iodothyronine*, m. p. 256° (decomp.), $[\alpha]_{\text{D}}^{25} +1.15^\circ$, was obtained and the latter was iodinated.

l-Tyrosine on iodination in ammonia yielded *3:5-di-iodotyrosine*, $[\alpha]_{\text{D}}^{25} +2.6^\circ$. *l*-Tyrosine does not suffer racemisation when reduced. *l*-Thyroxine is about three times as active physiologically as its *d*-isomeride.

S. S. ZILVA.

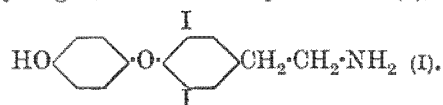
Derivatives of thyroxine. J. N. ASHLEY and C. R. HARRINGTON (Biochem. J., 1928, 22, 1436—1445).—Glycyl- and *dl*-alanyl-thyroxine have been prepared (a) by condensing chloroacetyl chloride and α -bromopropionyl chloride respectively with the methyl ester of *3:5-di-iodothyronine* followed by hydrolysis of the ester group and iodination, and (b) by condensing the acid chlorides with thyroxine methyl ester followed by hydrolysis of the ester group and treatment with ammonia. *3:5-Di-iodothyronine methyl ester hydrochloride*, m. p. 230° (decomp.), is prepared by treating the amino-acid in methyl alcohol with dry hydrogen chloride. From this compound the methyl ester, $\text{C}_{16}\text{H}_{15}\text{O}_4\text{NI}$, m. p. $174\text{—}175^\circ$, is obtained by neutralisation with sodium hydroxide. By condensing the ester with chloroacetyl chloride in

anisole, *chloroacetyl-3:5-di-iodothyronine methyl ester*, m. p. 160° , was prepared, which by hydrolysis with sodium hydroxide yielded *chloroacetyl-3:5-di-iodothyronine*, m. p. $166\text{—}168^\circ$. The latter compound when treated with ammonia gave *glycyl-3:5-di-iodothyronine*, $\text{C}_{17}\text{H}_{16}\text{O}_5\text{N}_2\text{I}_2$ (not melted definitely below 290°), which on iodination yielded *glycylthyroxine*, $\text{C}_{17}\text{H}_{14}\text{O}_5\text{N}_2\text{I}_4$. The following were the stages in the attempted synthesis of the alanyl derivative. *α -Bromopropionyl-3:5-di-iodothyronine methyl ester*, $\text{C}_{19}\text{H}_{18}\text{O}_5\text{NBrI}_2$, m. p. $161\text{—}162^\circ$, prepared in the same way as the corresponding chloroacetyl compound, by hydrolysis gave *α -bromopropionyl-3:5-di-iodothyronine*, m. p. $194\text{—}195^\circ$, which on treatment with ammonia gave *dl-alanyl-3:5-di-iodothyronine*, m. p. 207° . The iodination of the *dl*-alanyl derivative was not successful.

The second method of synthesis was carried out as follows. *Thyroxine methyl ester hydrochloride*, m. p. 221.5° (decomp.), obtained by treating thyroxine in methyl alcohol with dry hydrogen chloride, on hydrolysis gave *thyroxine methyl ester*, m. p. 156° ; this was condensed with chloroacetyl chloride in anisole, giving *chloroacetylthyroxine methyl ester*, m. p. $159\text{—}160^\circ$, and, by hydrolysis, *chloroacetylthyroxine*, m. p. $201\text{—}202^\circ$ (decomp.). *Glycylthyroxine*, m. p. $188\text{—}190^\circ$ (decomp.), identical with the product obtained by the first method, was prepared by heating the last with ammonia. Similarly, in the synthesis of the alanyl derivative the following compounds were prepared: *α -bromopropionylthyroxine methyl ester*, m. p. $199\text{—}201^\circ$ (decomp.); *α -bromopropionylthyroxine*, m. p. $193\text{—}194^\circ$ (decomp.); *alanylthyroxine*, m. p. $195\text{—}200^\circ$ (decomp.).

N-Lactylthyroxine, m. p. $199\text{—}200^\circ$ (decomp.), was prepared by treating with sodium hydroxide *N*-acetyl-lactylthyroxine methyl ester, $\text{C}_{21}\text{H}_{19}\text{O}_6\text{NI}$, obtained from acetyl-lactyl chloride and thyroxine methyl ester, in anisole.

The following amines were prepared: by heating *3:5-di-iodothyronine* with diphenylamine in a current of dry hydrogen, *3:5-di-iodothyronamine* (I), m. p.



$243\text{—}245^\circ$ (hydrochloride, m. p. $285\text{—}290^\circ$), and *thyroxamine*, $\text{C}_{14}\text{H}_{11}\text{O}_2\text{NI}$, m. p. 207° (decomp.) (chloroacetate, $\text{C}_{16}\text{H}_{14}\text{O}_4\text{NCl}$, m. p. 152°), by similar decarboxylation of thyroxine, as in the preceding preparation.

Glycyl-, *dl*-alanyl-, and *N*-lactyl-thyroxine are not more soluble in water than thyroxine and consequently do not possess a higher therapeutic value than the parent compound.

S. S. ZILVA.

Synthesis of esters of α - γ -dicyano- β -benzylglutaconic acid. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1928, 3, 316—320).—Phenylacetyl chloride condenses with ethyl sodiocyanoacetate in benzene solution with the formation of ethyl α -cyano- γ -phenylacetoacetate, which on ethylation with ethyl iodide afforded ethyl α -cyano- β -ethoxy- γ -phenylcrotonate (cf. Smith and Thorpe, J.C.S., 1907, 91, 1905). The condensation of the latter with ethyl

sodiocyanoacetate in ethyl-alcoholic solution gave the monohydrate of diethyl $\alpha\gamma$ -dicyano- β -benzylglutaconate, $\text{CO}_2\text{Et}\cdot\text{C}(\text{CN})\cdot\text{C}(\text{CH}_2\text{Ph})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, m. p. 131° , whilst methyl sodiocyanoacetate yielded the monohydrate of methyl ethyl $\alpha\gamma$ -dicyano- β -benzylglutaconate, m. p. about 115° . An isomeride of the last-named, m. p. about 115° , was produced by the condensation of methyl α -cyano- β -ethoxy- γ -phenylcrotonate and ethyl sodiocyanoacetate. In the above monohydrates, it is supposed that a cyano-group is hydrated to a carbamyl group.

A. I. VOGEL.

Phenylsuccinic acid series. IX. Resolution of *r*-diphenylsuccin- α - and β -naphthylamic acids into their optical antipodes. X. Racemisation phenomena observed during the action of water and bases on optically active diphenylsuccinic anhydrides. H. WREN and E. WRIGHT (J.C.S., 1929, 136—138, 138—141).—IX. *r*-Diphenylsuccin- α -naphthylamic acid, m. p. 217 — 219° (decomp.) (obtained by interaction of equivalent quantities of *r*-diphenylsuccinic anhydride and α -naphthylamine), was resolved into its optical antipodes by quinine in alcoholic solution, the salt of the *d*-acid being the more sparingly soluble. α -Diphenylsuccin- α -naphthylamic acid has m. p. 206 — 207° , $[\alpha]_D^{25} +205.8^\circ$ in acetone. *l*-Diphenylsuccin- α -naphthylamic acid, m. p. 206 — 207° , $[\alpha]_D^{25} -206.6^\circ$ in acetone, was separated by means of cinchonidine in alcohol from the crude *l*-acid obtained during resolution of the *r*-acid by quinine. α -Diphenylsuccin- α -naphthyl, m. p. 145° , $[\alpha]_D^{25} +139.2^\circ$ in acetone, $[\alpha]_D^{25} +123.3^\circ$ in chloroform (prepared by action of 3% ethyl-alcoholic hydrogen chloride on the corresponding acid), was readily racemised by alkali.

α -Diphenylsuccin- β -naphthylamic acid, m. p. 188° , $[\alpha]_D^{25} +386.9^\circ$ in acetone, was obtained by resolution of the corresponding *r*-acid, m. p. 201 — 202° , by quinine in alcoholic solution. α -Diphenylsuccin- β -naphthyl, m. p. 178 — 179° , $[\alpha]_D^{25} \pm 104.9^\circ$ in acetone, is described.

The marked diminution in specific rotation occasioned by conversion of the acids into the corresponding substituted imides and the irregularity of influence of aryl groups (β -naphthyl, phenyl, *p*-tolyl, α -naphthyl) on the specific rotations of the substituted diphenylsuccinamic acids and diphenylsuccinimides are pointed out.

X. The conversion of the active diphenylsuccinic anhydrides into the corresponding substituted amic acids by aniline, *p*-toluidine, α - or β -naphthylamine in cold benzene solution was not accompanied by any marked racemisation. The optical activity of the diphenylsuccinic acids which resulted from the action of water on the active anhydrides was found to be greatly influenced by the presence of a mutual solvent; thus from aqueous acetic acid, aqueous ether, aqueous acetone, and aqueous pyridine, acids were derived with the respective specific rotations -364.7° (from *l*-anhydride), $+232.7^\circ$, $+116.7^\circ$, and $+22.4^\circ$ (from *d*-anhydride) whereas the homogeneous acids had $[\alpha]_D \pm 383^\circ$. The partly racemised products always contained some mesodiphenylsuccinic acid. This was true also for the mixtures derived from *r*-diphenylsuccinic acid, although, in certain cases, the

proportion of meso-acid obtained from the *r*-anhydride greatly exceeded that derived from the active anhydrides under identical conditions. The authors consider, therefore, that even in dilute solution the *r*-compound does not behave as a simple mixture of *d*- and *l*-forms. *l*-Diphenylsuccin- β -naphthylamic acid, m. p. 188 — 188.5° , $[\alpha]_D^{25} -388.2^\circ$, is described.

R. J. W. LE FÈVRE.

Synthesis of isooipianic acid. S. N. CHAKRAVARTI and W. H. PERKIN, jun. (J.C.S., 1929, 193—196).—5-Nitro-2:3-dimethoxycinnamic acid (methyl ester, m. p. 154 — 155°) is obtained either by nitrating 2:3-dimethoxycinnamic acid or by condensing malonic acid and *o*-nitro-2:3-dimethoxybenzaldehyde in the presence of piperidine. It is smoothly reduced by ferrous sulphate and ammonia to *o*-amino-2:3-dimethoxycinnamic acid, m. p. 233° (decomp.), which is converted through the diazo-compound into *o*-cyano-2:3-dimethoxycinnamic acid, m. p. 251° . The cyano-acid is oxidised by potassium permanganate in presence of benzene to 5-cyano-2:3-dimethoxybenzaldehyde, m. p. 135° , which when heated with hydrochloric acid is converted into isooipianic acid.

R. J. W. LE FÈVRE.

Aldehydes from acetylenic carbinols. IV. 3-Methyl-6-isopropylcyclohexylideneacetaldehyde. H. RUPE and A. GASSMANN (Helv. Chim. Acta, 1929, 12, 193—204).—The action of acetylene on *d*-menthone in presence of benzene and sodamide yields 3-methyl-6-isopropyl-1-ethinylcyclohexan-1-ol, b. p. 101.5 — $102.5^\circ/12.5$ mm., $d_4^{25} 0.9257$, $[\alpha]_D^{25} +5.08^\circ$ (silver derivative), which when heated with 5 parts of 71% formic acid changes to 3-methyl-6-isopropylcyclohexylideneacetaldehyde (I), b. p. $111^\circ/12.5$ mm., $d_4^{25} 0.9115$, $[\alpha]_D^{25} +82.9^\circ$ (semicarbazone, m. p. 146 — 147°), the oxime, m. p. 101° , $[\alpha]_D^{25} +103.09^\circ$ in benzene, of which is hydrolysed by aqueous oxalic acid, forming menthone. Magnesium ethyl bromide converts I into a mixture of 3-methyl-6-isopropylcyclohexylethylcarbinol, b. p. $125^\circ/12$ mm., and α -3-methyl-6-isopropylcyclohexylidene- Δ^8 -butene, $\text{C}_{10}\text{H}_{18}\cdot\text{CH}=\text{CH}\cdot\text{CHMe}$, b. p. $99^\circ/12$ mm. Oxidation of I with alkaline potassium permanganate yields β -methyladipic and δ -isobutyryl- β -methyl-*n*-valeric acids (semicarbazone, m. p. 152°), whilst reduction with hydrogen and a nickel catalyst gives 3-methyl-6-isopropylcyclohexylacetaldehyde, b. p. 106 — $107^\circ/12$ mm., $d_4^{25} 0.9032$, $n_D^{20} 1.46111$, $[\alpha]_D^{25} -51.28^\circ$, purified through its semicarbazone, decomp. 222° (oxime, m. p. 102° , $[\alpha]_D^{25} +34.11^\circ$), together with the corresponding alcohol.

H. BURTON.

Arylidene 2:4-diphenylsemicarbazones from aldehydephenylhydrazones and phenylcarbinide. G. MINUNNI and S. D'URSO [with S. GUGLIELMINO, P. SALANITRO, D. TORRISI, and M. VASTA] (Gazzetta, 1928, 58, 808—820).—The interaction of benzaldehydephenylhydrazone and phenylcarbinide to give benzaldehyde-2:4-diphenylsemicarbazone, $\text{CHPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NHPH}$ (cf. Busch and Walter, A., 1903, i, 522), proceeds readily in benzene solution. In hot solution, the semicarbazone (new m. p. 174 — 175°) and some *s*-diphenylcarbamide are obtained; in the cold the former is produced more slowly, but in better yield, together with two yellow secondary products, one, a mixture, having m. p.

175—188°, and the other m. p. 194—196°. The semicarbazone is readily reduced to *s*-diphenylcarbamide, with a substance, m. p. 116—118°; when treated with phenylhydrazine it yields benzaldehyde-phenylhydrazone and other products.

o- and *m*-Nitrobenzaldehyde-phenylhydrazones do not react satisfactorily in benzene; with phenylcarbamide alone the corresponding semicarbazones are formed, m. p. 190—192° (decomp.) and 206—208° (decomp.), respectively, identified by reduction to the carbamides. The *p*-isomeride reacts very slowly in benzene, and more rapidly without solvent, giving the corresponding semicarbazone, m. p. 199—201°; piperonalphenylhydrazone gives, in cold benzene, piperonal-2:4-diphenylsemicarbazone, m. p. 169—169.5° (decomp.). E. W. WIGNALL.

Action of bromine on some hydrazones. II. R. CIUSA and P. MEGA (Gazzetta, 1928, 58, 831—840).—The compound described by Ciusa and Vecchiotti (A., 1916, i, 437) as *p*-bromobenzaldehyde-2:4-dibromophenylhydrazone is found to be ω -bromobenzaldehyde-2:4-dibromophenylhydrazone, since its aliphatic bromine atom will react with aniline, or can be determined by titration after boiling with sodium acetate in alcohol; the formation of *p*-bromobenzoic acid during oxidation must be attributed to bromination during the oxidation process, since benzoic acid is also formed. Similarly, anisaldehyde gives rise to ω -bromoanisaldehyde-2:4-dibromophenylhydrazone, m. p. 135°, and benzaldehyde-*p*-nitrophenylhydrazone to benzaldehyde-2-bromo-4-nitrophenylhydrazone, m. p. 171°; in each of these compounds the bromine may be determined as above, the second giving, with sodium acetate and acetic acid, the *O*-acetyl derivative of *N*-benzoyl-*N'*-2-bromo-4-nitrophenylhydrazine. The benzoyl group of the last compound may be removed by boiling with hydrochloric acid and alcohol, giving rise to 2-bromo-4-nitrophenylhydrazine, m. p. 143° (benzaldehyde-2-bromo-4-nitrophenylhydrazone, m. p. 166°). *m*-Nitrobenzaldehyde-*p'*-nitrophenylhydrazone is brominated to ω -bromo-*m*-nitrobenzaldehyde-2-bromo-4-nitrophenylhydrazone, m. p. 212—213°, from which the above hydrazine may again be prepared. Finally, the same hydrazine is synthesised by brominating the benzoyl derivative of *p*-nitroaniline, hydrolysing the product, and diazotising and reducing the 2-bromo-4-nitroaniline thus obtained. E. W. WIGNALL.

Trichloro- and tetrabromo-nitrobenzaldehydes, hexachloro- and octabromo-indigotins. C. VAN DE BUNT (Rec. trav. chim., 1929, 48, 121—146).—3:4:5-Tribromocinnamic acid, m. p. 215—216°, and its 2-nitro-derivative, m. p. 264—265° (decomp.), are obtained from the corresponding benzaldehydes by the Perkin reaction. Treatment of both these acids with warm absolute nitric acid yields 3:4:5-tribromo-2- ω -dinitrostyrene, m. p. 228—230° (decomp.), which could not be reduced successfully to tribromoindeole (cf. van der Lee, A., 1926, 179). When 3:4:5-tribromobenzaldehyde is treated with a mixture of absolute nitric and concentrated sulphuric acids at 100°, 3:4:5-tribromo-2:6-dinitrobenzoic acid, m. p. 245—248° (decomp.), is obtained. When crystallised from boiling alcohol this acid elimin-

ates carbon dioxide, yielding 4:5:6-tribromo-1:3-dinitrobenzene. Chlorination of *p*-aminobenzaldehyde hydrochloride in 75% acetic acid solution gives 3:5-dichloro-4-aminobenzaldehyde, m. p. 144° [phenylhydrazone, m. p. 156—157°; *p*-nitrophenylhydrazone, m. p. 288—289° (decomp.); semicarbazone, m. p. 248—250° (decomp.); semioxamazone, m. p. 269—270°; azine, m. p. 285—286°], chlorinated further to 2:4:6-trichloroaniline, and converted by the Sandmeyer reaction into 3:4:5-trichlorobenzaldehyde, m. p. 90—91° [phenylhydrazone, m. p. 147°; *p*-nitrophenylhydrazone, m. p. 342° (decomp.); semicarbazone, m. p. 252—254°, resolidifying with m. p. 284°; semioxamazone, m. p. 297—298° (decomp.); azine, m. p. 289—289.5°]. Nitration of this with cold absolute nitric acid yields 3:4:5-trichloro-2-nitrobenzaldehyde (I), m. p. 118.5—119° [phenylhydrazone, yellow and red, m. p. 229° (decomp.), modifications; *p*-nitrophenylhydrazone, m. p. 293—294° (decomp.); semicarbazone, m. p. 278—279° (decomp.); semioxamazone, m. p. 303—304° (decomp.); azine, m. p. 287—288° (decomp.)], oxidised by alkaline potassium permanganate to 3:4:5-trichloro-2-nitrobenzoic acid, m. p. 181—181.5°, and converted by absolute nitric and concentrated sulphuric acids into 3:4:5-trichloro-2:6-dinitrobenzoic acid, m. p. 219—221.5°. This acid also eliminates carbon dioxide in boiling alcoholic solution, forming 4:5:6-trichloro-1:3-dinitrobenzene. 3:4:5-Trichlorobenzoic acid has m. p. 210—210.5° (lit. 203°).

Nitration of 2:3:4:5-tetrabromobenzaldehyde with a mixture of absolute nitric and concentrated sulphuric acids at 50—60° affords 3:4:5:6-tetrabromo-2-nitrobenzaldehyde (II), m. p. 225—227° (decomp.) after previous darkening and sintering, whilst oxidation with potassium permanganate gives 2:3:4:5-tetrabromobenzoic acid, m. p. 234° (slight decomp.). This last compound is nitrated to 3:4:5:6-tetrabromo-2-nitrobenzoic acid, m. p. 238—240° (decomp.), which does not lose carbon dioxide when its alcoholic solution is boiled. 2:4-Dichloro-3:5-dibromobenzaldehyde, m. p. 110—111°, prepared by the Sandmeyer reaction from the 2-chloro-4-amino-compound, is nitrated to 4:6-dichloro-3:5-dibromo-2-nitrobenzaldehyde (III), m. p. 198—199°.

Conversion of the halogeno-2-nitrobenzaldehydes into the polyhalogenated indigotins is effected by warming with acetone and sodium hydroxide solution. Thus, 5:5':6:6':7:7'-hexachloro-, 4:4':5:5':6:6':7:7'-octabromo-, and 4:4':6:6':7:7'-tetrachloro-5:5':7:7'-tetrabromo-indigotins are obtained from I, II, and III, respectively.

H. BURTON.

Products with an odour of musk and carbon rings containing a large number of linkings. L. RUZICKA (Bull. Soc. chim., 1928, [iv], 43, 1145—1173).—A lecture surveying recent work on the constitution of muscone and civetone, and the synthesis and behaviour of carbon ring systems containing a large number of linkings (cf. A., 1926, 614, 615, 726, 727, 1142; 1927, 1189; 1928, 642, 887). In further elucidation of the constitution of muscone, it is shown that neither the *d*- β -methyltridecane- α -dicarboxylic acid, m. p. 69°, obtained by condensation with benzaldehyde and treatment of the benzylidene-

muscone with ozone and chromic acid nor its methyl ether can be racemised, and the inactivity of the mixture of two acids, $C_{15}H_{30}O_3$, obtained by oxidation of muscone is consequently due to mutual compensation of the two acids. Muscone is thus regarded as *l*-2-methylcyclopentadecanone (cf. A., 1926, 1143). *dl*-2-Methyltridecane-2 α -dicarboxylic acid obtained by synthesis has m. p. 76° (anilide, m. p. 133°), but shows no depression of m. p. when mixed with the degradation product of muscone. The molten acid on solidifying has m. p. 10° lower. Oxidation of exaltone with persulphuric acid affords the lactone of *o*-hydroxypentadecanoic acid (exaltolide).

R. BRIGHTMAN.

3 : 5-Diphenylcyclohexenone. A. D. PETROV (J. Russ. Phys. Chem. Soc., 1928, 60 1441—1445).—The reactions of 3 : 5-diphenylcyclohexenone with hydrogenating and dehydrogenating agents have been investigated. By hydrogenating the ketone at 240°/50 atm. in presence of nickel oxide as catalyst, 1 : 3-dicyclohexylcyclohexane was obtained in two isomeric forms, m. p. 66° and b. p. 202°/14 mm., respectively. By heating the ketone at 300° in presence of platinised charcoal, 3 : 5-diphenylphenol, m. p. 88—92°, was obtained, whilst reduction with absolute alcohol and metallic sodium gave a 50% yield of 3 : 5-diphenylcyclohexanol, m. p. 127°, easily oxidised to 3 : 5-diphenylcyclohexanone, m. p. 139—140°.

M. ZVEGINTZOV.

Use of zirconium tetrachloride in organic synthesis. P. KRISHNAMURTI (J. Madras Univ., 1928, [Reprint], 5 pages).—Zirconium tetrachloride may be used in place of aluminium chloride in condensations involving (a) elimination of hydrogen chloride (preparation of acetophenone, benzophenone, anisaldehyde, and diphenylmethane), (b) elimination of water (phenolphthalein), (c) elimination of alkyl halide (demethylation of anisole), and (d) condensations of phenylcarbimide with benzene and its derivatives. It is more easy to handle and more readily preserved than the older reagent.

J. W. BAKER.

Reduction of phenyl naphthyl ketones by the binary system, magnesium-magnesium iodide. W. E. BACHMANN and R. V. SHANKLAND (J. Amer. Chem. Soc., 1929, 51, 306—309).—Phenyl α -naphthyl ketone is reduced by the above system to an equilibrium mixture (I) of the green *ketyl* $-CPh(C_{10}H_7) \cdot OMgI$, and its *dimeride*, which is converted by water into $\alpha\beta$ -diphenyl- $\alpha\beta$ -di- α -naphthylethylene glycol (II), m. p. 220° (decomp.). When heated with acetyl chloride this is almost quantitatively converted into *benzoylphenyldi- α -naphthylmethane*, m. p. 216—217°, the naphthyl group wandering in preference to the phenyl. The second $\alpha\beta$ -diphenyl- $\alpha\beta$ -di- α -naphthylethylene glycol, m. p. 158° (Cohen, A., 1919, i, 124, 210), may be transformed into II by treatment with a Grignard reagent, when the radical formed by dissociation of the resulting iodomagnesium glycoloxide changes into I and is then decomposed by water. The second isomeride is converted by acetyl chloride into a substance, $C_{24}H_{24}O$, m. p. 232°, which is also formed from phenyl α -naphthyl ketone, zinc, and acetyl chloride and, unlike most pinacolins, is only slightly

attacked by boiling alcoholic potassium hydroxide. Phenyl β -naphthyl ketone is reduced by the binary system, or by zinc and acetic acid to $\alpha\beta$ -diphenyl- $\alpha\beta$ -di- β -naphthylethylene glycol, m. p. 175°, which undergoes naphthyl wandering in presence of acetyl chloride, giving *benzoylphenyldi- β -naphthylmethane*, m. p. 181—182°.

H. E. F. NOTTON.

Organic compounds of sulphur. XI. Comparison of the tendency of polymeric thioketones towards dissociation with that of the corresponding compounds of the ethane series. A. SCHONBERG (Ber., 1929, 62, [B], 195—199; cf. A., 1928, 896, 1375).—Replacement of the phenyl groups of hexaphenylethane by hydrogen or methyl causes a stabilisation of the ethane linking; the same effect is observed when the phenyl groups of the hypothetical hexaphenyltrithian are substituted by hydrogen or methyl. In both series the effect of hydrogen is more marked than that of methyl. If two phenyl groups of triphenylmethyl are replaced by the substituted methylene residue, radicals are obtained which cannot exist "free"; this is also the case with thioketones. Complete or partial replacement of the phenyl groups of hexaphenylethane by the radicals, $p\text{-OMe}\cdot C_6H_4\cdot$, $Ph\cdot C_6H_4\cdot$, $C_6H_4\cdot <O> C_6H_4\cdot$, $o\text{-OMe}\cdot C_6H_4\cdot$, $NMe_2\cdot C_6H_4\cdot$, $C_6H_4\cdot <S> C_6H_4\cdot$, leads to compounds with a tendency towards dissociation similar to or greater than that of hexaphenylethane itself. As expected, replacement of the phenyl groups of thiobenzophenone by these radicals leads to compounds which, like thiobenzophenone, do not tend to polymerise. In the ethane series, the substituted vinyl group behaves similarly to the phenyl group; this is also the case with thioketones. If one or two phenyl groups of thiobenzophenone are replaced by substituted vinyl groups, thioketones are produced which do not tend to polymerise. On the other hand, attempts to convert cyclohexanone into the corresponding thioketone give trithiocyclohexanone, which does not become depolymerised when heated. The close analogy can be explained only by the hypothesis that the dissociation of ethanes and polymeric thioketones is produced and regulated by the same causes.

H. WREN.

Benzoinanililide and benzoin-*p*-tolil-*p*-toluidide as ammono-benzoin acetals. H. H. STRAIN (J. Amer. Chem. Soc., 1929, 51, 269—273).—The formulation of these compounds as ammono-acetals of benzoin (cf. A., 1928, 1134) is in accordance with the following reactions. Benzoinanililide is hydrolysed by boiling alcoholic hydrochloric acid to benzoinanilide and aniline, and benzoin-*p*-tolil-*p*-toluidide to benzoin-*p*-toluidide and *p*-toluidine. They are nitrised by iodine in liquid ammonia, or in benzene by a current of air, to the ammono-benzils, benzildianil and benzildi-*p*-tolil. Ammonolysis by liquid ammonia at 130° for 10 hrs. affords a small yield of tetraphenylpyrazine, m. p. 252°. The mechanism proposed by Bischler (A., 1893, i, 519) for the formation of 2 : 3-diphenylindole from benzoin and aniline is confirmed by the almost quantitative conversion of benzoinanililide into this compound in benzene in presence of hydrogen chloride at 180—200°.

Benzoin-*p*-tolil-*p*-toluidide similarly yields 2:3-di-phenyl-5-methylindole. H. E. F. NOTTON.

Persistence of optical activity during elimination of water from optically active glycols. II. Production of optically active ketones by semipinacolinic transformation. R. ROGER and A. MCKENZIE (Ber., 1929, 62, [B], 272—284).—Ethyl *l*-mandelate is converted by magnesium benzyl chloride into *d*-2-hydroxy-2-phenyl-1:1-dibenzylethanol, m. p. 136—137°, $[\alpha]_D^{25} +80.3^\circ$ in ethyl alcohol, $[\alpha]_D^{25} +62.3^\circ$ in chloroform, $[\alpha]_D^{25} +96.8^\circ$ in acetone. The glycol is converted by concentrated sulphuric acid into *r*- α -diphenyl- γ -benzylacetone, m. p. 74.5—75.5°; this product is also obtained when the action is effected by boiling, dilute sulphuric acid, but is then accompanied by *d*- α -diphenyl- γ -benzylacetone, m. p. 77—78°, $[\alpha]_{589}^{25} +208^\circ$ in benzene, $[\alpha]_{589}^{25} +202^\circ$ in chloroform (among other values), and 1-phenyl-2-benzylindene, m. p. 100—102°, which appears to become isomerised to a product, m. p. 95—96°, when crystallised repeatedly from ethyl alcohol. The optically active ketone is racemised by concentrated sulphuric acid or by alcoholic potassium hydroxide; the latter change appears to be unimolecular. *d*-Methyldeoxybenzoin is likewise racemised by concentrated sulphuric acid. The first phase of the elimination of water from the *d*-glycol appears to consist of a semipinacolinic transformation yielding the *d*-ketone which, after transitory production of the sulphuric ester of the corresponding substituted vinyl alcohol, passes into the optically inactive ketone. The observation that triphenylacetaldehyde is converted by acids into phenyldeoxybenzoin suggests the possibility that aldehydes are intermediate products in the transformation of glycols to ketones in acid media (cf. Danilov and Venus-Danilova, A., 1927, 460; Tiffeneau and Orékhov, A., 1926, 171, 172). In the present instance and that recorded by McKenzie and Denler (A., 1927, 243), the intermediate formation of the corresponding aldehyde is impossible, since the compound would be optically inactive owing to the absence of an asymmetric carbon atom and thus could not give rise to an optically active ketone. The preservation of optical activity during the formation of the *d*-ketone has its parallel in the elimination of the amino-group from optically active amino-alcohols (cf. McKenzie, Roger, and Wills, A., 1926, 610). It is suggested that in this transformation an electric charge plays the part of a group, so that the dissymmetry of the molecule remains undisturbed.

l-Benzoin is transformed by magnesium benzyl chloride into 1-benzylhydrobenzoin (1- β -hydroxy- α - β -diphenyl- α -benzylethanol), m. p. 183—184.5°, $[\alpha]_{589}^{25} -61^\circ$ in chloroform, $[\alpha]_{589}^{25} -22^\circ$ in acetone (among other values), which is converted by protracted action of boiling acetyl chloride into 2:3-diphenylindene, m. p. 176—177°, isomerised by alcoholic potassium hydroxide to 1:2-diphenylindene, m. p. 107—108°; the last-mentioned compound is not affected by the protracted action of boiling acetyl chloride.

H. WREN.

Elimination of the amino-group from tertiary amino-alcohols. V. Semipinacolinic de-amination and Walden inversion. A. MCKENZIE and

A. K. MILLS (Ber., 1929, 62, [B], 284—288; cf. A., 1927, 457).—Ethyl *l*-phenylaminoacetate hydrochloride is converted by magnesium benzyl chloride into *d*- β -amino- β -phenyl- α -dibenzylethanol, $(\text{CH}_2\text{Ph})_2\text{C}(\text{OH})\cdot\text{CHPh}\cdot\text{NH}_2$, m. p. 144—145°, $[\alpha]_D^{25} +59.2^\circ$ in chloroform, which is transformed by sodium nitrite in dilute acetic acid solution into a mixture of *d*- α -diphenyl- γ -benzylacetone, m. p. 77.5—78°, $[\alpha]_D^{25} +283^\circ$ in benzene, and *d*- β -hydroxy- β -diphenyl- α -dibenzylethanol, m. p. 136—137°, $[\alpha]_D^{25} +81^\circ$ in ethyl alcohol, identical with the product obtained by Roger and McKenzie (preceding abstract). A further instance in favour of the semipinacolinic transformation and against the intermediate production of an aldehyde is afforded, since phenyldibenzylacetaldehyde could not yield an optically active ketone. H. WREN.

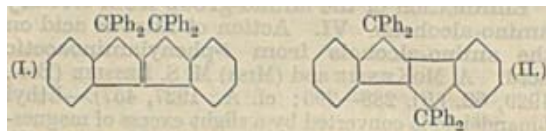
Elimination of the amino-group from tertiary amino-alcohols. VI. Action of nitrous acid on the amino-alcohols from *l*-phenylaminoacetic acid. A. MCKENZIE and (MISS) M. S. LESSLIE (Ber., 1929, 62, [B], 288—295; cf. A., 1927, 457).—Ethyl *l*-mandelate is converted by a slight excess of magnesium ethyl bromide into 1- β -hydroxy- β -phenyl- α -diethylethanol, m. p. 48—48.5°, $[\alpha]_D^{25} -26^\circ$ in ethyl alcohol, $[\alpha]_D^{25} -32^\circ$ in acetone. From ethyl *l*-phenylaminoacetate hydrochloride and magnesium ethyl bromide, 1- β -amino- β -phenyl- α -diethylethanol hydrochloride, m. p. 225—226°, $[\alpha]_D^{25} -28.7^\circ$ in water, $[\alpha]_D^{25} -17^\circ$ in ethyl alcohol, is derived. The amino-alcohol is converted by nitrous acid into a mixture of *r*- β -hydroxy- β -phenyl- α -diethylethanol, m. p. 88—89°, and a substance which is dextrorotatory in ethyl alcohol; the optical activity cannot be ascribed to the ketone, $\text{Et}\cdot\text{CO}\cdot\text{CHPhEt}$, formed by semipinacolinic deamination, since it persists unchanged after addition of alcoholic potassium hydroxide.

Ethyl *r*-phenylaminoacetate hydrochloride is transformed by magnesium methyl iodide into *r*- β -amino- β -phenyl- α -dimethylethanol, m. p. 82.5—83.5° (hydrochloride, m. p. 173—175°), from which methyl α -phenylethyl ketone is obtained by means of nitrous acid. The dissimilar course of the change in the cases of the dimethyl and diethyl derivatives is attributed to the superior saturating capacity of the methyl group, which causes a less firm union of hydroxyl to carbon in the methyl compound. Somewhat unexpectedly, *r*- β -amino- β -phenyl- α -di-*n*-propylethanol hydrochloride, m. p. 210—212° (from ethyl *r*-phenylaminoacetate hydrochloride and magnesium *n*-propyl bromide), is converted by nitrous acid into *r*- β -hydroxy- β -phenyl- α -di-*n*-propylethanol, m. p. 100—102°. Ethyl *d*-mandelate and magnesium *n*-propyl bromide afford *d*- β -hydroxy- β -phenyl- α -di-*n*-propylethanol, m. p. 67—68°, $[\alpha]_D^{25} +26.4^\circ$ in ethyl alcohol. 1- β -Amino- β -phenyl- α -di-*n*-propylethanol, m. p. 120—121°, $[\alpha]_D^{25} -93.4^\circ$ in ethyl alcohol (from ethyl *l*-phenylaminoacetate hydrochloride and magnesium *n*-propyl bromide), is transformed by nitrous acid into a mixture of *r*- and *d*- β -hydroxy- β -phenyl- α -di-*n*-propylethanol; the presence of the corresponding optically active ketone is excluded, since the activity of the product remains unchanged after treatment with alcoholic potassium hydroxide. H. WREN.

Phenylindene series. I. 3:3-Diphenylhydrindone. C. MOUREU, C. DUFRAISSE, and P. M. DEAN (Bull. Soc. chim., 1928, [iv], 43, 1367—1371).— $\beta\beta\beta$ -Triphenylpropionic acid, m. p. 179—180°, obtained in 76% yield by condensing triphenylcarbinol with malonic acid in presence of acetic anhydride at 170—180° (cf. Fosse, A., 1907, i, 764), is converted into 3:3-diphenylhydrindone, m. p. 129—130° (*oxime*, m. p. 155—156°), when warmed with sulphuric acid below 70°.

R. BRIGHTMAN.

Phenylindene series. II. Conversion of 3:3-diphenylhydrindone into 2:3-diphenylindone. C. MOUREU, C. DUFRAISSE, and F. BAYLOCC (Bull. Soc. chim., 1928, [iv], 43, 1371—1380).—To obtain confirmation of the structure advanced for rubrene (A., 1928, 53, 594, 628, 996, 1127) the synthesis of the isomeric hydrocarbons I and II from 3:3-diphenylhydrindone has been attempted. The



action of phosphorus pentabromide on 3:3-diphenylhydrindone or on its monobromo-derivative, m. p. 154—155°, gives a dibromo-derivative, m. p. 205°,

$C_6H_4 \cdot CPh_2 \cdot CBr_2CO$, in which the methylene hydrogen atoms are substituted, and accordingly the acetylene,

$C_6H_4 \cdot CPh_2 \cdot C \equiv C$, cannot be obtained by the usual methods. Phosphorus tribromide converts the dibromo-ketone into a substance, m. p. 143—144°, neither the tetrabromide $-CBr_2 \cdot CBr_2-$, nor the dibromide, $-CBr \cdot CBr-$, being obtained. When heated at 200°, 3:3-diphenylhydrindone, and its mono- and dibromo-derivatives are converted into 2:3-diphenylindone (yield 75% with the monobromo-ketone), the yield being improved in presence of sulphur with unsubstituted and of iron with the dibromo-ketone, a transformation which throws doubt on the structure of 3:3-diphenylhydrindone. Amyl nitrite and sodium ethoxide in alcohol convert the latter into an oximino-derivative, m. p. 220°, which with acetic acid and nitrosyl sulphate (cf. Bouveault and Locquin, A., 1904, i, 847) affords a substance (N 7.98%), m. p. 164—165° (decomp.), and not the expected diketone. $\beta\beta\beta$ -Triphenylpropionyl chloride, m. p. 120°, in presence of aluminium chloride in carbon disulphide at 50° is converted into 3:3-diphenylhydrindone. The yields of 2:3-diphenylindone claimed by Orekhov (A., 1920, i, 235) on heating the dibromide (m. p. 154—155°; cf. Stobbe and Niedenzu, A., 1902, i, 103) of benzylidenedecybenzoin were not obtained.

R. BRIGHTMAN.

Phenylindene series. III. Derivatives of 2:3-diphenylindone. C. MOUREU, C. DUFRAISSE, and M. BADOCHÉ (Bull. Soc. chim., 1928, [iv], 43, 1381—1388).—With phosphorus pentachloride at 165—170° 2:3-diphenylindone gives (yield 61%) a dichloro-derivative, $C_{21}H_{14}OCl_2$, m. p. 132—133°, from which with copper in benzene or magnesium in ether 2:3-diphenylindone is regenerated. Alcoholic potassium hydroxide removes only half of the chlorine,

yielding a substance, m. p. 148—160°. Sodium in ether yields a substance, $C_{21}H_{16}O_2$, m. p. 127—128°, identical with that obtained, together with a substance, $C_{21}H_{16}O$, m. p. 87—88° (cf. Schlenk and Bergmann, A., 1928, 1031), by the action of sodium on 2:3-diphenylindone. The former, $C_{21}H_{16}O_2$, with phosphorus pentoxide or zinc chloride loses 1 mol. of water and is re-converted into 2:3-diphenylindone, but its structure is undetermined. The second compound is also obtained by the action of iron and acetic acid on 2:3-diphenylindone or its dichloro-derivative, and is possibly stereoisomeric with Schlenk and Bergmann's compound. When heated with lead oxide it is converted into 2:3-diphenylindone.

R. BRIGHTMAN.

Diphthalimidobenzoquinones. M. COVELLO [with S. PALMA] (Rend. Accad. Sci. fis. mat. Napoli, 1928, [in], 34, 149—151).—2:3-, 2:5-, and 2:6-Diphthalimidoquinols, m. p. 250—300° (decomp.), obtained by condensation of the corresponding diaminoquinols with phthalic anhydride, yield, when oxidised with nitric acid (*d* 1.4): 2:3-, m. p. 320°; 2:5-, m. p. 305°, and 2:6-diphthalimidobenzoquinone, m. p. 277°.

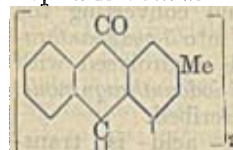
T. H. POPE.

Dehydration of o-benzoylbenzoic acid. A. H. GLEASON and G. DOUGHERTY (J. Amer. Chem. Soc., 1929, 51, 310—315).—Many substances, all of which are inferior to sulphuric acid, have been tried as catalysts in the condensation of benzoylbenzoic acid to anthraquinone. In presence of 96% sulphuric acid (6—10 parts) the reaction is unimolecular at 65—85° and k_{t+10}/k_t is greater than 3. Using 86—96% sulphuric acid, the reaction velocity is proportional to the initial concentration of the acid. Methyl, ethyl, and isopropyl o-benzoylbenzoates are converted into anthraquinone by sulphuric acid with approximately equal ease, the yield being slightly lower than from the free acid. Esters of the higher alcohols give poor yields. The acetate of enolic benzoylbenzoic acid condenses as readily as does the free acid itself. These results are explained by assuming that all the above compounds are rapidly transformed by sulphuric acid into the hydrogen sulphate of enolic benzoylbenzoic acid, which then passes with measurable velocity into a sulphuric acid additive product of anthraquinone. The smaller reaction velocity observed with the esters is due to the action of the alcohols on part of the sulphuric acid.

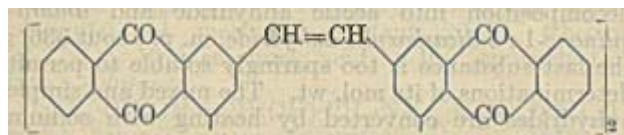
H. E. F. NOTTON.

Anthracene derivatives. III. Derivatives of 2-methylantraquinone and anthraflavone. P. RUGGLI and E. MERZ (Helv. Chim. Acta, 1929, 12, 71—99).—Bromination of 1-iodo-2-methylantraquinone in nitrobenzene solution at 160—170° gives 1-iodo-2-dibromomethylantraquinone, m. p. 210°. The crude bromination product can be freed from the monobromomethyl derivative by warming with pyridine, when some 1-iodo-2-anthraquinonylmethylpyridinium bromide is formed. Similarly, the crude bromination product of 1-nitro-2-methylantraquinone affords 1-nitro-2-anthraquinonylmethylpyridinium bromide, m. p. 262—269° (decomp.), together with the unaffected 2-dibromomethyl derivative. When 5:6:7:8-tetrachloro-2-dibromomethylantraquinone is treated with copper powder (Naturkupfer C) in

boiling nitrobenzene solution, *s-di*-(5:6:7:8-tetrachloro-2-anthraquinonyl)ethylene, m. p. above 300°, is obtained; no 1:1'-dianthraquinonyl derivative is formed by elimination of chlorine. 4-Bromo-1-amino-2-methylanthraquinone is converted by the usual method into 1-bromo-3-methylanthraquinone (I), m. p. 199—200°, which when treated with *p*-toluenesulphonamide in presence of amyl alcohol, anhydrous sodium acetate, and a trace of copper acetate yields 1-*p*-toluenesulphonamido-3-methylanthraquinone, m. p. 232—233°. This is hydrolysed by warm concentrated sulphuric acid to 1-amino-3-methylanthraquinone, m. p. 193°. Treatment of I with *p*-toluidine and anhydrous potassium acetate affords 1-*p*-toluidino-3-methylanthraquinone, m. p. 174—175°, whilst interaction with sodium sulphide in 80% alcoholic solution and atmospheric oxidation of the resulting violet solution yields 3:3'-dimethyl-1:1'-dianthraquinonyl disulphide. This is oxidised by concentrated nitric acid, giving 3-methylanthraquinone-1-sulphonic acid + 2H₂O (potassium salt), which when treated with hydrochloric acid and sodium chlorate affords 1-chloro-3-methylanthraquinone (II), m. p. 186—188°. When I is treated with copper powder in boiling nitrobenzene solution, 3:3'-dimethyl-1:1'-dianthraquinonyl, m. p. 354—355°, is produced. When a solution of this last compound in concentrated sulphuric acid is treated with copper powder at 55°,



3:3'-dimethylhelianthrone (3:3'-dimethylmesobenzdianthrone) (annexed formula), not melted at 300°, is obtained. Bromination of I in nitrobenzene solution at 150—160° gives 1-bromo-3-dibromomethylanthraquinone, m. p. 214—215°, which when treated with copper powder furnishes 4:4'-dianthraflavone,



m. p. above 300°. Similar bromination of II yields 1-chloro-3-dibromomethylanthraquinone, m. p. 223—224°, which with copper powder yields *s-di*-(4-chloro-2-anthraquinonyl)ethylene, m. p. above 300°.

Treatment of 4-bromo-2-methylanthraquinone-1-diazonium sulphate with potassium thiocyanate gives 1:4-dithiocyno-2-methylanthraquinone (III), m. p. 250—251°, which is converted by hot aqueous-alcoholic potassium hydroxide solution into 1:4-dithiol-2-methylanthraquinone, isolated as the diethyl ether, m. p. 195—205° (dibenzyl ether). Oxidation of III with boiling concentrated nitric acid affords 2-methylanthraquinone-1:4-disulphonic acid, + 3H₂O (potassium salt), converted by treatment with hydrochloric acid and sodium chlorate into 1:4-dichloro-2-methylanthraquinone, m. p. 185—186°. This on bromination yields 1:4-dichloro-2-dibromomethylanthraquinone, m. p. 180—181°, whilst treatment with *p*-toluenesulphonamide in presence of amyl alcohol, anhydrous sodium acetate, and a trace of copper acetate gives 1:4-di-*p*-toluenesulphonamido-2-methylanthraquinone, m. p. 206—207°. Hydrolysis of this

with hot concentrated sulphuric acid affords 1:4-diamino-2-methylanthraquinone, m. p. 246—248°.

H. BURTON.

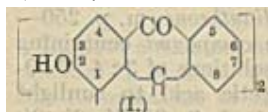
Inductive method for study of natural products. I. Naturally occurring anthraquinone derivatives. P. C. MITTER and H. BISWAS (J. Indian Chem. Soc., 1928, 5, 769—778).—Examination of the naturally occurring substituted anthraquinones shows empirically that not more than four groups are present in the benzene rings. Not more than three of these groups are hydroxyl and only one is methyl, hydroxymethyl, or carboxyl. Two of the substituents occupy α -positions and two (including methyl, hydroxymethyl, or carboxyl) occupy β -positions. If both β -substituents are in one ring then the other groups are in the same nucleus, but if they are in different rings the α -substituents are arranged symmetrically. Four fundamental types of anthraquinone derivatives are postulated, viz., 1:2:3-trihydroxy- (chayroot), 1:2:4-trihydroxy-3-methyl- (madder), 1:3:8-trihydroxy-6-methyl- (emodin), and 1:2:5-trihydroxy-6-methyl- (morindone). The products actually isolated from different plants conform, except in one or two doubtful cases, to the above types. The alizarin grouping occurs in three of the types.

1:5-Dimethoxy-6-methylanthraquinone, m. p. 176—177°, is demethylated by heating with a saturated solution of hydrogen chloride in acetic acid at 190—200°, to 1:5-dihydroxy-6-methylanthraquinone, m. p. 190° (diacetyl derivative, m. p. 230°), which resembles morindadiol (Oesterle and Tisza, A., 1908, ii, 527) in its colour reactions. Condensation of hemipinic anhydride with toluene in presence of aluminium chloride and treatment of the resulting 2-*p*-toluoylbenzoic acid derivative with boric and fuming sulphuric acids on the water-bath yields 1-hydroxy-2-methoxy-6-methylanthraquinone, m. p. 200° (acetyl derivative, m. p. 170°). This is demethylated by heating with aluminium chloride at 220° to 6-methylalizarin, m. p. 220° (acetyl derivative, m. p. 190°).

H. BURTON.

Reduction products of hydroxyanthraquinones.

X. R. W. HARDACRE and A. G. PERKIN (J.C.S., 1929, 180—193).—The dihydroxyhelianthrone (I) obtained from 3-hydroxyanthranol by gentle oxidation gives, after acetylation followed by halogenation in pyridine solution, 3:3'-di-iodo-2:2'-diacetoxyhelianthrone, m. p. 268—270° (decomp.), or 3:3'-dibromo-2:2'-diacetoxyhelianthrone. Monoiododihydroxyhelianthrone (Haller and Perkin, A., 1924, i,



301; Perkin and Yoda, A., 1925, i, 1160) cannot have an 8'-iodine atom (as previously supposed) because exposure of 3-iodo-2:2'-diacetoxyhelianthrone in

benzene solutions to sunlight caused formation of iododiacetoxynaphthodianthrone, m. p. above 340°, without elimination of iodine.

Treatment of 2-hydroxyanthraquinone with bromine and sodium hydroxide solution gives 1-bromo-2-acetoxyanthraquinone, m. p. 182—183°, and 1-bromo-2-hydroxyanthraquinone, m. p. 185—187° (methyl ether, m. p. 247°); the benzoyl derivative of the last compound, m. p. 229—230°, yields, when heated in

naphthalene solution with copper powder, 2:2'-dihydroxy-1:1'-dianthraquinonyl (similar treatment of 1-chloro-2-benzoyloxyanthraquinone, m. p. 228—230°, gave smaller yields), identical with the chromic acid oxidation product from dihydroxyhelianthrone (I), which is therefore the 2:2'-compound.

The action of excess of sodium hypobromite on 2-hydroxyanthraquinone gives 1:3-dibromo-2-hydroxyanthraquinone, m. p. 216—217° (acetyl derivative, m. p. 195°; methyl ether, m. p. 226—227°), mild fusion of which with 40% sodium hydroxide in an autoclave gives 3-bromoalazarin.

2:2'-Dihydroxy-1:1'-dianthraquinonyl by reduction with boiling aqueous ammonia and zinc dust gives, after acetylation, 3:9-diacetoxyanthracene, m. p. 157—158°, and tetra-acetyl-2:2'-dihydroxy-1:1'-dianthranolyl, m. p. 267—268°, which by chromic acid-acetic acid oxidation gives 2:2'-diacetoxy-1:1'-dianthraquinonyl. 2:2'-Dihydroxy-1:1'-dianthranolyl has m. p. about 290° (blackening at 270°). Reduction of 1-chloro-2-hydroxyanthraquinone by sulphuric acid and aluminium powder gives chlorodiacetoxyanthracene, m. p. 167—168°, and chlorohydroxyanthranol, m. p. 230°. Similarly 3-iodo-2-hydroxyanthraquinone, m. p. 278—279° (acetyl derivative, m. p. 224—225°; methyl ether, m. p. 228—229°) (prepared by direct iodination in pyridine solution), gives only 2-iodo-3-hydroxyanthranol, m. p. 239—240° (diacetyl derivative, m. p. 196°), which with ammonia and a trace of copper under pressure yields 3-amino-2-hydroxyanthraquinone (?), decomp. above 300°. 3-Iodo-2-benzoyloxyanthraquinone, m. p. 185°, when boiled in naphthalene solution with copper powder, gives 3:3'-diacetoxy-2:2'-dianthraquinonyl, m. p. 315°.

Oxidation of the diacetyl derivative of 2-iodo-3-hydroxyanthranol by ferric chloride in acetic acid solution gives 2:2'-di-iodo-3:3'-dihydroxydianthrone, m. p. 267—268° [previous darkening at 255°; diacetyl derivative, m. p. 227—228°, darkening at 215°; tetra-acetyl derivative, m. p. 293—295° (the following compounds with solvents were isolated: acetone, $C_{36}H_{24}O_8 \cdot I_2 \cdot 2C_3H_6O$, m. p. 200—220°; alcohol, $C_{36}H_{24}O_8 \cdot I_2 \cdot C_2H_6O$)]. Oxidation of 2:2'-di-iodo-3:3'-dihydroxydianthrone by alkaline potassium ferricvanide gives, after acetylation, 2:2'-di-iodo-3:3'-diacetoxydianthraquinone, whilst similar treatment using alkaline potassium persulphate gives 3:3'-di-iodo-2:2'-diacetoxyhelianthrone, m. p. 268—270°. Acetylanthrapurpurinanthranol is oxidised by ferric chloride in acetic acid solution to 3:4:6:3':4':6'-hexa-acetoxydianthrone, m. p. 250—251°, accompanied by a blue compound containing combined iron. Exposure of solutions of 3:4:6:9-tetra-acetoxyanthracene in acetic acid to sunlight results in slow formation of 3:4:6:9:3':4':6':9'-octa-acetoxydianthranol, m. p. 239—240°. The tetra-acetyl derivative of 3:3'-dihydroxydianthranol crystallises with benzene and chloroform of crystallisation. $C_{36}H_{20}O_8 \cdot C_6H_6$, m. p. 145—177°; $C_{36}H_{20}O_8 \cdot CHCl_3$, m. p. 161°. R. J. W. LE FEVRE.

Anthraquinone-1:5-dicarboxylic acid and certain simple and mixed anthraquinonecarboxylic anhydrides. R. SCHOLL, S. HASS, and K. H.

MEYER [with W. WINKLER, C. SEER, O. DISCHENDORFER, S. BRISSEMDJI, and W. MESSE] (Ber., 1929, 62, [B], 107—115).—1:5-Dichloroanthraquinone is converted by treatment with *p*-toluenesulphonamide, potassium carbonate, and copper acetate in nitrobenzene into 1:5-di-*p*-toluenesulphonamidoanthraquinone, m. p. 310—311°, transformed by concentrated sulphuric acid at 50—60° into 1:5-diaminoanthraquinone, m. p. 318—319° (corr.). The diamine, which must be homogeneous, is diazotised in concentrated sulphuric acid and the crystalline bisdiazonium sulphate is transformed in the usual manner into 1:5-dicyanoanthraquinone, m. p. about 390° (decomp.) after darkening at 370°. Hydrolysis of the dinitrile with sulphuric acid or, preferably, with sodium hydroxide affords anthraquinone-1:5-dicarboxylic acid, which gradually becomes red above 300° but does not melt below 390°. Purification of the crude acid is most simply effected by boiling with nitric acid (d 1.35), which attacks and dissolves only the impurities. The potassium, calcium, and pyridinium salts are described. The acid is transformed by phosphorus pentachloride and phosphoryl chloride into anthraquinone-1:5-dicarboxyl chloride, m. p. 260—263° (decomp.), from which methyl anthraquinone-1:5-dicarboxylate, m. p. 236°, is derived. An alternative method for the preparation of anthraquinone-1:5-dicarboxylic acid consists in diazotising 5-aminoanthraquinone-1-carboxylic acid in sulphuric acid and converting the greenish-yellow diazonium sulphate into 5-cyanoanthraquinone-1-carboxylic acid, which is hydrolysed with 20% sodium hydroxide. 1:5-Di-iodoanthraquinone, m. p. 308—309°, is incidentally described.

Anthraquinone-1:5-dicarboxylic acid is transformed by boiling acetic anhydride into acetic anthraquinone-1:5-dicarboxylic anhydride, $C_{14}H_6O_5(CO \cdot OAc)_2$, m. p. about 202°, with incipient decomposition into acetic anhydride and anthraquinone-1:5-dicarboxylic anhydride, m. p. about 336°; the last substance is too sparingly soluble to permit determinations of its mol. wt. The mixed and simple anhydrides are converted by heating with sodium hyposulphite in water or acetic acid into the red anthraquinol-1:5-dicarboxylic dilactone (to be described later). Similarly, anthraquinone-1-carboxylic acid and acetic anhydride afford acetic anthraquinone-1-carboxylic anhydride, m. p. 188—190°, which decomposes at about 220° into acetic anhydride and anthraquinone-1-carboxylic anhydride, m. p. 285—287°. Acetic 2-methylantraquinone-1-carboxylic anhydride, m. p. 173°, and 2-methylantraquinone-1-carboxylic anhydride, m. p. 268.5° (decomp.), are described. The simple and mixed anhydrides give olive-green solutions when treated with sodium amalgam in absolute alcohol. The simple structure is assumed for the mixed anhydrides, but the ultimate decision between this and a hydroxylactone constitution can be made only on spectroscopic evidence. H. WREN.

Oxidation of anthracene by nitrogen oxides. M. A. ILINSKI, B. V. MAKOROV, and N. V. ELIGIN.—See B., 1929, 88.

Anthraquinone solutions in sulphuric acid. P. I. SOKOLOV and V. P. DREVING.—See B., 1929, 88.

substance, as well as all four solutions of crude and pure caoutchouc, underwent appreciable change of viscosity, this change being the greater the higher is the b. p. of the solution. It follows that the caoutchouc undergoes degradation at fairly low temperatures, whereas guttapercha withstands higher temperatures. Degradation of caoutchouc in boiling xylene produces gummy products, mol. wt. about 4200, whilst guttapercha gives powdery products (mol. wt. about 2500). Both products are regarded as being lower members of the two different series of which caoutchouc and guttapercha respectively are complex members (evidence: both products contain one ethylenic linking per isoprene unit). At the higher temperature of boiling tetrahydronaphthalene, further degradation does not occur, although cyclisation of the open-chain residues takes place to some extent. It is only at temperatures above 300° that caoutchouc and guttapercha decompose to give identical products. The degradation of crude caoutchouc appears to be inhibited to some extent by the presence of the protein at temperatures up to 142°, but at higher temperatures it follows a course similar to that observed with pure caoutchouc. The interpretation of the results is, however, doubtful, owing to the uncertain function of the protein.

[With E. GEIGER.]—The pyrogenic decomposition of guttapercha begins at 285–290° at 11 mm., becomes vigorous at 300–315°, and then slackens (cf. the analogous decomposition of caoutchouc, A., 1926, 841). The product of such heating is a *polycycloguttapercha*, $(C_5H_8)_x$, mol. wt. (benzene at f. p.) 1950, reduced by hydrogen in presence of nickel at 275–285°/95 atm. to a *hydropolycycloguttapercha*, $(C_{2.5}H_{4.2})_x$, mol. wt. 1930, n_D^{20} 1.5238.

The cyclisation of caoutchouc and guttapercha by hydrogen chloride in the above solvents was studied. Crude caoutchouc in boiling tetrahydronaphthalene gave a *cyclocaoutchouc* (mol. wt. 2500), liquefying at about 123°, whilst guttapercha gave a *cycloguttapercha* indistinguishable from the caoutchouc product. At lower temperatures, however, caoutchouc and guttapercha gave different cyclisation products. The *cyclocaoutchoucs* obtained in boiling xylene and toluene have mol. wt. 4000–12,900 and 14,000, respectively. The *cycloguttaperchas* obtained in boiling xylene, toluene, and benzene have mol. wt. 2600–8100, 10,000, and about 8500, respectively. Cyclisation of caoutchouc and guttapercha in toluene solution at 20° gave different products with very high mol. wts.

The heat-degradation products of caoutchouc and guttapercha are hemicolloids, mixtures of polyprenes with an average mol. wt. of 10,000, which are relatively stable. This explains (1) the considerable solubility of the products, (2) the fact that the mol. wt. does not vary with concentration (as it would if the products had associated molecules merely), and (3) the fact that the viscosity of solutions of the products is roughly proportional to the concentration. Caoutchouc, on the other hand, is a eucolloid, consisting of a mixture of polyprenes having an average mol. wt. of 100,000. Even slight temperature elevation causes degradation. The macro-molecule is the colloid particle.

The conclusions of Pummerer (*loc. cit.*, and B., 1928, 793) are criticised on the grounds that at the m. p. of camphor caoutchouc undergoes considerable degradation. Further, had caoutchouc the formula $(C_5H_8)_n$, the heat-degradation products could be explained only as being due to polymerisation or condensation. The present authors agree with Meyer and Mark (A., 1928, 1252) as regards the suggestion that the isoprene molecules in caoutchouc are united with co-valencies, but differ from them in the conception of the colloid characters of caoutchouc, which is not regarded as a micelle. The structures of caoutchouc and guttapercha are discussed. The former contains about 1000 isoprene residues covalently united and may be a *trans*-compound. The molecule of guttapercha is smaller (about 300–500 isoprene residues), is more symmetrical, and is possibly a *cis*-compound. E. E. TURNER.

Menthone series. VI. Crystallisation of menthylamines with optically active bases. J. READ, C. C. STEELE, and P. G. CARTER (J.C.S., 1929, 23–32; cf. A., 1927, 772, 1080).—*dl*-Menthylamine and *d*-neomenthylamine are resolved by fractionally crystallising the hydrogen *d*-tartrates, the less soluble diastereoisomerides yielding *d*-menthylamine and *l*-neomenthylamine, respectively. No resolution was obtained when *dl*-isomenthylamine was similarly treated. *d*-Menthol is conveniently prepared by treating *d*-menthylamine with nitrous acid. The resolution of the three bases was also attempted with the *d*(or *l*)- α -bromocamphor- π -sulphonates, the *d*(or *l*)-camphor-10-sulphonates, and the normal *d*-tartrates, but complete resolution was not achieved. The observed molecular rotatory powers in dilute aqueous solution of the optically pure salts are in agreement with the calculated values except for the α -bromocamphor- π -sulphonates, the discrepancy being attributed to dynamic isomerism of the acid. When the salts of the three bases with *d*- α -bromocamphor- π -sulphonic acid or with *d*-camphor-10-sulphonic acid are fractionally crystallised, the rotatory powers of successive fractions oscillate irregularly, thus preventing complete resolution of the base. The following are described (rotations in water unless otherwise stated): Derivatives of *l*-menthylamine: *l*- α -bromocamphor- π -sulphonate, m. p. 183–184°, $[\alpha]_D$ –74.7°; *d*- α -bromocamphor- π -sulphonate, m. p. 225°, $[\alpha]_D$ +44.4°; *l*-camphor-10-sulphonate, $[\alpha]_D$ –28.9°; *d*-tartrate, $[\alpha]_D$ –24.6°, and hydrogen *d*-tartrate, $[\alpha]_D$ –8.0°; *d*-menthylamine hydrogen *d*-tartrate, m. p. 168°, $[\alpha]_D$ +37.1°, $[\alpha]_{5461}$ +39.1°, the derived *d*-menthylamine had $[\alpha]_D$ +36.6°; salicylidene-*d*-menthylamine, m. p. 56–57°, $[\alpha]_D$ +118° in chloroform, exhibits phototropic properties. Derivatives of *d*-neomenthylamine: *d*- α -bromocamphor- π -sulphonate, m. p. 166.5°, $[\alpha]_D$ +70.8°; *l*- α -bromocamphor- π -sulphonate, m. p. 171°, $[\alpha]_D$ –49.3°; *l*-camphor-10-sulphonate, m. p. 152°, $[\alpha]_D$ \pm 0°; *d*-camphor-10-sulphonate, m. p. 180°, $[\alpha]_D$ +24.0°; *d*-tartrate, m. p. 180°, $[\alpha]_D$ +25.0°, and hydrogen *d*-tartrate, m. p. 179°, $[\alpha]_D$ +27.4°; *l*-neomenthylamine hydrogen *d*-tartrate, m. p. 188°, $[\alpha]_D$ \pm 0°, resultant *l*-neomenthylamine hydrochloride, $[\alpha]_D$ –20.2°; salicylidene-*l*-neomenthylamine, m. p. 99°, $[\alpha]_D$ –31.3° in chloroform.

Derivatives of *d*-isomenthylamine: *d*- α -bromocamphor- π -sulphonate, $[M]_D +396^\circ$ to $+295^\circ$; *l*- α -bromocamphor- π -sulphonate, m. p. 206° (decomp.), $[M]_D -201^\circ$ to -249° ; *d*-camphor-10-sulphonate, m. p. 180° , $[\alpha]_D +24.6^\circ$; *l*-camphor-10-sulphonate, m. p. 188° , $[\alpha]_D \pm 0^\circ$; *d*-tartrate, m. p. 204° , $[\alpha]_D +32.9^\circ$, and hydrogen *d*-tartrate, m. p. 190° , $[M]_D +98^\circ$. Evaporation of aqueous solutions of *l*-menthylamine hydrochloride, salts of *d*-camphor-10-sulphonic acid with *d*-neo- and *dl*-neo-menthylamines, the normal *d*-tartrate of *d*-neomenthylamine and the normal and hydrogen *d*-tartrates of *dl*-neomenthylamine were accompanied by no change in rotatory power, whilst for the salts of *d*- α -bromocamphorsulphonic acid with *d*-neo- and *dl*-neo-menthylamine a decrease in molecular rotation was observed. A. I. VOGEL.

[Products of the addition of chlorine and bromine to pinene and their de-chlorination.] I. L. KONDAKOV (Ber., 1929, 62, [B], 151—152; cf. A., 1928, 526).—A reply to Aschan (A., 1928, 296, 893). H. WREN.

Ozonisation of nopinene and sabinene. H. SCHMIDT (Z. angew. Chem., 1929, 42, 126—127).—By the ozonisation of nopinene and subsequent decomposition with steam, nopinone was obtained as the chief product, which after purification by means of the semicarbazone had b. p. 209° , d^{20}_D 0.977, $[\alpha] +18.20^\circ$. In addition, smaller quantities of pinonic acid and pinonaldehyde were formed; the latter, which has $[\alpha] -13.8^\circ$, is probably isomeric with the compound, $[\alpha] +15^\circ$, obtained by Harries from pinene. Sabinene by similar treatment yields sabinaketone, b. p. $217-219^\circ$, d^{20}_D 0.957, $[\alpha] -23^\circ$. F. R. ENNOS.

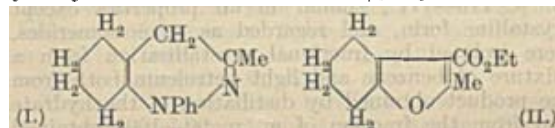
Transformation of pinocarveol and sabinol. H. SCHMIDT (Ber., 1929, 62, [B], 103—107).—When pinocarveol, b. p. $206-208^\circ/756$ mm., d^{20}_D 0.973, $\alpha_D -52^\circ$, is heated with aluminium isopropoxide, a vigorous reaction occurs at about 170° , whereby pinocamphone, b. p. $207^\circ/756$ mm., d^{20}_D 0.9572, $\alpha_D +14.20^\circ$, is produced. The semicarbazone, m. p. 223° , $\alpha_D +5.20^\circ$ in alcohol, non-crystalline oxime, $\alpha_D +38^\circ$, and the dibromide, $C_{10}H_{14}OBr_2$, m. p. $65-96^\circ$, are described. Increase in the duration of heating and the action of the catalyst diminishes the proportion of alcoholic components in the crude product, but increases the amount of resin. Sodium and pinocarveol react vigorously at 170° , giving a product, b. p. $207-211^\circ/756$ mm., d^{20}_D 0.955, $\alpha_D +3.8^\circ$, which affords a semicarbazone, m. p. 215° . Sabinol and aluminium isopropoxide at about 160° yield a product which, after treatment with boric acid to remove alcohols, yields two fractions: (i) b. p. $198-204^\circ$, d^{20}_D 0.912, $\alpha_D +32^\circ$, (ii) b. p. $204-208^\circ$, d^{20}_D 0.920, $\alpha_D +2^\circ$. The latter affords a semicarbazone, m. p. 206° , regarded as derived from isothujone. The crude semicarbazone, m. p. $128-131^\circ$, of the first fraction is hydrolysed to tanacetone, b. p. $199-202^\circ$, d^{20}_D 0.914, $\alpha_D +36.4^\circ$. Similar products are derived from sabinol and sodium at 160° . Tanacetone, when heated, is readily acted on by sodium, giving isothujone and is therefore probably the primary product of the action of sodium or aluminium isopropoxide on sabinol. The ring-unsaturated terpene alcohols verbenol and carveol, which also contain the hydroxyl

group in proximity to the double linking, are not isomerised to saturated ketones under the influence of aluminium alkoxide. The hemicyclic unsaturated pinocarveol and sabinol appear to be particularly unstable compounds. H. WREN.

[Essential oil and alcohol from] *Camphorosma Monspeliacum* from S. Cesarea (Lecce). F. P. MAZZA and G. SPAGNOLO (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], 34, 51—54).—The observation by Cassan (Thesis, Montpellier, 1901), that treatment of this plant with steam furnishes a yellow essential oil smelling of bitter almonds and containing nitrogen (the only essential oil stated to contain this element), is not confirmed. The steam distillate obtained by the authors is colourless, contains only traces of essential oil, and has not the above odour. By extraction with boiling benzene the plant gives a brown product; this when distilled in steam furnishes a volatile yellow oil, decomp. on heating, which contains no trace of nitrogen. Hydrolysis of the distillation residue by potassium hydroxide furnishes an alcohol, *camphorosmol*, $C_{14}H_{28}O_2$, m. p. $74-75^\circ$, which may be identical with an alcohol of the same formula, viz., glutanol, m. p. 76° , obtained by Euler (A., 1908, i, 40); it yields a *diacetyl* derivative, m. p. 80° . No other products were characterised.

E. W. WIGNALL.

Derivatives of *Bz*-tetrahydrocoumarone. F. EBEL, F. HUBER, and A. BRUNNER (Helv. Chim. Acta, 1929, 12, 16—19).—2-Chlorocyclohexanone condensed with ethyl sodioacetoacetate yields *ethyl cyclohexanonylacetoacetate*, b. p. $110-113^\circ/1.5$ mm., which on keeping for some time passes mainly into the enol form, b. p. $119-122^\circ/1.5$ mm. Hydrolysis of this ester with an excess of 2.5% alcoholic potassium hydroxide solution gives 3% of 2-acetonilycyclohexanone, b. p. $112^\circ/\text{vac.}$, which condenses with phenylhydrazine to form the *diazine* (I), m. p. 87° . When hydrolysis is effected with 15% hydrochloric acid

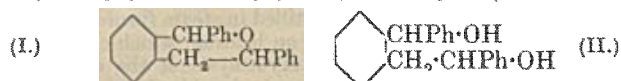


ethyl 1-methyl-3:4:5:6-tetrahydrocoumarone-2-carboxylate (II), b. p. $134^\circ/\text{vac.}$ (free acid, m. p. 156° , decomp. 159°), is obtained, whilst with 15% sulphuric acid there are formed, in addition to II, small amounts of acetonilycyclohexanone and a substance, m. p. 93° (probably II with $CO_2Et=H$). H. BURTON.

So-called "*o*- β -dimethylacroylphenol" of S. SKRAUP. K. VON AUWERS and W. MAUSS (Ber., 1928, 61, [B], 2545—2549).—Examination of the compound, m. p. 88° , obtained by Skraup and Beng (A., 1927, 560) by heating phenyl β -dimethylacrylate and regarded by them as *o*- β -dimethylacroylphenol, shows it to be 2:2-dimethyl-4-chromanone. Direct comparison shows that its properties differ entirely from those of *o*- β -dimethylacroyl-*p*-cresol. Skraup's compound is converted by bromine in carbon disulphide into 3:3-dibromo-2:2-dimethyl-4-chromanone, m. p. $95-96^\circ$; with *p*-nitrophenylhydrazine it affords 2:2-dimethylchromanone-*p*-nitrophenylhydrazone, m. p. $193-194^\circ$. Skraup's observation that

his compound is converted by alcoholic potassium hydroxide into *o*-hydroxyacetophenone does not establish its phenolic nature, since 2 : 2 : 6-trimethylchromanone affords *o*-aceto-*p*-cresol under these conditions. Attempts to synthesise the compound, m. p. 88°, were unsuccessful owing to the instability of the required β -bromoisovaleric acid and its derivatives; *ethyl* β -bromoisovalerate, b. p. 78–80°/16 mm., is incidentally described. H. WREN.

Organometallic derivatives. IV. Diphenylisochromans. A. GARCÍA BANÚS [with L. MEDRANO and M. DÍAZ ROLDAN] (Anal. Fis. Quím., 1928, 26, 372–398).—A further study has been made of the reaction which occurs when magnesium benzyl chloride is added to benzaldehyde, and of the mechanism by which diphenylisochroman (I) is formed (cf. A., 1913, i, 50; 1922, i, 734; 1924, i, 180).



Diphenylisochroman was unaffected by potassium-sodium alloy. Whilst vigorous treatment with acetic anhydride and a little sulphuric acid yielded diphenylindene, gentle treatment yielded a *diacetate*, m. p. 117–118°, which gave on hydrolysis “*diphenylisochroman hydrate*,” m. p. 114–115°, to which the constitution II is assigned. The new compounds developed the same green colour as diphenylisochroman with sulphuric acid. Oxidation of the hydrate by permanganate in acetone solution yielded benzoic and *o*-benzoylbenzoic acids and 2-benzoylbenzil. The hydrate has been previously assumed to be the parent substance of diphenylisochroman, and this is supported by its conversion into the latter when distilled with a small quantity of magnesium chloride and acetate. When heated with 50% sulphuric acid it yielded two *substances* (? phenyl-2-stilbenylcarbinols), m. p. 108–110°. Two forms of diphenylisochroman, m. p. 110–111°, similar in all properties except crystalline form, and regarded as stereoisomerides, were isolated by fractional crystallisation from a mixture of benzene and light petroleum both from the product obtained by distillation of the hydrate and from the fraction of m. p. 90–100° obtained from the product of reaction of magnesium benzyl chloride and benzaldehyde. The new β -form also yielded an unstable crystalline modification, the γ -form, m. p. 136–137°.

Attempts were made to demonstrate the presence of “*diphenylisochroman hydrate*” in the reaction mixture obtained from magnesium benzyl chloride and benzaldehyde. No crystalline compound could be obtained by treatment of the hydrolysed reaction mixture with acetic anhydride. Acylation of the reaction mixture before hydrolysis was also tried. In this way treatment with acetic anhydride or benzoyl chloride yielded $\alpha\beta$ -diphenylethyl acetate, b. p. 202–205°/10 mm., and $\alpha\beta$ -diphenylethyl benzoate, m. p. 70°, respectively, but no derivative of “*diphenylisochroman hydrate*” could be isolated. Similar treatment of the reaction product from magnesium benzyl chloride and anisaldehyde yielded β -phenyl- α -*p*-anisylethyl acetate, m. p. 81–82°, which gave *p*-methoxystilbene when hydrolysed by sulphuric acid, and β -phenyl- α -*p*-anisylethyl alcohol, m. p. 60–61°, when

hydrolysed by dilute sodium hydroxide. $\alpha\beta$ -Diphenylethyl alcohol yielded the *urethane*, m. p. 94–95°, with phenylcarbimide, but β -phenyl- α -*p*-anisylethyl alcohol was decomposed with the formation of an *isomeride* of *p*-methoxystilbene, m. p. 135–136°.

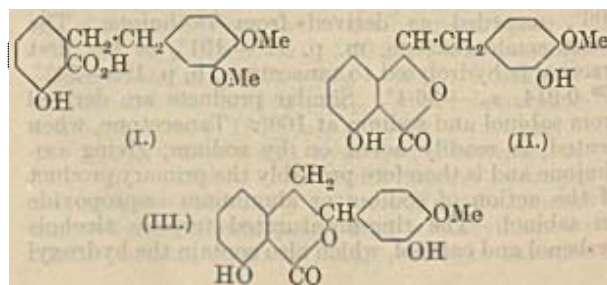
R. K. CALLOW.

Action of calcium hydride on diphenylene oxide. W. FUCHS (Ber., 1928, 61, [B], 2599–2600).—Diphenylene oxide is converted into diphenyl by passage over calcium hydride at 450° in an atmosphere of hydrogen. H. WREN.

Constitution of hydrangenol and phyllodulcin. Y. ASAHINA and J. ASANO (Ber., 1929, 62, [B], 171–177; cf. Asahina and others, J. Pharm. Soc. Japan, 1909, No. 330; 1916, No. 406; Maniwa, A., 1924, i, 1090).—2-Methoxybenzil is converted by hydrobromic and glacial acetic acids into 2-hydroxybenzil, m. p. 74°, which is isomerised by alkali hydroxide to the amorphous 2-hydroxybenzilic acid, yielding with acetic anhydride the crystalline *acetoxybenzilolactone*, $O \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown CO \end{smallmatrix} CPh \cdot OAc$, m. p. 115° (more readily

prepared by the action of bromine and potassium acetate on 2-hydroxydiphenylacetolactone). 2-Hydroxybenzilic acid and the acetylated lactone give a dark violet coloration with concentrated sulphuric acid, whereas the supposedly corresponding natural products give colourless solutions. Similarly, 2 : 4'-dimethoxybenzil is converted successively into 2 : 4'-dihydroxybenzil, m. p. 164°, 2 : 4'-dihydroxybenzilic acid, and the corresponding *acetylated lactone*, $C_{15}H_{14}O_8$, m. p. 215°, which give the characteristic benzilic acid colour with sulphuric acid. Also, *isophyllodulcin* is readily monomethylated, whereas the second hydroxyl group is more resistant; the *monomethyl ether*, $C_{15}H_{16}O_8(O_2Me)_2$, m. p. 115° (oxidised by permanganate in alkaline solution to veratric acid; *monoacetate*, m. p. 141°), gives a reddish-violet colour with ferric chloride, indicating the presence of a hydroxyl group in the *ortho*-position to the carbonyl. The constitutions assigned previously to hydrangenol and phyllodulcin are incompatible with these observations.

Treatment of *isophyllodulcin* in aqueous alcohol with sodium amalgam in the presence of hydrochloric acid affords deoxyphyllodulcinic acid, m. p. 158°, converted by methyl sulphate and alkali hydroxide into the corresponding *monomethyl ether*, m. p. 133°, obtained also by reduction of *isophyllodulcin monomethyl ether*. This, when oxidised by permanganate, affords β -2 : 3-dimethoxyphenylpropionic acid, m. p. 96–97°, in good yield. The constitutions I, II, and III are therefore assigned respectively to deoxyphyllodulcinic acid monomethyl ether, phyllodulcin, and *isophyllodulcin* :

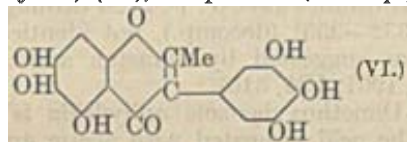


Benzylphthalide and 3-phenylhydroisocoumarin are reduced by sodium amalgam in faintly acid, aqueous alcohol to $\alpha\beta$ -diphenylethane-*o*-carboxylic acid and when heated with alkali are transformed through stilbene-*o*-carboxylic acid to *o*-toluic and benzoic acids. The production of these acids from isophyllodulcin and molten potassium hydroxide is therefore readily understood. It is highly probable that the hydrang-enols are demethoxyphyllodulcins. H. WREN.

Synthesis of naringenin and phloretin. K. W. ROSENMUND and M. ROSENMUND (Ber., 1928, 61, [B], 2608—2612; cf. this vol., 188).—Addition of benzoyl chloride to a solution of phloroglucinol and aluminium chloride in nitrobenzene gives benzoyl-phloroglucinol, m. p. 165°. The applicability of the method is established by the preparation of *phenyl-acetylphloroglucinol*, m. p. 164—166°, *anisylphloroglucinol*, m. p. 177—178°, β -*phenylpropionylphloroglucinol*, m. p. 137—138°, and *p-ethylcarbonatobenzoylphloroglucinol*, m. p. 172°. The additive compound of phloroglucinol and aluminium chloride in nitrobenzene is transformed by cinnamyl chloride at a temperature not exceeding 20° into much resinous matter, a compound, $C_{15}H_{12}O_4$, m. p. 202°, giving the reactions of a flavanone, and a substance, m. p. 210°. Under similar conditions, methylcarbonatocoumaryl chloride affords 2:4:6-trihydroxyphenyl 4'-methylcarbonatostyryl ketone, m. p. 166°, and 5:7-dihydroxy-4'-methylcarbonatoflavanone (*methylcarbonatoningenin*), m. p. 183—184°. Treatment of the last-named substance with ammonia yields naringenin, m. p. 247° (cf. Asahina and Inubuse, A., 1928, 1020), further characterised by transformation into its dimethyl ether, m. p. 115—116°. Contrary to Asahina (*loc. cit.*), naringenin is reduced by hydrogen in presence of palladium to phloretin (β -*p*-hydroxyphenylpropionylphloroglucinol). H. WREN.

isoFlavone group. IV. Synthesis of 2-methylirigenol. W. BAKER and R. ROBINSON (J.C.S., 1929, 152—161).—4:6-Dinitroguaiacol, m. p. 119—121.5°, prepared by the action of nitrous fumes on guaiacol in ethereal solution, was converted by methyl sulphate and potassium carbonate in xylene solution at 120° into 3:5(4:6)-dinitroveratrole, m. p. 99—100°. The latter was successively converted into 3:5(4:6)-diaminoveratrole, m. p. 106°, and 4:5-dimethoxyresorcinol (I) (monohydrate, m. p. 74°; anhydrous, m. p. 115°) by the method of Chapman and others (A., 1928, 183). Reduction of 3:4:5-trimethoxybenzoyl chloride in boiling xylene solution in the presence of palladised barium sulphate gave 3:4:5-trimethoxybenzaldehyde, m. p. 74—75°, converted by hippuric acid in presence of anhydrous sodium sulphate and acetic anhydride at 100° into the azlactone. Alkaline hydrolysis of the latter gave 3:4:5-trimethoxyphenylpyruvic acid (II) (quin-oxaline derivative, m. p. 196—197°); acetic anhydride at 100° converted the oxime of II into 3:4:5-trimethoxyphenylacetone, m. p. 77° (III) (corresponding amide, m. p. 121°). Saturation with hydrogen chloride of a cold ethereal solution of III and 4:5-dimethoxyresorcinol in the presence of anhydrous zinc chloride, followed by decomposition of the resulting ketimine with dilute hydrochloric acid, furnished 2:6-dihydroxy-3:4-dimethoxyphenyl 3:4:5-trimethoxy-

oxybenzyl ketone, m. p. 162° (IV). The constitution of this ketone follows from its conversion by anhydrous sodium acetate and acetic anhydride at 180° into the *acetyl* derivative, m. p. 232—233°, of 5-hydroxy-6:7:3':4':5'-pentamethoxy-2-methylisoflavone (2-methylirigenin 7:3'-dimethyl ether) (V), m. p. 179—180°, a chromone which has the properties of a 5- and not of a 7-hydroxy-derivative. Excess of methyl sulphate and methyl-alcoholic potassium hydroxide converted (V) into 5:6:7:3':4':5'-hexamethoxy-2-methylisoflavone (2-methylirigenin trimethyl ether), m. p. 166°; decomposition of the latter with concentrated alkali at 180° yielded antiarol (3:4:5-trimethoxyphenol), m. p. 147°, and 3:4:5-trimethoxyphenylacetic acid, m. p. 120°, thus establishing the direction of ring closure. Demethylation of V with excess of hydriodic acid at 130° afforded 5:6:7:3':4':5'-hexahydroxy-2-methylisoflavone (2-methylirigenol) (VI), m. p. 325° (decomp.), which



closely resembles irigenol (A., 1928, 646) in chemical and dyeing properties. When VI is methylated with methyl sulphate in an atmosphere of hydrogen its hexamethyl ether, m. p. 166°, identical with the methyl ether of 5-hydroxy-6:7:3':4':5'-pentamethoxy-2-methylisoflavone, is obtained.

When IV is heated with cinnamic anhydride and sodium cinnamate and the product is hydrolysed with alcoholic potassium hydroxide, 5-hydroxy-6:7:3':4':5'-pentamethoxy-2-styrylisoflavone, m. p. 270°, is produced; its methyl ether, m. p. 214—215°, obtained in acetone solution with methyl sulphate and aqueous potassium hydroxide, did not yield a substituted isoflavone-2-carboxylic acid when oxidised in pyridine solution with potassium permanganate. Iridamide (3-hydroxy-4:5-dimethoxyphenylacetamide), m. p. 113°, from ammonia and methyl iridate, could not be dehydrated to the nitrile.

The reactivity of some phenolic ethers is discussed with especial reference to the Hoesch reaction. Phenylacetone nitrile condenses with resorcinol monomethyl ether under the conditions of the Hoesch synthesis to give a mixture of 2-hydroxy-4-methoxyphenyl benzyl ketone, m. p. 90°, and 4-hydroxy-2-methoxyphenyl benzyl ketone, m. p. 68°, respectively insoluble and soluble in 1% sodium hydroxide; the orientation of the first follows from its conversion into 7-methoxy-2-methylisoflavone, m. p. 135.5°, by acetic anhydride and sodium acetate at 180°. Phenylacetone nitrile condenses similarly with orcinol monomethyl ether to produce 4-hydroxy-2-methoxy-6-methylphenyl benzyl ketone, m. p. 88°, together with some 2-hydroxy-4-methoxy-6-methylphenyl benzyl ketone, m. p. 110° (needles); the conversion of the latter into 7-methoxy-2:5-dimethylisoflavone, m. p. 165°, by sodium acetate and acetic anhydride establishes its constitution.

A. I. VOGEL.

Anthoxanthins. VIII. Synthesis of morin and of 5:7:2':4'-tetrahydroxyflavone. R. ROBINSON and K. VENKATARAMAN (J.C.S., 1929, 61—67).—When ω -methoxyphloracetophenone, 2:4-

dimethoxybenzoic anhydride, and sodium 2:4-dimethoxybenzoate are heated together at 180—185° and the product is hydrolysed with alcoholic potassium hydroxide, *morin* 3:2':4'-*trimethyl ether* (I), m. p. 132°, is formed. Methyl sulphate (4 mols.) and aqueous potassium hydroxide convert the latter into the pentamethyl ether, m. p. 155—157°, identical with morin pentamethyl ether. Demethylation of I gave a pale yellow compound, $C_{15}H_{10}O_4 \cdot H_2O$, m. p. 286—288°, identical with the compound, m. p. 290° (decomp.), synthesised by Kostanecki and others (A., 1906, i, 301) which exhibited all the reactions of natural morin [cf. Bablich and Perkin, J.C.S., 1896, 69, 792; m. p. of natural morin about 300° (decomp.)]. Condensation of phloracetophenone, 2:4-dimethoxybenzoic anhydride, and sodium 2:4-dimethoxybenzoate at 180—185° followed by hydrolysis of the product gave 5:7-dihydroxy-2':4'-dimethoxyflavone, $C_{17}H_{14}O_6 \cdot 0.5H_2O$, m. p. 258—259°. Demethylation of this substance gave 5:7:2':4'-tetrahydroxyflavone, m. p. 332—335° (decomp.), not identical with loto-flavin as suggested by Dunstan and Henry (Phil. Trans., 1901, 194, 515).

2:4-Dimethoxybenzoic anhydride is not formed when the acid is heated with acetic anhydride, but is obtained by treating the acid with thionyl chloride in ethereal pyridine. A. I. VOGEL.

Anthoxanthins. IX. Syringetin. T. HEAP and R. ROBINSON (J.C.S., 1929, 67—73).—When ω -benzoyloxyphloracetophenone (1 mol.) is heated at 180—185° with sodium *O*-trimethylgallate (1.5 mols.) and 3:4:5-trimethoxybenzoic anhydride (7 mols.; prepared by treatment of *O*-trimethylgallic acid with thionyl chloride at 0° in the presence of dry ether and pyridine) and the product is hydrolysed with alcoholic potassium hydroxide, *myricetin* 3':4':5'-*trimethyl ether*, m. p. 290—293°, is obtained; this forms an *O*-triacetyl derivative with acetic anhydride and pyridine and a monomethylmyricetinsulphonic acid (not melted at 330°) with fuming sulphuric acid. Benzoylation of syringic acid afforded *O*-benzoylsyringic acid, m. p. 229—232° (chloride, m. p. 116.5—118°), the anhydride, m. p. 200—228° (impure), of which did not give satisfactory results in an attempted synthesis of galangin. However, by heating a mixture of *O*-benzoylsyringic anhydride, m. p. 112—113° (7 mols.; prepared by treating the acid in dry ether-pyridine suspension with thionyl chloride at 0°), sodium benzylsyringate (1.5 mols.), and ω -benzoyloxyphloracetophenone, (1 mol.) at 180—185° and hydrolysing the product with alcoholic potassium hydroxide *syringetin* 4'-benzyl ether, m. p. 240—241° (triacetyl derivative, m. p. 191—194°), was obtained. This was converted by boiling hydrochloric acid and alcohol into *syringetin* (5:7:4'-trihydroxy-3':5'-dimethoxyflavonol) (II), m. p. 288—289° (tetra-acetyl derivative, m. p. 224—226°), which with methyl sulphate and potassium hydroxide furnished myricetin hexamethyl ether, m. p. 159—160° (lit. 154—156°). A. I. VOGEL.

Anthoxanthins. X. Synthesis of gossypetin and of quercetagetin. W. BAKER, R. NODZU, and R. ROBINSON (J.C.S., 1929, 74—84).—1:2:3-Tribenzoyloxybenzene, m. p. 70°, prepared by the benzylation of pyrogallol in the presence of anhydrous

potassium carbonate and acetone in an atmosphere of hydrogen, was converted by nitric acid (*d* 1.19) first into 5-nitro-1:2:3-tribenzoyloxybenzene, m. p. 139°, and then into 2:6-dibenzoyloxy-p-benzoquinone, m. p. 201—202°; the latter was reduced by zinc dust and alcoholic sulphuric acid to 2:6-dibenzoyloxyquinol, m. p. 116—117°, methylation of which with methyl sulphate, sodium hydroxide, and alcohol in an atmosphere of hydrogen gave 2:6-dibenzoyloxy-1:4-dimethoxybenzene, m. p. 82—83°. Hydrolysis of this ether with hydrochloric and acetic acids at 65—70° afforded 2:5-dimethoxyresorcinol (hydrated form, $C_8H_{10}O_4 \cdot 2H_2O$, m. p. 61—62°, anhydrous form, m. p. 86—88°), together with a small quantity of a substance, m. p. 180°. Saturation of a solution of anhydrous 2:5-dimethoxyresorcinol and of methoxyacetoneitrile in dry ether with hydrogen chloride, followed by decomposition of the resulting ketimine hydrochloride with water, gave 2:4-dihydroxy- ω :3:6-trimethoxyacetophenone, m. p. 150—151°. This was heated with potassium veratrate and veratric anhydride at 175—180° and the resulting product was hydrolysed with alcoholic potassium hydroxide, when there was obtained 7-hydroxy-3:5:8:3':4'-pentamethoxyflavone (*O*-pentamethylgossypetin), m. p. 253—254°; demethylation of the latter with hydriodic acid followed by treatment with sulphurous acid gave 3:5:7:8:3':4'-hexahydroxyflavone (I), m. p. 310—314°, the identity of which with natural gossypetin, m. p. 311—313°, was established by the m. p., by conversion (acetic anhydride and pyridine) into the *O*-hexa-acetyl derivative, m. p. 229—230°, and into 3:5:7:8:3':4'-hexamethoxyflavone (*O*-hexamethylgossypetin), by certain characteristic reactions, and by the dyeing properties. These results are irreconcilable with those of Nierenstein (A., 1917, i, 149), who describes the synthesis of I and states that it is identical with hydroxyquercetin derived from quercetone and is different from gossypetin and from quercetagetin. For the synthesis of quercetagetin, 2:6-dihydroxy- ω :3:4-trimethoxyacetophenone (Chapman and others, A., 1928, 183) was heated with veratric anhydride and sodium veratrate at 180—190° and the resulting resin was treated with warm dilute sodium carbonate solution followed by hydrolysis with alcoholic potassium hydroxide, when 5-hydroxy-3:6:7:3':4'-pentamethoxyflavone (*O*-pentamethylquercetagetin), m. p. 159—160°, was obtained. Demethylation of the latter with hydriodic acid afforded 3:5:6:7:3':4'-hexahydroxyflavone, m. p. about 316° (decomp.) (hydrate, $C_{15}H_{10}O_8 \cdot 2H_2O$, from 50% acetic acid), the identity of which with natural quercetagetin was established by conversion into the hexa-acetyl derivative, m. p. 210°, by certain colour reactions, and by the dyeing properties. Confirmation of the view that gossypetin and quercetagetin are derivatives of the same 1:3:4:5-tetrahydroxybenzene is provided by the fact that both 2:5-dimethoxy- and 4:5-dimethoxy-resorcinol yield the same 1:2:3:5-tetramethoxybenzene, m. p. 45—46°, when treated with methyl sulphate and sodium hydroxide in aqueous acetone solution. A. I. VOGEL.

Thiochromondiols. F. ARNDT and B. EISTERT (Ber., 1929, 62, [B], 36—44; cf. Arndt, A.,

1926, 177).—2:2-Dichloro-6-methylthiochromonol, $C_6H_3Me \begin{smallmatrix} CO \cdot CO \\ S - CCl_2 \end{smallmatrix}$, m. p. 138—139° (decomp.) (cf. A., 1925, i, 1312), is prepared by the action of sulphuryl chloride on 6-methylthiochromonol at the ordinary temperature and finally at 100°; 2:2-dichlorothiochromonol, m. p. 91—92° (decomp.), is prepared similarly under milder conditions. Decomposition of the methyl compound with boiling water yields 5-methylthionaphthenquinone and 6-methylthiochromondiol, $C_6H_3Me \begin{smallmatrix} CO \cdot C \cdot OH \\ S - C \cdot OH \end{smallmatrix}$ m. p. 224° (decomp.)

after softening at 205° when rapidly heated (diacetate, m. p. 176°), whereas the simpler compound affords thiochromondiol, m. p. 210° (decomp.) after softening at 190° (diacetate, m. p. 174°), and thionaphthenquinone, m. p. 120—121°. The diol is transformed by ethereal diazomethane into 2-methoxy-6-methylthiochromonol, $C_6H_3Me \begin{smallmatrix} CO \cdot C \cdot OH \\ S - C \cdot OMe \end{smallmatrix}$ m. p. 157°, soluble

in warm 2*N*-sodium hydroxide with production of a yellow sodium salt and smaller amounts of 2:3-dimethoxy-6-methylthiochromone, m. p. 120° (more readily prepared from the 2-methoxy-compound and an excess of ethereal diazomethane). Treatment of the dimethyl ether with boiling hydrochloric acid or of the diol with methyl sulphate and alkali hydroxide affords 2-hydroxy-3-methoxy-6-methylthiochromone, m. p. 125—126° (monohydrate, m. p. 106—107°), readily soluble in ammonia or sodium carbonate to colourless solutions. The compound is readily converted by diazomethane into a mixture of 2:3-dimethoxy-6-methylthiochromone, m. p. 120°, and a substance, $C_{12}H_{12}O_3S$, m. p. 52—53°, which does not react with ketonic reagents or bromine, is slowly soluble in boiling 2*N*-alkali hydroxide, and appears to yield an exceedingly unstable hydrochloride. The substance, together with 2:3-dimethoxy-6-methylthiochromone, is also derived by the action of an excess of ethereal diazomethane on the free diol.

The following method is adopted for the preparation of chromonols (cf. Arndt and Kallner, A., 1924, i, 411). Chromanone dissolved in amyl alcohol is treated successively with a solution of potassium in the same alcohol and amyl nitrite, whereby oximinochromanone, m. p. 155° (decomp.) (potassium salt), is produced, which is converted by boiling 2*N*-hydrochloric acid into chromonol (3-hydroxy-1:4-benzopyrone), m. p. 181°. 6-Methylchromanone similarly yields oximino-6-methylchromanone, m. p. 162° (decomp.) (potassium salt), and 6-methylchromonol, m. p. 175°. Treatment of the chromonols with sulphuryl chloride affords 2-chlorochromonol, m. p. 208°, and 2-chloro-6-methylchromonol, m. p. 192°.

H. WREN.

Synthesis of isonaphthathioxin. A. COHEN and S. SMILES (J.C.S., 1929, 209—213).—1-Bromonaphthalene-2-sulphinic acid, m. p. 146°, was prepared in 60% yield either by the interaction of alkaline sodium sulphite and 1-bromonaphthalene-2-sulphonyl chloride, m. p. 93—94° (prepared from β-naphthylamine-2-sulphinic acid through the diazo reaction and treating the resulting bromosulphonic acid with phosphorus pentachloride), or from 1-bromo-β-naphthylamine by diazotisation and subsequent treatment with copper

and sulphur dioxide, and yielded di-1-bromonaphthyl 2-disulphide, m. p. 161°, with sulphur dioxide and hydriodic acid in alcoholic solution. 1-Bromo-2-hydroxydinaphthyl 2:1'-sulphide (I), m. p. 154° or 135—136° (acetyl derivative, m. p. 116—117°), was obtained by brominating 2'-hydroxydinaphthyl 2:1'-sulphide in acetic acid solution or by heating 1-bromonaphthalene-2-sulphinic acid and β-naphthol at 95—100°. Heating of the sodium derivative of I with copper acetate at 160—170°/1 mm. gave a 50% yield of αββ'-naphthathioxin, m. p. 154°, identical with the substance obtained by dehydrating β-naphthol 1-sulphide (Mauthner, A., 1906, i, 447) or iso-β-naphthol (J.C.S., 1913, 103, 347, 909) or by treating dehydro-β-naphthol sulphide with acetyl iodide (J.C.S., 1914, 105, 1741). A. I. VOGEL.

Action of ammonia and amines on diphenylbenzylpyronone. J. SCHETTLE (J. Russ. Phys. Chem. Soc., 1928, 60, 1521—1533).—The compounds formed by the action of ammonia, methyl-, ethyl-, triethyl-, and propyl-amine, and of aniline on 3:5-diphenyl-2-benzylpyron-2-one were investigated. The compounds are somewhat unstable, ammonia or the corresponding amine being evolved on heating. Since the pyronone has distinctly acidic properties, the compounds are concluded to belong to the type of ammonium salts. With ammonia, diphenylbenzylpyronone gave a compound, m. p. 190—191°, which decomposed on prolonged heating below the m. p., giving ammonia and the original pyronone. If heated rapidly a partial conversion into the corresponding pyridonone took place. With methylamine, a compound, m. p. 180—182°, decomposed by heat was obtained. Ethylamine, triethylamine, propylamine, and aniline gave compounds of m. p. 180—183°, 122—123°, 186—190°, and 100—120°, respectively. The last two products are highly unstable, decomposing below the m. p. None of these compounds gave the corresponding pyridonone derivative. M. ZVEGINTZOV.

By-products of the hydrogenation of quinoline under pressure in presence of osmium and cerium oxides as catalysts. V. S. SADIKOV and A. K. MICHAÏLOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1557—1566).—When quinoline is hydrogenated by Ipatiev's method in presence of varying amounts of osmium and cerium dioxides, the properties of the resulting liquid mixtures depend both on the amounts and on the proportions in which the two catalysts are present. With cerium oxide, tetrahydroquinoline is formed almost exclusively. With osmium oxide, higher reduction products, up to decahydroquinoline, together with condensation products of hexahydroquinoline and alkylated derivatives due to the partial decomposition of the ring compounds, are obtained. If both osmium and cerium oxides are present, both condensation of hydrogenated quinoline derivatives and fission of the rings with formation of piperidine compounds, and secondary reactions, resulting in alkylamine derivatives, occur. Complex secondary reactions are especially prominent if the hydrogenation is carried on intermittently. Since the primary products of hydrogenation are very reactive, they must be removed as soon as formed. M. ZVEGINTZOV.

Phenylisatogen. M. BAKUNIN and T. VITALE (Rend. Accad. Sci. fis. mat. Napoli, 1927, [iii], 33, 270—278).—The red compound, m. p. 186—187°, obtained together with phenyl-*o*-nitrocinnamic acid when *o*-nitrobenzaldehyde is treated with sodium phenylacetate and acetic anhydride (Bakunin and Parlati, A., 1906, i, 664) is now found to be phenylisatogen (2-phenylindolone-1-oxide), $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NO} \end{smallmatrix} \text{CPh}$, and appears to be identical with the compound obtained by oxidising 3-isonitroso-2-phenylindole with acetic acid and chromic anhydride (Angeli and Angelico, A., 1904, i, 526). Treatment of phenylisatogen with hydroxylamine hydrochloride yields almost exclusively *C*- and *N*-oximes, but in presence of alcoholic sodium hydroxide the reaction gives 3-nitroso-2-phenylindole, m. p. 258° (cf. Mohlau, A., 1883, 342; Fischer and Schmidt, A., 1888, 698). The action of alcoholic sodium hydroxide solution on phenylisatogen, partly dissolved and partly suspended in alcohol, yields a compound, m. p. 209—210°, which is probably identical with the compound obtained by Pinner (A., 1894, i, 385) by boiling diphenyltetrazide with alcoholic potassium hydroxide and subsequently treating with dilute hydrochloric acid and with Bamberger and Szolayski's benzylidenebenzhydrazide (A., 1901, i, 84). The action of concentrated nitric acid on a chloroform solution of phenylisatogen in presence of a trace of sulphuric acid or ferric chloride or phosphoric anhydride yields 1-(or 3- or 3'- or 4'-)nitrophenylisatogen, m. p. 220°.

T. H. POPE.

Syntheses with diazomethane. VI. Reaction of ketones and aldehydes with diazomethane. F. ARNDT, B. EISTERT, and W. ENDER (Ber., 1929, 62, [B], 44—56; cf. A., 1928, 739).—*p*-Nitrobenzaldehyde is converted by ethereal diazomethane into a mixture of *p*-nitroacetophenone, m. p. 80°, *p*-nitrophenylacetone, m. p. 62°, and *p*-nitrophenylethylene oxide, m. p. 84—85°, which adds hydrogen chloride, benzoyl chloride, and acetic anhydride without giving crystalline compounds. Addition of methyl alcohol to the reactants increases the yield of nitrophenylacetone without affecting that of the other products. Since nitrophenylacetones are obtained by the prolonged action of ethereal diazomethane on *o*- or *p*-nitroacetophenone, the authors adopt Meerwein's interpretation of the change (A., 1928, 1217) and accept the possibility of radical migration. The results, considered in connexion with those of Mosettig (A., 1928, 887), show that the reaction between the aldehydic group and diazomethane may be accelerated by catalysts but is not altered in its qualitative results. Aldehydes of the type of chloral with "negative carbonyl" afford ethylene oxides and thereby the reaction is concluded, whereas those like benzaldehyde yield methyl ketones. The influence of catalysts is felt in its effect only on the further interaction of the methyl ketone with diazomethane. Thus piperonal without catalyst yields mainly acetylpipecrone, whereas in the presence of much methyl alcohol it affords piperonylacetone and other products.

Ethyl ketomalonate adds ethereal diazomethane in exothermic action without evolution of nitrogen, which occurs only when the solvent is evaporated; its

hydrate immediately evolves nitrogen briskly. In both cases, the main product of the change is ethyl as-ethylene oxide dicarboxylate, $\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} \text{C}(\text{CO}_2\text{Et})_2$, b. p. 127—128°/16 mm., characterised by conversion into the corresponding chlorohydrin, $C_8H_{13}O_5Cl$, b. p. 132—133°/15 mm., and glycoldiacetate, b. p. 152—156°/11 mm.

Repetition of the work of Biltz and Paetzold (A., 1923, i, 1233) has led to a different interpretation of the action of diazomethane on alloxan. Instead of 5:6-methylenedioxy-1:3-dimethyluracil, the primary product, m. p. 176°, is regarded as the ethylene oxide, $\begin{smallmatrix} \text{CO} & \text{NMe} & \text{CO} \\ & \text{NMe} & \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{O} \\ \text{CH}_2 \end{smallmatrix}$, which is transformed

by hydrogen chloride into 5-hydroxy-5-chloromethyl-1:3-dimethylbarbituric acid (benzyl derivative, m. p. 173—174°) and by acetic anhydride in the presence of ferric chloride into 5-acetoxy-5-acetoxymethyl-1:3-dimethylbarbituric acid, m. p. 97°.

As expected, the ketonic group in position 3 in isatin reacts with diazomethane, giving the intermediate product, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$, which gives

rise to the ethylene oxide, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$, m. p.

175°, or passes through 2:3-diketo-1:2:3:4-tetrahydroquinoline into 2:3-dihydroxyquinoline (cf. Heller and others, A., 1919, i, 283; 1926, 620); in addition, further methylation of dihydroxyquinoline occurs to a greater or smaller extent. The ethylene oxide is transformed by hydrochloric acid into 2:3-dihydroxy-3-chloromethylindoline, m. p. 182—183° (decomp.), which does not yield an immediate precipitate of silver chloride when treated with silver nitrate in aqueous-alcoholic solution. 3-Hydroxycarbostyryl, m. p. 257—258°, is converted by short treatment with 1 mol. of benzoyl chloride in boiling pyridine into 3-benzoyloxy-carbostyryl, m. p. 286—287°, readily hydrolysed by alkali hydroxide. With excess of benzoyl chloride the dibenzoyl derivative, m. p. 45—46°, is produced, hydrolysed by 2*N*-alkali hydroxide to the 2-monobenzoyl compound, but by concentrated hydrochloric acid to the 3-benzoyl derivative; 3-acetoxycarbostyryl has m. p. 211°. 3-Methoxycarbostyryl, m. p. (anhydrous) 194°, is obtained by the action of diazomethane on isatin or on hydroxycarbostyryl; the sodium salt and the benzoyl derivative, m. p. 130—131°, are described. In absence of water, 3-hydroxycarbostyryl is converted by diazomethane solely into the 3-monomethyl ether, which is not further attacked. In presence of water, the latter substance is slowly transformed into non-crystalline 2:3-dimethoxyquinoline (compound with mercuric chloride and hydrochloric acid). When preserved, the dimethoxy-compound becomes isomerised to 3-methoxy-1-methyl-carbostyryl, m. p. 70—71°.

H. WREN.

Subsidiary valency forces of pyrrole nitrogen. O. SCHMITZ-DUMONT (Ber., 1929, 62, [B], 226—234).—The co-ordinative valency of pyrrole compounds, with the exception of tripyrrole, is equal to the number of nitrogen atoms which they contain. The additive capacity of pyrrole nitrogen is greatly influenced by substituents and constitution. The additive com-

pounds of pyrroles and tin tetrahalides are prepared by mixing the components in an indifferent solvent and either removing the latter and excess of tin tetrachloride by evacuation or by filtering the product in absence of moisture. Pyrrole and tin tetrachloride give the pale yellow compound, $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_5\text{N}$, from which pyrrole cannot be regenerated; it is therefore regarded as derived from dipyrrole. Attempts to isolate the latter compound failed, but it appears relatively strongly basic, since it is not displaced from its additive compound by pyridine, a process which takes place quantitatively with all the other compounds investigated, giving the dipyridine compound of the tin tetrahalide. The basic properties of pyrrole are strengthened by its polymerisation, since tripyrrole yields the compounds $\text{SnCl}_4 \cdot (\text{C}_4\text{H}_5\text{N})_3$ and $\text{SnBr}_4 \cdot 2(\text{C}_4\text{H}_5\text{N})_3$. Introduction of methyl groups so increases the additive capacity of pyrrole that 2:4-dimethylpyrrole without polymerisation yields the crystalline substance, $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_3\text{Me}_2\text{N}$, from which the pyrrole component can be quantitatively regenerated. Replacement of the 1-hydrogen atom by methyl has little effect, since 1-methylpyrrole and tin tetrachloride do not give a compound from which the pyrrole can be obtained. $\alpha\beta$ -Di-*NN'*-2:5-dimethylpyrrolethane gives a compound, $2\text{SnCl}_4 \cdot \text{C}_{14}\text{H}_{20}\text{N}_2$, for which a structure is suggested which avoids the unusual co-ordination number 5 for tin. 2-Acetylpyrrole affords the compounds $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_4\text{AcN}$ and $\text{SnBr}_4 \cdot 2\text{C}_4\text{H}_4\text{AcN}$, and, since 2:5-diacetylpyrrole yields the substances $\text{SnCl}_4 \cdot \text{C}_4\text{H}_3\text{Ac}_2\text{N}$ and $\text{SnBr}_4 \cdot 2\text{C}_4\text{H}_3\text{Ac}_2\text{N}$, it is assumed that the subsidiary valency linking is essentially localised at the nitrogen atom. Di-3-carbethoxy-2:4-dimethylpyrrole yields a compound, $\text{SnCl}_4 \cdot \text{C}_4\text{HMe}_2\text{N}(\text{CO}_2\text{Et}) \cdot \text{CH} \cdot \text{C}_4\text{HMe}_2\text{N} \cdot \text{CO}_2\text{Et}$, in which the nitrogen atoms appear precisely equivalent, thus suggesting that the imino-hydrogen atom is not definitely attached to either nitrogen atom. The compound obtained by Tschelincev (A., 1917, i, 91, 93) does not add tin tetrachloride, whereas that obtained from cyclohexanone (A., 1917, i, 412) gives the

compound $\text{C}_4\text{H}_3\text{N} \begin{matrix} \text{C}_6\text{H}_{10} \\ \text{SnCl}_4 \\ \text{C}_6\text{H}_{10} \end{matrix} \text{C}_4\text{H}_3\text{N}$, whilst the substance obtained with tin tetrabromide has the unusual composition $\text{C}_{20}\text{H}_{26}\text{N}_2[\text{SnBr}_5\text{H}, \text{C}_{20}\text{H}_{26}\text{N}_2]_2$. H. WREN.

Formation of 2-aminopyridine. G. KOLLER and H. RUPPERSBERG (Monatsh., 1928, 50, 436—438).—When 2-chloropyridine is heated at 200° with pyridine an appreciable amount of 2-aminopyridine (*chloroaurate*, m. p. 231—232°) is formed, probably through the intermediate *N*-2-pyridylpyridinium chloride. A small quantity of the aminopyridine is produced also from 2-chloro- and 3-methylpyridine at 200°. H. BURTON.

Manufacture of 2-hydroxypyridine-5-carboxylic acid. C. RATH.—See B., 1929, 149.

5- and 8-Aminoquinolines. R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 147—154).—When 5-nitroquinoline is reduced with a mixture of stannous chloride and hydrochloric acid the impure 5-amino-derivative is obtained, but 8-nitroquinoline affords 8-aminoquinoline, 5-chloro-8-aminoquinoline, and a

small quantity of 3(?)-chloro-8-aminoquinoline, m. p. 85°. These halogenated derivatives are formed presumably through the intermediate hydroxylamine (cf. Blanksma, A., 1906, i, 345). An excess of a powerful reducing agent causes hydrogenation of the pyridine nucleus, and optimum yields (75%) of the 5- and 8-amino-compounds are best obtained with iron powder and 50% acetic acid. H. BURTON.

Manufacture of 8-hydroxyquinoline and derivatives thereof. I. G. FARBENIND. A.-G.—See B., 1929, 149.

Manufacture of ethers of 6:8-dihydroxyquinoline. I. G. FARBENIND. A.-G.—See B., 1929, 149.

Action of magnesium [alkyl] compounds on anhydrides of asymmetric polycarboxylic acids: action of magnesium ethyl iodide on cinchomeronic anhydride. F. P. MAZZA [with O. FICI] (Rend. Accad. Sci. fis. mat. Napoli, 1928, [iii], 34, 59—65).—The action of magnesium ethyl iodide on cinchomeronic anhydride in ether, followed by treatment with sulphuric acid, gives two diethylcinchomeronides, $\text{C}_5\text{H}_3\text{N} \begin{matrix} \text{CO} \\ \text{C}_6\text{H}_5 \\ \text{O} \end{matrix} \text{O}$, viz., 2- α -hydroxy- α -ethylpropylpyridine-3-carboxylic acid lactone, b. p. 132—133°/60 mm., hydrolysed to diethyl ketone and isonicotinic acid, and 3- α -hydroxy- α -ethylpropylpyridine-2-carboxylic acid lactone, b. p. 165—166°/60 mm., hydrolysed to diethyl ketone and nicotinic acid. E. W. WIGNALL.

Preparation of quinaldinyll chloride and ethyl quinaldinyllacetoacetate. D. L. HAMMICK and W. P. DICKINSON (J.C.S., 1929, 214—215).—Contrary to the statement of Besthorn and Ibele (A., 1905, i, 612) and in agreement with that of Meyer (A., 1905, i, 155, 666; cf. Besthorn, A., 1908, i, 681), it is found that only quinaldinyll chloride of m. p. 175—176° is obtained by the action of thionyl chloride (redistilled over quinaldinic acid) on the acid. The acid chloride, m. p. 97°, is, however, obtained by the action of phosphorus pentachloride on the acid or on ethyl quinaldinate, m. p. 36°, in light petroleum solution (b. p. 100—120°). Only hydrochloric and quinaldinic acids are obtained when the acid chlorides of high and low m. p. are treated with water. Ethyl 2-methylquinolinyllacetoacetate, m. p. 61° [copper derivative, m. p. 178° (decomp.)], is formed from quinaldinyll chloride and ethyl sodioacetoacetate in benzene. Dry ammonia in ether or a mixture of ammonia and ammonium chloride at 50° and ethyl quinaldinyllacetoacetate yield only quinaldinamide and no ethyl quinaldinyllacetate. A. I. VOGEL.

Derivatives of quinoneacridone. B. B. SCHARVIN and D. I. GALPERIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1423—1499).—The formation of the derivatives of quinoneacridone was investigated with the view of preparing vat dyes of the type $\text{R}'(\text{NHR})_2$, where R is an anthraquinone and R' a quinoneacridone derivative. Crystalline quinoneacridone can readily be obtained by hydrolysing the sulphate. The monochloro- and monobromo-derivatives can be obtained only with great difficulty, by the direct halogenation of quinoneacridone dissolved in phosphoryl chloride. Tetrabromoquinoneacridone was synthesised from *p*-benzoquinone and dibromoanthranilic acid by way of tetrabromoquinoneanthranilic

acid, m. p. 269°, which, when heated at 200° for 3 hrs. in sulphuric acid, gave dark red *tetrabromoquinone-acridone*. Sodium hydrogen sulphite reduces it to the di- and tetra-hydro-derivatives. By reducing dinitroquinoneacridone, the deep violet *diamino*-compound can be obtained; it gives coloured reduction and sulphonation products, and when diazotised and coupled with β -naphthol yields a violet dye. If the diamino-compound is benzoylated in nitrobenzene solution, a brown *dibenzoyl* derivative is obtained, whilst hydrolysis of the diazonium compound yielded a dark red *dihydroxyquinoneacridone*. All these derivatives can be reduced with sodium hydrogen sulphite, but since the reduction products are all insoluble, they cannot be used as vat dyes. If, however, the di- and tetra-bromo-derivatives are heated for 20 hrs. with β -aminoanthraquinone in nitrobenzene solution in the presence of alkali, *dianthraquinonyl*- and *tetra-anthraquinonyl-diaminoquinoneacridone* are obtained, which are dark brown vat dyes suitable for cotton. M. ZVEGINTZOV.

Derivatives of hydantoin-3-acetic acid. R. LOCQUIN and V. CHERCHEZ (Compt. rend., 1929, 188, 177—179; cf. A., 1928, 744).—Treatment of ethyl aminomalonate, either in the form of the sodium derivative or in the presence of pyridine, with carbonyl chloride yields *ethyl carbonyldiaminomalonate*, m. p. 167°, which gives *carbonyldiacetic acid*, m. p. 208° (efferv.), when heated at 100° with 4% sodium hydroxide and hydantoin-3-acetic acid, m. p. 195—196°, when refluxed with 10% hydrochloric acid. The 3-acetic acid, when heated with thionyl chloride, affords a *chloride*, which in turn yields *amides* with aniline, ethyl aminomalonate, ethyl aminoacetate, and 3-methyl-5-isopropylpyrazoline, m. p. 215°, 172—173°, 168°, and 185°, respectively. The interaction of aqueous ammonia and ethyl hydantoin-3-acetate yields *carbonyldiacetamide*, decomp. about 240°, and *hydantoin-3-acetamide*, m. p. 225—226° (cf. Gränacher and Landolt, A., 1928, 74; Fischer, A., 1901, i, 192; 1902, i, 350). G. A. C. GOUGH.

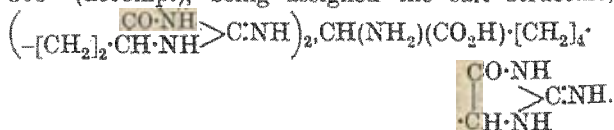
Hydantoins. XLVII. Polypeptidehydantoins from 2-thiohydantoin-3-acetic acid. A. G. RENFREW and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 254—259).—2-Thiohydantoin-3-acetic acid (A., 1925, i, 583) and *p*-anisaldehyde in glacial acetic acid in presence of sodium acetate yield 2-thio-5-*p*-anisylidenehydantoin-3-acetic acid, m. p. 280—282°. This is desulphurised by chloroacetic acid to 5-*p*-anisylidenehydantoin-3-acetic acid (cf. Gränacher, A., 1928, 74), which may also be obtained from hydantoin-3-acetic acid and *p*-anisaldehyde. 2-Thio-5-salicylidenehydantoin-3-acetic acid, m. p. 253—254° (decomp.), prepared similarly, is desulphurised to 5-salicylidenehydantoin-3-acetic acid, m. p. 273—274° (decomp.) (ethyl ester, m. p. 164°), which is reduced by hydriodic acid to 5-*o*-hydroxybenzylhydantoin-3-acetic acid, m. p. 189—190°. 2-Thio-5-piperonylidenehydantoin-3-acetic acid, m. p. 291° (decomp.), is desulphurised to 5-piperonylidenehydantoin-3-acetic acid, m. p. 275—276°, the constitution of which is established by the formation of its ethyl ester, m. p. 159—160°, from ethyl chloroacetate and the sodio-derivative of piperonylidenehydantoin. H. E. F. NOTTON.

Direct substitution on the nitrogen of 5:5-di-alkylbarbituric acids. A. W. DOX and E. G. JONES (J. Amer. Chem. Soc., 1929, 51, 316—318).—When 5:5-dialkylbarbituric acids (1 mol.) are refluxed with *N*-sodium hydroxide (1 mol.) and benzyl chloride or allyl bromide (1 mol.) the product contains mainly the trialkyl derivative with some unchanged material and tetra-alkyl derivative, and occasionally a little acetyldialkylcarbamide. In this way the following *barbituric acids* have been prepared: 1-benzyl-5:5-diethyl-, m. p. 127°; 1-benzyl-5:5-diallyl-, m. p. 116°; 1-benzyl-5-ethyl-5-isoamyl-, m. p. 90°; 5-phenyl-1-benzyl-5-ethyl-, m. p. 113°; 1-benzyl-5-sec-butyl-5-allyl-, m. p. 90—91°; 5:5-diethyl-1-allyl-, m. p. 75°; 1:5:5-triallyl-, m. p. 68—69°; 5:5-dipropyl-1-allyl-, m. p. 73°; and 5:5-dipropyl-1:3-diallyl-, m. p. 62—63°. H. E. F. NOTTON.

Colour on basis of molecular strain. V. Absorption spectra and dissociation constants of organic salts of violuric acid. N. GHATAK and S. DUTT (J. Indian Chem. Soc., 1928, 5, 665—672).—Although solid violuric acid is almost colourless, its aqueous solution is pink (Donnan and Schneider, J.C.S., 1909, 95, 956; Morton and Tipping, *ibid.*, 1925, 127, 2514). This is ascribed to the change $\cdot\text{CO}\cdot\text{C}\cdot\text{N}\cdot\text{OH}(\text{solid}) \rightarrow \cdot\text{C}(\text{OH})\cdot\text{C}\cdot\text{N}\cdot\text{O}(\text{solution})$; the highly strained nitroso-group is thus responsible for colour formation. The coloured alkali salts are also regarded as nitroso-compounds; the intensity of colour is greater with increasing basic strength of alkali (cf. Hantzsch, A., 1909, i, 331). This relationship is also true for the organic salts of violuric acid which have been examined. The absorption maxima and dissociation constants of *N*/128 aqueous solutions of the following salts are recorded: ammonium, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, *n*-propylamine, *n*-butylamine, aniline, *o*-, *m*-, and *p*-toluidine, *p*- and *o*-phenylenediamine, α - and β -naphthylamine, pyridine, piperidine, quinoline, α -picoline, nicotine, morphine, brucine, strychnine, cinchonine, quinine, and cocaine. The colours of the salts vary from orange to violet, whilst the aqueous solutions range from pale pink to violet-red. The above salts decompose when heated to about 85°, or when exposed to air for a long time.

H. BURTON.

Reaction between guanidine and esters of amino-acids. III. E. ABDERHALDEN and H. SICKEL (Z. physiol. Chem., 1929, 180, 75—89; cf. A., 1928, 511, 623).— $\alpha\alpha'$ -Diaminosuberic acid is converted (contrary to the statement of Neuberg and Neimann, A., 1905, i, 687) by 10 parts of methyl alcohol and anhydrous hydrogen chloride into the *methyl ester dihydrochloride*, decomp. 270° (the difficulty in esterification being the insolubility of the acid dihydrochloride in alcohol), which reacts with guanidine at 0° in the expected manner, the isolated compound, m. p. 305° (decomp.), being assigned the salt structure,



Guanidine similarly condenses with methyl *dl*- α -

amino- δ -benzamidovalerate [*hydrochloride*, m. p. 128—130° (corr.)] to yield the corresponding *cyanidine* derivative [2-amino-5-keto-4- γ -benzamido-4 : 5-dihydroglyoxaline], m. p. 198° (corr.) [*picrate*, decomp. 220° (corr.)], which by debenzoylation with hydrochloric acid yields 2-imino-4- γ -aminopropyl-5-glyoxalidone [isolated as its *dipicrate*, m. p. 230° (decomp.) (corr.)]; this is hydrolysed by *N*-sodium hydride at the ordinary temperature to yield δ -amino- α -guanidinovaleric acid (*isoarginine*) (*picrate*), which is not attacked by arginase. *as*-Dimethyl-, *N*-methyl-, and *N*-isoamyl-guanidine react only to a very small extent with glycine ester, no condensation product being isolated, whilst *N*- α -naphthyl- and *N*-acetyl-guanidine do not react. Guanidine condenses with ethyl hippurate at the ordinary temperature to yield *hippurylguanidine* (*picrate*, decomp. above 320°) and with acetyl-glycine to yield the *guanidonium* salt, m. p. 217—218°. J. W. BAKER.

N-Substituted derivatives of piperazine and ethylenediamine. I. Preparation of *N*-mono-substituted derivatives. T. S. MOORE, M. BOYLE, and V. M. THORN (J.C.S., 1929, 39—51).—Interaction of piperazine with substances capable of attacking the imino-groups usually gives the *N*-disubstituted derivatives. If the interaction takes place in two stages, the velocity of the reaction in the second stage would therefore appear to be much greater than that in the first stage. Theoretical considerations, based on the relative values of the primary and secondary dissociation constants of a diacid base and the ionic product of water, lead to the conclusion that the possibility of survival of a monosubstituted derivative is greatest in weakly acid solution, a result confirmed by experiment. Thus piperazine (3 mols.) reacts with ethyl chloroformate (2 mols.) at p_H 2.8—4.6 (constant) to give *ethyl piperazine-1-carboxylate* (I), b. p. 116—117°/12 mm. and 237°/760 mm., and ethyl piperazine-1 : 4-dicarboxylate in yields of 70% and 12%, respectively. Under similar conditions, benzoyl chloride gives a 22% yield of 1-benzoylpiperazine, m. p. 64°, whilst no monotoluenesulphonyl compound could be isolated with *p*-toluenesulphonyl chloride owing to the slowness of the reaction. Carbon dioxide and I form an additive compound, whilst carbon disulphide and I give the additive compound, $2C_4H_9N_2 \cdot CO_2Et \cdot CS_2$, m. p. 148° (decomp.). Benzoylation of I in the cold affords *ethyl 4-benzoylpiperazine-1-carboxylate*, m. p. 82° (shaking of the latter with cold 0.1*N*-sodium hydroxide gave chiefly sodium benzoate and a poor yield of *N*-benzoylpiperazine), whilst treatment with *p*-toluenesulphonyl chloride in weakly alkaline solution afforded *ethyl 4-p-toluenesulphonylpiperazine-1-carboxylate*, m. p. 121°, which yielded *N*-*p*-toluenesulphonylpiperazine, m. p. 110° [additive compound with carbon dioxide, $2C_{11}H_{16}O_2N_2S \cdot CO_2$, m. p. 107° (decomp.); additive product with carbon disulphide, $2C_{11}H_{16}O_2N_2S \cdot CS_2$, m. p. 171°]. Interaction of I with ethyl iodide in alcoholic solution gave an inseparable mixture of a quaternary iodide and ethylpiperazine-1-carboxylate, whilst interaction of I with excess of ethyl *p*-toluenesulphonate in dry alcohol at 100° in presence of sodium carbonate gave a 70—75% yield of *ethyl 4-ethylpiperazine-1-carboxylate*, b. p. 136°/28 mm.

The latter was converted by boiling concentrated hydrochloric acid into 1-ethylpiperazine dihydrochloride, which when heated with dry slaked lime gave 1-ethylpiperazine, b. p. 155—158° (*chloroplatinate*; *chloroaurate*; additive compound with carbon disulphide, $C_6H_{14}N_2 \cdot CS_2$). When I is heated with ethylene chlorohydrin and anhydrous sodium carbonate at 110°, *ethyl 4- β -hydroxyethylpiperazine-1-carboxylate*, b. p. 184°/17 mm., is formed; this is hydrolysed by concentrated hydrochloric acid, giving 1- β -hydroxyethylpiperazine dihydrochloride (*chloroplatinate*; *chloroaurate*). Ethyl chloroacetate and anhydrous sodium carbonate convert I into *ethyl 4-carbethoxypiperazinoacetate*, b. p. 183°/18 mm., hydrolysed by alkali or (better) hydrochloric acid, to *piperazinoacetic acid dihydrochloride*. Treatment of the latter with silver carbonate gave *piperazinoacetic acid* (+ H_2O), m. p. 279° (decomp.). *Ethyl 4-carbethoxypiperazino- β -propionate*, b. p. 198°/22 mm., and *ethyl 4-carbethoxypiperazino- γ -butyrate*, m. p. 207°/21 mm., were similarly prepared from ethyl β -iodopropionate and ethyl γ -chlorobutyrate, respectively. Further treatment of these two esters gave *piperazino- β -propionic acid dihydrochloride*, *piperazino- β -propionic acid*, m. p. 215° (decomp.), the *chloroplatinate* of *piperazino-butyric acid dihydrochloride*, and *piperazino- γ -butyric acid*, m. p. 235° (decomp.).

Ethylenediamine and ethyl chloroacetate (p_H controlled by bromocresol-green) react to give *carbethoxyethylenediamine*, b. p. 135°/20 mm., which yields ethylenecarbamide when heated or when treated during several days with dilute aqueous "soda" and gives an additive compound with carbon dioxide, m. p. 102—103°, which is best prepared by passing carbon dioxide into an ethereal solution. The following are described: *N*-benzoyl-*N'*-carbethoxyethylenediamine, m. p. 130°; *N*-*p*-toluenesulphonyl-*N'*-carbethoxyethylenediamine, m. p. 66°; *N*-*p*-toluenesulphonylethylenediamine, m. p. 121°; *ethyl N'*-carbethoxyethylenediamino-*N*-acetate (decomposes on distillation and affords the *hydrochloride* of β -aminoethylglycine on hydrolysis); β -aminoethylglycine, m. p. 144°.

A. I. VOGEL.

Quinoxalines from camphorquinone and aromatic o-diamines. A. HECKENDORN (Helv. Chim. Acta, 1929, 12, 50—60).—Camphanoquinoxalines have been prepared from camphorquinone (1 mol.) and the following 1 : 2-diamines (1 mol.): *o*-phenylenediamine, m. p. 74° (cf. Singh and Mazumder, J.C.S., 1919, 115, 574); *o*-tolylenediamine, m. p. 50°; 4-chloro-*o*-phenylenediamine, m. p. 98° after previous softening; 4-nitro-*o*-phenylenediamine, m. p. 149° [the quinoxaline derivative is reduced by stannous chloride and hydrochloric acid to the corresponding amino-derivative, m. p. 135° (*picrate*, m. p. 216°; *acetyl* derivative, m. p. 118°)]; 3 : 4 : 5-triaminobenzoic acid, m. p. 128—130° (decomp.) [*picrate*, m. p. 203° (decomp.); *acetyl* derivative, m. p. 279° (decomp.)]; 1 : 2-naphthylenediamine, m. p. 85—86°; 2 : 3-diaminoanthraquinone, m. p. 211°. 1 : 2 : 3 : 4-Tetraaminobenzene condenses with camphorquinone yielding a mixture of *diaminocamphanoquinoxaline*, m. p. 153—154° (*picrate*, m. p. 175°), and *dicamphanoquinoxaline*, m. p. 245°. From 1 : 2 : 4 : 5-tetra-amino-benzene and 1 mol. of the quinone a *diaminocamphano-*

quinoxaline, m. p. 165° after softening at 130—140° (*picrate*, m. p. 176° after softening), is obtained. This furnishes three types of salts with sulphuric acid, namely, mono- (orange), di- (permanganate-red), and tri- (colourless). With 2 mols. of camphorquinone a *dicamphanoquinoxaline*, m. p. 333—335°, results.

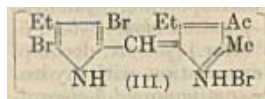
H. BURTON.

Syntheses of heterocyclic nitrogen nuclei.
III. Triaryl derivatives of 1 : 2 : 4-triazole from arylidene [aromatic aldehyde] 2 : 4-diphenylsemicarbazones. G. MINUNNI and S. D'URSO [with S. GUGLIELMINO, P. SALANITRO, D. TORRISI, and M. VASTA] (*Gazzetta*, 1928, **58**, 820—831; cf. this vol., 196).—1 : 3 : 4-Triphenyl-1 : 2 : 4 : 5-triazolone (new m. p. 221.5—222°) is readily obtained by oxidising benzaldehyde-2 : 4-diphenylsemicarbazone with amyl nitrite in benzene solution (cf. Busch and Walter, A., 1903, i, 522; Minunni, A., 1927, 1073). *o*-Nitrobenzaldehydediphenylsemicarbazone reacts less readily, but with excess of amyl nitrite, in absence of solvent, 1 : 4-diphenyl-3-*o*-nitrophenyl-1 : 2 : 4 : 5-triazolone, m. p. 135—137° (decomp.), is formed. Under similar conditions the *m*- and *p*-compounds are oxidised to the 3-*m*- and 3-*p*-nitrophenyltriazolones, m. p. 199—200° (decomp.) and 193—194°, respectively. The *o*-nitrophenyltriazolone is reduced by zinc and acetic acid to 1 : 4-diphenyl-3-*o*-aminophenyl-1 : 2 : 4 : 5-triazolone, m. p. 192.5—193.5° (decomp.), with a secondary product, m. p. 244—247°; similar treatment of the *p*-compound gives a substance, m. p. 235—238°, which is not the *p*-aminophenyl derivative, since it contains 14.16—14.28% N. The piperonal semicarbazone gives rise to 1 : 4-diphenyl-3-piperonyl-1 : 2 : 4 : 5-triazolone, m. p. 169—170°.

E. W. WIGNALL.

Synthesis of octaethylporphyrin. H. FISCHER and R. BAUMLER (*Annalen*, 1929, **468**, 58—98).—Reductive condensation (using zinc dust and acetic acid) of the isonitroso-derivative of ethyl propionacetate with acetylacetone produces ethyl 3-acetyl-2-methyl-4-ethylpyrrole-5-carboxylate, m. p. 115°, converted by the Wolff-Kishner method into 2-methyl-3 : 4-diethylpyrrole (I), b. p. 104—105°/13 mm. or 202—203°/760 mm., d_{20}^{25} 0.90996, n_D^{25} 1.49879 (*picrate*, m. p. 101°). Hydrolysis of the above ester affords the acid, m. p. 208°, and this when heated passes into 3-acetyl-2-methyl-4-ethylpyrrole (II), m. p. 129°, b. p. 280—290°. Since ethyl propionacetate is not readily obtainable by Willstätter's method (A., 1914, i, 286) I was synthesised by the Wolff-Kishner method from II, obtained by the Friedel-Crafts reaction from 2-methyl-4-ethylpyrrole, the latter being obtained from ethyl 5-propionyl-2-methyl-4-ethylpyrrole-3-carboxylate by means of sulphuric acid. Both methods of synthesis were abandoned in favour of the following: Reductive condensation of the isonitroso-derivative of dipropionylmethane with acetylacetone gives 3-acetyl-5-propionyl-2-methyl-4-ethylpyrrole, m. p. 137°, converted by diluted sulphuric acid at above 70° into 2-methyl-4-ethylpyrrole, but by the same reagent at 65—70° into II. The latter (II) affords 5-bromo-3-acetyl-2-methyl-4-ethylpyrrole, m. p. 149°, when treated in glacial acetic acid with 1 mol. of bromine; in hot acetic acid, the requisite bromine gives rise to 3 : 5-dibromo-2-methyl-4-ethylpyrrole, m. p. 161°, which

withstands further attempts at bromination; 4 mols. of bromine convert II into the *perbromide* (III), not melting at 260°. This substance does not brominate



acetone, so that the bromine is unusually non-reactive, and cannot be converted into the parent base, or into a porphyrin, or into a copper salt. Proof that in the formation of III an acetyl group is eliminated is given by the fact that oxidation of III with chromic anhydride in warm glacial acetic acid affords bromoethylmaleimide, m. p. 128°.

Excess of bromine converts 2 : 4-dimethylpyrrole-5-aldehyde into the methene obtained by brominating 2 : 4-dimethylpyrrole (Fischer and Scheyer, A., 1924, i, 80), but ethyl 2 : 4-dimethylpyrrole-5-aldehyde-3-carboxylate under similar conditions merely gives the hydrobromide of the methene derived from ethyl 2 : 4-dimethylpyrrole-3-carboxylate. Ethyl 2 : 4-dimethylpyrrole-3-carboxylate shows a marked tendency to pass into methenes. Thus it condenses with ethyl 3-methyl-4-ethylpyrrole-5-aldehyde-2-carboxylate, the aldehyde group of the latter being eliminated in the process.

Boiling aqueous formaldehyde, in absence of hydrochloric acid, converts II into *bis*-(3-acetyl-2-methyl-4-ethyl-5-pyrrolyl)methane, m. p. 259°, a fact which demonstrates the great reactivity of II as compared with that of lower homologues. Bromination of the methane gives (3-bromo-2-methyl-4-ethyl-5-pyrrolyl)-(3'-bromo-4'-ethyl-2'-bromomethyl-5'-pyrrolyl)-methene hydrobromide, convertible with difficulty into a porphyrin.

Stepwise bromination of ethyl 3-acetyl-2-methyl-4-ethylpyrrole-5-carboxylate gives, first, ethyl 3-acetyl-4-ethyl-2-bromomethylpyrrole-5-carboxylate (impure, m. p. 120°, converted by warm dilute alcohol into ethyl 3-acetyl-4-ethyl-2-hydroxymethylpyrrole-5-carboxylate, m. p. 101°) and, secondly, into ethyl 3-bromo-4-ethyl-2-bromomethylpyrrole-5-carboxylate, m. p. 170°. The latter is the product of excess bromination of the above ester and also results by the excess bromination of ethyl 2-methyl-4-ethylpyrrole-5-carboxylate. The stepwise bromination of the latter produces, immediately, ethyl 3-bromo-2-methyl-4-ethylpyrrole-5-carboxylate, m. p. 124°. The fact that the acetyl radical resists replacement by bromine appears to explain why in the conversion of II into III only one acetyl group is lost. This conversion appears to involve: (1) 5-bromination, (2) bromination in the 2-methyl group, and (3) displacement of the 3-acetyl group by a bromine atom (giving possibly a *perbromide*). The resulting substance is exceedingly reactive, and condenses with unchanged 5-bromo-derivative to give III. This explanation accords with the facts regarding the bromination of ethyl 2 : 4-dimethylpyrrole-3-carboxylate. In this case, bromine in ether produces ethyl 5-bromo-2 : 4-dimethylpyrrole-3-carboxylate, m. p. 96° (decomp.), whilst further bromination (in acetic acid) gives (5-bromo-3-carbethoxy-4-methyl-5-pyrrolyl)-(3'-carbethoxy-2' : 4'-dimethylpyrrolyl)methene hydrobromide, not melting at 260° (free methene has m. p. 153°).

The above ethyl 3-acetyl-4-ethyl-2-bromomethyl-

pyrrole-5-carboxylate reacts with boiling methyl alcohol to give the corresponding 2-methoxymethyl compound, and not *bis*-(2-carbethoxy-4-acetyl-3-ethyl-5-pyrryl)methane, m. p. 115°, which results when the bromomethyl compound is heated with aqueous formaldehyde. 2-Methyl-3:4-diethylpyrrole (I), the physiological action of which (on rats and mice) has been studied (it is a weak poison), is convertible (1) into a well-defined *picrate*, (2) into well-defined, although unstable, *azo-dyes*, and (3), by Gattermann's hydrogen cyanide method, into 2-methyl-3:4-diethylpyrrole-5-aldehyde, m. p. 74° (copper acetate additive compound of the intermediately formed aldimine hydrochloride is described). This aldehyde is transformed by sodium nitrite and diluted sulphuric acid into the monoxime of diethylmaleimide, m. p. 194°, and by nitric acid into diethylmaleimide, which is not an oil as stated by Küster (A., 1908, i, 303), but melts at 68° (crystallographic data by STEINMETZ). Repetition of Küster's synthesis of the imide gave an identical solid product.

2-Methyl-3:4-diethylpyrrole is readily brominated in acetic acid, giving the well-defined *perbromide hydrobromide*, m. p. 132°, converted by benzene-light petroleum crystallisation into the *hydrobromide*, m. p. 194°, of (5-bromo-3:4-diethyl-2-pyrryl)(2'-methyl-3':4'-diethyl-5'-pyrrolenyl)methene, m. p. 97°, obtained by treating the perbromide hydrobromide with alcoholic ammonia. The methene, or either of the salts, is converted into *octaethylporphin*, m. p. 318° (hydrochloride, m. p. 318°), either by fusion, or by concentrated sulphuric acid, or by boiling formic or acetic acid, or best, either by the action of hydrogen bromide in glacial acetic acid under pressure, or by succinic acid fusion (35% yield in the last case). Treatment of the last-named perbromide hydrobromide or of the hydrobromide with zinc dust and glacial acetic acid produces *octaethylporphyrinogen*, m. p. 184°, passing slowly if pure, but rapidly if impure, into *octaethylporphin* (m. p. 322° ?) by aerial oxidation. The mechanism of the synthesis of the porphyrinogen is regarded as involving first of all the formation of 5-bromo-2'-methyl-3:4:3':4'-tetraethyl-2:5'-dipyrrylmethane, since the picrate of I was isolated from the product containing the porphyrinogen.

Octaethylporphin is spectroscopically identical with *ætioporphyrin* (data tabulated). In hydrochloric acid the porphin shows the same spectrum as *ætioporphyrin*; after some time another spectrum is observed and a hydrochloride separates.

Iron is readily introduced into octaethylporphin in good yield. All three *hæmins* of the formula $C_{36}H_{44}N_4FeX$, where $X = Cl, Br, \text{ or } I$, are obtainable in well-defined forms. They are spectroscopically different in pyridine solution, in which additive compound formation probably takes place. The *copper salt*, $C_{36}H_{44}N_4Cu$, is described (spectroscopic data given). The *phyllin* is well defined (m. p. not below 400°) and forms a *copper salt*.

Octaethylporphin is oxidised by oxygen to diethylmaleimide, forms a *tetrabromo-compound*, and is oxidised by lead dioxide in chloroform and glacial acetic acid to the yellow *octaethylxanthoporphinogen*. The latter contains xH_2O , difficult to remove, and decomposes at 274°.

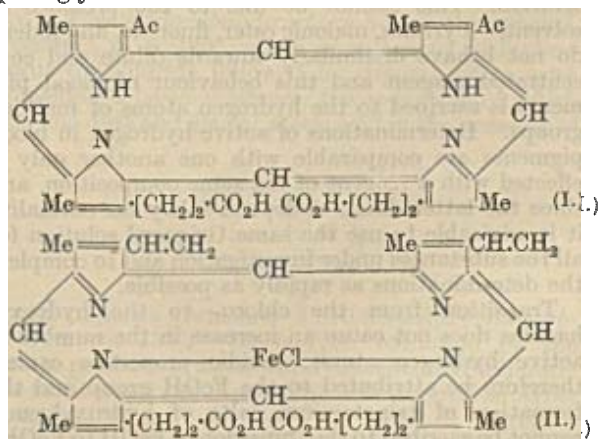
Octaethylporphin was also synthesised as follows: Magnesium ethyl bromide, followed by ethyl chloroformate, converts I into ethyl 2-methyl-3:4-diethylpyrrole-5-carboxylate. The latter, with bromine in absolute ether, passes into a bromo-compound which, when boiled with methyl alcohol and then submitted to hydrolysis, affords 3:4:3':4'-tetraethyl-2:2'-dipyrrylmethane-5:5'-dicarboxylic acid, m. p. 186°. When air is passed through a formic acid solution of this substance at 40°, octaethylporphin, m. p. 326°, is produced. Bromination of the same acid in glacial acetic acid affords (5-bromo-3:4-diethyl-2-pyrryl)-(5'-bromo-3':4'-diethyl-2'-pyrrolenyl)methene hydrobromide, decomp. 206°.

Condensation of I with formic acid in presence of hydrochloric, hydrobromic, or perchloric acid gives either the *hydrochloride*, or the *hydrobromide*, m. p. 202°, or the *perchlorate*, m. p. 173°, of the expected *methene*, m. p. 92° (copper salt, $C_{38}H_{54}N_4Cu$, m. p. 176°). Bromination of the methene at 100° in glacial acetic acid gives (3:4-diethyl-5-bromomethyl-2-pyrryl)(3':4'-diethyl-5'-bromomethyl-2'-pyrrolenyl)methene, which when submitted to succinic acid fusion with the above methene, m. p. 92°, gives octaethylporphin.

Ethyl 2:4-dimethylpyrrole-5-carboxylate reacts with isovaleryl chloride in presence of aluminium chloride to give ethyl 3-isovaleryl-2:4-dimethylpyrrole-5-carboxylate, m. p. 99°.

E. E. TURNER.

Synthesis of hæmatoporphyrin, protoporphyrin, and hæmin. H. FISCHER and K. ZEILE (Annalen, 1929, 468, 98—116).—Although deuteroporphyrin cannot be condensed with acetic anhydride in presence of aluminium or stannic chloride, deuterohæmin is converted into the *CC*-diacetyl derivative when it is treated with acetic anhydride and stannic chloride at the ordinary temperature (cf. Stadnikov and Rakovski, A., 1928, 427). A poor yield of the diacetyl derivative is obtained when aluminium chloride is used, but in both cases removal of iron from the product (using hydrogen bromide and glacial acetic acid at 40°), followed by esterification, gives the *methyl ester*, m. p. 234°, of *diacetyldeuteroporphyrin* (I). The latter forms a soluble ammonium salt, a sparingly soluble potassium salt, and a still more sparingly soluble sodium salt.



The methyl ester is converted by a solution of iron in

glacial acetic acid, in presence of sodium chloride and hydrochloric acid, into the complex iron salt, $C_{36}H_{36}O_6N_4FeCl$, m. p. 229°, and by copper acetate in presence of pyridine and acetic acid into the complex copper salt, $C_{36}H_{36}O_6N_4Cu$, m. p. 230°.

When an absolute alcoholic potassium hydroxide solution of diacetyldeuteroporphyrin is boiled, hæmatoporphyrin is formed. Its hydrochloride is crystallographically (STEINMETZ) and spectroscopically identical with natural hæmatoporphyrin hydrochloride. At 105° in a high vacuum, the free hæmatoporphyrin passes almost quantitatively into protoporphyrin, the methyl ester of which melts at 228°. Both substances are identical with the products derived from blood.

The synthetic hæmatoporphyrin hydrochloride is converted by hydrogen iodide in glacial acetic acid (Fischer and Kogl, A., 1924, i, 1130) into mesoporphyrin, the sparingly soluble sodium salt of which reacts with methyl-alcoholic hydrogen chloride to give mesoporphyrin dimethyl ester, m. p. 210°, identical with an authentic specimen. From the synthetic protoporphyrin, hæmin, $C_{34}H_{32}O_4N_4FeCl$, has been prepared (cf. Fischer and Pützer, A., 1926, 854). The product is crystallographically and spectroscopically identical with natural hæmin. At the moment the authors regard II as the most satisfactory formula for hæmin. E. E. TURNER.

Porphyrins and their metallic salts. F. HAUROWITZ and K. ZIRM (Ber., 1929, 62, [B], 163—170).—The lack of constancy in the results of determination of active hydrogen in blood pigment derivatives (cf. Fischer, A., 1926, 630; 1927, 1099; 1928, 903) by Zerevitinov's method is attributed to change in concentration of the Grignard reagent which rapidly loses strength if exposed to oxygen. This is usually unimportant, since the majority of organic compounds evolve methane quantitatively provided that the reagent is at least 0.8*N*. Compounds containing water of crystallisation require a 1.5*N*-reagent if both hydrogen atoms are to react quantitatively. The porphyrins appear to behave similarly to hydrated compounds, containing hydrogen atoms which react only with the concentrated reagent. With a dilute solution chlorohæmin indicates 2—3 active hydrogen atoms, whereas 3—6 are found with the concentrated solution. This cannot be due to the presence of solvent. Pyrroles, malonic ester, fluorene, and indene do not behave dissimilarly towards dilute and concentrated reagent and this behaviour of blood pigments is ascribed to the hydrogen atoms of methine groups. Determinations of active hydrogen in blood pigments are comparable with one another only if effected with a reagent of the same composition, and since the latter does not depend solely on normality it is advisable to use the same Grignard solution for all the substances under investigation and to complete the determinations as rapidly as possible.

Transition from the chloro- to the hydroxy-hæmins does not cause an increase in the number of active hydrogen atoms. Acidic properties cannot therefore be attributed to the FeOH group and the formation of tripotassium salts of hydroxyhæmin cannot be ascribed to the transition of FeOH to FeOK; the third acidic group is possibly the NH group of a

pyrrole ring. The number of active hydrogen atoms of porphyrins is diminished at most by one equivalent by the formation of complex metallic compounds with Cu, Zn, or FeCl. (The experiments are made with the dimethyl ester of mesoporphyrin.) These complex derivatives are therefore not formed analogously to potassium pyrrole by simple salt production involving two pyrrole hydrogen atoms. The organic porphyrin skeleton suffers marked alteration by union with metals.

The FeCl compound of mesoporphyrin ester contains the same number of active hydrogen atoms as the zinc or copper salt, suggesting that the residue is bivalent and the iron atom tervalent. Porphyrins do not, however, in general form hæmins with ferric salts unless a reducing agent is present. The possibility that ferrous passes into ferric iron by reducing the solvent appears unlikely, since no evidence could be obtained of the reduction of water to hydrogen or of valeric acid to the aldehyde or alcohol. Elimination of iron from hæmins by acid occurs in the ferric form without production of ferrous iron. The apparent contradiction is not fully explained. H. WREN.

1 : 3 : 4-Oxodiazines. III. J. VAN ALPHEN (Rec. trav. chim. 1929, 48, 163—172).— α -Bromopropionyl bromide reacts with β -acetylphenylhydrazine in benzene solution forming β -acetyl- α -(α' -bromopropionyl)phenylhydrazine, which when treated with anhydrous potassium carbonate in acetone yields Δ^2 -5-keto-4-phenyl-2 : 6-dimethyl-1 : 3 : 4-oxodiazine, b. p. 165—170°/15 mm., n_D^{20} 1.5583. The following substituted 5-keto-1 : 3 : 4-oxodiazines are obtained similarly from the appropriate α -halogenoacetyl halide and β -acetylphenylhydrazine: 4-phenyl-2-methyl-6-ethyl-, b. p. 146—148°/12 mm., n_D^{20} 1.5512; 4-phenyl-2 : 6 : 6-trimethyl-, b. p. 150—153°/15 mm., n_D^{20} 1.5423; 4 : 6 : 6-triphenyl-2-methyl-, m. p. 136°, isolated directly from β -acetylphenylhydrazine and diphenylchloroacetyl chloride; 2 : 4 : 6-triphenyl-, m. p. 141°; 2 : 4 : 6 : 6-tetraphenyl-, m. p. 151°, from β -benzoylphenylhydrazine and diphenylchloroacetyl chloride; 4-phenyl-2- β -phenylethyl-, m. p. 79°, hydrolysed by aqueous-alcoholic sulphuric acid to β -phenylpropionphenylhydrazide; 4-phenyl-2-styryl-, m. p. 128°, from cinnamphenylhydrazide and chloroacetyl chloride. The action of 10% aqueous-alcoholic sulphuric acid on the above and previously described oxodiazines (A., 1928, 780, 1386) shows that fission of the oxodiazine ring is partly inhibited with three methyl groups in the 2 and 6 positions, and completely stopped by one phenyl or styryl group in position 2.

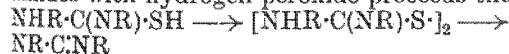
Δ^2 -5-Keto-2 : 4 : 6-triphenyl-1 : 3 : 4-oxodiazine is soluble in boiling aqueous-alcoholic sodium hydroxide, reacting in its enol form. This modification appears to be fairly stable, since the freshly-precipitated solid from an alkaline solution forms a chloroform-soluble copper salt, whereas the original compound does not. β -Benzoyl- α -phenylchloroacetylphenylhydrazine has m.p. 136°, not sharp. H. BURTON.

Dioximes. LI. G. PONZIO and M. MILONE (Gazzetta, 1928, 58, 844—853).—On the basis that the components of solid solutions resemble one another in molecular structure, the structure of dioxime peroxides is deduced from cryoscopic data, formation of

solid solutions being indicated by elevation of apparent mol. wt. The two structures in question are $\text{MeC} \begin{smallmatrix} \text{---} \text{C} \text{Ar} \\ \text{O} \cdot \text{N} \cdot \text{O} \cdot \text{N} \end{smallmatrix}$ (I) and $\text{MeC} \begin{smallmatrix} \text{---} \text{C} \text{Ar} \\ \text{N} \cdot \text{O} \cdot \text{O} \cdot \text{N} \end{smallmatrix}$ (II) (cf. A., 1928, 888). Compounds of type I, oxadiazole *N*-oxides, would be expected to form solid solutions with the oxadiazoles themselves, and actually it is found that 3-phenyl-, 3-*p*-bromophenyl-, and 3-*p*-anisyl-4-methyl-1:2:5-oxadiazole-5-oxides show elevation of apparent mol. wt. in 3-*p*-anisyl-4-methyl-1:2:5-oxadiazole. The last is therefore used as a test substance, and it is found that bromo- and nitro-anisyl-methyloxadiazole oxides, m. p. 109° and 88°, respectively, show increased mol. wt., and thus probably have similar structures, i.e., are *N*-oxides, whilst the corresponding compounds of m. p. 115–116° and 112° have normal mol. wt., and are thus probably described correctly as bromo- and nitro-anisylglyoxime peroxides. Determinations of the apparent mol. wt. of the test substance in oxadiazole oxides, and of the compounds of m. p. 109° and 88° in bromo- and nitro-anisylmethyloxadiazoles, respectively, have also been made.

E. W. WIGNALL.

Oxidation. II. Action of ferric chloride and hydrogen peroxide on *s*- and *as*-disubstituted thiocarbamides and synthesis of thiodiazoles. T. CHAKRAVARTI and S. DE (J. Indian Chem. Soc., 1928, 5, 661–664).—Oxidation of diarylthiocarbamides with hydrogen peroxide proceeds thus:



$\begin{smallmatrix} | \\ >\text{S} \end{smallmatrix}$ (I). The following substituted 1:3:4-

thiodiazoles were obtained from the requisite *s*-diarylthiocarbamide: 2:5-*di*-phenylimino-3:4-*di*-phenyl- (I, R=Ph), m. p. 228–230°; 2:5-*di*-*p*-tolylimino-3:4-*di*-*p*-tolyl-, m. p. 261°; 2:5-*di*-*o*-tolylimino-3:4-*di*-*o*-tolyl-, m. p. 249°; 2:5-*di*-*m*-xylylimino-3:4-*di*-*m*-xylyl-, m. p. 247°; 2:5-*di*- α -naphthylimino-3:4-*di*- α -naphthyl-, m. p. 285°, and 2:5-*di*- β -naphthylimino-3:4-*di*- β -naphthyl-, m. p. 288° after sintering at 268°. From the necessary *as*-disubstituted thiocarbamides: 2:5-*di*-(phenylmethylamino)-, m. p. 94°, 2:5-*di*-(phenylethylamino)-, m. p. 107–109°, and 2:5-*di*-(diphenylamino)-1:3:4-thiodiazoles, m. p. 155°, were prepared.

H. BURTON.

3-Chlorotropin. The non-existence of the bellatropine of Hesse. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1928, 188, 179–181).—Bellatropine, the hydrolytic product obtained by treating belladonine with hydrochloric acid at 140° and considered by Hesse to be an isomeride of tropine, is actually 3-chlorotropin, b. p. 163–165° (partial udecomp.) (hydrochloride, m. p. 234°; picrate, m. p. –217°). The methiodide, m. p. 306°, affords tropin methiodide when treated with zinc dust and hydrochloric acid. 3-Chlorotropin yields a crystalline *mu*ic oxide (hydrochloride, m. p. 210°; picrate, m. p. 175°; chloroplatinate, m. p. 252°; chloroaurate, m. p. 168° after darkening and softening at 150°). The use of hydrobromic acid in the hydrolysis leads to the formation of 3-bromotropin. Belladonine yields partly polymerised atropic acid, tropine, and tropidine when hydrolysed with alcoholic potassium

hydroxide or 2% sulphuric acid. [Throughout the paper the authors write the formulæ of 3-chlorotropin and its derivatives as containing an atom of oxygen.]

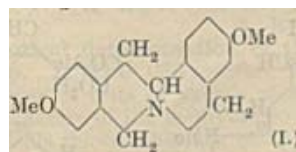
G. A. C. GOUGH.

Amine oxides of hydrastrine and narcotine. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1929, 188, 341–343).—Hydrastrine is converted by an acetic acid solution of 30% hydrogen peroxide into *hydrastrine oxide*, $[\alpha]_D +88^\circ$ in 3% chloroform solution (hydrochloride, m. p. about 125°, $[\alpha]_D +160^\circ$ in 12% aqueous solution; picrate, m. p. 128°). The oxide behaves like an amine oxide in most respects, although it slowly passes into a yellow substance, $\text{C}_{20}\text{H}_{18}\text{O}_7\text{NMe}$, m. p. 189° (hydrochloride, m. p. 196°), which behaves differently. Similarly, narcotine affords *narcotine oxide*, $[\alpha]_D +135^\circ$ in chloroform (hydrochloride, m. p. 193°, $[\alpha]_D +100^\circ$; picrate, m. p. 130°; chloroplatinate, m. p. 175°), changing into a substance, m. p. 228–229°, identical with that obtained by Drummond and McMillan (A., 1926, 1263) except that it is optically inactive.

G. A. C. GOUGH.

Synthesis of 3:10-dimethoxytetrahydroprotoberberine. S. N. CHAKRAVARTI and W. H. PERKIN, jun. (J.C.S., 1929, 196–201; cf. A., 1927, 1096).—*m*-Methoxybenzoic acid, m. p. 109–110° (methyl ester, b. p. 121–124°/10 mm.), was obtained in 90% yield by oxidising *m*-methoxybenzaldehyde with potassium permanganate in aqueous acetone solution. It condenses with formaldehyde in the presence of hydrochloric acid or, better, of the latter together with glacial acetic acid to give 4-methoxyphthalide, m. p. 120°. This is converted by manganese dioxide and sulphuric acid or alkaline potassium permanganate into 4-methoxyphthalic acid, m. p. 168–170° (decomp.), and not into the expected 4-methoxyphthalaldehydic acid which was required for the synthesis of 4-methoxyphthalidecarboxylic acid. The latter was, however, prepared by condensing methyl 4-methoxybenzoate with chloral hydrate in presence of a large excess of sulphuric acid. The 4-methoxytrichloromethylphthalide, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{---} \text{CH} \text{CCl}_3 \\ \text{CO} \cdot \text{O} \end{smallmatrix}$, so obtained m. p.

135°, was hydrolysed by aqueous sodium hydroxide to 4-methoxyphthalidecarboxylic acid, m. p. 170°. Condensation of the acid chloride of the latter with β -*m*-methoxyphenylethylamine in benzene solution gave 4-methoxyphthalidecarboxy- β -*m*-methoxyphenylethylamide, m. p. 129°, which when heated with phosphorus oxychloride followed by decomposition with ice yielded a basic substance, the reduction of which with zinc dust and glacial acetic acid in the presence of



copper sulphate furnished 3:10-dimethoxyprotoberberine, m. p. 180°. Electrolytic reduction of the latter in presence of alcohol and concentrated sulphuric acid furnished 3:10-dimethoxytetrahydroprotoberberine (I), m. p. 139°.

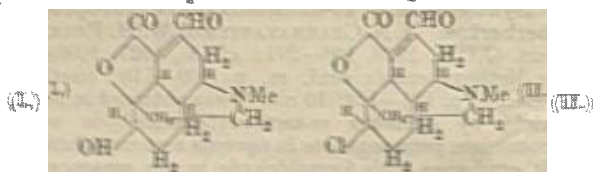
A. I. VOGEL.

Dehydrogenation of yohimbine. F. MENDELIK and J. P. WIBAUT (Rec. trav. chim., 1929, 48, 191–

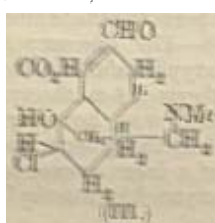
—Dehydrogenation of rohimbine with powdered selenium at 300–310° (cf. Diels, A., 1928, 51) gives a colourless compound, $C_{18}H_{16}N_2$, m. p. –1–213° (corr.), soluble in dilute acids with a blue fluorescence, and giving various alkaloidal precipitation reactions, together with a substance, m. p. 326°, yellow, not obtained pure, which dissolves in alcohol with a bluish-green fluorescence. H. BURTON.

Fissions with ozone in the morphine series. E. SNEYK (Ber., 1929, 62, [B], 209—218; cf. Wieland Small, this vol., 81).—Thebaine is converted by short treatment with 30% hydrogen peroxide into (189—190°); the presence of two carboxyl groups is established by potentiometric titrations. The monohydrated hydrochloride, m. p. 242° (decomp.), is described.

Oxalhydracetic acid hydrochloride (cf. Speyer and Popp, A. 1926, 532) is transformed by condensation in aqueous solution into methyl glyoxylate (phenylhydrazones, m. p. and dihydroacetal (I)

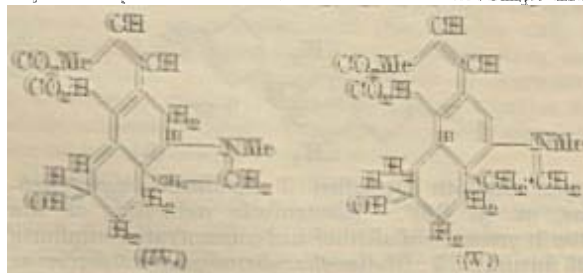


(amorphous phenylhydrazones and its derivatives, decm. 24°). Similarly, exothermally hydrazonophore (loc. cit.) acids dihydroxycinnal and ethyl glyoxalate:



dihydroacetaldehydeacetaldehyde di-
acompases at 275° (chloroac-
etaldehydeacetaldehyde dissolved in a
mixture of ethyl alcohol, chloro-
acetic acid, and perchloric acid
is transformed to oxalacetic
acid).

in. n. 216—217° (decamp.) [*perchlorate* (hydrated) softening at 165° (anhydrous, decamp. 270°)] whereas in acetic acid solution it affords *chloroal hydroradinal perchlorate* (cf. III), decamp. 216°, α_D^{20} —22.48° in water (also monohydrate). Chlorodihydroacetaldehyde in alcohol containing perchloric acid is ozonised to chlorodihydroacetal and methyl glyoxylic acid, whereas in formic acid solution it yields chlorodihydroacetal. Hydroxydihydroacetaldehyde in acetic acid solution and dihydroamphetamine in formic acid when ozonised yield respectively a substance, decamp. 245°.



and dihydroacetal. Ozonodihydroacetaline hydrochloride is converted by alcoholic sodium ethoxide at a temperature not exceeding 35° into 5-ozonodihydra-

codeine (IV), m. p. 170.5°, $[\alpha]_D^{25} +24.4^\circ$ in absolute alcohol, in 93% yield. If the reaction is allowed to proceed at 45–50°, γ -ozodihydrocodeine (V),⁴ m. p. 175°, $[\alpha]_D^{25} -8.2^\circ$ in alcohol, is produced. The β -compound is transformed into the γ -derivative by alcoholic sodium ethoxide at 50°. H. WREN.

Synthesis of aromatic arsenic compounds containing iodine. A. D. MACULLUM.—See B., 1929, 150.

Organo-antimony compounds. III. S. C. NITTOGI (J. Indian Chem. Soc., 1928, 5, 753—757).—Carbamide and *p*-aminophenylstibinic acid react in boiling aqueous suspension to give "ureastibamine" (Brahmachari, Indian J. Med. Res., 1922, 10, 508; 1924, 12, 423), proved to be ammonium 4-carbamido-phenylstibinate (sodium and potassium salts) by its preparation from cyanic and *p*-aminophenylstibinic acids. ammonia. H. BURTON.

Attempt to prepare mercury compounds of triphenylmethane dyes. F. R. GREENBAUM (Amer. J. Pharm., 1929, 101, 34—46).—Mercuration of brilliant-green, malachite-green, gentian-violet, night-blue, and basic fuchsin with mercuric chloride gave mixtures of mono- and di-mercury compounds which were almost insoluble in alcohol and water. Alkali-soluble dimercury compounds were obtained by mercuration of the condensation products of benzotrichloride and phenol and resorcinol.

E. H. SHAPLES.

Aromatic compounds containing tellurium. F. P. MARRA and E. MILCARONA (Rend. Accad. Sci. fis. mat. Napoli, 1928, [m], 34, 54-59).—*Diphenyltelluride-o-o'-dicarboxylic acid*, m. p. 215° (soluble in sodium salt), is obtained from an alkali telluride and dicarboxylic anhydride acid. The method of Emys (A., 1901, iii, 44) for the preparation of potassium telluride not being satisfactory, sodium telluride was prepared by the reaction between sodium and tellurium in liquid ammonia in an atmosphere. When the above acid was reduced by zinc and potassium hydroxide, and treated with sodium chloroacetate, *o-o'-carboxyphenylphenyltelluric acid*, m. p. 195°, was obtained. This decomposed when treated with fused potassium hydroxide, but when boiled with acetic anhydride it furnished 3-phenylphenyltellurindigotin, m. p. 200° (after decamp. at 146°) (acetyl derivative). By analogy with the corresponding selenium compound (Lewer and Weiss, A., 1902, i, 642) this was expected to yield tellurindigotin, but all attempts to carry out this oxidation were unsuccessful. F. W. WIGGALL.

Metal-protein compounds. VII. Changes in properties of egg-~~albumin~~
treated with oobakt powder. G. B. SORDO
A. Giannino (Arch. Sci. Ital., 1928, 11, 212-216;
Chem. Zentr., 1928, II, 1191-1192).—The electrical
conductivity and ρ_m of dialysed egg-~~albumin~~ solutions
are increased by addition of oobakt powder.

1. 1. 1960

Action on carbon monoxide in catalysis. H. A. KILKS (Birmingham, J., 201, 489).—Dixon's suggestion (A., 1928, 1149) solutions on were used by the author as incorrect. That Dixon obtained no evidence of

inhibition by carbon monoxide is due to his having used impure reagents. J. H.

Inhibition of ferrocysteine catalysis by carbon monoxide. W. CREMER (Biochem. Z., 1928, 201, 490).—Dixon's failure (A., 1928, 1149) to obtain inhibition of ferrocysteine catalysis is due to his having used the ratio of carbon monoxide to oxygen (P_{CO}/P_{O_2}) applicable to human. This is unsuitable for ferrocysteine. J. H. BIRKINSHAW.

Micro-Dumas apparatus. S. OMLD (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8).—Improvements in Dumas's micro-method for nitrogen determination are described: (a) by passing carbon dioxide through the preheated combustion tube while still red hot, to avoid occlusion of air, and (b) by use of a three-way cock between the carbon dioxide generator and the bubble counter. B. W. ANDERSON.

Determination of iodine (halogen) in organic material. J. SCHWAIBOLD (Chem.-Ztg., 1929, 53, 22—23).—For the determination of small amounts of iodine in organic material, a weighed amount (up to several grams) of the dried substance is burnt in a porcelain or nickel boat in a stream of oxygen in a wide combustion tube. The vapours pass over heated platinumed asbestos and through wash-bottles containing very dilute potassium carbonate. The boat and tube are finally washed out, the extract is combined with the potassium carbonate, the whole evaporated, and iodine determined by an appropriate method. Examples are given of the determination of iodine in thyroid extract, milk, urine, and soil.

R. K. CALLOW.

Micro-determination of iodine in organic material. J. F. REITH (Chem. Weekblad, 1929, 26).—The author claims a method similar to that of Schwaibold (preceding abstract) but arrived at independently. The material is burned in oxygen and the gases are drawn through alkaline solutions, which are added to the ash. S. I. LEVY.

Determination of sulphur in organic compounds. I. MAREK (Bull. Soc. chim., 1928, [iv], 43, 1405—1408).—The organic substance is burnt in a quartz, pyrex, or Jena glass combustion tube (50 cm. \times 18—20 mm.), the forward end of which is bent over at right angles, constricted slightly, and drawn out. Moist oxygen is admitted through a sealed-in side tube at the opposite end and the combustion boat can be pushed forward into the heated zones by means of a nickel rod. The combustion products are swept into water containing 2% of dissolved oxygen, and the sulphuric acid is determined by titration or, in presence of halogen, phosphorus, nitrogen, or arsenic, by gravimetric methods. Halogen can be determined in the same way, using a 3% solution of equal parts of sodium carbonate and sodium sulphite as absorbent. R. BRIGHTMAN.

Microchemical detection of glycerol, ethylene glycol, and d-mannitol. H. ALBER (Mikrochem., 1929, 7, 21—29).—The sensitivity of the following:

for the detection of glycerol, glycol, and mannitol has been determined and the conditions for carrying out microchemically have been standardised:

Fischer and Tafel's hypobromite method and its various modifications (A., 1888, 358), Glaser and Moravski's formic acid method (A., 1890, 20), and Rose's boric acid method (Diss., Erlangen, 1902).

A. R. POWELL.

Micro-determination of the acetyl value. F. PREGL and A. SOLTYS (Mikrochem., 1929, 7, 1—9).—The substance (3—5 mg.), preferably compressed into a pastille, is introduced into a small pear-shaped flask, the bulb of which is then filled with dry glass beads. The flask is connected by means of a side tube at the top of the bulb to a purifying and drying apparatus for air, and by means of a side tube in the neck with a U-tube packed with glass beads moistened with a saturated solution of potassium dihydrogen phosphate to absorb any sulphur dioxide. The other limb of the U-tube is connected by a silver tube and condenser to the absorption flask containing standard sodium hydroxide. The flask is heated in a water-bath for 20—40 min. while 1 c.c. of a 25% solution of toluene-*p*-sulphonic acid is introduced by means of a dropping funnel. The flask is then cooled and a slow current of purified air is drawn through it by attaching the side tube of the absorption flask to a vacuum pump capable of exhausting the apparatus to 15 mm. pressure. After 10 min., 1 c.c. of water is allowed to drop into the decomposition flask and the air current continued for another 10 min. without interrupting the suction. The U-tube is then immersed in hot water and the suction continued for a further 10 min. to ensure that all the acetic acid distils into the absorption flask. The solution in the latter is finally titrated with hydrochloric acid, using a slight excess which is determined by titration with 0.01N-sodium hydroxide. A. R. POWELL.

Microchemical determination of hydrocyanic acid by the Brunswik reaction. W. P. MALITZKY and M. T. KOSLOVSKY (Mikrochem., 1929, 7, 94—99).—The sensitivity of the Brunswik reaction is increased by the use of a silver nitrate solution acidified with nitric acid. The material to be tested is placed in a small tube together with a few drops of a saturated solution of oxalic acid and 2—3 drops of potassium permanganate solution if sulphides are present; the tube is covered with a watch-glass to the bottom of which is attached a small drop of the silver nitrate solution coloured with methylene-blue. If cyanides are present a turbidity due to silver cyanide appears in a few minutes; under the microscope blue needles are seen. The sensitivity of the test is 6×10^{-8} g. of hydrogen cyanide.

A. R. POWELL.

Microchemical determination of the methylimino-group. P. HAAS (Mikrochem., 1929, 7, 69—87).—A number of tests of Pregl's method for the micro-determination of the methylimino-group using various alkalis showed that low results are almost invariably obtained, especially when the substance contains more than one NMe group. The errors seem to be due to the difficulty of removing the whole of the NMe from the substance and to the incomplete absorption of the hydrogen iodide by the red phosphorus suspension even when two or three absorption vessels are used. A. R. POWELL.

Biochemistry.

Hæmoglobin. III. Equilibrium between oxygen and hæmoglobin in relation to changing p_H . R. M. FERRY and A. A. GREEN (J. Biol. Chem., 1929, 81, 175—203).—Horse-blood corpuscles diluted with 1.5% sodium chloride at 2° were run through a Sharples centrifuge, the concentrated cell suspension was added to distilled water and the solution again centrifuged, the mother-liquor was stirred and adjusted to about p_H 6.6 by addition of phosphate or dilute hydrochloric acid, and the hæmoglobin was recrystallised by dissolving in dilute potassium hydroxide and readjustment to p_H 6.6. Oxygen dissociation curves for the hæmoglobin thus prepared were determined at varying p_H in solutions buffered with phosphate or borate. The affinity of hæmoglobin for oxygen passed through a minimum at p_H 6.55. The combination of hæmoglobin with oxygen does not follow the simple mass law unless hæmoglobin be regarded as acting as a mixture of substances. Mathematical consideration of the results leads to the development of an empirical equation expressing the equilibrium, and to a theoretical expression for the change of the dissociation curve with p_H , based on the theory of intermediate compound formation (cf. Adair, A., 1925, i, 849). C. R. HARINGTON.

Structure of the hæmoglobin molecule. I. Nitrogen distribution in the hæmoglobin molecule of horse's blood. II. Nitrogen distribution in the globin molecule of horse hæmoglobin. A. POLJAKOV (Biochem. Z., 1929, 204, 88—96, 97—105).—I. After repeated crystallisations of horse hæmoglobin elementary analyses and determinations of nitrogen in the various fractions obtained after hydrolysis were made. The content of arginine is 6.25%, histidine 13.78%, cystine 1.2%, and lysine 5.76%.

II. Globin was prepared by adding an aqueous solution of pure hæmoglobin to alcohol containing hydrochloric acid, precipitation by ether, washing with alcohol, and precipitating the aqueous solution with alcohol and ether. A globin hydrochloride was obtained. Analysis showed arginine 6.1%, histidine 13.25%, cystine 1.2%, lysine 6.2%.

J. H. BIRKINSHAW.

Formation of hæmatin from carboxy- and oxy-hæmoglobin by dilute acids. W. LINTZEL and T. RADEFF (Biochem. Z., 1928, 203, 212—217).—When oxy- and carboxy-hæmoglobin solutions of the same molar concentration are treated with dilute acids the amount of hæmatin formed is 5—10% less for oxy- than for carboxy-hæmoglobin, whilst iron in an ionised form appears in the solution from the former but not from the latter. Oxyhæmoglobin, therefore, appears to undergo partial decomposition by the acid treatment. P. W. CLUTTERBUCK.

Synthesis of hæmatoporphyrin, protoporphyrin, and hæmin. H. FISCHER and K. ZEILE.—See this vol., 333.

Relation of proteins and lipins of blood-serum to osmotic pressure. E. H. FISHBERG (J. Biol.

Chem., 1929, 81, 205—214).—The relationship between the protein concentration and the (colloid) osmotic pressure of blood-serum is expressed by $p = e^{\alpha v}$, p and v being the reciprocals of the osmotic pressure and of the protein concentration, and α a constant specific for an individual serum. In lipæmic blood the osmotic pressure per g. of protein is greater than in normal blood diluted to a similar content of protein; this indicates that the lipins exercise an osmotic pressure, and that the development of lipæmia in hæmorrhage and in nephrosis represents an attempt to compensate, as regards the osmotic pressure, for the loss of protein.

C. R. HARINGTON.

Viscosity of blood-serum as a function of temperature. P. L. DU NOÛY (J. Gen. Physiol., 1929, 12, 363—377).—The viscosity of serum at various temperatures was determined by the rotating-drum method. Heating decreases the viscosity until the critical temperature, 55°, is reached; above this the viscosity rises rapidly, and heating above 57° for short periods causes a permanent increase in viscosity. This effect is due to the change in hydration of the protein. E. BOYLAND.

p_H of arterial and venous blood. A. LUMIÈRE, (MME.) R. H. GRANGE, and R. MALAVAL (Compt. rend., 1929, 188, 364—367).—Determination of the p_H of arterial and venous blood-serum of the dog by means of the hydrogen electrode and with precautions against the displacement of part of the carbon dioxide by atmospheric oxygen, gives 7.78 and 7.43 as the respective average values. When the serum, the plasma, or the whole blood is placed in a vacuum, the p_H values rise towards 8 and consequent heating of these liquids at 56° causes a further rise to p_H 8.4.

G. A. C. GOUGH.

Physiological ontogeny. A. Chicken embryos. XIV. Hydrogen-ion concentration of the blood of chicken embryos as a function of time. A. E. COHN and A. E. MIRSKEY (J. Gen. Physiol., 1929, 12, 463—468).—The p_H of the blood of 8—20-day chicken embryos was determined with a glass electrode. At 8 days the p_H of the reduced blood was 6.92; at 20 days, 7.22, whilst the blood of normal adults is 7.30. There was a tendency for the p_H to remain at about 7.15 between the 10th and 14th days. The change in p_H seems to follow the same course as the oxygen consumption (cf. Murray, A., 1925, i, 1353), so that the change in p_H probably follows the change in metabolism. E. BOYLAND.

[p_H of blood.] J. HOLLÓ and E. WEISS (Bull. Soc. Chim. biol., 1928, 10, 1372—1375).—A reply to criticisms by Bigwood (A., 1928, 564) of the author's method for the determination of the p_H of blood.

G. A. C. GOUGH.

[p_H of blood.] E. J. BIGWOOD (Bull. Soc. Chim. biol., 1928, 10, 1376—1377).—Whilst no objection is made to the method of Holló and Weiss (preceding abstract), it is doubtful whether their method is more accurate than those of Cullen and Hastings.

G. A. C. GOUGH.

Behaviour of ethyl iodide in the body. I. STARR and C. J. GAMBLE (*Amer. J. Physiol.*, 1928, **87**, 474—485).—Ethyl iodide is constantly present in the venous blood of men or dogs inhaling it and exerts pressure against gases in contact with it.

B. A. EAGLES.

Absorption of ethyl chloride by blood, serum, and water. M. NICLOUX and L. SCOTTI-FOGLIENI (*Compt. rend. Soc. Biol.*, 1928, **98**, 229—232; *Chem. Zentr.*, 1928, ii, 682).—The solubility of ethyl chloride in pig or ox blood is greater than in the corresponding serum, and greater still than in water.

A. A. ELDRIDGE.

Role of the blood in transmineralisation. C. OEHME and P. TOROK (*Deut. Arch. klin. Med.*, 1928, **160**, 233—248; *Chem. Zentr.*, 1928, ii, 1114).

Determination of calcium in blood. J. H. ROE and B. S. KAHN (*J. Biol. Chem.*, 1929, **81**, 1—8).—A modification of the authors' method (A., 1926, 763) is described, calcium being precipitated as phosphate and the phosphorus in the precipitate determined by the method of Fiske and Subbarov (A., 1926, 443).

C. R. HARRINGTON.

Micro-determination of free phosphate in blood. E. JORPES and H. MAGNUSSEN (*Acta Paed.*, 1927, **7**, No. 1—2, 14 pp.; *Chem. Zentr.*, 1928, ii, 925—926).—The phosphate in blood deproteinised by means of trichloroacetic acid is precipitated as phosphomolybdate and collected on a micro-filter. Organic non-lipoid phosphorus in adults amounted to 0.25–0.35 mg. % (4–9% of the total non-lecithin phosphorus), and the phosphorus as free phosphate to 3.44 mg. %.

A. A. ELDRIDGE.

Is there an iodine value of the blood dependent on the thyroid gland? F. BLUM (*Schweiz. med. Woch.*, 1927, **57**, No. 34, 14 pp.; *Chem. Zentr.*, 1928, ii, 1111).—The thyroid gland does not pass iodine into the blood. Fellenberg's method for the determination of iodine is not suitable for blood.

A. A. ELDRIDGE.

Peptide-nitrogen of blood. R. MARTENS (*Bull. Soc. Chim. biol.*, 1928, **10**, 1336—1371).—Peptide-nitrogen is determined as the difference between the amino-nitrogen content after hydrolysis and elimination of ammonia and the original amino-nitrogen content of the filtrate from deproteinisation with 20% trichloroacetic acid, the method of Folin being used (A., 1922, ii, 536, 540). The trichloroacetic acid solution does not effect complete precipitation of leucylglycine, glycine, or proteoses. Blood from pathological cases is examined. G. A. C. GOUGH.

Amide-nitrogen of blood. II. **Determination.** III. **Muscular exercise; role of ammonia in neutralisation of lactic acid.** S. BLISS

B. *Chem.*, 1929, **81**, 129—135, 137—158).—II. The proteins of blood are precipitated with tungstic acid, the precipitate is hydrolysed by heating at 100° with 4*N*-sulphuric acid, and the ammonia liberated determined in the usual way. The amide-nitrogen of blood determined in this manner amounts normally to 134—144 mg. per 100 c.c.

III. A dog is able to tolerate an amount of ammonium carbonate administered intra-arterially which, if given intravenously, causes toxic symptoms; after

the intra-arterial administration an increase in the amide-nitrogen of the venous blood is observed, which, in dogs with normal kidneys, is of short duration only. After muscular exercise the amide-nitrogen of the arterial blood is diminished and that of the venous blood increased; this is accounted for in part by the increased excretion of ammonia, and in part on the view that ammonia, derived from the amide-nitrogen of the blood, is utilised in the neutralisation of lactic acid formed during exercise. C. R. HARRINGTON.

Hypobromite method for the determination of small quantities of ammonia, particularly of residual nitrogen in blood. W. ENGELHARDT and M. LJUBIMOVA-KREMLEVA (*J. exp. Biol. Med.* [Moscow], 1927, No. 16, 26 pp.; *Chem. Zentr.*, 1928, ii, 1241).—The iodometric hypobromite method is combined with the micro-Kjeldahl method for the determination of residual nitrogen in blood.

A. A. ELDRIDGE.

Distribution of uric acid in blood, and cause of errors in the determination of blood-uric acid. R. VLADESCO (*Compt. rend. Soc. Biol.*, 1928 **98**, 462—464; *Chem. Zentr.*, 1928, ii, 682).—The determination of uric acid in whole blood is more exact than that in serum; it must be preceded by complete haemolysis of the red cells. Tungstic acid is preferred as a clarifying agent to trichloroacetic acid.

A. A. ELDRIDGE.

Blood-sugar regulation in mammals. I. **Action of cold and hunger on blood-sugar.** B. KISCH, A. SIMONS, and P. WEYL (*Biochem. Z.*, 1929, **204**, 179—191).—Temperatures around 0° caused no marked increase in the blood-sugar of dogs and rabbits in the open air. When the animals were placed in an ice-box for 5—11 hrs. dogs showed an initial increase in blood-sugar of 10—30% followed by a decrease to below normal. Fasting rabbits showed a small decrease; when freshly fed there was a transient hyperglycemia as with dogs. At 23—26° the blood-sugar regained its normal value. Fasting caused only a slight fall in the blood-sugar.

J. H. BIRKINSHAW.

Blood-catalase. H. BISCHOFF (*Arch. Kinderheilk.*, 1927, **82**, 189—198; *Chem. Zentr.*, 1928, ii, 1113).—The catalase content of the blood of children does not differ greatly from that of adults, but varies according to the point of extraction of the sample. The value is unchanged in infection or irradiation.

A. A. ELDRIDGE.

Interfacial adsorption as a factor in the clotting of blood-plasma. J. M. JOHLIN (*J. Biol. Chem.*, 1929, **81**, 99—113).—The blood-plasma of fishes, which can normally be kept indefinitely without clotting, can be induced to clot by emulsification with air, ether, or chloroform (but not with paraffin), or by treatment with barium sulphate, kaolin, or powdered glass; ether-extracted plasma will cause normal plasma to clot, whilst the ethereal extract contains a substance which antagonises the accelerating effect of kephalin on clotting. The phenomena are regarded as being due to the adsorption of an antiprotease at the interface of the plasma with the various substances mentioned.

C. R. HARRINGTON.

Hæmolysis. K. C. SEN, A. C. RAY, and N. N. MITRA (*Nature*, 1929, **123**, 242).—Both acceleration and retardation of hæmolysis in presence of normal serum can readily be obtained in taurocholate and oleate hæmolysis by varying concentrations of the reacting substances. Similar curves are obtained when the serum is replaced by a dilute solution of sodium hydroxide. Acceleration with saponin has not been observed. A. A. ELDRIDGE.

Hæmolysis. III. Photochemical transformation of lecithin in the presence of hæmatoporphyrin. R. FABRE and H. SIMMONET (*Bull. Soc. Chim. biol.*, 1928, **10**, 1306—1325).—Irradiation of an alcoholic solution of lecithin and hæmatoporphyrin by the light of a mercury-vapour lamp leads to the formation of a substance which, when dissolved in normal saline, exerts a powerful hæmolytic action on the red blood-corpuscles of the dog (cf. Fabre, A., 1926, 750). The hæmolytic agent is not altered by dialysis or by boiling in an isotonic solution for 1 hr.; it is insoluble in ether but partly soluble in acetone and in alcohol. It is unaffected by 0.1*N*-hydrochloric acid, but treatment with 0.1*N*-sodium hydroxide increases its activity nearly tenfold.

G. A. C. GOUGH.

Time-dilution curves in hæmolytic systems. K. C. SEN and N. N. MITRA (*J. Indian Chem. Soc.*, 1928, **5**, 683—695; cf. MacLean and Hutchinson, A., 1909, ii, 816; Ponder, A., 1922, i, 292; 1923, i, 975; 1926, 751; 1927, 585).—The time-dilution curves for the hæmolysis of sheep's erythrocytes by hydrochloric acid, sodium hydroxide, potassium oleate, and saponin are all normal, the time of hæmolysis decreasing with increasing concentration of added substance. With sodium taurocholate marked abnormality is observed over the range of concentrations studied (approx. 1 in 50—16,000), but at low concentrations (below 1 in 1400) using small amounts of erythrocytes the curve is normal. The differences in results obtained by various workers (*loc. cit.*) are probably due to the concentrations of the hæmolytic systems. Sodium hydroxide retards the hæmolytic action of saponin, and inhibits completely that of sodium taurocholate over the range of concentrations examined. With potassium oleate and sodium hydroxide an acceleration is found for low oleate concentration; at higher oleate concentration inhibition takes place. With the same concentration of oleate hæmolysis always takes place first in presence of alkali. H. BURTON.

Immuno-chemical investigations on globin and globin derivatives. L. HEKTOEN and K. SCHULHOF (*Biochem. Z.*, 1929, **204**, 125).—A reply to Ottensooser and Strauss (A., 1928, 540).

Relation of lipins to proteins and immunity. S. BELFANTI (*Z. Immunitats.*, 1928, **56**, 449—463; *Chem. Zentr.*, 1928, ii, 1116).—The hæmolytic action of animal poisons on addition of lecithin is due to lecithinase whereby lysocithin is produced. A corresponding lipin has been isolated from the pancreas. Egg-yolk contains two proteins, one coagulable and the other soluble; with these is associated a large part of the lecithin, together with lysocithin, which may be extracted with alcohol. The soluble portion of egg-

vitellin detoxicates lysocithin. Wasp- and hornet-poisons decompose lysocithin. A. A. ELDRIDGE.

Rôle of lipins in immunisation. V. BRAZIL and J. VELLARD (*Z. Immunitats.*, 1928, **56**, 191—208; *Chem. Zentr.*, 1928, ii, 1116).—Animals could be immunised against animal and bacterial poisons with lipins prepared from serum and liver.

A. A. ELDRIDGE.

Concentration of sera containing anti-bodies by physico-chemical methods. (Electrodialysis and adsorption.) M. EISLER and M. SPIEGEL-ADOLF (*Biochem. Z.*, 1929, **204**, 28—45).—The use of electrodialysis in the concentration of serum agglutinating typhoid bacilli had no special advantages over half saturation with ammonium sulphate. A method depending on repeated precipitation of the active component by means of aluminium hydroxide and subsequent elution by 0.01*N*-sodium hydroxide is described. It was applied to typhoid-agglutinating serum of the horse, to hæmantitoxic sera of the horse, rabbit, and goat, and to diphtheria-antitoxic serum of the horse. By this method the protein content of the agglutinating serum was reduced to one sixth of its original volume without serious loss of agglutinin. In the case of antitoxic sera, only a single treatment could be applied and the protein content of the product corresponded with the original albumin content.

J. H. BIRKINSHAW.

Proteins in egg-white and their relationship to the blood-proteins of the hen as determined by the precipitin reaction. L. HEKTOEN and A. G. COLE (*J. Infect. Dis.*, 1928, **42**, 1—24).—Ovalbumin, ovomucin, and ovomucoid may be completely separated from ovoglobulin and conalbumin. Antisera against ovalbumin, ovoglobulin, ovomucin, and ovomucoid gave no reactions when tested with solutions of fibrinogen, euglobulin, or albumin prepared from the blood-plasma. An antiserum against the whole egg-white reacts with the blood-albumin only; the reaction is due to conalbumin, which is, probably, chemically identical with blood-albumin.

CHEMICAL ABSTRACTS.

Agglutination and colloidal reactions. F. W. MULSOW (*Proc. Iowa Acad. Sci.*, 1927, **34**, 85).—The agglutination reaction appears to be dependent on changes in surface tension and other colloidal properties. Alkalis have a stronger inhibiting action than acids. The effect of sodium or potassium hydroxide is much greater than that of ammonia, whilst strong and weak acids have an equal inhibiting action. Certain colloidal solutions, saponin, bile, and bile salts also have an inhibiting effect.

CHEMICAL ABSTRACTS.

Hæm and tissue-iron. M. L. ANSON and A. E. MIRSKY (*J. Gen. Physiol.*, 1929, **12**, 401—405).—The hæm of muscle and of yeast is estimated as pyridine-hæmochromogen, by spectroscopical examination of the band, corrected for the absorption by other pigments. Both yeast and muscle appear to contain about 40% of their total iron combined as hæm.

E. BOYLAND.

Occurrence of lead in hen's eggs. W. B. S. BISHOP (*Med. J. Austral.*, 1928, **1**, 480—488).—The wet material (100 g.) contained the following amounts

of lead: shell 0.1—1.6 mg., yolk 0.2—1.0 mg., white 0.12—0.48 mg. **CHEMICAL ABSTRACTS.**

Occurrence of molybdenum in hen's eggs. W. R. MANKIN (Med. J. Austral., 1928, 2, 87).—Egg-white contains 0.01 mg. of molybdenum in 100 g. A modification of Koppel's method was employed. **CHEMICAL ABSTRACTS.**

Connexion of ropiness and structure in egg-white. J. JOCHIMS (Biochem. Z., 1928, 203, 142—146).—The ropiness of egg-albumin depends on the presence of substances which readily form filaments. When an albuminous rope is coagulated or when the albumin is dropped into boiling water a fibrillar coagulum is obtained, but when the albumin is whipped into a froth and allowed to reliquify ropiness is lost and a fibrillar coagulum is no longer obtained.

P. W. CLUTTERBUCK.

Copper content of normal and pathological organs. I. Method. II. Copper content of normal and hæmochromatose liver, gallstones, and whole blood. R. SCHONHEIMER and F. OSHIMA (Z. physiol. Chem., 1929, 180, 249—258).—I. The solution obtained by heating 5—10 g. of the organ with concentrated nitric and sulphuric acids is treated with hydrogen sulphide, and subsequently with a few drops of bromine water, when the precipitated sulphur carries down the copper sulphide with it. This mixture is then washed free from iron, incinerated with a small amount of Neumann's reagent, and subsequently treated with ammonium thiocyanate and pyridine (cf. Fleming, A., 1924, ii, 502). The coloured complex is dissolved in chloroform and determined microcolorimetrically. The method is sensitive within the following limits of error: for 0.01 mg. 5%, for 0.008 mg. 8%.

II. The copper content of normal liver is 1.09—3.92 mg. per kg. (extreme values for 17 varying specimens), whilst hæmochromatose liver contains 98.6—63.29 mg. (extreme values for 16 cases). There is also a large increase in the amount of iron. Pigmented gallstones contain varying amounts (0.0159—0.206%), and blood has a content of 1.13—1.44 mg. per kg. in the three cases examined. H. BURTON.

Cerebronic acid. P. A. LEVENE and F. A. TAYLOR. Also E. KLENK.—See this vol., 321.

Succinic acid as a product of decomposition of organs. L. VAN ITALLIE and A. J. STEENHAUER (Pharm. Weekblad, 1929, 66, 14—15).—The acid has been identified in the ethereal extracts of acid aqueous solutions obtained by treatment of partly decomposed organs, and is regarded as a normal decomposition product. S. I. LEVY.

Determination of the carbohydrates in animal organs and in blood by characteristic colour reactions. I. Colour reactions of the carbohydrates and their use in the microchemical determination of different sugars in dilute solution. Z. DISCHE (Mikrochem., 1929, 7, 33—68).—The solution (1 vol.) is mixed with 0.1 vol. of 10% α -naphthol solution and 8 vols. of concentrated sulphuric acid without cooling—a brown colour indicates glycuronic acid and a red colour glycollaldehyde or a sugar. In the latter case a further portion of the

solution (1 vol.) is heated with 9 vols. of a mixture of 8 vols. of concentrated sulphuric acid and 1 vol. of water for 3 min. in a water-bath, cooled, and treated with 0.2 c.c. of a 5% α -naphthol solution—a brown colour develops in 10 min. if glycollaldehyde or a triose is present and a red colour in other cases. If a red colour is obtained, a third portion of the original solution (2 vols.) is heated for 30 min. in a water-bath with 4 vols. of a mixture of 100 vols. of concentrated hydrochloric acid, 80 vols. of glacial acetic acid, and 20 vols. of a 10% alcoholic solution of diphenylamine; pentoses give a brown, hexoses a blue, and carbohydrates or thymonucleic acid a violet-red colour. To distinguish between glycollaldehyde and trioses the solution (1 vol.) is mixed with 0.1 vol. of a 10% α -naphthol solution and 4 vols. of concentrated sulphuric acid without cooling; glycollaldehyde gives a greenish-blue and the trioses a red colour. The presence of the latter may be confirmed by mixing 1 vol. of the sugar solution with 4 vols. of sulphuric acid, cooling, and adding 0.1 vol. of a 10% α -naphthol solution; a green colour indicates trioses. If the hexose test is positive 1 vol. of the original solution is mixed with 0.1 c.c. of a 2% alcoholic solution of α -naphthol and 9 vols. of 75 vol.-% sulphuric acid; a blue colour indicates lævulose or hexosediphosphoric acid and a red colour aldoses. On dilution with water the red solution becomes colourless and a red precipitate is formed, but the blue solution is stable. The aldoses are differentiated by repeating the diphenylamine test previously mentioned but heating only for 1.5 min.; galactose produces a violet, mannose a brown, and dextrose a blue solution. To distinguish lævulose from hexosediphosphoric acid the diphenylamine test is repeated with only a 3 min. heating; the acid gives a violet and lævulose a brown colour. All the above tests serve to detect the respective compounds when they are present alone in a solution, but it is possible to use the tests for the approximate determination of lævulose, mannose, and galactose in the presence of dextrose by indirect analysis. A. R. POWELL.

Micro-determination of glycogen in the liver. H. BIERRY and B. GOUZON (Compt. rend. Soc. Biol. 1928, 99, 186—188; Chem. Zentr., 1928, ii, 1132).—The liver is treated in an autoclave at 120° for 30 min. with 35% potassium carbonate solution; an excess of hydrochloric acid is then added and the heating at 120° for 30 min. repeated. After neutralisation and removal of protein with mercuric nitrate the dextrose is determined by a micro-method.

A. A. ELDRIDGE.

Plasmalogen. I. Properties of plasmalogen and preparation and nature of plasmal. R. FEULGEN, K. IMHAUSER, and M. BEHRENS (Z. physiol. Chem., 1929, 180, 161—179).—Ox brain contains about ten times as much phosphatide as horse flesh, and this can be precipitated from ethereal solutions by acetone, or from alcoholic solution by alcoholic cadmium chloride solution. This precipitate contains the plasmalogen (cf. Feulgen and Voit, Pflüger's Archiv, 1924, 206, 404). Treatment of plasmalogen emulsion (*loc. cit.*) with dilute acids or mercuric chloride and precipitation with acetone gives

plasmal. When the emulsion is made alkaline with sodium hydroxide solution and then extracted with ether both plasmalogen and phosphatides go into solution, but after alkaline hydrolysis plasmalogen is not extracted. Acidification of the soap produced and subsequent extraction gives plasmal and fatty acids. Whereas plasmal is a powerful reducing agent plasmalogen does not contain a free aldehyde group. So far plasmalogen has only been obtained associated with phosphatides. Distillation of the emulsion from 10 kg. of horse flesh after treatment with mercuric chloride, with steam in an atmosphere of carbon dioxide gives crude plasmal, which when treated with thiosemicarbazide yields 1–2 g. of plasmalthiosemicarbazone, sinters at 105°, melts at 106°, and becomes clear at 107–107.5°. This m. p. is unaltered by repeated crystallisation from alcohol. Analysis indicates that it is essentially a mixture of stearaldehydethiosemicarbazone (10%) and palmitaldehydethiosemicarbazone (90%). The m. p. of such a mixture does not depress the m. p. of plasmalthiosemicarbazone, nor do the colour reactions (A., 1927, 369) of the two differ. H. BURTON.

Occurrence of methylguanidine in animal organism. I. Detection of methylguanidine in dog's muscle. I. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1929, 180, 192–197).—Methylguanidine picrate has been isolated from the aqueous muscle extract either by direct precipitation with picric acid solution, or by precipitation of the extract with mercuric chloride and sodium acetate, and after removing mercury from this precipitate treatment of the residue with methyl and ethyl alcohols, platinum chloride, and finally picric acid. The yield of methylguanidine by this last method is 0.0134%.

H. BURTON.

Relation between cystine yield and total sulphur in wool. C. RIMINGTON (Biochem. J., 1929, 23, 41–46).—The whole of the sulphur of wool is liberated as cystine when the protein is hydrolysed by acid. The cystine determinations were carried out by the Sullivan and by the Folin and Looney methods in each case.

S. S. ZILVA.

Enzymes in the fluid of ovarian cysts. I. Amylase. T. TACHIBANA (J. Kinki Gynæcol. Soc., 1927, 10, 1–14; Chem. Zentr., 1928, ii, 1221).

Analysis of the liquid from a splenic cyst. S. GRILLON (Bull. Soc. Chim. biol., 1928, 10, 1382).—The liquid, d 1.124, contained 24.27% of solid matter, which, when incinerated, gave 52.41% of an ash containing 0.431% Cl, 5.9% P_2O_5 , and 6.59% $CaCO_3$. The cholesterol, protein, carbamide, and fat contents were 0.1, 8.25, 0.043, and 2.28%, respectively.

G. A. C. GOUGH.

Membrane studies with the human amnion. H. RUNGE and H. SCHMIDT (Biochem. Z., 1928, 203, 394–399).—When sacks made of the amnion of a freshly-born placenta and containing methylene-blue-Tyrode solution are placed in Tyrode solution at 37°, in some cases the epithelial and in others the connective-tissue side being in contact with the outer fluid, it is found by colorimetric examination of the outer fluid at intervals that diffusion is always greater when the dye is in contact with the epithelial

side. Similar results are obtained with patent-blue, the direction of diffusion being unaffected by the presence of cyanide or mercuric chloride. Similar results are also obtained with Congo-red and cyanol at 37° and 2°.

P. W. CLUTTERBUCK.

Histochemistry of the insect skeleton. W. KUHNELT (Zool. Anzeiger, 1928, 75, 111–113; Chem. Zentr., 1928, ii, 1109–1110).

Staining of elastic tissue. R. W. FRENCH (Stain Tech., 1929, 4, 11–12).—The addition of dextrin to crystal-violet and basic fuchsin is advantageous in staining elastic tissue by Weigert's method.

H. W. DUDLEY.

Staining of glial cells. R. ALTSCHUL (Atti R. Accad. Lincei, 1928, [vi], 8, 594–595).—By mordanting nervous tissue with a solution containing 2 c.c. of hydrobromic acid and 2 g. of ammonium bromide to 100 c.c. of water, staining with either methyl-violet or Victoria-blue, and differentiating with xylene-aniline oil, the glial cells are revealed more certainly and more simply than by Weigert's process.

T. H. POPE.

Differentiation of safranin in cytology. R. HAYNES (Stain Tech., 1929, 4, 27–28).—An acid dye, such as "light green SF yellowish," is preferable to hydrochloric acid for the differentiation of safranin.

H. W. DUDLEY.

Colloid chemistry of cerebrospinal fluid. J. KISS (Deut. Z. Nervenheilkunde, 1927, 98, 227–272; Chem. Zentr., 1928, ii, 1229–1230).—Cerebrospinal fluid is best studied by means of gold sol.

A. A. ELDRIDGE.

Digestive enzymes in stomach juices of snails. E. GRAETZ (Z. physiol. Chem., 1929, 180, 305–307).—The stomach juices from *Helix pomatia*, *Limax maximus*, *L. flavus*, *Agriolimax agrestis*, and *Arion emericorum* all cause fission of Witte's peptone at pH 7–8 and 37°. Caseinogen and fibroin are also digested by *H. pomatia*. The action of the juices on fats is also manifested, more particularly with the lower neutral fats. Sucrose, maltose, raffinose, and arbutin are also hydrolysed.

H. BURTON.

Protease content of pylorus secretion. O. KESTNER, R. WILLSTATTER, and E. BAMANN (Z. physiol. Chem., 1929, 180, 187–191).—The secretion gives a slight reaction for pepsin and trypsin, and a somewhat greater one for erepsin. After removal of leucocytes by centrifuging the secretion has no proteolytic action.

H. BURTON.

Studies in milk secretion based on the variations and yields of butter fat and milk produced at morning and evening milkings. S. BARTLETT (J. Agric. Sci., 1929, 19, 36–47).—Numerous milking records are presented and examined. Lower yields of milk and fat in morning milkings were general, but most notable in heifers and in heavy-milking, small-uddered cows. The possibility of the reabsorption of milk in these cases is discussed. The summer stimulus to milk secretion, usual in May and June, is more effective in the evening milk than in the morning.

A. G. POLLARD.

Clarification and decolorisation of urine. FISCHER and HORKEIMER (Pharm. Ztg., 1929, 74,

45—46).—Adsorption of sugar may be avoided by using only a small proportion of animal charcoal (0.7 g. for 25 c.c.) or by shaking with freshly-ignited kieselguhr. S. I. LEVY.

Graph for urine analysis. J. DÉCADE (Bull. Soc. Chim. biol., 1928, 10, 1383—1384).—In the graph described the acidity and normal total nitrogen, carbamide, uric acid, phosphorus pentoxide, and sodium chloride contents are multiplied by a suitable factor so that each possesses an equal numerical value. Thus, when analyses of pathological and normal urine are compared graphically, the deviations from the normal may be easily read. G. A. C. GOUGH.

Ammonia coefficient of urine and its dependence on various sources of nitrogen. M. POLONOVSKI and P. BOULANGER (Compt. rend. Soc. Biol., 1928, 99, 233—235; Chem. Zentr., 1928, ii, 1117).—The urinary ammonia is independent of the p_H and of the nitrogen excretion. The alkali reserve and the acid content of the food, particularly the sulphur and phosphorus content of the proteins, are, however, concerned. A. A. ELDRIDGE.

Analysis of the acid-base equilibrium in the urine. F. MAINZER and A. JOFFE (Biochem. Z., 1928, 203, 50—87).—The quotients "alkali-sparing tendency" measured by the ratio $100[\text{NH}_3 + \text{titratable acid} - \text{hydrogen carbonate}]/\text{total nitrogen}$ and the "alkali-sparing effect," measured by the ratio $100[\text{NH}_3 + \text{titratable acid} - \text{hydrogen carbonate}]/\text{total base}$, are introduced and their theoretical importance is explained. The "base-sparing effect" permits the quantitative comparison of urines of the same titratable acidity but of different p_H . The practical importance of the quotients for an analysis of acid-base equilibrium is illustrated in a series of experiments on the effect of administration of ammonium chloride and hydrogen carbonate. The determination of titratable acidity is critically examined. The simultaneous variation of the excretion of ammonia and carbon dioxide—fixed as hydrogen carbonate—makes possible the regulation of acid-base equilibrium by the kidney irrespective of the material excretion requirement and it is therefore unjustifiable to regard increased ammonia and acid excretion as indicating acidosis; it is rather the symbol of the alkali-sparing tendency of the organism. A method for determination of the fixed carbon dioxide of urine is laid down and the influence of the concentration of the urine on the solubility of carbon dioxide and its apparent dissociation constant discussed. Preliminary balance experiments indicate that a considerable amount of unknown organic bases is present in urine.

P. W. CLUTTERBUCK.

Bile pigments in urine. C. KUHN (J. Pharm. Chim., 1928, [viii], 8, 546—549).—The following method for the detection of bilirubin is described. 2 c.c. of a phosphoric acid (d 1.71) diluted with 20 c.c. of water are added to a mixture of 20 c.c. of the urine, 2 c.c. of a mixture of 2 vols. of 5% aqueous copper sulphate (crystals) solution, and 1 vol. of ammonia solution (d 0.924), and, immediately after mixing, 6 drops of toluene are added and the mixture is vigorously shaken. After a time biliverdin, formed by the action of the alkaline copper solution on bilirubin

and liberated in the free state on acidification, rises to the surface; 3-4 c.c. of 95% alcohol are then carefully added. If the bile pigments are present in appreciable quantity a green zone is rapidly formed at the boundary of the two liquids, and the alcohol is quickly coloured green, most of the biliverdin dissolving. If bile pigments are absent the alcohol remains colourless or assumes a faint rose or greyish-blue colour. The presence of protein, dextrose, indoxyl, uric acid, or urobilin does not interfere. E. H. SHARPLES.

Detection of bile pigment in urine. L. VAN ITALLIE (Pharm. Weekblad, 1929, 66, 13—14).—The pigment is adsorbed on filter-paper or talc, and, after washing with water, removed again in acid alcohol solution; treatment of the solution with an oxidising agent gives the characteristic green coloration. S. I. LEVY.

Uric acid elimination and diuresis. R. GOIFON (Compt. rend. Soc. Biol., 1928, 98, 941—943; Chem. Zentr., 1928, ii, 1229).—The uric acid concentration of the urine of an individual is constant.

A. A. ELDRIDGE.

Uric acid in organic fluids. R. MENASCI (Folia clin. chim. micros., 1927, 2, No. 5, 12 pp.; Chem. Zentr., 1928, ii, 1229).

Concentration of acid and base in blood-serum in normal pregnancy. H. C. OARD and J. P. PETERS (J. Biol. Chem., 1929, 81, 9—27).—During pregnancy there is a reduction of about 5% in the total base concentration in the blood-serum which is accounted for by disappearance of sodium; at the same time, there is equivalent reduction in the total anions, due principally to diminution in the hydrogen carbonate and organic acid, and, to a smaller extent, in the protein. There is thus no true acidosis in normal pregnancy. C. R. HARRINGTON.

Physical chemistry of cerebrospinal fluid and serum diagnosis. Lange's gold sol reaction. G. ETTISCH and O. EINSTEIN (Biochem. Z., 1928, 203, 389—393).—Many of the reactions obtained by Lange (Z. Chemother., 1913, 1, 44) with cerebrospinal fluid and gold sol, claimed to be characteristic of pathological conditions, may be obtained merely by alteration of the p_H of the gold sol added. Thus the reaction with normal fluid may be made to approximate to that of fluid in progressive paralysis by acidifying the sol, and the reaction of a fluid in paralysis may be converted into normal by making the sol alkaline. P. W. CLUTTERBUCK.

Metabolism of under-nourished children. III. Urinary nitrogen; creatinine. C. C. WANG, M. FRANK, R. KERN, and B. B. HAYS (Amer. J. Dis. Children, 1926, 32, 360—366).—Creatinine-nitrogen increased with increasing weight and age; creatine was always present; ammonia and total nitrogen were fairly constant. The creatinine coefficient was 5.5—9.5; creatinine excretion was constant in individuals. CHEMICAL ABSTRACTS.

Deposition of sulphur in the skin after extirpation of the adrenals. M. LOEPER, J. DECOURT, and A. LESURE (Compt. rend. Soc. Biol., 1928, 98, 1098—1099; Chem. Zentr., 1928, ii, 1231).

Saponin hæmolysis in anæmic blood. H. D. KESTEN and T. F. ZUCKER (Amer. J. Physiol., 1928, 87, 274—279).—Red blood-cells from persons with severe secondary anæmia are hæmolyzed more slowly by saponin than are those from normal individuals.

B. A. EAGLES.

Saponin hæmolysis of reticulocyte-containing blood. T. F. ZUCKER and H. D. KESTEN (Amer. J. Physiol., 1928, 87, 280—287).—The curve of saponin hæmolysis of a reticulocyte-containing blood shows a rate of hæmolysis which at first is faster and later slower than that of normal blood. B. A. EAGLES.

Splenic substance in Gaucher's disease. H. BEUMER (Klin. Woch., 1928, 7, 758; Chem. Zentr., 1928, ii, 679).—After death from Gaucher's disease investigation of the spleen showed that a mixture of cerebrin and kersin was concerned.

A. A. ELDRIDGE.

Splenic substance in Gaucher's disease. E. ERSTEIN and H. LIEB (Klin. Woch., 1928, 7, 1035; Chem. Zentr., 1928, ii, 679).—Examination of the spleen in Gaucher's disease has never revealed the presence of cerebrin (phrenosin) as well as kersin (cf. preceding abstract).

A. A. ELDRIDGE.

Reaction for diagnosis of cancer. A. H. ROFFO (Z. Krebsforsch., 23, 39—98; Chem. Zentr., 1928, ii, 1018).—The serum (2 c.c.) is coloured red on addition of a neutral-red solution (0.1%, 5 drops).

A. A. ELDRIDGE.

Activation of proteolysis in animal organs and its significance in the metabolism of malignant tumours. E. WALDSCHMIDT-LEITZ, I. J. BER, and J. KAHN (Naturwiss., 1929, 17, 80).—Proteolytic enzymes such as kienokathepsin are accompanied by an activator which extends the specificity of the enzyme. The activator of the protease of the spleen may be replaced by hydrocyanic acid or by hydrogen sulphide. As these latter substances check cell respiration there appears to be a connexion between arrest of cell respiration and increased proteolysis. This connexion may be extended to tumours.

W. E. DOWNEY.

Protein metabolism of normal and malignant *in vitro*. F. DEMUTH and I. VON RIESSEN (Z., 1928, 263, 27—49).—Hen sarcoma cultures readily liquefy the clot of hen plasma, the being converted from the gel into the sol and the fibrin network being dissolved. The amount of the smaller decomposition products, not precipitable by molybdate, does not increase. The liquefaction is an enzymic process. The action of the enzymic system in a medium of plasma and embryonic extract proceeds so slowly (if at all) that it cannot be detected, but substances present in small amount in normal tissues, and in very much greater amount in sarcoma, are able to activate the enzyme. This activator is heat-stable and to some extent ultrafiltrable. Activation is favoured by the hydrogen, acetate, and lactate ions, but is inhibited by calcium. This fibrinolysis is not specific for the sarcoma cell.

P. W. CLARKE.

Protein metabolism in cystinuria. W. GIBSON (Biochem. J., 1929, 23, 228—235).—The cystinuric

patient oxidised cystine to inorganic sulphate normally. The amount of the cystine in the urine appeared to bear a relation to the protein consumed. The administration of sodium hydrogen carbonate but not of disodium hydrogen phosphate was accompanied by a marked disturbance of the sulphur fractions of the urine. The excretion of cystine was not affected to any extent by either of these compounds. Tyrosine, leucine, putrescine, and cadaverine were not found in the urine. S. S. ZILVA.

Connexion between sodium chloride elimination and insulin administration in diabetes. M. TINKER and A. SAIDENBERG (Russ. Klin., 1927, 8, 223—235; Chem. Zentr., 1928, ii, 1229).—In diabetes there is sodium chloride insufficiency, but retention of sodium chloride in the tissues is prevented by polyuria; excess of administered salt is retained, but the smaller the concentration of sugar in the urine, the greater is then the sodium chloride concentration. On administration of insulin the diminished urinary excretion of sugar is paralleled by an increase in the sodium chloride concentration, but the water retention leads to sodium chloride retention in the tissues. The sodium chloride concentration in the blood is increased.

A. A. ELDRIDGE.

Protein and energy economy in pancreatic diabetes of dogs. E. ENDERLEN, H. GLATZEL, and P. (Arch. exp. Path. Pharm., 1929, 139, 20—31).—The protein metabolism of depancreatized dogs is raised 28—66% and the basal metabolism is 3—28% above normal.

B. A. EAGLES.

Amino-acid content of the blood in leucæmia. E. WIECHMANN (Munch. med. Woch., 1928, 75, 1115—1116; Chem. Zentr., 1928, ii, 907).—The amino-acid content of the plasma and erythrocytes is normal whilst that of the leucocytes and whole blood is high, if the leucæmia is accompanied by a high leucocyte count.

A. A. ELDRIDGE.

Metabolism of salts in nephritis. I. G. L. BOYD, A. M. COURTNEY, and I. F. MACLACHLAN. II. G. L. BOYD and A. M. COURTNEY. III. G. L. BOYD, A. M. COURTNEY, and I. F. MACLACHLAN (Amer. J. Dis. Children, 1926, 32, 29—39, 192—199; 1927, 34, 218—233).—The blood-phosphate (of children) was usually increased, and blood-calcium decreased, the calcium balance being independent of the blood-calcium. The relation between calcium and phosphate is discussed. Plasma-potassium was normal but plasma-magnesium was low, and there was usually retention of sulphate. Sodium and chlorides were determined in the food, faeces, urine, and plasma: high values are usually obtained in the plasma except in chronic azotæmic nephritis.

CHEMICAL ABSTRACTS.

Albuminuria in the mechanism of detoxification. E. ANDREWS, W. A. THOMAS, and W. F. WELKER (Arch. Int. Med., 1929, 43, 139—143).—The urine of nephritic patients contains, besides the normal blood-proteins, a relatively non-toxic peptone combined with or adsorbed by serum-proteins and also a highly toxic blood-protein so highly dispersed in solution as to pass readily through a colloidal membrane.

B. A. EAGLES.

proteases and antiproteases of pleural exudates. C. WEISS (J. Insect. Dis., 1927, 41, 467—471).—The activity of proteases and antiproteases of pleural exudates over a range of p_H values was studied. **CHEMICAL ABSTRACTS.**

Tetany of fasting in experimental rickets. T. WILDER (J. Chem., 1929, 81, 65—72).—Rachitic rats, when starved for 24—36 hrs., show tetanic convulsions, whilst normal animals similarly treated show no such symptoms; there is no marked but a slight decrease in the calcium of the blood, and a marked rise in the inorganic phosphate, the latter being apparently derived from endogenous tissue breakdown (cf. Cavins, A., 1924, 5, 680). **C. K. HARRINGTON.**

Inorganic blood-phosphate. E. M. KOCH and M. H. CLEGG (Amer. J. Dis. Children, 1927, 34, 187—197).—In rats on a rachitic diet the inorganic blood-phosphate is lowered; for mature, but not young, animals the value is raised by irradiation, whilst addition of cod-liver oil raises the value in both cases. Non-irradiated cholesterol produces normal values, but does not prevent rickets. **CHEMICAL ABSTRACTS.**

Creatine-phosphoric acid content of white and red muscle in experimental scurvy and polyneuritis. A. PALLADIN and S. EPELBAUM (Biochem. Z. 1929, 204, 140—149).—The creatine-phosphoric acid in guinea-pigs suffering from scurvy was below normal, especially in red muscle, and the lactacidogen was above normal. In the heart-muscle creatine-phosphoric acid was absent and lactacidogen was diminished. In chronic polyneuritis of pigeons similar effects were observed to those for scurvy, but acute polyneuritis creatine-phosphoric acid was lowered and lactacidogen was diminished. **J. H. BIRKINSHAW.**

Variations of the potassium : calcium quotient in the lymph in experimental sepsis. W. F. PETERSEN, G. MILLES, and E. F. MÜLLER (Z. ges. exp. Med., 1928, 60, 336—354; Chem. Zentr., 1928, 5, 790).

Experimental uræmia and chloride content of the cortex. F. LEÖVEY and E. KERPEL-FRONTUS (exp. Path. Pharm., 1929, 138, 373—378).—Rabbits suffering from sodium chloride starvation show a smaller decrease of chloride in the grey substance of the brain than in the white or in the other organs. Conversely, if excess of sodium chloride is administered to a rabbit after ligation of the ureters, the largest increase of chloride is found in the grey substance. **W. O. KERMACK.**

Parenteral absorption of colloids. I. M. JACOBY (Biochem. Z., 1928, 203, 278—279).—Introductory to work not yet published. **P. W. CLUTTERBUCK.**

Carbon dioxide from the unsevered vagus or the snake. G. H. PARKER (J. Gen. Physiol., 1929, 12, 419—425).—The nerve produced 0.0017—0.0032 mg. of carbon dioxide per g. per min. Separation of the nerve from the brain and heart produced no appreciable change in the carbon dioxide output. **E. BOYLAND.**

Metabolism of two breeds of pigs. T. DEMENTON (J. Agric. Sci., 1929, 19, 140—184).—Calorimetric investigations of the metabolic changes in Middle White and Berkshire pigs are recorded. Internal and external thermal changes during fasting catabolism are examined. The bearing of the experimental results on the energy relationships of an animal during experiment and on the computation of maintenance rations is discussed. **A. G. POLLARD.**

Spleen and calcium metabolism. F. P. UNDERHILL and E. G. CROSS (J. Biol. Chem., 1929, 81, 163—165).—In rabbits no alteration in the calcium metabolism was produced by splenectomy or by injection of nucleoprotein prepared from the spleen. **C. R. HARRINGTON.**

Factors influencing calcium balance. I. Influence of potential alkalinity on the utilisation of supplementary calcium lactate in the mature rat. V. V. COLE, J. H. SPEER, and F. W. HEYL (J. Amer. Pharm. Assoc., 1929, 18, 36—42).—To maintain calcium balance, adult rats fed on an acidotic, calcium-deficient diet required a daily addition of 4—5 mg. of calcium lactate, and with calcium carbonate the rat came into calcium balance at about the same level. Calcium carbonate was probably entirely dissolved at this level and it gave a much better utilisation of the phosphorus than was secured with calcium lactate. Small additions of alkaline citrate to calcium lactate increased the percentage utilisation of both calcium and phosphorus; larger additions caused a greater, although not proportional, increase. Alkalinity probably had a favourable influence on the magnesium balances. **E. H. SHARPLES.**

Factors influencing the excretion of calcium. B. HAMILTON and M. MORIARTY (Amer. J. Dis. Children, 1928, 36, 450—462).—The amount of calcium excreted by breast-fed infants depends only on the amount of calcium, magnesium, sodium, and potassium in the milk. Increase in p_H of the (naturally buffered) intestinal contents may favour the formation of calcium soaps and phosphate. Addition of alkali or acid to the milk respectively increases or decreases the proportion of calcium excreted. **CHEMICAL ABSTRACTS.**

Creatine and creatinine excretion in women. P. HODGSON and H. B. LEWIS (Amer. J. Physiol., 1928, 87, 288—292).—In women with physical development greater than that of the ordinary woman, creatinine coefficients of the same order of magnitude as those of men were observed. Creatine was present in 93% of the urines analysed, indicating that creatinuria in women is probably not related to the difference in muscular development between men and women. **B. A. EAGLES.**

Influence of hunger on the creatine content of muscle and on the creatine and creatinine excretion of cats. A. PALLADIN and S. EPELBAUM (Biochem. Z., 1929, 204, 150—164).—Fasting cats show creatine present in the urine at the fourth to sixth day and continually increasing; creatinine gradually falls so that the two curves cross. The sum of creatine- and creatinine-nitrogen increases throughout. The creatine content of the muscles

increases during fasting up to the third fasting period and then diminishes. J. H. BIRKINSHAW.

Have histidine and arginine any influence on purine synthesis in the growing human organism? P. GYORGY and S. J. THANNHAUSER (Z. physiol. Chem., 1929, 180, 286—304).—Addition of histidine and arginine to the ordinary milk diet of babies of 4—8 months had no effect on uric acid or creatinine excretion. Addition of histidine to a synthetic diet consisting of caseinogen hydrolysate freed from histidine and arginine had no noticeable effect on the purine or other constituents of the urine. There is no evidence of any direct relation between histidine administered and the purine metabolism. J. H. BIRKINSHAW.

Cholesterol metabolism. H. BEUMER and F. HEPNER (Klin. Woch., 1928, 7, 1470; Chem. Zentr., 1928, ii, 1121).—After injection of cholesterol (1—2 g.) no marked increase of the bile cholesterol or bile acid was observed in dogs with biliary fistula, but after intravenous injection of cholesterol into normal dogs the faecal cholesterol was increased.

A. A. ELDRIDGE.

Animal calorimetry. XXXVIII. Specific dynamic action of meat in hypophysectomised dogs. O. H. GAEBLER (J. Biol. Chem., 1929, 81, 41—47).—The specific dynamic effect of protein in dogs was not altered by removal of the pituitary gland; the magnitude of the specific dynamic effect does not run parallel with changes in the amino-acid nitrogen of the blood. C. R. HARRINGTON.

Physiology of the liver. XVI. Respiratory quotient and basal metabolic rate following removal of the liver and injection of dextrose. F. C. MANN and W. M. BOOTHBY (Amer. J. Physiol., 1928, 87, 486—496).—The total amount of heat produced in dogs is not directly affected by the total loss of hepatic tissue. The respiratory quotient increases immediately after removal of the liver. Dextrose has a greater specific dynamic action in the dehepatised animal than in the normal one.

B. A. EAGLES.

Physiology of the liver. XVII. Specific dynamic action after removal of liver. C. M. WILHELMJ, J. L. BOLLMAN, and F. C. MANN (Amer. J. Physiol., 1928, 87, 497—509).—Intravenous injection of alanine or glycine into hepatectomised animals fails to raise the level of the consumption of oxygen but elevates the respiratory quotient. It is suggested that the specific dynamic action of amino-acids is not the result of direct stimulation brought about by the presence of unchanged amino-acids in the tissues.

B. A. EAGLES.

Significance of adenylic acid for muscle function. II. Deamination of adenylic acid by minced muscle and ammonia formation on muscle contraction. G. EMBDEN, C. RIEBELING, and G. E. SELTER. III. Ammonia formation in muscular work under various conditions. G. EMBDEN and H. WASSERMAYER. IV. Fission and resynthesis of the ammonia-producing substance in muscle activity. G. EMBDEN, M. CARSTENSEN, and H. SCHUMACHER. V. Source of the ammonia formed on contraction. G. EMBDEN and H.

WASSERMAYER (Z. physiol. Chem., 1928, 179, 149—160, 161—185, 186—225, 226—237).—II. The formation of ammonia by fresh minced muscle on keeping is considerably increased in presence of adenylic acid, but not of urea. More than 80% of the amino-group of the adenylic acid added may appear as ammonia. Electrical stimulation of frog's muscle even for 1 sec. leads to an increase in the ammonia content. After prolonged stimulation the ammonia figure may be nine times its original value.

III. *Rana esculenta* has in May a higher content of ammonia-forming substance in the muscle than in winter or summer. Prolonged jumping causes a considerable increase in the ammonia content of the gastrocnemius. A similar effect is produced by electrical stimulation. After resting, especially in the dark, the ammonia decreases. In the autumn *R. temporaria* maintained at 26—27° showed effects similar to those observed in *R. esculenta* in May. Phosphorus poisoning likewise caused an increase in the ammonia content of the muscle. The ratio of lactic acid to ammonia showed wide variations.

IV. The formation of free ammonia on the contraction of isolated frog's muscle (gastrocnemius) is a reversible change. The recombination of the ammonia eliminated is most easily demonstrated in spring and summer frogs. In winter the reversibility is greater, so that it is difficult to show the initial increase in the ammonia under electrical stimulation except when this is so prolonged as to damage the muscle-tissue, thus interfering with the resynthesis. If the number of stimuli per sec. is doubled or quadrupled, however, the resynthesis can be demonstrated; the ammonia shows a definite increase, the intervals being now too short for complete re-amination.

V. Extracts from the hind-limb muscle of the frog and from the biceps femoris of the rabbit were investigated. The nitrogen in the copper-lime precipitate together with that of the ammonia originally present in the extract was found to be equal to five times the nitrogen of the ammonia obtained after complete deamination by 2% sodium hydrogen carbonate solution. It is concluded that adenosine-phosphoric acid and probably adenosine are the sole sources of the ammonia formed by muscle activity.

J. H. BIRKINSHAW.

Enzymic deamination in muscle. G. SCHMIDT (Z. physiol. Chem., 1928, 179, 243—282).—Adenylic acid from muscle and adenosine are easily deaminated by muscle juice from the rabbit, but adenine, guanine, guanosine, and guanosinephosphoric acid are unaffected. The ammonia production is due to two different deaminases, one specific for adenylic acid, the other for adenosine. A highly active muscle extract of adenylic acid deaminase was prepared by adsorption on aluminium hydroxide, from which it could be eluted by sodium phosphate solution. The adenosine deaminase remains in solution during the adsorption process. The optimum p_H for the adenylic acid enzyme is 5.9.

Adenylic acid from muscle differs chemically from that of yeast, since the latter is unattacked by the muscle enzyme. The inosinic acid obtained by enzymic deamination of muscle-adenylic acid was isolated. J. H. BIRKINSHAW.

Action of ions on the ageing of muscle press-juice, and the influence of hydrogen-ion concentration. H. WASSERMEYER (*Z. physiol. Chem.*, 1928, 179, 283—311).—Muscle juice in comparison with minced muscle shows a much smaller "ageing" effect as measured by loss of power to synthesise complex phosphoric acids. The artificial production of "ageing" by the addition of various substances to rabbits' muscle juice was examined. Sodium hydrogen carbonate, sodium hydroxide, and ammonia increase the rate of ageing. All these substances increase the p_H of muscle juice which is normally low, but carbon dioxide has a similar ageing effect although lowering the p_H value.

J. H. BIRKINSHAW.

Lactacidogen in denervated muscle. L. DE CARO (*Boll. Soc. Ital. Biol. sper.*, 1927, 2, 642—646; *Chem. Zentr.*, 1928, ii, 784).—Denervated muscle contains less lactacidogen and free calcium ions than normal muscle. The results accord with the known smaller content of lactic acid and greater content of glycogen.

A. A. ELDRIDGE.

Presence and exchange of pyrophosphate in cells. II. Amount of readily hydrolysable phosphorus compounds in animal and plant cells. III. Physiological behaviour of pyrophosphate. K. LOHMANN (*Biochem. Z.*, 1928, 203, 164—171, 172—207).—II. Yeasts and striated muscle of vertebrates and invertebrates have the highest pyrophosphate content, muscles containing 0.4—0.9 mg., and yeast 1.6—1.8 mg. P_2O_5 per g. moist wt. In frogs and rabbits, the pyrophosphate content of the heart and smooth muscle, liver, kidney, spleen, testicles, brain, and red blood-cells is smaller, corresponding with the smaller acid-soluble P_2O_5 content, and amounts to 0.1—0.4 mg. P_2O_5 per g. moist wt. With the roots of pea seedlings, 9% of the total acid-soluble phosphate is present as pyrophosphate. Three kinds of bacteria gave similar figures and it appears therefore that all cells which can utilise carbohydrate possess readily hydrolysable phosphorus compounds.

III. The pyrophosphate content of the intact frog's muscle remains unchanged while resting for 20 hrs. in oxygen and also during moderate stimulation, but when the stimulation is prolonged, hydrolysis of pyrophosphate and formation of orthophosphate occur. In heat and chloroform rigor, almost all the pyrophosphate is hydrolysed. Pyrophosphate does not diffuse out of muscle into Ringer's solution, but is probably present in the cell and in the extract as a (protein) adsorption complex. The pyrophosphate of frog's muscle-pulp or of the hydrogen carbonate-potassium chloride extract is completely hydrolysed during autolysis at 40°, about 75% of the orthophosphate arising during such autolysis being thus formed from pyrophosphate. The remaining 25% (i.e., 0.2—0.3 mg. P_2O_5 per g. moist wt. of frog's muscle) arises only in part from Embden's lactacidogen. Enzymic hydrolysis of pyrophosphate is inhibited by orthophosphate. Respiration and the degradation of carbohydrates by the cell are independent of the pyrophosphate fraction. The hydrolysis of pyrophosphate existing in fresh muscle pulp is accelerated by 0.5*M*- and by 0.01—0.003*M*-

potassium fluoride, but is inhibited by intermediate concentrations (0.1*M*), whereas hydrolysis of $\alpha\beta$ pyrophosphate is always inhibited by Pyrophosphate administered by the mouth is in the urine as orthophosphate.

P. W. CLITTERBUCK.

Extraction of pyrophosphate containing iron from muscle. O. MEYERHOF and K. LOHMANN (*Biochem. Z.*, 1928, 203, 208—211).—Some of the iron contained in muscle is but loosely combined and may be removed along with pyrophosphate by treatment with a solution of mercuric chloride in hydrochloric acid. It could not be decided, however, whether the iron was combined with the pyrophosphate in the cell.

P. W. CLITTERBUCK.

Muscle-lactic acid in decapsulated rats. P. MAZZOCCO (*Compt. rend. Soc. Biol.*, 1928, 99, 174—176; *Chem. Zentr.*, 1928, ii, 1121).—After tetanisation the muscle-lactic acid is somewhat greater in decapsulated than in normal rats.

A. A. ELDRIDGE.

Metabolism of carbohydrates in normal conditions and in starvation. G. MOURIQUAND and A. LEULIER (*Compt. rend. Soc. Biol.*, 1928, 98, 1110—1113; *Chem. Zentr.*, 1928, ii, 1230—1231).—With normal rabbits the liver-glycogen varies from 0.14 to 12.86%; values for muscle are 0.07—1.52%. Starvation values are 0.16—1.34 and 0.10—0.48, respectively. The blood-sugar of normal guinea-pigs is 0.93—1.50, and is reduced in starvation to 0.85—1.38.

A. A. ELDRIDGE.

Metabolism of lævulose; determination in blood and urine. R. C. CORLEY (*J. Biol. Chem.*, 1929, 81, 81—98).—Lævulose may be determined in aqueous solution, diluted urine, and protein-free blood-filtrates by heating with hydrochloric acid and diphenylamine, followed by treatment of the solution with phenol and alcohol; the resulting blue colour is compared with that obtained by similar treatment of a standard solution of lævulose. The error of the method is $\pm 5\%$. After oral administration to rabbits of 6—7 g. per kg. of lævulose, small amounts of the latter appear in the blood; after intravenous injection of 2 g. per kg. the excess lævulose disappears from the blood within 90 min. Hepatic poisons had little effect on the metabolism of lævulose; the latter exercises a protective effect against overdosage with insulin, although its rate of disappearance from the blood is not affected by the presence of excess of insulin.

C. R. HARRINGTON.

Physico-chemical theory of the cause of sweet and bitter taste. N. W. TAYLOR (*Protoplasma*, 1928, 4, 1—17; *Chem. Zentr.*, 1928, ii, 901).—A discussion.

A. A. ELDRIDGE.

Distribution in the organism of oil injected in the arterial system. L. BINET and R. FABRE (*J. Pharm. Chim.*, 1929, [viii], 9, 16—19).—Distribution of the oil was followed by examination of solvent extracts of the organs with Wood's light ($\lambda=3650 \text{ \AA}$) after injection of olive oil containing 0.01% of diphenylanthracene. Extracts of the lungs, heart, skeletal muscle, liver, kidney, and spleen of a rabbit were examined. Visual examination with Wood's light

showed that the lung extract contained most of the diphenylanthracene. Photographic examination was necessary to compare the remaining extracts and, after the lungs, the muscle, followed by the liver and kidneys, showed the strongest deposition. Injection of aqueous suspensions of diphenylanthracene gave extracts from the organs which were only very faintly fluorescent.

E. H. SHARPLES.

Explanation of oligodynamic action. H. FREUNDLICH and K. SOLLNER (Biochem. Z., 1928, 203, 3—13).—When 40 sq. cm. of pure silver foil are kept in 100 c.c. of tap-water or distilled water for 3 days, 2×10^{-5} g. of silver per litre is dissolved and can be determined by Haber's method (A., 1926, 699). Algae brought into such solutions adsorb most of the dissolved silver, the algae suffering oligodynamic injury. The silver adsorbed in 1 g. of dry algae amounts to 5×10^{-5} g. The silver is present in these solutions as silver ions, and the poisonous action on algae may be imitated by a solution of silver nitrate containing the same concentration of silver ions. The fact that a glass surface which has been brought into contact with a silver solution retains its oligodynamic activity after washing is confirmed and depends on the adsorption of the silver by the glass, the silver penetrating deeply into its structure. When dilute solutions of silver nitrate are evaporated in glass vessels, the silver is almost completely adsorbed by the glass and may be recovered therefrom after careful washing away of all traces of the solution.

P. W. CLUTTERBUCK.

Neutralisation of the oligodynamic power of copper by solutions of electrolytes. Application to mineral waters. P. L. VIOLE and A. GIBERTON (Compt. rend., 1929, 188, 409—411).—The property of distilled water of becoming toxic (e.g., to fish) when placed in contact with a copper surface for a few hours at the ordinary temperature is due to copper in the colloidal state, and the antitoxic effect of certain mineral waters is due to its precipitation by the ions of the dissolved salts. The antitoxic properties of anions increase with the valency, whilst cations are usually toxic and only calcium has a protecting effect.

J. GRANT.

Chemical nature of allergic substances. L. F. LOEB (Biochem. Z., 1928, 203, 226—236).—Guinea-pigs are sensitised specifically against an aqueous extract of goose-feathers. The extract contains 0.4 mg./c.c. of total nitrogen, about half of which is colloiddally dispersed and precipitable by colloidal ferric hydroxide and gives reducing, sulphosalicylic acid, ninhydrin, and Molisch reactions. The colloiddally dispersed nitrogenous substance may be precipitated by alcohol and then contains only a trace of reducing substance and gives a positive sulphosalicylic acid reaction, a negative ninhydrin, and a doubtful Molisch reaction. Specific sensitisation is similarly obtained with this alcohol precipitate, but not with the filtrate, which contains only molecular dispersed nitrogen and considerable amounts of reducing substance and gives positive ninhydrin and Molisch reactions. Guinea-pigs are similarly sensitised against aqueous extracts of pollen of the ordinary pine (*Pinus sylvestris*) and against the alcoholic precipitate

thereof, the latter containing only the colloiddally dispersed nitrogen and no reducing substance.

P. W. CLUTTERBUCK.

Value of dextrose in maintaining acid-base equilibrium of the blood in pregnant animals. II. Effect of period of chloroform anaesthesia in pregnant animals: lack of protection conferred by dextrose. W. DE B. MACNIDER (J. Pharm. Exp. Ther., 1929, 35, 31—48).—The degree of protection afforded by the administration of a solution of dextrose to pregnant dogs against the toxic effects which follow periods of ether anaesthesia was greatest in young dogs in the early stages of pregnancy. No protection is afforded when chloroform is substituted for ether as the anaesthetic. The toxic action of the chloroform is revealed in a decrease in the reserve alkali of the blood, in the elimination of phenolsulphonephthalein, and in urine formation; albumin, casts, and acetoacetic acid also appear in the urine.

F. C. HAPFOLD.

Fixation of colloids caused by chloroform. G. SPAGNOL (Atti R. Accad. Lincei, 1928, [vi], 8, 515).—If colloidal mercuric sulphide (0.15 g.) is injected into the ear vein of a rabbit and at the same time chloroform is applied to the side of the animal by means of a pad of cotton-wool, the subcutaneous tissue beneath the chloroformed spot shows a distinct black deposit of the sulphide when the rabbit is killed (after 2 hrs. or 8 days). A similar result is observed when trypan-blue (0.001 g.) is injected into the jugular vein of a guinea-pig.

T. H. POPE.

Ethylisoamylbarbituric acid (amytal) as anaesthetic for cats. M. G. MULINOS (J. Pharm. Exp. Ther., 1928, 34, 425—435).—Subcutaneous doses of 0.1 g. of amytal per kg. body-weight give a safe anaesthesia with quiet induction. This anaesthetic does not affect the blood-sugar or interfere with the effect of insulin.

E. BOYLAND.

Binding power of serum for alkaloids, and the inhibition of this effect by homologous alcohols. Theory of narcosis. R. BEUTNER and E. HYDEN (J. Pharm. Exp. Ther., 1929, 35, 25—30).—The relative amounts of the alcohols of the series propyl to octyl alcohol which will set free a trace of the bound pilocarpine in mixtures of cattle-serum with pilocarpine have been determined. It is suggested that the action is one of adsorptive replacement. The activity of hexyl alcohol represents a maximum in this series. Since the narcotic power of these alcohols increases continuously with the length of the carbon chain, it is suggested that these results support a theory of narcosis based on lipid solubility rather than Traube's theory of surface action.

F. C. HAPFOLD.

Occurrence of caffeine in human milk after ingestion of coffee. E. SCHILF and R. WOHINZ (Klin. Woch., 1928, 7, 1186; Chem. Zentr., 1928, ii, 684).—Of the ingested caffeine, 1% was found in the milk.

A. A. ELDRIDGE.

Influence of choline on blood-sugar. F. P. UNDERHILL and J. PETRELLI (J. Biol. Chem., 1929, 81, 159—162).—Subcutaneous injection of sub-lethal

doses of choline causes in rabbits (but not in dogs) marked hyperglycæmia but no glycosuria.

C. R. HARRINGTON.

Changes in blood-dextrose in rabbits after intravenous injections of histamine. M. L. MENTEN and H. M. KRUGH (*J. Infect. Dis.*, 1928, **43**, 117—120).—Experiments with normal and immunised rabbits are described.

CHEMICAL ABSTRACTS.

Influence of ergotamine on blood-sugar concentration. L. RICÉ and L. VESZELSZKY (*Arch. exp. Path. Pharm.*, 1929, **139**, 10—13).—Small doses of ergotamine (0.5—1.5 mg. per kg.) in rabbits produce a hypoglycæmia; larger amounts (2.0—2.5 mg. per kg.) cause a hyperglycæmia. B. A. EAGLES.

Influence of ergotamine on the blood-sugar of animals and man. M. BUFANO and A. MASINI (*Riforma Med.*, 1927, **43**, No. 38, 21 pp.; *Chem. Zentr.*, 1928, ii, 908).—Administration of ergotamine causes a fall in the blood-sugar which is ascribed to diminished glycogenolysis in the liver.

A. A. ELDRIDGE.

Reduction processes in muscle under the action of guanidine. L. CALIFANO and M. D'ALISE (*Riv. Pat. sper.*, 1927, **2**, 288—293; *Chem. Zentr.*, 1928, ii, 1121).—The muscular oxidation processes of *Bufo* are increased by guanidine.

A. A. ELDRIDGE.

Effect of hydrazine, hydroxylamine, and aminoguanidine on the excretion of uric acid. N. NIELSEN and G. E. WIDMARK (*Upsala Lakarefor. forh.*, 1927, [ii], **33**, 327—333; *Chem. Zentr.*, 1928, ii, 1229).—The uric acid excreted by normal rats was 7—8 mg. per kg. per day; the administration of hydrazine, hydroxylamine, or aminoguanidine did not cause increased elimination of uric acid.

A. A. ELDRIDGE.

Effects of drugs on secretion of uric acid in the fowl. O. S. GIBBS (*J. Pharm. Exp. Ther.*, 1929, **35**, 49—62).—The immediate response of the blood-uric acid content and the uric acid output to procedures which change the renal activity renders the fowl especially suitable for studies of renal function. Clamping of the ureters leads to a rise in the blood-uric acid concentration; there does not, however, appear to be any storage of uric acid by the kidneys. The effects of atropine, pilocarpine, physostigmine, adrenaline, pituitrin, atophan, hexamine, and uric acid were studied, but no changes suggestive of nervous control other than vascular effects were observed. Uric acid stimulated its own excretion, pituitrin caused a decrease in the urinary water secreted, and atophan of the uric acid.

F. C. HAPFOLD.

Action of certain heterocyclic compounds on the autonomic nervous system. R. HUNT and R. R. RENSHAW (*J. Pharm. Exp. Ther.*, 1929, **35**, 45—98).—The muscarine- and nicotine-like actions of certain compounds on the circulation have been studied. 1-Carboxymethylpyridinium bromide gave a weak muscarine effect, the action was more marked with methyl nicotinate and 1-acetoxyethyl-1-methylpiperidinium iodide and it became intense with 1-carbethoxymethylpyridinium bromide and 3-carbomethoxy-1-methylpyridinium iodide. In all cases

there was an absence of nicotine-like action. 1-Acetoxyethylpyridinium chloride had a weak nicotine-like stimulating action, and methyl 1-methyltetrahydronicotinate and 3-carbomethoxy-1-methyl-1-ethylpiperidinium bromide gave an even more definite action in addition to an active muscarine effect. 1-Carbethoxymethyl-2-methylpyridinium bromide had a brief, weak, paralysing, nicotine-like action. 1-Carbethoxymethylpiperidinium bromide, 1-methyl-2-pyridone, 1-ethyl-2-pyridone hydrobromide, and 1-diethylpyrrolidinium bromide were devoid of muscarine or nicotine actions. The muscarine-like actions of 1-carbethoxymethyl-1-methylpiperidinium iodide and 1-carbethoxymethyl-1-ethylpiperidinium bromide were not very pronounced but were more marked after the administration of large doses of nicotine, although neither salt had a marked nicotine-like stimulating action. *N*-Dimethylhexamethylenammonium bromide had no muscarine-like action. Other effects are noted and the relationship between chemical constitution and pharmacological action is discussed.

F. C. HAPFOLD.

Comparative studies of ephedrine, *r*-ephedrine, and ψ -ephedrine. II. Comparative toxicity. C. PAK and B. E. READ. III. Effects on the nasal mucous membranes. T. KING and C. PAK (*Chinese J. Physiol.*, 1929, **3**, 81—92, 95—108).—II. In rabbits, frogs, rats, and dogs ephedrine is definitely more toxic than *r*-ephedrine (ephedrine) and the latter is more toxic than ψ -ephedrine.

III. Ephedrine, *r*-ephedrine, and ψ -ephedrine cause shrinkage of the nasal mucous membrane, the activity being greatest with the first compound and smallest with the last.

W. O. KERMACK.

Biochemical properties of pyridine and quinoline derivatives. A. BINZ and C. RATH (*Biochem. Z.*, 1928, **203**, 218—222).—The chemotherapeutic action of a number of derivatives of pyridine and quinoline containing arsenic and iodine (A., 1927, 580, 890) is investigated with the view of establishing a relationship between chemical constitution and biological activity. The dose of 2-hydroxypyridine-5-arsinic acid just tolerated by a mouse is 30 times as great as that of atoxyl and 2.66 times that of trypanamide. Rabbits tolerate 1 g./kg. body-weight, the arsenic content of which is 75 times the normal toxic dose of arsenic. The curative dose of this acid for mice which had been infected with trypanosomes was 1.2 mg./g. body-weight. 5-Iodo-2-hydroxypyridine has no action on animals infected with trypanosomes, but a decidedly beneficial action in staphylococcal and streptococcal infections. 2-Aminopyridine-5-arsinic acid behaves similarly to the corresponding hydroxy-derivative. Pyridine-3-arsinic acid causes only a transient decrease of the number of trypanosomes. 2-Halogenopyridine-5-arsinic acids are more toxic and have less action on trypanosomes, but when the halogen is in the *ortho*-position to a hydroxy-group, e.g., in 3-chloro-2-hydroxypyridine-5-arsinic acid, the action on trypanosomes is retained and increases with increasing weight of the halogen. Chemotherapeutic action appears therefore to depend on the presence adjacent to nitrogen of a group which permits tautomerism. Similarly, whereas unsubsti-

tuted quinolinecarboxylic acids have no chemotherapeutic action, the corresponding 2-hydroxy- (carbostyryl) derivatives are strongly parasitotropic.

P. W. CLUTTERBUCK.

Tobacco smoking. II. A. WINTERSTEIN and E. AROSNOV (*Z. Hyg. Infekt.-Krankh.*, 1928, 108, 530—553; *Chem. Zentr.*, 1928, ii, 689—690).—The main current from a cigarette carries about 25% of the nicotine into the mouth, at least 50% passing into the air; from a cigar 60% reaches the mouth. The main current from cigarettes of light tobaccos contains markedly less nicotine than that from dark tobaccos.

A. A. ELDRIDGE.

Pharmacology of pyridylpyrroles and derivatives of 2-aminopyridine. E. DINGEMANSE and J. P. WIBAUT (*Arch. exp. Path. Pharm.*, 1929, 138, 379; cf. A., 1928, 919).—A question of priority.

W. O. KERMAK.

Chemical changes in muscle produced by drugs. H. N. ETS (*Amer. J. Physiol.*, 1928, 87, 399—405).—Pilocarpine produces a decrease and atropine an increase in the sodium, potassium, calcium, and magnesium content of trichloroacetic acid extracts of the small intestine. Adrenaline produces an increase in the sodium and calcium and a decrease in the potassium and magnesium.

B. A. EAGLES.

Relationship between chemical constitution and physiological action. II. Miotic activity of urethanes derived from the isomeric hydroxybenzylidimethylamines. E. STEDMAN (*Biochem. J.*, 1929, 23, 17—24).—The following urethanes were prepared: methylurethane of *m*-hydroxybenzylidimethylamine, m. p. 86° (hydrochloride, m. p. 175°; methiodide, m. p. 162°); ethylurethane of *m*-hydroxybenzylidimethylamine, an oil (hydrochloride, m. p. 156°; methiodide, m. p. 155—156°); phenylurethane of *m*-hydroxybenzylidimethylamine, m. p. 93° (hydrochloride, m. p. 175°); methylurethane of *p*-hydroxybenzylidimethylamine, m. p. 72° [hydrochloride, m. p. 180°; methiodide, m. p. 188° (decomp.); methochloride, m. p. about 110°]; ethylurethane of *p*-hydroxybenzylidimethylamine (hydrochloride, m. p. 165°; methiodide, m. p. 186°); phenylurethane of *p*-hydroxybenzylidimethylamine, m. p. 126° (hydrochloride, m. p. 182°); methylurethane of *o*-hydroxybenzylidimethylamine, m. p. 76° (hygroscopic hydrochloride; methiodide, m. p. 175°); ethylurethane of *o*-hydroxybenzylidimethylamine (methiodide, m. p. 149°); phenylurethane of *o*-hydroxybenzylidimethylamine, m. p. 90° (methiodide, m. p. 171°); methylurethane of choline iodide, m. p. 174°; methylurethane of tropine, m. p. 126° (hydrochloride, m. p. 263°).

Miotic activity was confined to the methylurethanes of the isomeric hydroxybenzylidimethylamines, the urethanes of choline iodide and tropine being inactive in 2% solutions. The activities of the methylurethanes of the isomeric hydroxybenzylidimethylamines are in the order $o > p > m$. Conversion of the tertiary basic group into the quaternary ammonium group increased the activity of the *o*-, diminished that of the *m*-, and abolished that of the *p*-compound.

S. S. ZILVA.

Bio-assay of aconite and its preparations. I. Lethal dose of aconitine to rats. J. C. MÜNCH

and G. S. GITTINGER (*J. Amer. Pharm. Assoc.*, 1929, 18, 17—24).—The fatal dose of aconitine (killing 2 out of 3 animals), when injected subcutaneously into white rats by the U.S.P. method, is 0.175 mg./kg. Wild rats are equally or somewhat less susceptible. Injected intraperitoneally the fatal dose is 0.10 mg./kg. Variations in susceptibility of individual rats are large and a number of test animals must be used.

E. H. SHARPLES.

Adsorption of poisons by "adsorbin," kieselguhr, and kaolin. Y. TAKAHASHI (*Okayama Ig. Zasshi*, 1927, 39, 1123—1132; *Chem. Zentr.*, 1928, ii, 970).—The poisonous action on excised rabbit's intestine of strychnine, cocaine (strongly absorbed), adrenaline, strophanthin, or pilocarpine (absorbed with difficulty) is inhibited by adsorption from the nutrient solution or from the tissue by the above substances, in order of decreasing effect. Animal charcoal is more effective.

A. A. ELDRIDGE.

Adsorptive effect of barium sulphate on intestinal toxins. I. SPADOLINI (*Boll. Soc. Ital. Biol. Sper.*, 1927, 2, 597—601; *Chem. Zentr.*, 1928, ii, 1002).

Action of magnesium salts on blood-sugar. S. LANG and L. RIGÓ (*Arch. exp. Path. Pharm.*, 1929, 139, 1—9).—Subcutaneous injection of small quantities of magnesium salts (0.0025—0.1 g. of magnesium chloride and 0.0025—0.005 g. of the sulphate per kg.) in rabbits produces a decrease in the blood-sugar concentration; larger doses result in an increase. Ergotamine increases the blood-sugar-raising action of magnesium salts.

B. A. EAGLES.

Action of chlorates, in particular potassium chlorate, on blood in animals. J. L. ULRICH and V. A. SHTERNOV (*J. Pharm. Exp. Ther.*, 1928, 34, 391—406).—Toxic doses of chlorates were given orally and intraperitoneally. Potassium chlorate, which converts hæmoglobin into methæmoglobin *in vitro*, does not always do so *in vivo*. Magnesium and calcium chlorates are both toxic and produce no methæmoglobin *in vivo*. Definite doses of sodium chlorate (6—8 g. per kg. body-weight) invariably produced methæmoglobin. Such doses were toxic in 45 min.

E. BOYLAND.

Comparative [toxic] action of hypertonic solutions of chlorates and chlorides of potassium, sodium, calcium, and magnesium. J. L. ULRICH and V. A. SHTERNOV (*J. Pharm. Exp. Ther.*, 1929, 35, 1—15).—Hypertonic solutions of the above salts were administered either intraperitoneally or orally to rabbits, guinea-pigs, cats, and albino rats. Approximately isotonic solutions were also occasionally injected intravenously. The average lethal doses of these salts for rats were determined for the two methods of administration. The chlorides were gram for gram more toxic than the chlorates, but if the average lethal doses were expressed on a molecular basis and administered intraperitoneally the chlorates of sodium and calcium were more toxic than the chlorides, i.e., a greater number of chloride molecules were required to produce death. This was also true with orally administered magnesium salts. The toxicity of the chlorates decreased in the order

calcium, magnesium, potassium, and sodium, irrespective of the method of administration; when injected intraperitoneally the chlorides decreased in toxicity in the order magnesium, calcium, potassium, and sodium, but administered orally the decrease followed the order potassium, magnesium, calcium, and sodium. The effect of these salts on the heart and respiration has been studied and the general symptoms are described and discussed. The salts were toxic only in large doses; their toxicity is ascribed to the cations rather than to the common chloride and chlorate anions. F. C. HALPOLD.

Influence of calcium on the fauna of peaty waters. I. A. SMORODINCEV and A. N. ADOVA (Bull. Soc. Chim. biol., 1928, 10, 1298—1305).—Water from *Carex* swamps (average p_H 7.728, average calcium content per litre, 46.83 mg.) contains large numbers of the larvæ of *Anopheles*, whilst water from sphagnum swamps (average p_H 5.04, average calcium content per litre, 10.61 mg.) is invariably devoid of these larvæ. Examination of other peaty waters shows that low calcium contents generally accompany low p_H and small number of larvæ.

G. A. C. GOUGH.

Pharmacology of bismuth salts. V. Distribution of bismuth in tissues. C. S. LEONARD. VI. Permeability of the placenta to bismuth. C. S. LEONARD and R. B. LOVE. VII. Concentration of bismuth in the blood of dogs after intramuscular injection of bismuth antiluetics. C. S. LEONARD and A. F. SEIBERT (J. Pharm. Exp. Ther., 1928, 34, 333—346, 347—354, 355—364).—V. Lethal and sub-lethal doses of soluble bismuth salts were injected intramuscularly into rabbits and the bismuth present in different organs was determined by the method previously described (A., 1926, 975). The average order of fixation was: kidney (highest), spleen, adrenals, liver, lung, brain, and heart. Twenty-four hrs. after injection of the bismuth compound blood contained 0.0035 mg. bismuth per c.c., whilst bile contained 0.03 mg. per c.c. The significance of this in the bismuth treatment of neuro-syphilis is discussed.

VI. Intramuscular injection of dipotassium bismuth tartrate and sodium bismuth tartrate in rabbits and cats produced no trace of bismuth in foetal organs, unless the lethal dose were exceeded, when appreciable amounts were found in the foetal kidneys. The placenta, however, always contained bismuth.

VII. The bismuth content of blood and urine of dogs was determined after injection of 40—50 mg. Bi (as dipotassium bismuth tartrate) per kg. body-weight. The urine always had a higher concentration of bismuth than the blood. With massage of the injection site, bismuth was found in the blood 24 hrs. after injection; without massage this took 48 hrs.

The maximum concentration in the blood of 0.001—0.003 mg. per c.c. is maintained for 48 hrs. after the injection, after which it declines, although bismuth is detectable in the blood for some weeks.

E. BOYLAND.

Liposoluble bismuth compounds. C. LEVADITI (Ann. Inst. Pasteur, 1928, 42, 1489—1535).—The tolerated dose of basic bismuth α -carbethoxy- β -

methylnonoate in the rabbit after intramuscular injection is 0.033 g. of bismuth per kg. body-weight. Its therapeutic efficiency in rabbits infected with *Spirochaeta cuniculi* depends on its rapid resorption, the creation of a local bismuth depot, and its gradual assimilation.

B. A. EAGLES.

Adsorption of dyes by the serum in lead poisoning. A. SEITZ (Klin. Woch., 1928, 7, 1234—1235; Chem. Zentr., 1928, ii, 1115—1116).—Inhibition by serum of the diffusion of dyes is less marked in lead poisoning.

A. A. ELDRIDGE.

Marked action of organic compounds of lead on experimental carcinoma in mice. E. KRAUSE (Ber., 1929, 62, [B], 135—137).—The following compounds have been used: lead tri-*n*-propyl fluoride, triisobutyl bromide, triisomyl bromide, lead tricyclohexyl and its iodide, lead triphenylcyclohexyl, lead tetraphenyl, triphenyl, triphenyl bromide, triphenyl fluoride, diphenyl dibromide, tin tetraphenyl, triphenyl, triphenyl bromide, and triphenyl *n*-propyl. The toxicity of organo-metallic compounds depends to a greater extent on constitutive influences than on solubility in water, which is possessed to a sensible degree only by lead tri-*n*-propyl fluoride. The latter compound is particularly effective against carcinoma. Lead triisobutyl bromide and lead tetraphenyl are very useful and lead tricyclohexyl is relatively active. The other compounds are less useful and the tin derivatives are unsuitable.

H. WREN.

Influence of heavy metals on the basal metabolism of guinea-pigs. G. SOSTBERG and M. STEUBER (Biochem. Z., 1928, 203, 385—388).—Injection of Ringer's solution and of "electroferrol" had no effect on basal metabolism but of "collargol" caused a 12% and of "solganol" (a gold preparation) a 20% increase.

P. W. CLUTTERBUCK.

Behaviour of the blood-sugar values after oral administration of yeast. A. BICKEL and G. NIGMANN (Biochem. Z., 1928, 203, 421—428).—Oral administration of 5 g. of dried yeast in 100 c.c. of water to normal dogs which had been starved for 24 hrs. caused a considerable decrease of blood-sugar 4—6 hrs. after administration.

P. W. CLUTTERBUCK.

Effect of oral administration of yeast on carbon- and oxidation-quotients of urine. P. HOFFMANN (Biochem. Z., 1929, 204, 208—214).—Dried yeast orally administered to rabbits decreases the carbon and oxidation quotients of the urine when these have been artificially raised by feeding dextrose. The action is very similar to that of insulin.

J. H. BIRKINSHAW.

Concentration of the [respiratory] enzyme-iron in the cell. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1928, 203, 95—98).—1 g. of baker's yeast (dry substance) contains less than 4×10^{-7} g. of iron combined as the respiratory enzyme. Since 1 g. of baker's yeast (dry weight) contains about 10^{-4} g. of iron, less than 1/250 of the iron is present as iron of the respiratory enzyme.

P. W. CLUTTERBUCK.

Bioluminescence. VI. Mechanism of luminescence in *Cypridina*: luciferin and luciferase. S. KANDA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1929, 9, 265—269).—When equal volumes of an

aqueous solution of luciferase and a methyl-alcoholic solution of luciferin are mixed in the dark no luminescence is observed, but if distilled water is then added slowly luminescence becomes just perceptible in presence of about 60% of water and 40% of methyl alcohol. When further water is added the intensity of luminescence reaches a maximum and then gradually decreases. A theory is suggested to explain these phenomena. P. W. O. KERMAK.

Separation of the enzymes of barley malt. III. **Amylase and maltase.** H. PRINGSHEIM and E. THILO (Biochem. Z., 1928, 203, 99—102).—When malt is kept for 3 days at the ordinary temperature with 87% glycerol, the extract freed from glycerol by dialysis contains a highly active amylase, but is free from maltase. The residue containing maltase is not, however, completely freed from amylase by such extraction. Extraction with glycol effects a similar separation, but the maltase activity is considerably decreased (cf. A., 1926, 202, 976).

P. W. CLUTTERBUCK.

Complement of the amylases. VII. J. BONDI (Biochem. Z., 1928, 203, 88—94).—Egg-albumin digested with pepsin has only a slight, but digested with trypsin a greater, complement action, whilst albumin digested first with pepsin and then with trypsin has a still greater action. It is suggested that the activator contained in yeast complement is formed from the yeast-protein by the proteolytic enzymes of the yeast (cf. A., 1928, 1280).

P. W. CLUTTERBUCK.

Enzymes and light. XIII. L. PINCUSSEN. **Action of light on takadiastase in presence of sensitizers.** Y. KAMBAYASHI (Biochem. Z., 1928, 203, 334—342).—The variation of the extent of inactivation of takadiastase on irradiation with ultra-violet light with changes of p_H and of purity and dilution of enzyme is investigated in presence and absence of the sensitizers eosin, sodium anthraquinone-disulphonate, and sodium dichloroanthracenedisulphonate. With a concentration of 0.01% of sensitizer, the action of light is no greater than in its absence. The degree of inactivation decreases with increasing concentration of sensitizer but to different extents with the three substances. The action of light on takadiastase purified by adsorption on aluminium hydroxide and eluted with phosphate is considerably greater than on the untreated enzyme, 16—22% of the untreated and 36—48% of the purified enzyme being destroyed. Dilute enzyme solutions are more strongly inactivated than concentrated. Injury of the purified enzyme by light is never greater and often less in presence than in absence of sensitizers (cf. A., 1926, 432, 757; 1928, 795). P. W. CLUTTERBUCK.

Specificity of enzymic fission of maltose. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1928, 788—795).—Leibowitz has assumed the existence of two types of maltase, viz., glucosido-maltase present in yeast, and gluco-maltase present in barley and in takadiastase, the latter type being incapable of hydrolysing α -methylglucoside or maltosazone (cf. A., 1925, 184; 1926, 322). This view is not shared by the author, who found that α -methylglucoside is readily hydrolysed by barley maltase if sufficiently

concentrated enzyme solutions are used. The fact that maltase in different materials may exert its maximum activity at different p_H values does not disprove the identity of the enzyme in the different materials, since the effect of activating and inhibiting substances has to be considered. J. H. LANE.

Enzymic fission of sucrose. II. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1928, 781—787; see also A., 1928, 1157, 1281).—Of the two sucrose-splitting enzymes in yeast, viz., α -glucosidase and β -*h*-fructosidase, the former is present in much smaller amount than the latter and is inactive at p_H 4.7, the optimum reaction for fructosidase. Their behaviour towards raffinose affords a means of distinguishing them, since α -glucosidase has no action, whilst the fructosidase produces melibiose and laevulose. Melezitose, a glucosidofructosidoglucose in which the fructosidoglucose portion of the molecule is supposed to have the constitution of sucrose, is not attacked by fructosidase, but is completely hydrolysed to hexoses by α -glucosidase; hence it appears to be α -glucosido- β -*h*-fructosido- α -glucoside. J. H. LANE.

Liberation of invertase from yeast. R. WILLSTATTER and W. GRASSMANN (Biochem. Z., 1928, 203, 308—312).—Yeast is treated with ethyl acetate and digested with pepsin or trypsin and the invertase finally liberated into aqueous solution from the residue by treatment with malt diastase or papain. Activation of papain by hydrogen cyanide accelerates the liberation of invertase (cf. A., 1921, i, 823).

P. W. CLUTTERBUCK.

Formation of acetaldehyde from pyruvic acid in the autolysis of red and white muscle. A. UTEVSKI (Biochem. Z., 1929, 204, 81—87).—In the autolysis of white muscle of the rabbit, cock, and hen, smaller amounts of acetaldehyde are formed than in the red muscle and in the breast muscle of the pigeon. Only red muscle and the breast muscle of the pigeon can convert sodium pyruvate into acetaldehyde. J. H. BIRKINSHAW.

Titration method for lipase. L. GÓZONY, J. GSELL, and F. HOFFENREICH (Biochem. Z., 1929, 204, 126—139).—Mono- or tri-butyrin is added to serum in a number of known dilutions, and caseinogen dissolved in sodium hydroxide and brought to p_H 5.6 is then added; the free acid liberated by the serum-lipase precipitates the caseinogen. The dilution at which turbidity just ceases is observed. A comparative series of lipase determinations in various animal sera is given and the effect of various substances on lipase action is studied. J. H. BIRKINSHAW.

Stereochemical specificity of liver- and pancreas-lipase. H. H. WEBER and R. AMMON (Biochem. Z., 1929, 204, 197—207).—The dissociation constant of the compound of liver-lipase with methyl *d*-mandelate is $10^{-3.75}$ and with the *l*-mandelate $10^{-2.9}$. The ratio of the hydrolysis constants is 1:1.75. The dissociation constants of the corresponding compounds of pancreas-lipase are equal and have the value $10^{-1.8}$. The ratio of the hydrolysis constants is 1:1.7 in favour of the *l*-ester. The optical decomposition specificities peculiar to the two lipases agree quantitatively in spite of the opposite nature of their optical total specificity. J. H. BIRKINSHAW.

Hydrolysis of ethyl lactate by liver-esterase. P. RONA and R. ITELSOHN-SCHUCHTER (Biochem. Z., 1928, 203, 293—297).—Of the ethyl esters of *d*-, *l*-, and *dl*-lactic acid, the esterase of pig's liver hydrolyses the *d*-ester most readily. P. W. CLUTTERBUCK.

Activation of *Ricinus* lipase by acids. S. MUKAI (J. Soc. Chem. Ind. Japan, 1928, 31, 759—765).—There is a magnesium compound in castor seeds which inhibits the activity of lipase, and acids used for the activation of lipase dissolve and remove this compound. The activated lipase, which had been previously treated with 0.05*N*-sulphuric acid, showed nearly the same activity from *p*_H 3.5 to 6.8.

Y. TOMODA.

An enzyme [effecting hydrolysis of allantoin]. R. FOSSE and A. BRUNEL (Compt. rend., 1929, 188, 426—428).—A new enzyme, *allantoinase*, which hydrolyses allantoin to allantoic acid, is found in the seeds of many leguminous plants. G. A. C. GOUGH.

Enzymic proteolysis. IV. E. MISLOWITZER (Biochem. Z., 1928, 203, 323—333).—The amino-groups liberated during hydrolysis of the CO-NH groups of protein belong to the lower degradation products and the carboxyl groups to the colloidal residue. In the initial hydrolysis of caseinogen (cf. A., 1928, 923, 1401) the amino-groups present in the colloidal fraction show scarcely any change, whilst the carboxyl groups increase considerably.

P. W. CLUTTERBUCK.

Specific action of proteolytic enzymes and its significance in determining the structure of proteins. E. WALDSCHMIDT-LEITZ (Collegium, 1928, 543—554).—Clupeine, salmine, and scombrine are strongly hydrolysed by trypsin-kinase, and moderately by trypsin and papain-hydrocyanic acid, but not by erepsin, pepsin, and papain. Histone, caseinogen, fibrin, gelatin, gliadin, and albumin are not hydrolysed by erepsin or trypsin, but are moderately hydrolysed by trypsin-kinase, pepsin, or papain, and, except albumin, are strongly hydrolysed by papain-hydrocyanic acid. Globulin is hydrolysed by trypsin-kinase and pepsin. Silk fibroin and keratin are not hydrolysed by any of these enzymes. Synthetic dipeptides, derived from amino-acids occurring in proteins, *e.g.*, glycyl- and leucyl-glycine, glycyltyrosine, and histidyl-glycine, are hydrolysable by erepsin only, except in certain instances, *e.g.*, phenylalanylarginine and glutamyltyrosine, which are hydrolysable by trypsin and trypsin-kinase also. Mere lengthening of the peptide chain does not induce hydrolysis. The introduction of a tyrosine molecule renders tri-, tetra-, and pentapeptides capable of hydrolysis by trypsin and trypsin-kinase, respectively. Leucyltriglycyltyrosine is not split by erepsin, which shows that the modes of action of erepsin and trypsin are different. The trypsin eliminates tyrosine from the carboxyl group, whereas erepsin eliminates the amino-acids carrying free amino-groups and then proceeds to the complete hydrolysis of the peptide. These observations explain the effects of fractional hydrolysis. Leucylglycyltyrosine would give a hydrolytic ratio 1:1 with trypsin followed by erepsin, whereas leucyltriglycyltyrosine would show 1:3. The action of yeast polypeptidase and yeast erepsin depends on the length of

the peptide chain, independent of its composition. Dipeptides are attacked by yeast erepsin only, and tri- and higher peptides by polypeptidase only. Yeast erepsin requires the close proximity of both a free amino-group and a free carboxyl group; the polypeptidase requires a free amino-group without the close proximity of the carboxyl group. A certain electronegative property is required in trypsin substrates. Dipeptides, which are specific erepsin substrates, can be converted into specific pancreatic trypsin substrates by introducing acyl groups.

D. WOODROFFE.

Specific action of erepsin, trypsin, and trypsin-kinase. Effect of the addition of α - and β -amino-acids, amines, etc. to the substrate-enzyme mixture. E. ABDERHALDEN, E. RINDTORFF, and A. SCHMITZ (Fermentforsch., 1928, 10, 233—250; cf. Abderhalden and Gigon, A., 1907, ii, 892).—That the action of erepsin, trypsin, and trypsin-kinase on various polypeptides is not affected in the same manner by the addition of various amino-acids or amines is shown by a study of the hydrolysis of *dl*-leucylglycine, glycyl-*dl*-leucine and its phenylurethane, *dl*- α -aminobutyrylglycine, and benzoyl-*dl*-leucylglycine by these enzymes at various concentrations, with or without the addition of a large number of amino-acids. The hydrolysis of *dl*-leucylglycine by erepsin (*p*_H 7.8) for 20 hrs. at 37° is slightly increased by the addition of β -aminobutyric acid, whilst *l*-leucine, glycine, *l*-valine, *l*-alanine, β -alanine, *d*-alanine, sarcosine, *l*-phenylalanine, and hippuric acid have a retarding effect which increases in the order given. A small retarding action is also observed by addition of α - and β -naphthylamine, *p*-toluidine, and colamine, which again increases in the order given. On the other hand, with trypsin-kinase (*p*_H 8.3) at 37° for 20 hrs. the retarding action on the hydrolysis of benzoyl-*dl*-leucylglycine increases in the order, *d*-alanine, hippuric acid, sarcosine, *l*-phenylalanine, *l*-leucine, glycine, *l*-alanine, and β -aminobutyric acid; and in the second series, in the order, colamine, α - and β -naphthylamine, and *p*-toluidine. Similarly for the hydrolysis of glycyl-*dl*-leucine by erepsin for 30 hrs. the retarding effect increases in the order glycine, β -aminobutyric acid, *l*-leucine, *d*- and *l*-valine, sarcosine, benzoyl-*dl*-alanine, *d*-alanine, *l*-alanine, β -alanine, hippuric acid, and *l*-phenylalanine; and in the second series, in the order colamine, β -naphthylamine, carbamide, *p*-toluidine, and α -naphthylamine. The corresponding order for the hydrolysis of the phenylurethane of glycyl-*dl*-leucine with trypsin-kinase for 30 hrs. is sarcosine, *l*-valine, *l*-leucine, β -aminobutyric acid, β -alanine, *l*-alanine, benzoyl-*dl*-alanine, phenylalanine, glycine, and hippuric acid; and in the second series, α - and β -naphthylamine, *p*-toluidine, carbamide, and colamine. The hydrolysis of *dl*- α -aminobutyrylglycine by erepsin is similarly retarded in the order *l*-leucine, glycine, *d*-alanine, *l*-alanine, sarcosine, *l*-phenylalanine, hippuric acid, the last two having a very large effect. The interaction of the enzyme-complex with the original substrate (polypeptide) and its fission products (amino-acids) is discussed, and on the basis of the above results it is concluded that neither the free amino-group nor the carboxyl group of itself is responsible for the specific action of the

enzyme, but that this depends in a complicated manner on the whole structure of the substrate and its fission products. J. W. BAKER.

Proteases of gastric mucosa. R. WILLSTATTER and E. BAMANN (Z. physiol. Chem., 1928, 180, 127—143).—A glycerol extract of the gastric mucosa of the pig or dog contains kathepsin, a protease having its optimum activity at p_H 4. Erepsin is also present. B. A. EAGLES.

Enzymic synthesis of protein. P. RONA and H. A. OELKERS (Biochem. Z., 1928, 203, 298—307).—The formation of sparingly soluble products by the action of pepsin and trypsin on the concentrated aqueous solution of protein decomposition products at a suitable p_H as reported by Wasteneys and Borsook (A., 1925, i, 97, 102, 472, 865) is confirmed and the conclusion of the latter that this represents synthesis of protein, previously contested (Rona and Chrometzka, A., 1927, 1220), is now regarded as proved correct in the case of peptic digestion, since the process is accompanied by a decrease of amino-nitrogen and carbonyl groups, but the authors' view that these products are the result of further hydrolysis is maintained in the case of tryptic digestion, there being a further increase in amino-nitrogen and carbonyl groups during the formation of the products. The less soluble products obtained during the action of pepsin, on digestion again with pepsin under optimal conditions again break down with the formation of free carbonyl groups and an increase in amino-nitrogen. P. W. CLUTTERBUCK.

First phases of the chemistry of the dissimilation of the hexoses. II. A. J. KLUYVER and A. P. STRUYK (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 882—893; cf. A., 1928, 398).—When dextrose is fermented by maceration juice from yeast under certain conditions the amount of hexosemonophosphoric acid formed may exceed that of the hexosediphosphoric acid. The smaller the concentration of maceration juice used to ferment a mixture of dextrose and disodium hydrogen phosphate the larger is the ratio of hexosemonophosphoric acid to hexosediphosphoric acid. The ratio between the number of molecules of carbon dioxide and of hexosediphosphoric acid formed is frequently greater than 2. Various theories of alcoholic fermentation are discussed. W. O. KERMACK.

Biochemical conversion of dihydroxyacetone into hexose by fermentation and the velocity of fermentation of dihydroxyacetone in relation to its heat of combustion. I. C. NEUBERG and M. KOBEL (Biochem. Z., 1928, 203, 452—462).—The velocity of fermentation of dihydroxyacetone by fresh *Saccharomyces Ludwigii* is never greater than the velocity with dextrose. From the energy content (heat of combustion) of dihydroxyacetone, which is higher than that of dextrose, it follows that dihydroxyacetone is fermented, not as such, but after condensation to hexose. This is confirmed by the isolation as products of fermentation of hexosemono- and hexosediphosphoric acid. Using dried *S. Ludwigii* to which co-enzyme of bottom yeast had been added, the chief product is optically active hexosemonophosphate [α_D of the barium salt in two preparations

+17.7° ($c=2.63$), +13.8° ($c=1.7$)] consisting of a little of Neuberg's and a large amount of Robison's ester together with decreasing amounts of hexosediphosphate. P. W. CLUTTERBUCK.

Mechanism of the fermentation of dihydroxyacetone. K. IWASAKI (Biochem. Z., 1928, 203, 237—266).—Fermentation of dihydroxyacetone by *Saccharomyces Ludwigii*, using either the living yeast or the maceration extract, leads to the conclusion that fermentation depends on the condensation of dihydroxyacetone to hexose, direct fermentation of the triose not taking place. With living yeast, the maximal rate of fermentation of 0.10% dextrose solution is not increased by adding dihydroxyacetone, but with lower concentrations of sugar the rate becomes maximal, but never exceeds it on adding dihydroxyacetone. The oxidation quotient for the fermentation of dihydroxyacetone is at first low, but eventually increases to the same value as for the fermentation of sugar. The calorimetrically determined heat of fermentation of dihydroxyacetone is 70—80 g.-cal. per g. higher than for dextrose. The activity of maceration juice from freshly-prepared dry yeast in fermenting dihydroxyacetone corresponds with that of the living yeast from which the dry yeast is prepared. When by storage its activity decreases, the original activity is restored by mixing with dried yeast before macerating. The velocity of fermentation of dihydroxyacetone by extract is 30—40% of that of sugar in the phosphate period. Inorganic phosphate becomes esterified and the esters examined after 80 min. consisted of 80% of hexosediphosphate and 20% of Robison's hexosemonophosphate. The rate of fermentation of dihydroxyacetone is limited by the rate of condensation of triose to hexose. P. W. CLUTTERBUCK.

Desmolytic formation of methylglyoxal by the enzymes of yeast. C. NEUBERG and M. KOBEL (Biochem. Z., 1928, 203, 463—468).—By keeping magnesium hexosediphosphate for 3 days with an enzyme solution (prepared by suspending for 2 days at 37° dried yeast in distilled water, adding toluene, shaking occasionally, and centrifuging) and removing the protein with trichloroacetic acid, a clear solution was obtained containing considerable amounts of methylglyoxal, characterised as the 2:4-dinitrophenylosazone. P. W. CLUTTERBUCK.

Bacteriological conductivity culture cell and some of its applications. L. B. PARSONS, E. T. DRAKE, and W. S. STURGES (J. Amer. Chem. Soc., 1929, 51, 166—171).—A conductivity cell which can also be used as a growth vessel is described. The cell is used to investigate the effect of environment factors (e.g., p_H , temperature, oxygen pressure) on the biochemical activity or growth of ammonia-producing anaerobes, the conductivity change being used to measure the ammonia production. Other possible applications are suggested. S. K. TWEEDY.

Biological reactions on the concentration of gels. S. PRÁT (Kolloid-Z., 1929, 47, 36—38).—When micro-organisms are grown in agar, the forms developed vary with the concentration of the gel. E. S. HEDGES.

Microbiology of aqueous solutions. K. C. BERTHELSSEN (Pharm. Zentr., 1929, 70, 37—44).—A study of the types of growth colonies found in simple aqueous solutions of a large number of inorganic salts and of the commoner alkaloids. B. A. EAGLES.

Relation of the growth of certain micro-organisms to the composition of the medium. IV. Addition of mannitol. V. READER (Biochem. J., 1929, 23, 61—67).—The anomalous results obtained by Orr-Ewing and Reader (A., 1928, 556) with *Streptothrix corallinus* when crude aqueous extracts of yeast were added to the medium can be artificially reproduced by adding mannitol to the purer extracts. The increased weight of bacteria grown in the presence of mannitol is not due to increased fat production. The amount of growth is independent of the concentration of the mannitol. Dulcitol, sorbitol, glycerol, or inositol could not replace mannitol in this respect. S. S. ZILVA.

Metabolism of the *Bacillus abortus-melitensis* group. II. Nitrogen. III. Dextrose utilisation. J. G. McALPINE and C. A. SLANETZ (J. Infect. Dis., 1928, 42, 66—71, 73—78).—Differences in sugar and nitrogen metabolism are employed for the differentiation of human and porcine from bovine *B. abortus* and from *B. melitensis*.

CHEMICAL ABSTRACTS.

Gas production by bacterial symbiosis with special reference to the influence of nitrogenous substances. M. ISHIKAWA (J. Infect. Dis., 1927, 41, 238—256).—Non-proteolytic bacteria cannot produce gas from carbohydrates and formates in media containing only complex nitrogenous substances unless proteolytic bacteria or simple nitrogenous substances are present. Probably the simple nitrogenous compounds increase the activity or production of formiase, which is considered to be responsible for the production of gas. CHEMICAL ABSTRACTS.

Influence of anions and cations on the viability of *Bacillus coli*. C. H. BOISSEVAIN and E. WEBB (J. Lab. Clin. Med., 1928, 13, 1027—1035).

CHEMICAL ABSTRACTS.

Reduction potential, energy exchange, and cell growth. Experiments with *B. coli*. J. H. QUASTEL and W. R. WOOLDRIDGE (Biochem. J., 1929, 23, 113—137).—Succinate inhibits anaerobic growth of *B. coli* in a lactate-formate medium. Cysteine (or thiol compounds) also inhibits growth. Formate at relatively low concentrations increases the rate of proliferation of the organism. Rate of growth of *B. coli* is not dependent on the oxidation or reduction intensity of its environment (cf. Quastel and Stephenson, A., 1926, 1177). S. S. ZILVA.

Resting bacteria. J. H. QUASTEL (Bull. Soc. Chim. biol., 1928, 10, 1282—1292).—A discussion of work already published (A., 1926, 434, 868; 1927, 280, 1113; 1928, 797). G. A. C. GOUGH.

Lactic acid fermentation. A. I. VIRTANEN (Förrh. III nord. Kemistmötet, 1928, 217—226).—A résumé of recent work on the lactic acid fermentation of sugar. H. F. HARWOOD.

Precipitation of organic iron compounds by bacteria. I. M. LEWIS (Zentr. Bakt. Par., II, 1928,

75, 45—52; Chem. Zentr., 1928, ii, 677).—When grown on a medium containing certain iron salts and tap, spring, or river water, various bacteria caused precipitation of iron, the effect depending to some extent on the amount of phosphorus present.

A. A. ELDRIDGE.

Nitrogen-fixing bacteria of the genus *Rhizobium*. R. H. WALTER (Iowa Agric. Exp. Sta. Res. Bull., 1928, 113, 371—406).—Legume bacteria attack monosaccharides with a greater production of acid than in the case of di- or tri-saccharides, dulcitol, inositol, or dextrin. Agglutination and gelatin liquefaction were studied. CHEMICAL ABSTRACTS.

Bacteria. XXIV. Timothy-grass bacillus. R. D. COGHILL and O. D. BIRD (J. Biol. Chem., 1929, 81, 115—122).—Dried Timothy-grass bacilli (*Mycobacterium phlei*) when extracted with ether and chloroform yielded 2.72% of fat; after hydrolysis of the residue with hydrochloric acid a further 14.9% of fat could be extracted. The dried organisms, after defatting with ether, were extracted successively with water and 0.5% sodium hydroxide; the water removed 12—15% of the total nitrogen, and yielded a protein and a carbohydrate fraction, the latter containing reducing sugars. The alkaline extract contained about 16% of the total nitrogen, of which about 6% was represented by a second protein; the insoluble residue contained about 60% of the nitrogen, the remainder having been lost as ammonia. This organism therefore, although biologically similar to the tubercle bacillus, differs markedly from the latter in chemical composition (A., 1926, 1277).

C. R. HARRINGTON.

Pneumococcal hæmolysin. L. COTONI and N. CHAMBRIN (Ann. Inst. Pasteur, 1928, 42, 1536—1572).—Media containing dextrose are favourable to the production of pneumococcal hæmolysins. Cultures grown on media containing animal sera are entirely lacking in hæmolytic activity. B. A. EAGLES.

Oxidations by *Bacterium xylinum*. II. Formation of gluconic and 5-ketogluconic acids [from dextrose]. K. BERNHAUER and K. SCHÖN (Z. physiol. Chem., 1929, 180, 232—240).—A bacterium resembling *B. xylinum* (cf. A., 1928, 1285) can convert dextrose, in acid solution, into gluconic acid. The change proceeds best in presence of 0.02*N*-butyric acid when 79% of the acid is obtained after 23 days. Formic and acetic acids are not so suitable. The conversion takes place also in presence of calcium carbonate. When the reaction mixture is slightly alkaline (p_H 8) 5-ketogluconic acid is obtained, but the yield diminishes from 64 to about 40%, when 36% of the experiments were infected with *Aspergillus niger*. This mould contamination is prevented by addition of 0.006*N*-butyric acid. H. BURTON.

Formation of acid by species of *Penicillium* (Link). T. CHRZASZCZ and D. TINKOV (Biochem. Z., 1929, 204, 106—124).—The titratable acidity, citric and oxalic acids, and acids having soluble calcium salts were determined for 42 species of *Penicillium*. All species produced acid. Citric acid is a normal product of metabolism and is produced in considerable amount by some species; oxalic acid is formed only by a few species and is not regarded

as a stage in the normal oxidation process. The acid (or acids) with soluble calcium salt appears regularly. Some species form fatty substances, possibly esters.

J. H. BIRKINSHAW.

Resins of *Aspergillus niger*. C. PONTILLON (Compt. rend., 1929, 188, 413—415).—The alcoholic extract of the mycelium of *A. niger* yields resins when freed from fats by dilution with water to a concentration of 70% followed by filtration. The resins may also be isolated by virtue of their solubility in sodium carbonate or by the difference between the solubility of the magnesium resins and the magnesium soaps arising from the hydrolysis of the fats. The resin is soluble in ether, light petroleum, and concentrated solutions of chloral hydrate.

G. A. C. GORCH.

Disinfectants for preserving the amylase solution of *Aspergillus oryzae*. K. OSHIMA (J. Soc. Chem. Ind. Japan, 1928, 31, 750—753).—The following antiseptics were proved to be suitable for preserving the amylase solution: cresol (0.15—0.5%); phenol (0.4—1.5%); thymol (0.05—0.20%); phenol+cresol (0.3%+0.1%); 0.2%.

Y. TOMODA.

Grouped organisms. Action of alkaloids on *Cumulus Roscoffensis*. J. A. THOMAS (Compt. rend., 1929, 188, 190—197).—The time of survival of groups of these organisms in dilute solutions of various alkaloids is sometimes greater and sometimes smaller than that of the individual organisms. In many cases a particular concentration is observed at which the groups possess a greater time of survival. Increase in pH generally increases the toxicity and the addition of quinal decreases the toxicity in some instances.

G. A. C. GORCH.

'Bactericidal' action of sodium ricinoleate. A. KOZLOWSKI (J. Bact., 1928, 16, 203—209).

Bactericidal properties of the acyl and alkyl derivatives of resorcinol. B. HAYAT (J. Infect. Dis., 1928, 43, 33—40).—The bactericidal properties of acyl- and alkyl-resorcinol depend on the composition of the medium: the inhibitory power of organic material increases from *n*-butyl- to *n*-octyl-resorcinol, where disinfectant power has disappeared. The bactericidal power is greater at 37° than at 20°. At 45°, acyl- and octyl-resorcinol are bactericidal in aqueous solution. By increasing the solubility, addition of sodium carbonate (1%) increases the bactericidal action of hexyl and higher derivatives. Alkyl derivatives of resorcinol (*n*-butyl- to *n*-decyl-) are more potent at 37° than at 20°; they are ineffective in a standard organic medium at 37°. With hexyl-, heptyl-, and octyl-resorcinol a specificity in disinfectant action was observed. CHEMICAL ABSTRACTS.

Thermodynamic activity and biochemical action. Disinfecting power and activity of mercury ion. I. A. SHENKOVICH and G. B. SOLOVY (Arch. Sci. Biol., 1928, 22, 411—416; Chem. Zentr., 1928, 1, 2138).—The activity of the mercuric ion and the disinfecting power diminish with increasing addition of sodium chloride to the solution. When as compared against *loc. cit.* where n is the number of *E. coli* destroyed after 6 mins.

a straight line is obtained except for very high sodium chloride concentrations. A. A. ELDRIDGE.

Bactericidal action of nitroso-compounds. E. A. COOPER and R. B. HAINES (Biochem. J., 1929, 23, 10—16).—The hydrochloride and methiodide of nitrosoanilines are weaker germicides than the bases from which they are derived. Nitrosophenol, nitrosoaniline, and nitrosodimethylaniline have little or no action on amino-acids and proteins, but react gradually with nucleic acid, forming a dark green, insoluble product. The nitroso-compounds are readily absorbed by lecithin. The nitroso-compounds, therefore, most probably owe their slow germicidal action and marked inhibitory power to their gradual chemical interaction with the nuclear constituents of the cell. S. S. ZILVA.

Chemical action of quinones on proteins and amino-acids. II. E. A. COOPER and R. B. HAINES (Biochem. J., 1929, 23, 4—9).—Saline constituents of Ringer's solution accelerate considerably the reaction between benzoquinone and glycine, but have only a slight effect with toluquinone. Benzoquinone loses much of its germicidal activity on forming an additive compound with anthranilic acid. The temperature coefficient of disinfection in the case of quinones is 6 or even higher; on the other hand, the coefficient for the chemical action on glycine is normal (2 for 10°). In the case of phenol the temperature coefficient for germicidal action is approximately 3 and agrees more closely with the coefficient for the process of protein-coagulation by phenol. The velocity of coagulation by *m*-cresol is only very slightly increased by rise in temperature, as is also that of its bactericidal action. It is suggested that the main factor in the germicidal action of the quinones is the interaction with the amino-acids, but another factor fundamental in the action of oxidising disinfectants is operating simultaneously.

The chemical reactivity ratio benzoquinone/toluquinone with the nitrogenous constituents of urines is highest in glycosuria (3.5), intermediate in value with leucemia (2), and lowest in nephritis, jaundice, and hematuria (1.4). S. S. ZILVA.

Production of monochromatic X-rays of long wave-length. Quantitative action on micro-organisms. F. HOLWACK (Compt. rend., 1929, 188, 197—199).—X-Rays of 4 and 8 Å., emitted from the silver cathode of a Coolidge tube through a silver window 5 thick and a cellophane sheet 20 thick, possess a bactericidal action on *B. pyocyaneus*. In the quantitative experiments the technique of Lacassagne (following abstract) is used. Mathematical investigation shows that, when light of 4 Å. is used, one quantum is sufficient to kill one organism and the number of surviving organisms is an exponential function of the time of irradiation. With light of 8 Å. at least 4 quanta are required and the mathematical relationship is more complex.

G. A. C. GORCH.

Action of X-rays of long wave-length on micro-organisms. Statistics of the mortality of the irradiated bacteria. A. LACASSAGNE (Compt. rend., 1929, 188, 199—202).—An appropriate amount of a culture of *E. pyocyaneus*, suspended in water, is

evenly distributed on the surface of gelatin in a Petri dish so that a field of 10 cm. diameter contains 100 bacteria. A number of fields are then irradiated by X-rays (penetrating absorption) of known intensity, the dishes incubated, and the resultant colonies in the irradiated fields compared with those in control dishes. It is assumed that each bacterium possesses a sensitive zone, which, if it absorbs a certain minimum of muricic acid, is destroyed by irradiation; the mathematical development depends on this assumption.

G. A. C. GORCH.

Probability curves describing the action of X-rays on bacteria. (Mém.) P. CURIE (Compt. rend. Sér. 188, 302—304).—The equations of curves relating the time of irradiation to the probability of survival of bacteria irradiated by X-rays are given (see preceding abstracts).

G. A. C. GORCH.

Staining methods for bacteria and yeasts. W. E. MAXEVAL (Stain Tech., 1929, 4, 21—25).—In order successfully to stain the flagella of bacteria and actively motile organisms 20—24 hrs. old must be used. They should be transferred to sterile water, and after 30 min. droplets should be evaporated on slides. These should then be treated for 2—4 min. with the following mordant: 50 c.c. of 10—20% acetic acid, 10—15 c.c. of 5% ferric chloride, 5 c.c. of carbolfuchsin (Ziehl-Nielsen), 6—8 c.c. of 3% hydrogen peroxide. The slides should be washed and then treated for 2—3 min. with a mixture of 10 c.c. of saturated alcoholic basic fuchsin, 5 c.c. of a solution of aniline (1 part) in 95% alcohol (3 parts), 30 c.c. of water, 1 c.c. of 4% acetic acid, after which they should be washed with water. Gutstein's methods of staining bacteria and yeasts are satisfactory.

H. W. DUDLEY.

Loeffler's methylene-blue. H. J. CONN (Stain Tech., 1929, 4, 27).—Instead of using Loeffler's formula for making up methylene-blue for use as a stain it is recommended that an alcoholic solution of the dye diluted with water be used.

H. W. DUDLEY.

Simultaneous determination of the adrenaline secretion, sugar content, and coagulation time of the blood in non-fasted, non-anæsthetised dogs after hæmorrhage. S. SAITO, B. KAMEI, H. TACHI (Tohoku J. Exp. Med., 1928, 11, 205—217).

CHEMICAL ABSTRACTS.

Significance of the augmented adrenaline secretion after hæmorrhage in dogs in the simultaneous occurrence of hyperglycæmia. H. TACHI and S. SAITO (Tohoku J. Exp. Med., 1928, 11, 205—217).

CHEMICAL ABSTRACTS.

Influence of adrenaline and insulin on distribution of glycogen. N. R. BLATHERWICK and M. SALTIN (J. Biol. Chem., 1929, 81, 123—127).—The conclusion of Cori and Cori (A., 1928, 1286) that adrenaline causes increased deposition of glycogen in the liver is confirmed by experiments on rabbits.

C. R. HARRINGTON.

Action of insulin in normal young rabbits. M. W. GOLDBLATT (Biochem. J., 1929, 23, 83—98).—Young rabbits 6—10 weeks old of the same litter when starved for 24 hrs. show a very satisfactory

uniformity in their liver-glycogen (average of twelve animals was 50 mg. per liver). On treating such starved animals with insulin a rise in liver-glycogen invariably occurs (average for twelve animals 237 mg. per liver). An increased liver- and a considerable muscle-glycogen content is observed even in animals dying in hypoglycæmic convulsions. Adrenaline, whilst relieving hypoglycæmia, does not interfere with the action of insulin in increasing liver-glycogen. On the other hand, in continuous deep anaesthesia insulin fails to bring about this increase. Light ether anaesthesia relieves hypoglycæmic convulsions. Hypoglycæmic animals are very susceptible to strychnine poisoning. Continuous strychnine convulsions can prevent the typical action of insulin in promoting an increased glycogen content of the liver. In fed animals insulin does not bring about an increase in liver-glycogen and the animal goes into hypoglycæmic convulsions with large quantities of glycogen in the liver. Muscle-glycogen is definitely lowered. It is suggested that the immediate effect of insulin is to inhibit the release of liver-glycogen.

S. S. ZILVA.

Glycogen content of the liver and muscle of rabbits; comparison of insulin and decamethylenediguanidine (synthalin). P. RUBINO, J. A. COLLAZO, and B. VARELA-FUENTES (Compt. rend. Soc. Biol., 1928, 99, 178—180; Chem. Zentr., 1928, ii, 1113).—Insulin, but not synthalin, stimulates not only the utilisation of dextrose in the tissue, but also the synthetic process leading to the formation of dextrose.

A. A. ELDRIDGE.

Insulin. III. Standardisation of insulin. K. FREUDENBERG and W. DIRSCHERL. IV. Action of pepsin on insulin and its acetyl derivative. W. DIRSCHERL (Z. physiol. Chem., 1929, 180, 212—216, 217—231).—III. The standard used by the authors is the amount of insulin necessary to reduce the blood-sugar of a 2-kg. rabbit from an initial value of 0.1% to 0.045%. This unit is equivalent to 1.8 standard units. Abel's crystalline insulin is found to contain 26 standard units/mg. (cf. du Vigneaud and others, A., 1928, 1160).

IV. The action of pepsin on insulin, "regenerated" insulin, and acetylinsulin (A., 1928, 675) at different p_H values and temperatures has been examined. The results show that the inactivation of insulin is comparable to the pepsin digest of a protein and optimum activity is at p_H 1.8 and 45°. A suspension of acetylinsulin was only slightly affected after 3 hrs. The acetylinsulin obtained by Jensen and Gelling (A., 1928, 1160) probably differs from the author's, since a different method of preparation was employed.

[With H. EYER.]—Formol titration of the pepsin digest of insulin shows an increase in the amino-nitrogen. Acetylinsulin shows only a slight increase after 24 hrs.

H. BURTON.

Insulin content of the pancreas following intoxication of rabbits with paratyphoid-B filtrate and dysentery bacilli. M. L. MENTEN and H. M. KRUGH (J. Infect. Dis., 1928, 43, 121—125).

Insulin-like plant extracts. III. Phaseolin. E. KAUFMANN (Z. ges. exp. Med., 1928, 60, 285—288;

Chem. Zentr., 1928, ii, 674).—The insulin-like effect of phaseolin on the blood-sugar is recorded; the active principles of such substances may be biogenic amines.
A. A. ELDRIDGE.

Denaturation of insulin protein by concentrated sulphuric acid. F. BISCHOFF and M. SAHYUN (J. Biol. Chem., 1929, 81, 167—173).—Various preparations of insulin were dissolved in ice-cold sulphuric acid, or in a mixture of the latter with acetic acid, and the solution was poured on to ice; the product was acid-insoluble and retained half the physiological activity of the original material. Addition of nitrite to the sulphuric acid reduced the activity to one third, and addition of formaldehyde abolished it entirely, whilst cyanide and methyl sulphate had no effect. The denaturation by sulphuric acid is irreversible.
C. R. HARRINGTON.

Hyperglycæmia following injection of secretin. H. HERMAN (Rev. franç. Endocrinol., 1929, 4, 381—415; Chem. Zentr., 1928, ii, 1115).—The hyperglycæmia following intravenous administration of Bayliss and Starling's secretin is due to the presence of impurities which depress the blood-pressure and cause the adrenals to produce adrenaline.

A. A. ELDRIDGE.

Sexual hormone in the urine of males. S. LOEWE, H. E. VOSS, F. LANGE, and A. WÄHNER (Klin. Woch., 1928, 7, 1376—1377; Chem. Zentr., 1928, ii, 1111—1112).—Testicular hormone is present in the urine of males, although it does not respond to the Allen-Doisy test. Testicular and ovarian hormones can be separated by fractionation.

A. A. ELDRIDGE.

Sexual hormone in blood. E. FELS (Arch. Gynakol., 1927, 130, 606—625; Chem. Zentr., 1928, ii, 1111).—From the sixth month of pregnancy the serum contains much ovarian hormone; the hormone of the anterior lobe of the pituitary is not then found.

A. A. ELDRIDGE.

Hormones and tissue respiration. I. Function of the thyroid gland. M. MAEDA (Folia Endocrinol., 1928, 3, No. 4, 2 pp.; Chem. Zentr., 1928, ii, 1111).—By feeding of thyroid to rabbits the oxygen consumption of thyroid tissue is reduced, whilst in the spleen, pancreas, sexual glands, and liver it is increased. The respiratory quotient in the liver is unchanged, but in the kidneys it is increased. After removal of the thyroid gland the oxygen consumption of the suprarenals is increased, but that in other organs is reduced. The respiratory quotient falls in the liver and remains unchanged (the oxygen and carbon dioxide both diminishing) in the kidneys.

A. A. ELDRIDGE.

Thyroid hormone regulating cerebral excitability. (MILLE.) G. FUCHS, J. RÉGNIER, D. SANTENOISE, and P. VARE (Compt. rend., 1929, 188, 419—421).—The thyroid gland, taken from a dog in which the vagus nerve has been excited by eserine, yields an extract which, when injected into the brain of a second dog, considerably lowers the chronaxia of the sigmoid convolution of the brain. It is suggested that the extract contains a hormone which regulates the excitability of this part of the brain.

G. A. C. GOUGH.

Resolution of *dl*-thyroxine. C. R. HARRINGTON.
—See this vol., 313.

Derivatives of thyroxine. J. N. ASHLEY and C. R. HARRINGTON.—See this vol., 313.

Vitamin content of honey. E. HOYLE (Biochem. J., 1929, 23, 54—60).—A fresh English comb honey and a West Indian honey were found to contain no appreciable quantities of vitamins-A, -B, -C, and -D.
S. S. ZILVA.

Vitamin-A action of lipochromes. B. VON EULER, H. VON EULER, and H. HELLSTROM (Biochem. Z., 1928, 203, 370—384).—The vitamin-A colour reaction (antimony chloride and chloroform) is given by pure carotin and lycopin. The spectra of the blue solutions so obtained and the displacement of the absorption maxima by fat are determined spectrophotometrically. Carotin in daily doses of less than 0.005 mg. causes an increase in the weight of young rats, the action being similar to the growth-promoting characteristic of vitamin-A. The antimony reaction of blood-serum and of butter runs parallel with their carotin content.
P. W. CLUTTERBUCK.

Vitamins. L. S. FOGLIENI (Arch. Fisiol., 1928, 26, 83—153; Chem. Zentr., 1928, ii, 1118).—In absence of air, vitamins-A, -B, and -C withstand exposure to 120—134° without loss of activity. Vitamin-B consists of two components which separately have only a small and transient action; one gives Folin's reaction, is non-volatile, and has no effect on yeast growth, whilst the other gives Folin's reaction, is largely volatile between 120° and 134°, and stimulates the development of yeast. Similarly, vitamin-C appears to consist of two substances; one is non-volatile, gives Bezssonoff's test, and alone has a healing effect on acute, but not chronic, scurvy, whilst the other is volatile, fails to respond to Bezssonoff's test, and has no antiscorbutic action. In both cases the substances together exert a strong effect. When a solution containing vitamin-C is made slightly alkaline with sodium hydroxide, and heated, the vitamin is rapidly inactivated.

A. A. ELDRIDGE.

Homogeneity of vitamin-B. E. SCHMITZ and E. GEORGE (Biochem. Z., 1929, 204, 165—178).—By feeding sunflower seeds along with polished rice to pigeons an attempt was made to induce the neuritic symptoms unaccompanied by secondary phenomena such as loss in weight. This was found to be impossible. When the ration of seeds was sufficiently reduced all the symptoms of B-avitaminosis appeared simultaneously. The work of di Mattei (Arch. Fisiol., 1927, 25, 56) is therefore not confirmed.

J. H. BIRKINSHAW.

Attempt to separate the antineuritic vitamin with fuller's earth. L. RANDOIN and R. LECOQ (Compt. rend. Soc. Biol., 1928, 99, 148—150; Chem. Zentr., 1928, ii, 1119).—In aqueous medium fuller's earth extracts from yeast almost all the antineuritic vitamin, together with a certain quantity of vitamins essential for nutrition. Fuller's earth activated in alcoholic medium contains almost exclusively antineuritic vitamin.
A. A. ELDRIDGE.

Effect of desiccation on the antiscorbutic principle. P. LAVIALLE (Bull. Soc. Chim. biol., 1928, 10, 1293—1297).—A diet of bread, meat, water, and salts, heated at 130° for 45 min., resulted in the development of scurvy in a dog in 9—10 months, whilst a similar animal fed on malted biscuit powder, milk, and sugar dried under reduced pressure resisted scurvy for at least 18 months. A freshly-weaned dog, fed on the last-named diet, resisted scurvy for 16 months.

G. A. C. GOUGH.

Experimental rickets. XXVIII. Does vitamin-D pass into the milk? E. V. MCCOLLUM, N. SIMMONDS, J. E. BECKER, and P. G. SHIPLEY (Amer. J. Dis. Children, 1927, 33, 230—243).—Experiments with rats suggest that vitamin-D passes into the milk when cod-liver oil is fed to the mother, but the amount is considerable only when the oil is administered during pregnancy as well as during lactation.

CHEMICAL ABSTRACTS.

Vitamin content of olive oil irradiated with ultra-violet rays. G. RIGOBELLO (Rev. sud-amer. endocrinol., 1928, 11, 456—466).—The bone calcification of rats receiving irradiated olive oil was almost normal, and 25% greater than that of the controls; young rats exhibit increased, although abnormal, bone growth. Increase in weight and alleviation of severe avitaminosis were observed. The effect is not regarded as being truly antirachitic.

CHEMICAL ABSTRACTS.

Action of the cholesterol of cod-liver oil on the photographic plate. L. HUGOUNENQ and E. COUTURE (Compt. rend., 1929, 188, 349—350).—Cholesterol obtained from cod-liver oil, when allowed to rest directly on the sensitive coating of a photographic plate or placed above it on a quartz plate for 3—15 days, produces a latent image which gives rise to dark markings on development; these effects are not produced by cholesterol from ox brain or gallstones nor are they produced if a glass plate is interposed between the cholesterol and the sensitive film.

G. A. C. GOUGH.

Antirachitic potency of ergosterol irradiated by ultra-violet light and by exposure to cathode rays. A. KNUDSON and C. N. MOORE (J. Biol. Chem., 1929, 81, 49—64).—The highest degree of antirachitic potency was induced in ergosterol by ultra-violet irradiation for 15 sec. to 3 min.; exposure to cathode rays rendered ergosterol antirachitic, although the highest activity was 1/25 of that obtainable with ultra-violet irradiation. The material exposed to cathode rays showed a similar ultra-violet absorption spectrum to that irradiated with ultra-violet light.

C. R. HARRINGTON.

Spectrographic determination of the activation of ergosterol by ultra-violet light. G. TIXIER (Compt. rend., 1929, 188, 206—208).—The maximum absorption of light of wave-length 2537 Å. during the irradiation of ergosterol does not correspond with the maximum antirachitic activity. Under standardised conditions, however, this may be determined from the absorption by an empirical rule.

G. A. C. GOUGH.

Comparative value of biological and physical determinations of the [antirachitic activity of] irradiated ergosterol. R. FABRE and H. SIMONNET (Compt. rend., 1929, 188, 424—426).—Ergosterol, irradiated in an inert atmosphere for 20 min., is sufficient to prevent avitaminosis in rats in doses of 0.001 mg. per 100 g. body-weight. The fraction of this preparation capable of precipitation by digitonin is almost as great as that of the original sterol. Longer irradiation gives a product which is not entirely crystalline, but, although the fractions show different absorption spectra, they possess approximately the same activity.

G. A. C. GOUGH.

Specific colour reaction for ergosterol. O. ROSENHEIM (Biochem. J., 1929, 23, 47—53).—Both chloral hydrate and trichloroacetic acid give a characteristic blue colour reaction with ergosterol, whilst all the other naturally occurring sterols investigated when purified from ergosterol remain colourless under the same conditions. Anhydrous chloral is non-reactive. The production of an immediate red colour with either of these reagents is specific for the $\Delta^{1:2}$ (or $\Delta^{1:13}$) linking of the sterol ring.

S. S. ZILVA.

Toxic action of milk and other substances exposed to ultra-violet radiation. P. REYHER and E. WALKHOFF (Munch. med. Woch., 1928, 75, 1071—1073; Chem. Zentr., 1928, ii, 909—910).—Ultra-violet irradiation gives rise to no antirachitic vitamin, but to a toxic substance which causes calcium deposition in rachitic bones, and in organs (heart, kidneys), together with pathological symptoms. The toxic effect is more marked if the diet of the animal is poor in vitamins, and is greatest in pregnancy. The vitamin-C content of milk is reduced proportionally to the oxygen present, and to the duration and intensity of irradiation by ultra-violet light.

A. A. ELDRIDGE.

Presence of an ozonide in the vitamin-rich fraction of cod-liver oil. J. A. DE LOUREIRO (Compt. rend. Soc. Biol., 1928, 97, 878—879; Chem. Zentr., 1928, ii, 685).—The unsaponifiable fraction of cod-liver oil gives with petroleum a precipitate. This insolubility is characteristic of ozonides.

A. A. ELDRIDGE.

Diet and reproduction. III. G. GREJNS, K. DE HAAN, and J. A. VAN DER LOEFF (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 721—732).—The addition of serum-albumin to a diet poor in reproductive vitamins results in a marked improvement in the milk secretion, which has previously (Sure, A., 1926, 981) been shown to be dependent on a factor associated with that necessary for fertility but more readily destroyed by heat. It is not clear whether the albumin itself or a small quantity of some associated compound is responsible for the improvement in lactation. Various experiments are described demonstrating the effect of diet on reproduction.

W. O. KERNACK.

Changes in the chlorophyll of a green alga. A. PERRIER (Compt. rend., 1929, 188, 339—341).—Cultivation of a unicellular alga in media composed of gelatin, inorganic salts, and organic substances

shows that chlorophyll is formed in the absence of light and that growth is rapid in the presence of ethyl or methyl alcohol, but slower in the presence of glycerol, mannitol, or arabinose. In the absence of nitrogenous organic matter, the chlorophyll is gradually replaced by an orange-red substance (greenish-white in the absence of light).

G. A. C. GOUGH.

Natural colour preserved in sectioned green plant tissue. E. A. JIROUCH (Stain Tech., 1929, 4, 17—19).—The tissue is fixed in Keefe's solution (Science, 1926, 64, 331), frozen in a 20% gum arabic solution, sectioned, and finally mounted in glycerol jelly.

H. W. DUDLEY.

Forcing [of plants] by warm baths. III. K. BORKSCH (Biochem. Z., 1928, 202, 180—201).—The fermentative processes of hazel catkins are followed in terms of the alcohol and acetaldehyde liberated and the oxygen utilised. By placing the buds in luke-warm water, the amount of oxygen they can obtain becomes insufficient for their needs and metabolic products of anaerobic respiration (alcohol and aldehyde) accumulate. The oxygen utilisation of the buds 19 hrs. after treatment is still only one half that of the controls, whilst 42 hrs. afterwards it has attained the control value and after a further 2 days it has become greater than the control. It seems probable that some causal relationship exists between the injury to respiration and the forcing of the buds.

P. W. CLUTTERBUCK.

Influence of radiations on the germination of seeds and the growth of plants. G. MEZZADROLI and E. VARETON (Zymologica, 1928, 3, 172—173).—The presence of an oscillating circuit increases the percentage germination of seeds by 25—50%. This influence continues, usually to the third or fifth day after germination, the plants showing double the aerial development of those not treated in this way. The waves used (0.5—2 metres in length) appear to be without further effect on the plants, since by the twelfth or fifteenth day both the treated and the untreated plants show the same aerial growth.

T. H. POPE.

Dynamics of the waxy gene in maize. II. Nature of waxy starch. R. A. BRINK (Biochem. J., 1928, 22, 1349—1361).—The waxy and non-waxy maize starches contain nearly equal proportions of α - and β -amylose (amylopectin and amylose) if determined by the Ling and Nanji method (J.C.S., 1923, 123, 2666). Both starches on hydrolysis with malt amylase yield mainly maltose together with traces of dextrose associated with dextrinous materials. The common maize starch is converted to maltose in this way more rapidly than is waxy starch. Intermediate products of a lower specific rotatory power appear during the conversion of waxy starch than during the hydrolysis of common maize starch. The pure starch of the latter origin contains more than twelve times as much organic phosphorus as does waxy starch. This difference in the organic phosphorus content is not due to a deficiency of this element in the endosperm tissue. The total phosphorus content of waxy and common endosperm meal is nearly the same.

S. S. ZILVA.

Relationship of tetra-araban to tetragalacturonic acid, the chief complex of pectin. F. EHR- LICH and F. SCHUBERT (Biochem. Z., 1928, 203, 343—350).—Further examination of the crude araban obtained from hydropectin of beet by treatment with alcohol (A., 1926, 441) shows that it can be precipitated from solution as a white amorphous powder, the elementary analysis and mol. wt. determinations of which indicate that it is tetra-araban or tetra-anhydrotetra-arabinose, $C_{20}H_{32}O_{16}$, $[\alpha]_D^{20}$ —123°, and yields *l*-arabinose on hydrolysis with mineral acids. The substance under aseptic conditions is very slowly but almost completely hydrolysed to *l*-arabinose by takadiastase. The fact that tetragalacturonic acid, $C_{24}H_{36}O_{24}$, must lose 4 mols. of carbon dioxide to give a compound of the same empirical formula as tetra-araban and the close spatial similarity of *d*-galacturonic acid and *l*-arabinose make it probable that the tetra-araban component of pectin is formed from tetragalacturonic acid by loss, as a result of enzymic processes, of the four free carbonyl groups.

P. W. CLUTTERBUCK.

Iodine liberator from *Laminaria*. T. DILLON (Nature, 1929, 123, 161—162).—An aqueous extract of the fresh fronds of *Laminaria*, when acidified, liberates iodine from potassium iodide. Preliminary experiments suggest that the agent is a dialysable organic substance.

A. A. ELDRIDGE.

Favourable action of potassium iodide on the volatilisation of iodine [in sea-weeds]. P. DANGEARD (Compt. rend., 1928, 187, 1156—1158).—Sea-water containing 0.1% of potassium iodide greatly increases the evolution of iodine from certain sea-weeds (e.g., *Laminaria flexicaulis*), whilst it is without effect on other species (e.g., *Fucus platycarpus*).

G. A. C. GOUGH.

High- and low-frequency measurements with *Laminaria*. L. R. BLINKS (Science, 1928, 68, 235).—Osterhout's view that the observed change of resistance is actually a change in the permeability of protoplasm to ions is supported by the author's experiments.

A. A. ELDRIDGE.

Osmotic pressure of cell-sap of plants. H. WALTER (Ber. deut. bot. Ges., 1928, 46, 539—549).—The osmotic pressure of the cell-sap from the leaves of certain plants has been determined and comparisons have been made of the living sap and the sap from plants killed in various ways.

E. A. LUNT.

Cell-sap of *Valonia* and *Halicystis*. W. C. COOPER, jun., and L. R. BLINKS (Science, 1928, 68, 164—165).—Determinations of potassium are recorded.

CHEMICAL ABSTRACTS.

Penetration of strong electrolytes [into plant cells]. W. C. COOPER, jun., M. J. DORCAS, and W. J. V. OSTERHOUT (J. Gen. Physiol., 1929, 12, 427—433).—The addition of ammonium chloride to sea-water causes *Valonia* cells to float, because the very permeable salt reduces the specific gravity of the sap. Cæsium chloride causes flotation because it raises the specific gravity of the water but does not penetrate the cell-wall. Strong electrolytes penetrate very slowly. Potassium is absorbed much more rapidly than sodium. Lithium, rubidium, bromides,

bromates, iodides, iodates, and selenites are able to penetrate, but most of the complex anions and the heavy metals are unable to penetrate the cell-wall.

E. BOYLAND.

Spectrophotometric studies of penetration. V. Resemblances between the living cell and an artificial system in absorbing methylene-blue and trimethylthionine. M. IRWIN (J. Gen. Physiol. 1929, 12, 407—418).—The partition coefficients of methylene-blue and azure-B between water, chloroform, and sap as determined by spectroscopic methods are compared with the penetration of these dyes in cells. The layer of protoplasm of *Valonia* at p_H 9.5 behaves like a layer of chloroform in absorption of these dyes, but the sap of *Nitella* dissolves more azure-B from chloroform than it does from protoplasm.

E. BOYLAND.

Permeability test with radioactive indicators. K. LARK-HOROVITZ (Nature, 1929, 123, 277).—By the use of thorium-B as radioactive indicator, it is shown that lead ions do not enter the sap of living cells of *Valonia macrophysa* even if the cells are kept for several months in lead nitrate solution; lead ions, however, readily enter the sap of dead cells. Radium emanation quickly becomes evenly distributed between the sap of living cells and the surrounding sea-water.

A. A. ELDRIDGE.

E.M.F. in plants arising on contact with potassium chloride solutions of different concentrations. K. STERN and E. BUNNING (Biochem. Z., 1928, 203, 400—408).—The current of injury found with *Nitella* by Osterhout and Harris (J. Gen. Physiol., 1928, 11, 673; 12, 167) to be positive when the cell is in contact with concentrated solutions and negative with dilute solutions, is found with a variety of leaves always to be negative whether the solution is of higher or lower concentration than that of the cell sap.

P. W. CLUTTERBUCK.

Permeability. Viscosity and interfacial surface tension. J. TRAUBE and S. H. WHANG (Biochem. Z., 1928, 203, 363—369).—The velocity of flow through a capillary of aqueous solutions of surface-active materials increases inversely with the surface tension, and the permeability and therefore the absorption of a fluid are dependent on its surface activity. The velocity of flow of water in a glass tube provided with a membrane layer of cholesterol or lecithin is increased, but with a layer of gelatin, albumin, or peptone is scarcely altered in comparison with the velocity without these layers. In plants a decrease of surface activity causes therefore an increased movement of sap and so may result in accelerated growth.

P. W. CLUTTERBUCK.

Formation of plant membranes. K. HESS (Biochem. Z., 1928, 203, 409—420).

P. W. CLUTTERBUCK.

Preparation of lipins from organs containing chlorophyll. B. REWALD (Biochem. Z., 1928, 202, 399—402).—By means of a process involving extraction with cold acetone, lipins, free from chlorophyll, can be obtained from vegetables.

W. MCCARTNEY.

Nature of the unsaponifiable fraction of the lipid matter extracted from green leaves. E.

CLENSHAW and I. SMEDLEY-MACLEAN (Biochem. J., 1929, 23, 107—109).—Crystals containing about 5% of oxygen, m. p. 72—75°, separate from the hot alcoholic solution of the unsaponifiable matter from cabbage leaves after the removal of the sterols. Hentriacontane is also present in this fraction. Similar treatment of the unsaponifiable matter from spinach yielded only hentriacontane.

S. S. ZILVA.

Constancy of the essential oil of seedlings of aniseed fruit. N. V. IVANOV and V. F. GRIGORJEVA (Biochem. Z., 1928, 202, 284—293).—In seedlings of aniseed fruit during germination in the dark for 20 days the essential oil remains unchanged both in amount and in composition. No physiological explanation for the presence of the oil has so far been found.

W. MCCARTNEY.

Composition of the root of *Geum urbanum*, L. J. CHEYMOL (Schweiz. Apoth.-Ztg., 1928, 66, 283—284; Chem. Zentr., 1928, ii, 457).—The glucoside geoside, m. p. 146—147°, $[\alpha]_D$ -53.80° in water, on acid hydrolysis affords eugenol, dextrose, and l-arabinose; hydrolysis by gease affords eugenol and vicianose; by emulsin, eugenol, dextrose, and arabinose. Gease is present in the root as an insoluble compound, e.g., with tannin. Dry gease is decomposed above 98°; in aqueous solution, above 75°. It is inactivated by sulphuric or acetic acid. The action of gease on geoside is not specific.

A. A. ELDRIDGE.

Glutamine and allantoin in beetroot. C. RAVENNA and R. NUCCORINI (Annali Chim. Appl., 1928, 18, 509—512).—The aqueous extract of the roots is treated with a slight excess of basic lead acetate, to the filtrate is added a small excess of mercuric nitrate, and the precipitate, suspended in water, is decomposed with hydrogen sulphide. The filtrate, freed from hydrogen sulphide by distillation in a vacuum, is neutralised with ammonia and concentrated to a syrup under diminished pressure. Sufficient alcohol is then added to cause separation of a syrup, which is redissolved by addition of a few drops of water. On keeping, the liquid deposits crystalline glutamine.

As the growth of the beet proceeds, the percentage of glutamine present increases from 0.035 (June) to 0.112 (October). If the beets are stored during the winter and planted again at the beginning of spring, the glutamine gradually disappears, its place being taken by allantoin, which itself disappears later.

T. H. POPE.

Total alkaloids of *Datura fastuosa*, L., and *Datura alba*, Nees, from the Philippines. J. M. MARANON (Philippine J. Sci., 1928, 37, 251—260).—The total alkaloid content of different parts of *Datura fastuosa* and *D. alba*, collected at Manila at different times of the year, has been determined. *D. fastuosa* contains more alkaloids in its leaves, seeds, fruits, and roots than does *D. alba*; the latter contains a higher percentage than the former in its flowers. As the fruit ripens there is a migration of alkaloids from the pericarp to the seeds. Apart from the seeds, the younger portions of different parts of the plants contain more alkaloid than the

more mature portions. The possible mode of formation of alkaloids in plants is discussed.

C. W. GIBBY.

Hydrocyanic acid in *Lotus*. P. GUERIN (Compt. rend., 1928, 187, 1158—1160).—Mainly qualitative investigations show that a large number of the plants of this genus contain hydrocyanic acid. The leaves and the growing cotyledons contain most of this constituent. The hydrocyanic acid of *L. corniculatus* (0.02% in the fresh plant) is probably insufficient to injure cattle.

G. A. C. GOUGH.

Physiology of apples. X. Chemical changes in stored apples. F. HAYNES and H. K. ARCHBOLD (Ann. Bot., 1928, 42, 905—1017).—Methods of determining the principal chemical constituents of the apple are described. The properties which favour keeping are found to be: low nitrogen and high sucrose contents and probably a large amount of cell-wall material. Exhaustion of sucrose and acid is coincident with the death of the apple, and it is therefore suggested that acid metabolism may be an essential part of the respiratory cycle of this fruit.

E. A. LUNT.

Composition of the juices of some American apples. J. S. CALDWELL (Fruit Prod. J. Amer. Vinegar Ind., 1928, 8, 14—18).—Climatic conditions during development and maturity produce consistent and sustained effects on the composition of apples. Analytical data for various varieties are recorded.

CHEMICAL ABSTRACTS.

Boron compounds in fruits and vegetable products. A. S. DODD (Analyst, 1929, 54, 15—22).—The proportion of boric acid present in currants and raisins was small but over 100 parts per million; in miscellaneous dried fruits it varied from 40 parts per million in prunes to 300 in apricots and peaches, enough being present to make it necessary to allow for the presence of boron in jams, tarts, etc. In fresh fruits boron compounds were small, from 31 to 62 in 10^6 , but calculated on the dried fruits boric acid varied from 240 to 1090 in 10^6 . The prepared dried acid fruits lose boric acid as the drying process is carried out without the presence of an alkaline fixing agent.

D. G. HEWER.

Boric acid in oranges. J. T. DUNN and H. C. L. BLOXAM (Analyst, 1929, 54, 28—29).—Three Californian, three South African, and one West Indian samples of oranges were examined for the presence of boric acid in the rind and pulp. In every case it was present in quantities comparable with that found as a natural constituent of a large number of vegetable substances, and no evidence of addition was adduced.

D. G. HEWER.

Zinc content of vegetable foods. G. BERTRAND and B. BENZON (Compt. rend., 1928, 187, 1098—1101).—The zinc content of a wide variety of fruits and vegetables is of the order of 1—3 mg. per kg. of the fresh material. In general, the amount of zinc increases with the chlorophyll content. Garlic and onion bulbs, millet, maize, lentil, and similar grains contain 10—50 mg. per kg. Polished rice contains

about 2 mg., whilst the husks give values as high as 30 mg. per kg.

G. A. C. GOUGH.

Biology of metals. I. Localisation of lead by growing roots. II. Retardative influence of lead on root growth. F. S. HAMMETT (Protoplasma, 1928, 4, 183—186, 187—191).—Lead absorbed by growing roots of *Allium cepa*, *Phaseolus vulgaris*, and *Zea mais* from solutions of the nitrate was deposited in the regions of growth by cell division as a compound. Lead (10^{-5} to 5×10^{-4}) retards the root growth of seedlings. CHEMICAL ABSTRACTS.

Effect of hydrogen-ion concentration on the fixation image of various salts of chromium [in plants]. C. ZIRKLE (Protoplasma, 1928, 4, 201—227).—Experiments with root tips of *Zea mais* are described. It is assumed that the fixation consists of a double decomposition in which the cation of the fixative unites with certain elements of the cell and the anion with others, followed by reduction of part of the chromate to a chromium salt, the chromium then being combined with the tissue both as anion and as cation. CHEMICAL ABSTRACTS.

Chlorosis of fruit trees. II. Composition of leaves, bark, and wood of shoots in cases of lime-induced chlorosis. III. Chlorosis of plums due to potassium deficiency. T. WALLACE (J. Pomology, 1928, 7, 172—183, 184—198).—The leaves and bark of chlorotic shoots in the apple, pear, plum, and raspberry exhibit a high percentage of ash in the dry matter, and low calcium and high potassium contents in the ash itself. In the wood of chlorotic shoots the changes in the calcium and potassium contents do not obtain.

III. A chlorosis of plum trees due to deficiency of potassium is described in which the chlorotic leaves show a low ash content, and high iron, calcium, magnesium, and phosphorus, and low potassium contents in the ash. The conditions in which this disease is observed suggest water-logging as a possible cause.

E. A. LUNT.

Micro-determination of carbon. M. NICLOUX. —See this vol., 204.

Determination of iodine. J. SCHWAIBOLD; also J. F. REITH.—See this vol., 337.

Dehydration apparatus. W. D. COURTNEY (Science, 1928, 67, 653—654).—An apparatus for biological use is described. A. A. ELDRIDGE.

Use of Hildebrand hydrogen electrode in biological solutions. R. E. CORNISH (J. Amer. Chem. Soc., 1928, 50, 3310—3311).—The Hildebrand hydrogen electrode (A., 1913, ii, 721) may be brought rapidly to equilibrium in those biological solutions in which it normally attains equilibrium only very slowly by repeated saturation with hydrogen, which is attained by squeezing a rubber bulb inserted in the hydrogen lead, so that the solution level is forced entirely below the platinum a few times.

S. K. TWEEDY.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1929.

General, Physical, and Inorganic Chemistry.

Perturbation theory in quantum mechanics. A. H. WILSON (Proc. Roy. Soc., 1929, A, 122, 589—598).—Mathematical. It is shown that, although the series of perturbations does not in general converge, yet it usually possesses the same asymptotic character as in the classical theory, and its use can therefore be justified. The investigation is limited to systems possessing only discrete spectra, and the method does not seem adequate to deal with systems with continuous spectra. L. L. BIRCUMSHAW.

Assignment, especially of multiplet terms to series limits. F. HUND (Z. Physik, 1928, 52, 601—609).—A discussion of the theory of multiplet series. E. B. ROBERTSON.

Light scattering and the hydrogen spectrum. H. S. ALLEN (Nature, 1929, 123, 127).—An examination of the secondary spectrum of hydrogen suggests that many of the lines arise by light scattering, as described by Raman and Krishnan (this vol., 240). The lines of the Balmer series are emitted by atoms of hydrogen, and the neighbouring molecules are subjected to bombardment by light quanta of corresponding frequency. A. A. ELDRIDGE.

Spectral phenomena of spark discharges. W. CLARKSON (Phil. Mag., 1929, [vii], 7, 322—331).—A general account of the electrical and optical properties of spark discharges is given and the phenomena are discussed on the basis of the dynamic principles previously laid down (*ibid.*, 1927, [vii], 4, 849 etc.). The observed phenomena are in good agreement with the theoretical deductions. The variation of the arc and spark lines of helium with the initial condenser voltage is discussed and a double maximum in the arc intensities is attributed to a duplication of flashes. The subsequent reduction of spark intensities is attributed to the diversion of energy to other spectra derived from the activated state of the gas. With suitable corrections for these effects, the resulting intensity curve is in good agreement with the theory. A. E. MITCHELL.

Absorption in excited helium. J. C. McLENNAN, R. RUEDY, and E. ALLIN (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 273—277).—The amount of light absorbed when light from a discharge tube containing helium is passed through a weakly excited column of the gas has been determined quantitatively. The percentage absorption is measured for the wavelengths 6678, 5876, 5016, 3889 Å. It is pointed out that the amount of absorption observed is a lower limit necessary for producing distinct reversals in the apparatus used. A. J. MEE.

Band spectrum of helium. W. WEIZEL (Z. Physik, 1928, 51, 328—340).—Three new bands are reported at 4720, 4400, and 4140 Å.; one of these has been identified as the $2'p-4's$ band of the para-system. It is thought the available evidence can be construed to show that the helium molecule arises from the combination of two excited metastable helium atoms, and not from one normal and one excited atom. R. W. LUNT.

New bands in the helium spectrum. W. WEIZEL (Z. Physik, 1928, 52, 175—196).—Nine new bands in the He_2 spectrum between 3785 and 4470 Å. have been discovered and examined with a grating spectrograph. They are partly higher members of series already known, and exhibit to a marked degree anomalies which occur to a slight extent in bands already investigated. It appears that the band spectrum of helium gives the electronic terms required by Hund's theory of molecular spectra (A., 1927, 183, 495, 801, 809). The doubling of the rotational terms of the $-$ and Δ levels is explained by the uncoupling of the rotational impulse of the electron from the axis, owing to rotation, and this uncoupling explains also the anomalies of many of the terms. He_2 is as yet the only case in which this kind of uncoupling is observed, and the only band spectrum in which all the terms predicted by theory are found by experiment. E. B. ROBERTSON.

Helium bands. V. FUJIOKA (Z. Physik, 1928, 52, 657—667).—The difference in the relative intensities of the helium bands when excited (a) in the gas at a pressure of 2.5 cm. by a condensed discharge at 20,000 volts and (b) in the gas at 8 mm. pressure by a direct discharge at 500 volts has been investigated. In the bands at 4650 and 4540 Å. the intensity maximum is found to lie in regions of higher rotational quantum number in the condensed than in the direct discharge. The band at 4540 Å. is relatively much stronger in the latter than in the former, although in both cases the absolute intensity of the band at 4650 Å. is much the greater. A table is given of the relative intensities of a number of ortho- and parahelium bands in the direct and condensed discharges, referred to 4650 Å. as standard.

The bands at 4950 and 5350 Å., which are relatively stronger in the negative glow of the direct discharge, have been analysed under a dispersion of 8 Å./mm., and their origin is discussed. E. B. ROBERTSON.

Triplets of helium. J. A. GAUNT (Proc. Roy. Soc., 1929, A, 122, 513—532, and Phil. Trans., 1929,

A, 228, 151—196.—Heisenberg's calculation (A., 1927, 5), based on Schrodinger's equation, of the triplet separations of helium is open to a number of objections, the chief being that the radius of the inner orbit is neglected in comparison with that of the outer, even when the principal quantum number of the latter is only 2. The theory of an atom with two electrons is now developed on the basis of Dirac's q -number theory (cf. A., 1928, 344, 456), as interpreted in terms of wave-mechanics by Darwin (*ibid.*, 570). The main differences between the present method and that of Heisenberg are that (1) part of the spin effect is included from the start in Dirac's equation, whereas Heisenberg first applies the perturbation by the electrostatic interaction of the electrons with a complete neglect of spin, and then superposes the much smaller spin perturbation, and (2) the spin energies are calculated in a straightforward manner by means of integrals involving the wave-functions, and are not taken from a model built up of precessing vectors. The method of calculation for a helium atom with one excited electron is outlined and the resulting triplet separations are given. A perturbation theory is developed for nearly degenerate systems. The spin energy terms used are practically the same as Heisenberg's, with the omission of those which are already accounted for in Dirac's equation. It is shown, however, that this energy not only corresponds with classical theory, but also arises naturally from Dirac's theory. A simple formula is obtained for the mutual potential energy of two electrons. L. L. BIRCUMSHAW.

Effect of combined electric and magnetic fields on the helium spectrum. J. S. FOSTER (Proc. Roy. Soc., 1929, A, 122, 599—603).—A study has been made of the effect of simultaneous parallel electric and magnetic fields on certain of the more intense helium lines. The light was analysed with a prism spectrograph of high dispersion (cf. A., 1924, ii, 323). Photographs are recorded showing the perpendicular components of the parhelium group $2P-5Q$ (4388 Å.) in an electric field of 63,000 volts/cm. and a magnetic field of 1650 gauss, and of the parallel and perpendicular components of the ortho-helium group $2p-4q$ (4471 Å.), taken when fields of 60,000 volts/cm. and 2250 gauss were applied to the source. The expected combined effect has been found for all principal and sharp series lines which appeared on the plates (4713, 5015, 4438 Å.), and for the components of the diffuse lines which are resolved. The magnetic separation is independent of the magnitude of the Stark effect. Certain Stark components which were known to vanish in moderate fields now reappear under the action of stronger fields, as predicted in the quantum mechanical explanation of the Stark effect for helium. L. L. BIRCUMSHAW.

Effect of electric and magnetic fields on the helium spectrum. J. S. FOSTER (Nature, 1929, 123, 414).—Many lines which are not ordinary Stark components have been observed; they show no decided polarisation and are well-defined. A magnetic field of 15,000 gauss perpendicular to an electric field of 0—15,000 volts per cm. was employed.

A. A. ELDRIDGE.

Anomalous g -values in the spectrum of ionised argon (A II). C. J. BAKKER (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 1041—1045).—Theoretical. It is found that for the Zeeman effect in the spectrum of simply ionised argon (cf. this vol., 3) the g -values of many terms differ from the Landé g -formula. The g -values belonging to four different coupling schemes for the terms arising from the coupling of the $4p$ and $5s$ electron are calculated and compared with those found experimentally.

N. M. BLIGH.

Zeeman effect in the argon spark spectrum (A II). C. J. BAKKER, T. L. DE BRUIN, and P. ZEEMAN (Z. Physik, 1928, 52, 299—300).—In the authors' previous work on this subject (this vol., 3), in which measurements were made on the grating photographs by means of a comparator, there was apparently a slight discrepancy in the law of summation of the g -terms for terms of the $4p$ electron with $j=1$. The work has been checked, using a photo-electric photometer, and the discrepancies appear to have been due to errors in the optical method, too high results having been obtained for the widths of very close doublets.

E. B. ROBERTSON.

Structure of induction spectra of rare gases. A. T. WILLIAMS (Univ. nac. La Plata, estud. cien., 1928, No. 82, 253—281).—The induction method of excitation facilitates the separation of different orders of the spectra of an element. The spectra of argon, krypton, and xenon were examined. Two new lines, 3354 Å., $3(1S_3-6p_8)$ and 3355 Å., $4(1S_3-6p_9)$ in the argon spectrum are classified with Meissner's terms.

CHEMICAL ABSTRACTS.

Intensities of the light of the oxygen green line in the night sky. J. C. McLENNAN, J. H. McLEOD, and H. J. C. IRETON (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 397—412).—In order to obtain some information on the origin of the excitation of the non-polar aurora and on the composition and physical state of the upper atmosphere, some experiments were made to determine whether the intensity of the oxygen green line varied during a single night. The apparatus is fully described. There was no regular diminution in intensity immediately after sunset, but it reached a maximum about an hour after midnight, and then diminished until sunrise. Measurements on the total intensity of the green line radiation for a series of successive moonless nights showed large variations. The origin of the maximum value attained about midnight is associated with solar radiation. It may be that when oxygen in the upper atmosphere is irradiated with light of very short wave-length it passes into the atomic state from which spontaneous transitions take place, giving rise to the green line. Light of longer wave-length may inhibit the process and prevent the accumulation of oxygen in the atomic state. In order to explain the time of maximum intensity, it is possible that the upper atmosphere may be irradiated at night with solar light refracted or scattered laterally into it from beams that are projected over the earth and graze its surface. The ratio of the energy of scattered solar light waves of wave-length less than 2070 Å. to that of those longer than 2500 Å. would, in the region of very low pressure,

increase after sunset up to midnight and then decrease. If this view is true the upper atmosphere must always be glowing more or less feebly with a faint green light.

A. J. MEE.

Arc spectrum of nitrogen in the extreme ultra-violet. K. T. COMPTON and J. C. BOYCE (Physical Rev., 1929, [ii], 33, 145—153).—Lines in the arc spectrum of nitrogen excited by controlled electron impact were photographed in a vacuum spectrograph in the region from 500 to 1200 Å. These lines, together with all other available data, are tabulated and used for a fairly complete analysis of the spectrum, in good agreement with the predictions of the Hund theory. A Grottrian diagram of the nitrogen atom is constructed. The ionisation potential is 14.48 volts, and the metastable levels 2D and 2P have energies corresponding with 2.37 and 3.56 volts, respectively, in good agreement with the predictions of Kaplan and Cario from a study of active nitrogen (cf. A., 1928, 683).

N. M. BLIGH.

Excitation of the aurora green line in active nitrogen. J. KAPLAN (Physical Rev., 1929, [ii], 33, 154—156; cf. A., 1928, 566).—The auroral green line has been excited in the nitrogen afterglow when oxygen was present in the discharge in which the active nitrogen was produced and observed. The interpretation of the phenomenon is based on Kaplan and Cario's explanation of active nitrogen (cf. preceding abstract).

N. M. BLIGH.

Arc spectrum of chlorine. K. MAJUMDAR (Nature, 1929, 123, 131).—Lines which Laporte (A., 1928, 805) ascribed to the transition $4M_2(N \rightarrow N_2)$ are attributed to $4M_2(O_2)$, and the ionisation potential of chlorine is estimated to be about 13 volts.

A. A. ELDRIDGE.

Analysis of first spark spectrum of sulphur. D. K. BHATTACHARYYA (Proc. Roy. Soc., 1929, A, 122, 416—429; cf. Ingram, A., 1928, 1068).—Saha's extension of the irregular doublet law, which shows that, knowing the spectra of two elements in any group of successive elements which are reduced by electric discharge to the same electronic constitution, then the spectra of the remaining elements can be predicted (cf. A., 1928, 209), has been successfully applied to the analysis of the first spark spectrum of sulphur, and 59 lines are classified. In an attempt to identify the doublet spectrum of S II, 84 lines have been measured in the region 5712—7715 Å., a pure sulphur tube of Wood type being employed. With two exceptions, none of the lines agrees with those previously found by Bungartz (A., 1925, ii, 609), who apparently used a lower excitation and did not get lines of S II. An interesting band spectrum of sulphur was observed in the near infra-red, extending from 7574 to 7057 Å., the bands having a close resemblance to the A, B, α, α' bands of oxygen.

L. L. BIRCUMSHAW.

Polarisation of resonance radiation and the breadth of spectral lines. A. ELLETT (Proc. Iowa Acad. Sci., 1927, 34, 283).—Observations on the polarisation of the D -line resonance radiation of sodium indicate that the transition probabilities for the various components of the Zeeman pattern are substantially in agreement with the predictions of

the summation rule. The distribution of energy in the exciting line is due practically entirely to the Doppler effect.

CHEMICAL ABSTRACTS.

Magneto-optical determination of the intensity of the first two members of the principal series of potassium and the vapour pressure of potassium. J. WEILER (Ann. Physik, 1929, [v], 1, 361—399).—See A., 1928, 1067. The ratio of the first to the second member (temp. 253—296°) is now given as 98.5:1+5%, and the formula for the vapour pressure as $\log pT = -20,590/4.571T + 10.133$ or $-21,100/4.571T + 10.37$ according to the method used.

Beryllium spectrum in the region λ 3367—1964 Å. S. N. BOSE and S. K. MUKHERJEE (Phil. Mag., 1929, [vii], 7, 197—200).—The lines of beryllium at 2351, 2175, 2126, 2056, and 2033 Å., reported as singlets by Bowen and Millikan (A., 1926, 985), are shown to be doublets of approximate wave-number difference 2.6. These are probably triplets due to the triplet P -terms, but it was impossible to separate the P_2 and P_3 lines. The earlier results of Rowland and Tatnall and of Glaser (A., 1922, ii, 675) have been verified. Four new lines, a doublet at 3019, a triplet at 2986, and singlets at 3110 and 2738 Å., have been discovered. By feeding a large quantity of the metal or its salt into an arc the lines at 3321, 2651, 2494, and 2175 Å. have been obtained in reversal, indicating the common origin of the lines in the p -level as classified by Bowen and Millikan. The vacuum spark spectrum comprises ten bands degraded towards the red. The measurements of the edges vary over the range 2474.2—2189.0 Å.

A. E. MITCHELL.

Transition probabilities in the Ca II spectrum. A. ZWANN (Naturwiss., 1929, 17, 121—122).—If f denotes the strength of a spectral line expressed as a ratio of the dispersion or absorption of the line to the dispersion or absorption of an elastic and isotropic electron, vibrating with the same frequency and defined according to the classical theory, then f for the two components of the calcium line 2^2S-2^2P together equals 1.08 and for the three components of the line 3^2D-2^2P together, equals 0.09. The corresponding values of Einstein's A are 1.55×10^8 and 1.3×10^7 , respectively.

W. E. DOWNEY.

Fine structure of the principal series of caesium and rubidium. A. FILIPPOV and E. GROSS (Naturwiss., 1929, 17, 121).—The caesium lines 4593 and 4555 Å. have been examined in absorption by means of an echelon grating of 30 plates. Each line shows two components. The rubidium emission lines at 4215 and 4201 Å. also show two components each.

W. E. DOWNEY.

First spark spectrum of mercury, Hg II. F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1928, 536—546).—An apparatus is described for investigating the first spark spectrum of mercury, Hg II. The wave-lengths of a large number of lines are given and a term table is drawn up. The spectrum is discussed.

A. J. MEE.

Second spark spectrum of mercury, Hg III. J. C. McLENNAN, A. B. McLAY, and M. F. CRAWFORD

(Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 247—251).—The extreme ultra-violet spectrum of a mercury spark in hydrogen has been reinvestigated, wave-length measurements being made in the range 1935—1350 Å. A zinc-aluminium spark was used as a comparison spectrum. The spectrum of an alternating discharge through mercury vapour in a vacuum was also studied. By the use of an inductance in series with the discharge the number of lines between 1750 and 700 Å. was reduced considerably. The lines classified in this region appeared in the lower excitation discharge spectrum, so that they probably belong to the Hg^{++} spectrum and not to any more highly ionised mercury spectrum. In the analysis Carroll's wave-lengths are used below 1350 Å. There is similarity between the Au II and Hg III spectra.

A. J. MEE.

First spark spectrum of thallium, Tl II. J. C. McLENNAN, A. B. McLAY, and M. F. CRAWFORD (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 241—245).—The spectrum of the thallium spark has been investigated and analysed, aluminium and zinc spark spectra being used as standards. A table giving frequency, intensity, and term combination of each line is drawn up. The intensities of all the classified lines are in good agreement with theory. A comparison of the 3P and 3D intervals of Ga II, In II, Tl II, and Hg I is made, and indicates points of similarity between these spectra. The relative positions of the singlet and triplet term systems of Tl II agree well with those of the corresponding systems of Zn I, Cd I, and Hg I.

A. J. MEE.

Wave-length measurements in the vacuum spark spectrum of lead from 2200 to 5000 Å. S. SMITH (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 331—335).—The work of Carroll on wave-lengths of the vacuum spark spectrum of lead up to 1936 Å. is extended to 5000 Å. A table of wave-lengths is given. (Cf. A., 1926, 214.)

A. J. MEE.

Black body [radiation] at the m. p. of palladium by the tube method. G. RIBAUD and S. NIKITINE (Compt. rend., 1929, 188, 618—620).—Measurements on an electrically-heated palladium tube, 80×1.5 mm., by 0.5 mm. thickness, and with a cavity 0.3 mm., give constant values for the filament current when the mechanical tension of the tube is below 2.5 g./mm.^2 ; at higher tensions the temperature of rupture is lowered sharply 8° , and the phenomenon is attributed to an allotropic transformation of palladium 8° below its m. p. The tube method gives an excellent pyrometric bench mark, since the temperature can be followed closely to the fusion point.

R. BRIGHTMAN.

Intensities of some Fe^+ multiplets in the arc and chromosphere spectra. W. CLARKSON (Phil. Mag., 1929, [vii], 7, 98—105).—Intensity measurements of the $2^4F-2^2F'$ and 2^4F-2^4D multiplets for ionised iron, the iron arc, and the chromosphere have been examined. In all cases there are wide divergences from the theoretical intensities of individual lines. In each multiplet there is one line 4520 and 4549 Å., which is abnormal relative to the others. Ionised iron is similar to ionised nickel and cobalt in that the multiplet summation rules apply only when extended

to cover the total series of both multiplets. The total summation rule shows the iron arc spectrum to be free from self-absorption whilst it demonstrates the self-reversal of the solar spectrum.

A. E. MITCHELL.

Predicted lines of Cr II in the spectra of the sun and of α Persei. T. DUNHAM, jun., and C. E. MOORE (Astrophys. J., 1928, 68, 37—41).

Influence of a hydrogen atmosphere on the arc spectra of certain metals. H. CREW (Phil. Mag., 1929, [vii], 7, 312—316).—Many of the effects of a hydrogen atmosphere on arc spectra previously observed (A., 1901, ii, 81) are attributed to pole effects in the apparatus employed. A new apparatus eliminating pole effects has been devised and by its use many of the effects previously observed have disappeared. Some notable results attendant on the change of atmosphere round an arc from air to hydrogen are recorded in the arc spectra of magnesium, zinc, aluminium, cadmium, and carbon. The general effects are the broadening of certain reversals, the reduction in intensity of most of the lines, particularly triplets, the reduction in intensity of lines due to impurities in magnesium and zinc, and the enhancement of such lines in the spectra of aluminium, cadmium, and carbon.

A. E. MITCHELL.

K-Radiation of the lightest elements. M. SODERMANN (Z. Physik, 1929, 52, 795—807).—By using an optical glass grating with 220 lines per mm., the wave-lengths of the K-series X-ray spectral lines of the elements from beryllium to aluminium have been measured. The results obtained are compared with those of previous investigators.

J. W. SMITH.

Absorption spectra of the vapours of tin, silver, and manganese between 5500 and 2140 Å. R. G. LOYARTE and A. T. WILLIAMS (Physikal. Z., 1929, 30, 68—75).—The absorption spectra of tin, silver, and manganese vapours have been obtained at temperatures between 1200° and 2200° . For tin and manganese the results of Zumstein (A., 1926, 107, 453) and of McLennan, Young, and McLay (A., 1925, ii, 454) are confirmed. Lines corresponding with the ionised atom have been observed in the spectrum of silver. The results are in agreement with Hund's theory as to the relation between the deeper atomic levels and absorption spectra. The equation $N'/N = e^{-E/RT}$, N' being the number of excited atoms, N the total number of atoms, has been applied to the data on tin with satisfactory results.

R. A. MORTON.

Series of the arc spectrum of tin. A. T. WILLIAMS and F. CHAROLA (J. Phys. Radium, 1928, [vii], 9, 377—385).—A number of hitherto unclassified terms in the arc spectrum of tin have been investigated and identified and origins are assigned to them. A table is given in which all the known terms are summarised, and this is illustrated by a Grotrian diagram. It is shown that the structure of the spectrum is in accord with the theory of Hund.

J. L. BUCHAN.

Intercombinations in the arc spectrum of carbon. D. S. JOG (Nature, 1929, 123, 318).—In a heavy arc spectrum of Acheson graphite in the region 2000 Å. the following inter-combination lines were

identified: $51313, {}^1D_2-{}^3P_1$ ($2L_2 \leftarrow L_2M$; $51356, {}^1D_2-{}^3P_2$ ($2L_2 \leftarrow L_2M_1$); $39862, {}^1S_0-{}^3P_1$ ($2L_2 \leftarrow L_2M_1$), whence ${}^3P_1-{}^1S_0=20474$, corresponding with $\lambda 4884.2 \text{ \AA.}$, which was not observed in the coronal spectrum.

A. A. ELDRIDGE.

Relative intensities of the Stark effect components of the [Balmer] H_β and H_γ lines. H. MARK and R. WIERL (Z. Physik, 1929, 53, 526—541).—A more detailed account of work already published (A., 1928, 1168).

Critical potential of the Geiger point counter. O. KLEMPERER (Z. Physik, 1928, 51, 341—349; cf. Geiger and Klemperer, *ibid.*, 49, 753).—For all dimensions of the counter and gas pressures the initial potential at which the current in the point counter increases from 10^{-13} to 10^{-10} amp. is dependent on only two constants: the number of positive ions required to liberate an electron from a metal surface and the range of the electrons. It was the same for air, hydrogen, and carbon dioxide. Variations from this condition appear only at very high ionic velocities.

J. W. SMITH.

Ionisation potentials of the rare-earth elements in relation to their position in the periodic system. L. ROLLA and G. PICCARDI (Phil. Mag., 1929, [vii], 7, 286—301).—A method for the determination of the ionisation potential of a metal, based on the measurement of the current flowing between two electrodes in a gas flame in which a salt of the metal is being volatilised, has been developed and shown to yield results in agreement with those calculated from spectroscopic data. The method is applied to determinations of the ionisation potentials of the rare-earth metals, which are shown to lie between 5.49 volts for lanthanum and 7.06 volts for yttrium. Comparison with the other elements places the rare-earth metals at the end of the fifth period of the periodic system, a result in general agreement with their chemical properties. With the exception of cerium the ionisation potentials increase regularly with increasing atomic number. Gadolinium exhibits no special peculiarities, indicating that such peculiarities must have their origin in the inner zones of the atomic structure. The results indicate that, with the possible exception of cerium, the external electronic shell is the same for all the rare elements. The ionisation potential of cerium, 6.91 volts, is attributed to the less basic character of this element.

A. E. MITCHELL.

Photo-electric effect at low temperatures. J. C. McLENNAN, L. A. MATHESON, and C. D. NIVEN (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 279—287).—When a potassium photo-cell is cooled to liquid air temperatures the emission for all wave-lengths of incident light is decreased, that for longer wave-lengths being affected most. The measurements have been extended with potassium down to the temperature of liquid hydrogen (-252°), and the current is still found to decrease. The results are discussed. It is possible that an electrical double layer at the surface of the potassium is responsible to a large extent for the change. The temperature variation of the threshold frequency may be related to the Thomson

coefficient in metallic conduction. Also a change in the absorption coefficient with temperature may be partly responsible for the change in emission, but this cannot be the sole cause.

A. J. MEE.

Influence of adsorbed gas on the photo-electric sensitivity of coconut charcoal. O. VON AUWERS (Z. Physik, 1928, 51, 618—637).—The photo-electric sensitivity of coconut charcoal to mercury arc light has been determined in relation to the nature of the adsorbed gas; the effects due to hydrogen, nitrogen, and air have been examined. Only small differences are found between these gases. The sensitivity of the charcoal surface diminishes as the adsorbed gas is removed, and its value in the presence of adsorbed gas is approximately independent of the pressure of the gas.

R. W. LUNT.

Oscillations in ionised gases. L. TONKS and I. LANGMUIR (Physical Rev., 1929, [ii], 33, 195—210).—Langmuir's theory of electronic and ionic oscillations in an ionised gas is developed, and experimental investigation is made over a frequency range of 1—1000 megacycles. The very rapid electronic oscillations leave the heavier positive ions unaffected, whilst the ionic oscillations are so slow that the electron density has its equilibrium value at all times. They vary in type according to wave-length, from the shorter ones similar to the electron vibrations to the longer ones similar to sound waves, an approximate transition range being established.

N. M. BLYTH.

Characteristic oscillation of free electrons in a constant magnetic field. S. BENNER (Naturwiss., 1929, 17, 120—121).—The theory of Appleton and Barnett (Electrician, 1925, 94, 398) has been experimentally proved.

W. E. DOWNEY.

Influence of the level of origin of the photo-electrons on the distribution in space of their initial directions. P. AUGER (Compt. rend., 1929, 188, 447—550; cf. A., 1926, 1188).—Electrons from the K -level behave as if they possess no motion before their photo-electric expulsion, whilst those from the L -level show a considerable supplementary dispersion, appreciable even for low values of this level, which indicates the existence of electronic motion in the atom itself before excitation.

J. GRANT.

Diffraction of electrons by crystalline powders. Electronic analysis. M. PONTE (Compt. rend., 1929, 188, 244—246).—A stream of electrons produces diffraction phenomena with crystalline powders analogous to those of X-rays. It is shown that in the case of zinc oxide, with the ordinary X-ray apparatus for crystal analysis, electronic analysis gives results in a short time with the expenditure of little energy, and having a maximum deviation from Broglie's law of 2%.

J. GRANT.

Motion of slow electrons in the rare gases. F. VON KOROSY (Z. Physik, 1928, 51, 420—428).—The work of Ramsauer and Meyer is considered from the point of view that the maximum effective target area is to be anticipated for that electron velocity which is equal to the orbital velocity of the electrons in the outermost shell. Approximate calculations of the orbital velocities are given which agree satisfactorily with the observed maxima.

R. W. LUNT.

Groups of electrons in the Geissler discharge. K. G. EMELEUS and W. L. BROWN (Phil. Mag., 1929, [vii], 7, 17—31).—The previous work of Emeleus (A., 1927, 293) and of Emeleus and Harris (A., 1927, 490) has been extended. Measurements of the collector characteristics in the Geissler discharge from a cold cathode in argon, neon, hydrogen, and oxygen at about 0.1 cm., under conditions approximating to the normal cathode potential drop, have been made. The results indicate that in the negative glow and in the Faraday dark space there is a group of fast electrons with approximately Maxwellian velocity distributions and an average energy of about 25 volts. The initial production of these is attributed to the passage of electrons into the negative glow from the cathode dark space and persistence by reason of a process the reverse of ionisation by collision. The persistence of two groups of slow electrons in the discharge is attributed to an effect of the Ramsauer minimum of the free paths of electrons.

A. E. MITCHELL.

Three-dimensional motion of an electron in the field of a non-neutral atom. M. A. HIGAB (Phil. Mag., 1929, [vii], 7, 31—52).—Mathematical.

A. E. MITCHELL.

Radiometer effect of positive ions. C. T. KNIPP and W. S. STEIN (Phil. Mag., 1929, [vii], 7, 70—79).—The effects of a stream of positive ions on an aluminium vane 0.1 mm. thick in residual air at 0.0003 mm. have been investigated. There is definitely both a radiometer and a mechanical effect, the energy loss in the apparatus being accounted for approximately as residual air effect 4%, mechanical effect 68%, and radiometer effect 28%. At a pressure of 0.009 mm. the distribution is roughly residual air effect 32%, mechanical effect 39%, and radiometer effect 28%.

A. E. MITCHELL.

Electronic charge e . R. T. BIRGE (Nature, 1929, 123, 318).—The evaluation of e is discussed.

A. A. ELBRIDGE.

Internal energy of electron evaporation in the electron emission of silver. J. M. ADAMS (Z. Physik, 1929, 52, 882).—It is pointed out that the result obtained by Rosenfeld and Witmer (A., 1928, 936), who calculated from the energy of evaporation of electrons from a silver surface that the number of valency electrons of this element was 3, is quite possible, since several examples are available of silver in a bivalent or trivalent state.

J. W. SMITH.

Electron scattering in helium. E. G. DYMOND and E. E. WATSON (Proc. Roy. Soc., 1929, A, 122, 571—582; cf. Dymond, A., 1927, 392).—The velocity distribution and angular distribution of electrons from a tungsten filament scattered by single collisions in helium have been measured, using an apparatus very similar to that previously employed. With the object of reducing stray effects due to electrons being scattered by the walls of the collision chamber, this was lined with thin aluminium sheet at all points where the main electron beam might strike. The gas pressure varied from 0.08 to 0.12 mm. of mercury. Curves are reproduced showing the velocity distribution of electrons scattered through 10° for initial velocities of 102, 226, and 386 volts. For each curve, besides

the peak corresponding with elastic collisions, two others appear, due to excitation and ionisation of the atom, respectively. That due to excitation reaches its maximum value at 21—22 volts, indicating that the excitation of the triplet system, requiring 19.8 volts, is very small at these high velocities. The effect of ionisation is at a maximum relative to that of excitation in the neighbourhood of 200 volts. It was found previously (*loc. cit.*) that the curve did not drop after the ionisation point, but even tended to rise. It is now found that the continuous loss of energy in the curves is much smaller, and is substantially the same, relative to the loss due to excitation, at 382 as at 226 volts. There seems to be no reason why it should not be attributed to the normal processes of ionisation. The scattering curves of both elastic and inelastic collisions (energy loss 21 volts) for an initial velocity of 210 volts are also reproduced. At large angles, many more elastically reflected electrons occur than inelastically reflected electrons, but for smaller angles they approximate in number, and for higher initial velocities (400 volts) the inelastic group may considerably exceed the elastic group for 5° angle of scattering. The reasons for the discrepancies between the present results and those found in previous work are discussed. The peaks in the curves relating scattered intensity with angle of scattering were most probably due to reflexion at the glass walls.

L. L. BIRCHMSEAW.

Probability of excitation by electron impact in neon. R. D'E. ATKINSON (Proc. Roy. Soc., 1929, A, 122, 430—442).—The recent data of Townsend and McCallum (A., 1928, 567) allow an estimate to be made of the "average of the sum of all probabilities" of the excitation of a quantum jump by electron impact in the case of neon. From the point of view of the quantum theory, a method is developed of analysing the results obtained by the Townsend type of experiment, in which currents of the form $i = i_0 e^{\alpha x}$ are found on varying the distance x between two parallel plates in a gas at comparatively high pressures. By assuming the first critical potential and the ionisation potential to be already known, the mean probability that at potentials in the range between them a collision, if it occurs, will be inelastic can be approximately evaluated. The chief uncertainty is due to the difficulty of calculating the total number of collisions that occur, since the Hertz formula, $\nu dx = 3x/\lambda^2 \cdot \log a/x \cdot dx$, rests on two assumptions, neither of which is fulfilled in the present case (Z. Physik, 1925, 32, 305). It is calculated that the average value of the sum of all excitation probabilities is about 5% in neon, and evidence is adduced in support of this figure. The relation between the Townsend theory of ionisation by collision and the general scheme provided by the quantum theory is discussed. It is shown that some modification is required in the definition of the quantity α (on which the Townsend collision formula rests) as "the average number of new ions produced per ion per cm. in the direction of the field." The measured α of the curves and the "average number of ions per ion per cm." would be identical only on the assumption that the probability of ionisation is independent of the distance

travelled since the last ionisation, *i.e.*, of the energy of the electron.

L. L. BIRCUMSHAW.

Diffraction of electrons at ruled gratings. B. L. WORSNOP (*Nature*, 1929, **123**, 164—165).

Eddington's hypothesis and the electronic charge. E. BÄCKLIN (*Nature*, 1929, **123**, 409—410).—The distribution of individual values of the electronic charge, e , obtained by Millikan, Wadlund, and the author, respectively, is examined, and the probable error is estimated. It is not possible to decide whether 136 or 137 is the better value for Eddington's relation $hc/2\pi e^2$ (this vol., 231).

A. A. ELDRIDGE.

Angular distribution of Compton recoil electrons. D. SKOBEŁTZYN (*Nature*, 1929, **123**, 411—412).

Attachment of electrons to the molecules HCl and NH₃. V. A. BAILEY and A. J. HEGGS (*Phil. Mag.*, 1929, [vii], **7**, 277—286).—The method of Bailey (*A.*, 1925, ii, 1019) has been extended to an examination of electron attachment in hydrogen chloride and in ammonia. The probability of attachment is shown to be proportional to the electric moment of the molecule (*cf.* this vol., 231).

A. E. MITCHELL.

Efficiency of electron impact leading to resonance in helium. G. GLOCKLER (*Physical Rev.*, 1929, [ii], **33**, 175—188; *cf.* *A.*, 1926, 552).—The efficiency of resonance impact between electrons and helium atoms was studied as a function of the energies of the impinging electrons. The transition investigated is $1^1S \rightarrow 2^3S$ leading from normal parahelium to metastable orthohelium, from 19.77 to 20.55 volts. The efficiency of inelastic electronic impacts rises to a maximum estimated to be 0.002 at 0.18 volt beyond the resonance potential of 19.77 volts and then decreases. The measurements were carried out by comparing the velocity distribution of the electrons leaving an equipotential surface, with the drop in current as observed in the inelastic impact method of Franck, and by comparing the velocity distribution of the electrons with the distribution of the positive current caused by them in a Lenard experiment. Both types of measurement gave similar results.

N. M. BLIGH.

Mobility of positive ions in flames. H. E. BANTA (*Physical Rev.*, 1929, [ii], **33**, 211—216).—The mobility of positive ions of potassium, rubidium, and caesium in the Bunsen flame was calculated from measured values of the current density, cathode drop of potential, and the thickness of the layer at the cathode in which the potential varies rapidly. The excess of ionisation over recombination in the layer was assumed to be proportional to $(1 - x/x_1)^m$, where x is the distance from the cathode, the thickness of the layer at the cathode, and m is a constant. The calculated mobility depends on the value assumed for m , and is 1.8 when $m = 2$ and 1.07 cm./sec. per volt/cm. when $m = 3$, and is known from other investigations to be approximately 1 cm./sec. per volt/cm. The mobility is found to be the same for salts of the three metals, and is independent of the concentration of the salt, but a small increase with electric intensity is indicated.

N. M. BLIGH.

Ion mobilities using the Erikson method on gases of controlled purity. J. J. MAHONEY (*Physical Rev.*, 1929, [ii], **33**, 217—228).—The change of mobility with the age of the ion was investigated using a form of Erikson's apparatus modified to allow a better control of the purity of the gas, and to extend the measurements to mixtures of known constitution. No ageing effect was found in carefully and moderately dried air, and mobilities were normal. Ordinary and moist air showed an ageing effect. The effects of various percentages of added ammonia, hydrogen chloride, and acetylene were investigated. The results obtained are compared with those of Erikson, and theoretical explanations are suggested (*cf.* Erikson, *A.*, 1926, 989; 1927, 1002).

N. M. BLIGH.

Emission of electrons from metals. F. ROTHER and E. MUNDER (*Physikal. Z.*, 1929, **30**, 65—68).—Millikan and Eyring (*A.*, 1926, 219) found the pulling-out of electrons from a thoriated tungsten cathode by intense electric fields to be independent of temperature, and Gossling (*A.*, 1926, 448) found the temperature effect up to 1700° Abs. on electron emission to be negligibly small. Gossling, in contrast to Millikan and Eyring, observed sudden changes in the characteristic curves for the discharge. According to Schottky's theory (*Z. Physik*, 1923, **14**, 80), the relation between $\log i$ (i being the current) and the root of the voltage gradient (volt/cm.)¹ should be linear, but Millikan and Eyring did not obtain such results. Repetition of the work shows that $\log i$ is proportional to the square root of the field strength rather than to the reciprocal of the field strength (*cf.* Fowler and Nordheim, *A.*, 1928, 681). The origin of the experimental discrepancies is discussed and the validity of Schottky's theory is accepted.

R. A. MORTON.

Emission of electrons from a metallic surface by slow positive ions. O. KLEMPERER (*Z. Physik*, 1928, **52**, 650—656).—Difficulties of direct measurement render it necessary to calculate the probability of emission of an electron by a slow positive ion from a metallic surface from known data. This is done in two fundamentally different ways: (i) from known current potentials of the Townsend discharge; (ii) from the minimum spark potential and the energy associated with the formation of an ion pair.

G. E. WENTWORTH.

Isotope of oxygen, mass 18. W. F. GIAUQUE and H. L. JOHNSTON (*Nature*, 1929, **123**, 318).—The weak doublets of the atmospheric absorption bands of oxygen originate from a molecule consisting of an oxygen atom of mass 18 combined with one of mass 16. The average and maximum deviations of observed minus calculated separations of the isotopic doublets are, respectively, -0.05 and -0.13 cm.⁻¹ The data show that the normal state of the oxygen molecule has one half unit of vibration, in agreement with the wave-mechanics theory.

A. A. ELDRIDGE.

Fundamental at. wts. VII. At. wt. of potassium. II. Analysis of potassium bromide. O. HONIGSCHMID and J. GOUBEAU (*Z. anorg. Chem.*, 1928, **177**, 102—108).—The most probable value for the at. wt. of potassium, derived from the ratios

potassium bromide:silver and potassium bromide:silver bromide is 39.104 ± 0.0020 , identical with that obtained by analysis of the chloride. The reason for the discrepancy between this value and that of Richards (39.095) has not been explained.

H. F. GILLBE.

Fundamental at. wts. VIII. At. wts. of silver and barium. Analysis of barium perchlorate. O. HONIGSCHMID and R. SACHTELEBEN (Z. anorg. Chem., 1929, 178, 1—32; cf. A., 1927, 806).—The ratio $\text{Ba}(\text{ClO}_4)_2 : \text{BaCl}_2$ has been determined by heating carefully purified and dried barium perchlorate in a current of hydrogen chloride at 550° . The barium chloride obtained was then titrated gravimetrically with silver nitrate and from the results the ratio $\text{Ag} : 4\text{O}$ calculated. The mean of five determinations gave the value of 107.880 ± 0.001 for the at. wt. of silver. The at. wt. of barium was calculated from the ratios $\text{Ba}(\text{ClO}_4)_2 : \text{BaCl}_2$, $\text{Ba}(\text{ClO}_4)_2 : 2\text{Ag}$, and $\text{BaCl}_2 : 2\text{Ag}$. The mean value found as the result of five determinations of each ratio was 137.355.

A. R. POWELL.

At. wt. of copper from the Lake Superior region and from [Chuquicamata] Chile. T. W. RICHARDS and A. W. PHILLIPS (J. Amer. Chem. Soc., 1929, 51, 400—410).—Cupric chloride was analysed, the copper being determined electrolytically and the chloride by nephelometric titration against pure silver (cf. Richards, Proc. Amer. Acad. Arts Sci., 1890, 25, 195). The at. wt. of copper was found to be 63.557 ($\text{Ag} = 107.880$), independent of the geographical origin of the metal. S. K. TWEEDY.

At. wt. of cerium. Analysis of cerium trichloride. O. HONIGSCHMID and H. HOLCH (Z. anorg. Chem., 1928, 177, 91—101).—The most probable value of the at. wt. of cerium, derived from the ratios $\text{CeCl}_3 : 3\text{Ag}$ and $\text{CeCl}_3 : 3\text{AgCl}$, is 140.125 ± 0.007 , the at. wt. of silver and chlorine being taken as 107.880 and 35.457, respectively.

H. F. GILLBE.

Mass-spectrum of uranium-lead and the at. wt. of protoactinium. F. W. ASTON (Nature, 1929, 123, 313).—The mass-spectrum of lead tetramethyl prepared from uranium-lead (from broggerite) includes lines corresponding with isotopes of at. wt. 206 (arbitrary intensity 100), 207 (intensity 10.7 ± 3) and 208 (intensity 4.5 ± 2). There is no indication of isotopes of at. wt. 203 or 205. These values correspond with the percentages 86.8, 9.3, and 3.9 which, with a packing fraction of 0.8×10^{-4} , give a mean at. wt. of 206.19. The line 207 is not due to ordinary lead, radium, or thorium; it is concluded that it is the end product of the disintegration of actinium. Extrapolation of the packing fraction curve then gives the value 231.08 for the at. wt. of protoactinium.

A. A. ELDRIDGE.

Relative velocities of the α -particles emitted by certain radioactive elements. G. C. LAWRENCE (Proc. Roy. Soc., 1929, A, 122, 543—551).—A direct comparison has been made of the velocities of the α -particles emitted from thorium-C and -C' and radium-F with those from radium-C'. The apparatus employed is similar to that described by Briggs (A., 1927, 392; 1928, 569), a combined source, consisting

of the two radioactive elements to be compared, being used. The ratio of the radii of curvature of the paths of the α -particles, measured in the usual way, is equal to the ratio of the velocities of the particles (after applying a small correction for the increase in mass at high velocities). In this way, the ratios are found to be $\text{Ra-F} : \text{Th-C} : \text{Ra-C}' : \text{Th-C}' = 0.8277 : 0.8885 : 1.000 : 1.0679$, with a probable error of 0.05%. Using Briggs' value of the velocity of radium-C' α -particles, 1.923×10^9 cm./sec. (*loc. cit.*), the others are calculated to be: thorium-C, 1.709, thorium-C', 2.054, and radium-F, 1.592×10^9 cm./sec.

L. L. BIRCHUMSHAW.

Ranges of β -rays. B. W. SARGENT (Trans. Roy. Soc. Canada, 1928, [III], 22, III, 179—191).—The absolute ranges of β -rays have been obtained by using the data of various workers on the loss of energy of the rays on passing through metal foils. Curves are given from which the ranges of rays with energies from 25,000 to 1,363,000 equivalent volts can be readily obtained. The values derived are somewhat greater than the usually accepted effective ranges, but it is considered that they are correct to within 10%. In the determination of relative ranges the intensity of a β -ray beam is measured by ionisation, and in the theory it is assumed that the quantity of the rays is unaltered for all substances for the same depth of penetration. There is some doubt whether this assumption holds for the β -rays from radium-E. The rays appear to be hardened by their passage through substances. true secondary β -radiation could not have this property. Since the β -rays from radium-E are thus modified it is necessary to revise previous estimates of the relative ranges in different substances. A repetition of the experiments shows that for the β -rays of radium-E the ratio of the stopping power of an atom to its atomic number Z decreases slowly with increasing Z . Previous results have shown that generally the mass range of β -rays in different elements is nearly proportional to A/Z , where A is the at. wt. Hence it follows that the stopping power of any atom for β -rays is proportional to its atomic number.

A. J. MEE.

Spatial distribution of the γ -radiation of radium in slightly dispersive media. M. BRUZAU (Ann. Physique, 1929, [x], 11, 5—140).—Compton's theory of scattering is reviewed and considered in relation to γ -radiation. A comparison of the absorption of scattered and primary γ -radiation by certain media was made, using methods of absolute and comparative absorption for the determination of the quality of the radiation. The intensity of the γ -radiation was determined experimentally through the ionisation effect. For this purpose an improved type of ionisation apparatus was designed, and adapted to the study of dispersive media. The intensity of the current in the ionisation chamber due to the radiation is proportional to the product of the intensity of the exciting radiation and the absorption coefficient of the chamber boundary. The sensitivity of such a chamber is a function of the atomic number of the element forming the boundary wall and of the wave-length. The energy emitted per sec. in the form of γ -rays by 1 g. of radium was calculated. The difference in the

qualities of the two radiations was shown, and the effect produced at different depths on a mass of water was evaluated. The pseudo-transparency of the dispersive media is due to the selectivity of the ionisation chamber for primary and scattered radiation. The selectivity being a function of the atomic number, the difference between the ionisation currents due to the respective radiations increases with increase of atomic number. The methods employed are important for their adaptability to radio-therapy; they can be extended to the study of the spatial distribution of X-rays. The results obtained were applied to deduce certain modifications in Millikan's measurements on cosmic rays. N. M. BLIGH.

Long-range α -particles from radium-C. K. PHILIPP and K. DONAT (Z. Physik, 1929, 52, 759—766).—The long-range α -particles from radium-C have been investigated by Wilson's cloud method, and new data concerning their range and the frequency of their appearance obtained. Wilson's apparatus was so adapted that stereoscopic photographs could be taken on a cinematographic film. Out of 3000 exposures, 221 long-range α -particles were observed; the ranges of these particles indicated two velocity groups with ranges of 9.2 and 11.0 cm., respectively. A few particles were observed with a path even longer than 11 cm. To every 10^6 normal α -particles there were 29 with a range of 9.2 cm., 4 of 11.0 cm., and 0.5 with a range greater than this. The data confirm the results of Rutherford and Chadwick (A., 1924, ii, 814). J. W. SMITH.

Ranges of the long-range α -particles from thorium-C and radium-C, using an expansion chamber. R. R. NIMMO and N. FEATHER (Proc. Roy. Soc., 1929, A, 122, 668—687).—The relative advantages of the scintillation and expansion chamber methods for measuring the ranges of long-range particles are discussed, and a detailed description is given of experiments made to determine accurately the ranges of the long-range α -particles from thorium-C and radium-C, using a special form of Wilson expansion apparatus. Two different arrangements are used, specially designed to furnish as few protons as possible within the interval of range in which long-range particles were expected—i.e., between 7 and 15 cm. for radium-C' and 8.6 and 15 cm. for thorium-C'. In one arrangement, the radioactive source was surrounded by a gas (carbon dioxide or oxygen) to avoid the production of disintegration protons. The results indicate that thorium-C gives out two groups of α -particles with extrapolated ionisation ranges of 11.70 and 9.90 cm., respectively. A few tracks were found, also thought to be due to α -particles emitted by the source, of which the range was greater than 12.5 cm. The ratio of the numbers of particles in the 9.9 and 11.7 cm. groups is found to be 1:5.1, which differs considerably from the value 1:2.8 obtained by Meitner and Freitag (A., 1926, 772). The conclusions for radium-C are less definite. There is certainly a group of α -particles having an extrapolated ionisation range of 9.16 cm. in standard air, but besides these particles there are others with ranges between 7.5 and 12.5 cm. No absolute decision can be made as to whether these particles are emitted in

groups of constant velocity, but there is strong evidence for additional groups at 8.1 and 11.0 cm. with a doubtful group at about 10 cm. The results make it quite clear that radium-C does not emit only two groups of long-range α -particles of 9.3 and 11.3 cm. range, as has hitherto been supposed on the evidence of scintillation experiments (cf. Rutherford and Chadwick, A., 1924, ii, 814).

L. L. BIRCUMSHAW.

Separation and preparation of radium-D, radium-E, and polonium (radium-F). O. ERBACHER and K. PHILIPP (Z. Physik, 1928, 51, 309—320).—Methods of determination of radium-D and -E and polonium are described, in which the milligram radium equivalent of a radium-D preparation is determined by means of a β -ray electroscope. This preparation is then compared with a mixture of radium-D and -E, which is itself compared with polonium in an α -ray apparatus depending on the ionisation produced by the α -rays between the plates of a condenser at 2000—4000 volts.

The preparation of pure radium-D and -E and polonium is described; the first is produced by the electrolysis of an acid solution of radium-D with a current of 3×10^{-4} amp., pure radium-D separating out at the anode under those conditions. Pure radium-E is deposited from an acid solution of the impure substance on to nickel foil on keeping, and pure polonium is similarly, but more slowly, deposited on silver foil. Tables of experimental results are given, showing that a degree of purity of 95% and upwards is readily obtained. D. W. BANDEY.

Behaviour of the radio-active deposit during the operations used for the removal of emanation from water. H. HERSZFINKIEL (Rocz. Chem., 1928, 8, 519—526).—The shaking out from radioactive mineral waters of the radioactive deposit together with the emanation observed by Hammer and Vohsen (A., 1913, ii, 622) is only apparent; this phenomenon is due to the Lenard effect, as well as to adsorption of the deposit on the walls of the vessel in which the solution is shaken. A similar effect is obtained by boiling the solutions or by aerating them.

R. TRUSZKOWSKI.

Temperature coefficient of γ -ray absorption. L. BASTINGS (Phil. Mag., 1929, [vii], 7, 337—345).—Measurements have been made on the absorption of γ rays by lead, tin (solid and liquid), iron, and aluminium at various temperatures. Within the limits of experimental error the temperature coefficient of the atomic absorption of γ -rays is in close numerical agreement with the coefficient of linear expansion of the metal. This suggests that the atomic absorption is probably a function of the distance between the atoms of the absorber and not of the atomic target, as might have been expected.

A. E. MITCHELL.

Two simple methods of purifying radium emanation. W. G. MORAN (Phil. Mag., 1929, [vii], 7, 399—404).—In the first method oxygen and hydrogen are ignited by means of a hot copper oxide filament which serves also to oxidise any excess of hydrogen. In the second method the oxygen and hydrogen are ignited by an electric spark and any excess of hydrogen is removed by diffusion through a

heated palladium tube. In both methods potassium hydroxide solution is employed to remove carbon dioxide. The apparatus is described in detail. The methods are applicable particularly to the preparation of specimens for therapeutic purposes, and since concentrations of the order of 125 millicuries per mm.³ are obtained it is not considered necessary to remove water vapour. A. E. MITCHELL.

Waves associated with β -rays and the relation between free electrons and their waves. G. P. THOMSON (Phil. Mag., 1929, [vii], 7, 405—417).—A mathematical analysis, on the basis of de Broglie's theory of wave mechanics, of β -ray emission is made and it is shown that the variation in speed of the electrons in the continuous β -ray spectrum may be regarded as due to the dispersion of a short-wave group associated with each ray. The mean velocity is of the order of that to be expected if the group had the form of an error function of sufficient spread to give the observed velocity range. The velocity of an electron associated with a given wave is considered and is shown to be capable of variation even in force-free space, a result which offers an explanation of the results of Ellis and Wooster (A., 1927, 393) on the heat generated in the disintegration of radium-E.

A. E. MITCHELL.

Ultra-violet radiation of substances subjected to γ -rays. L. MALLET (Compt. rend., 1929, 188, 445—447; cf. A., 1926, 885).—A new quartz spectrograph is described which has a high luminosity and may be used to analyse the very feeble ultra-violet radiations emitted by liquids subjected to γ -rays. In general, pure liquids (e.g., water) emit such radiations when subjected to high-frequency γ -rays, and the continuous spectrum of the radiations may extend from the visible to the extreme ultra-violet region and is limited only by the absorptive power of the substance concerned.

J. GRANT.

"Packing fractions" of the atoms and their interpretation. A. C. BURTON (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 379—395).—The work of Aston on "packing fractions," defined by him as the divergence of a given atom from the whole-number rule divided by its mass number, is discussed. To find the deviation, the actual mass found should be subtracted from ($1.00778 \times$ mass number) instead of from the nearest whole number, 1.00778 being the mass of the hydrogen atom, i.e., of one proton and one electron, the two being so far apart that there will be a negligible loss due to packing. It is enunciated that if it is found that in any two cases the addition of the same quantity to the nucleus in passing from one atom to the next produces the same extra loss in mass, it can be concluded that the addition has probably been made in the same way, and this is used in interpreting the results. It is believed that when more accurate data are available, the application of this method will give rise to a quantitative scheme of nucleus building. A graph is drawn of the total loss in mass due to packing against the mass number for the first twenty elements. The packing is not very different in the different elements, i.e., the whole-number rule is not very far from accurate. Atoms of the type mass = $4n$ are at maxima in the

curve, i.e., packing is peculiarly close for these elements. If the nuclei are made up of assemblages of helium nuclei, the packing effect per α -particle can be calculated. The loss in mass due to packing of proton and electron in a single α -particle is 0.0290. The theory of packing developed gives evidence for the existence of neutrons (Rutherford), and the packing loss due to a loosely added neutron is calculated to be between 0.008 and 0.007. A graph of the packing per α -particle against the number of α -particles in the core is plotted. Starting at the packing loss of a single α -particle the loss at first increases, due to the packing effect of the α -particle on its neighbours in the core. The loss reaches a maximum in the region of mass 60 or 70, where there is a maximum stability of the nuclei of elements. The packing effect then decreases. The nuclei of the lighter elements where there is an extra proton or electron in the nucleus are more difficult to investigate, but some attempt is made to apply the above principles to them. A. J. MEE.

Significance of the "packing fraction." M. FRANÇON (J. Physical Chem., 1929, 33, 296—300).—Previous views of other authors are summarised and the possible significance of the packing fraction in determining the evolution and abundance of the elements is discussed. L. S. THEOBALD.

Absorption of penetrating radiation. L. H. GRAY (Proc. Roy. Soc., 1929, A, 122, 647—668).—Assuming that penetrating radiation is an ultra- γ -radiation, its absorption in the atmosphere is investigated from the theoretical point of view, and an attempt is made to establish a quantitative correlation between the ionisation produced in an electroscope by penetrating radiation and the scattering absorption coefficient of the radiation. The extent to which the surrounding medium may influence directly the ionisation produced in an electroscope by changing the number and velocity distribution of the ionising particles is considered in detail. Assuming that a β -particle traversing a solid medium loses the same amount of energy in travelling a distance Δx short compared with its range as it would do in traversing $\rho \Delta x$ of air, where ρ is a proportionality factor independent of the velocity of the particle, it is calculated that, for a small air cavity in an extended solid medium traversed by penetrating radiation in any arbitrary manner, the variations in intensity of the radiation in distances comparable with the dimensions of the cavity being negligible, the energy lost per unit volume by β -particles in the cavity is $1/\rho$ times the energy lost by γ -rays per unit volume of the solid. The relative magnitudes of the ionisation produced by primary and scattered radiations at any point are calculated by approximate methods, and depth-ionisation curves are reproduced, computed both on the basis of the Compton scattering formulæ and on that of the new scattering formulæ proposed by Klein and Nishina (Nature, 1928, 122, 398). The relation between the apparent absorption coefficient of a homogeneous isotropic radiation and the true scattering coefficient of the primary radiation is discussed in the light of the results obtained. The validity of the Klein-Nishina formulæ is considered.

The points of contact of theory and experiment are studied for the formulæ of Dirac, Compton, and Klein and Nishina, and conclusions are reached which are favourable to the new formulæ.

L. L. BIRCUMSHAW.

Velocity of cadmium atoms regularly reflected from a rock salt crystal. A. ELLETT and H. F. OLSON (*Science*, 1928, 68, 89).—The velocities of cadmium atoms constituting a beam reflected (at an angle to the normal equal to that of the incident beam) from a cleavage face of rock salt are very nearly equal; between 200° and 500° the velocity is independent of the temperature of the crystal. The results obtained for various angles are shown to be in accord with de Broglie's equation $\lambda = h/MV$ for the wave-length of a phase wave associated with a particle of mass M and velocity V , and with Davisson and Germer's form of Bragg's law. A. A. ELDRIDGE.

Polarisation of Compton scattering according to Dirac's new relativistic dynamics. Y. NISHINA (*Nature*, 1929, 123, 349).—A correction (cf. this vol., 5). A. A. ELDRIDGE.

Penetrating radiation. II. J. CLAY (*Proc. K. Akad. Wetensch. Amsterdam*, 1928, 31, 1091—1097; cf. A., 1928, 569).—An accurate determination of the capacity of the electrometers has shown that the values previously used were incorrect. A redetermination has been made of the residual ionisation and of the constants of the penetrating radiation. The origin of the latter is discussed, and its intensity is shown to decrease as the equator is approached.

N. M. BLIGH.

More elementary treatment of the hydrogen atom in wave mechanics generalised for the moving nucleus. J. K. L. MACDONALD (*Trans. Roy. Soc. Canada*, 1928, [iii], 22, III, 417—422).—Mathematical. The problem of the hydrogen atom is solved by wave mechanics in a more elementary and familiar way, the motion of the nucleus and of the atom as a whole being considered. A. J. MEE.

Chemical combination as an electrostatic phenomenon. A. E. VAN ARKEL and J. H. DE BOER (*Chem. Weekblad*, 1929, 26, 66—69).—A summary of the present conception of atomic structure is given. S. I. LEVY.

Sommerfeld's electronic theory of metals and the mean free path of electrons. L. BRILLOUIN (*Compt. rend.*, 1929, 188, 242—244).—It is shown that in the calculation of the mean free path of electrons from Sommerfeld's application of Fermi statistics to the case of free electrons in metals (A., 1928, 467), the results for light and electrons cannot be similar, since the former is subject to Bose-Einstein statistics. A modified calculation is suggested (cf. Houston, *loc. cit.*). J. GRANT.

Regularities in the table of the elements. D. STROMHOLM (*Z. anorg. Chem.*, 1928, 177, 303—312, and *Phil. Mag.*, 1929 [vii], 7, 691—705).—The percentage electron content of the atomic nucleus increases rapidly with increase of at. wt.; this increase occurs in five stages, of which the second commences at scandium, the third at gadolinium or germanium, the fourth at indium, and the fifth probably at

hafnium. The significance of these stages is discussed, particularly as regards formation and disintegration of the elements. H. F. GILLBE.

Statistical periodic table. H. H. STEPHENSON (*Chem. News*, 1929, 138, 129—130).—The author has arranged the elements in order of atomic number, calculated the percentage increase of at. wt. of each element over that of its predecessor, and arranged the resulting numbers in columns of six. The table is said to be "statistically periodic" and to exhibit chemical relationships. A. A. ELDRIDGE.

Relations between doublets of stripped atoms in five periods of the periodic table. R. C. GIBBS and H. E. WHITE (*Physical Rev.*, 1929, [iii], 33, 157—162).—The periods considered are Li—O, Na—Cl, K—Mn, Rb—Zr, and Cs—Pr. Combining the available data for the one-electron system, certain regularities between the successive elements in each period and between corresponding elements in successive periods are found by the application of the regular and irregular doublet laws. That the latter is closely followed for all five periods is shown by a graph giving the linear progression of frequency with atomic number for transitions involving no change in the total quantum number. The term values of any sequence when plotted on a Moseley diagram show very nearly a straight-line relation. Previous identifications of the principal doublet of cerium are corrected. Evidence indicates that the unexcited state of cerium involves a $5d$ rather than a $4f$ electron. New data are given for vanadium, chromium, and lanthanum. N. M. BLIGH.

Origin of actinium and the age of the earth. (Sir) E. RUTHERFORD (*Nature*, 1929, 123, 313—314).—It is supposed that the new lead isotope "actino-uranium" (Aston, this vol., 370) is of mass 235, and that it undergoes first an α - and then a β -ray transformation into protoactinium. The β -ray substance is probably uranium-Y, whence the successive transformations follow the order $\alpha\beta\alpha\beta$ instead of $\alpha\beta\beta\alpha$, as in the main uranium series. From the half-value period (4.5×10^9 years) of transformation of uranium it is computed that the period of actino-uranium is 4.2×10^8 years. If it is supposed that the production of uranium in the earth ceased as soon as the earth separated from the sun, the earth cannot be older than 3.4×10^9 years. If the age of the sun is of the order 7×10^{12} years, uranium and similar elements were being formed in the sun 4×10^9 years ago, and the process still continues.

A. A. ELDRIDGE.

Scattering of radiation by free electrons according to Dirac's new relativistic quantum mechanics. O. KLEIN and Y. NISHINA (*Z. Physik*, 1929, 52, 853—868).—Mathematical. Using the principles of Dirac's theory the intensity of the Compton scattered radiation is calculated.

J. W. SMITH.

Stability of the silver atom. J. KAPLAN (*Z. Physik*, 1929, 52, 883; cf. Adams, this vol., 368).—It is suggested that although the shell of the $4d$ -electrons in silver is quite stable in almost all chemical reactions, this may not be so stable with respect to electrical conductivity and that some of them may

enter into this process. It is suggested that the appearance of tervalent silver mentioned by Adams indicates that the $4d$ -electrons are not equally stable.

J. W. SMITH.

Ionisation and chemical combination of gases. A. DE HEMPTINNE (Bull. Acad. roy. Belg., 1928, [v], 14, 450—454).—An experiment is described to investigate the relationship between ionisation and chemical reaction for mixtures of hydrogen and oxygen and of hydrogen and nitrogen. The ratio of the total number of ions formed to the number of combined molecules is calculated, and from the result it is shown that there is an intimate relationship between the amount of combination and the number of ions present. For the combination of hydrogen and nitrogen the ratio of ions to molecules combining varies only from 15 to 20, whilst the current through the gas is ten times as great in the second case as in the first.

A. J. MEE.

Quantum mechanics and radioactive disintegration. R. W. GURNEY and E. U. CONDON (Physical Rev., 1929, [ii], 33, 127—140).—Theoretical. The statistical nature of the new quantum mechanics renders it very suitable for the treatment of radioactive decay. The method of wave mechanics is employed and a simple deduction of the disintegration constant is made. It is shown qualitatively that the nucleus can disintegrate without the absorption of energy, a result opposed to classical theory. The equivalent of the Geiger-Nuttall relation between the rate of disintegration and the energy of the emitted α -particle is deduced quantitatively. The law of force between the emitted α -particle and the rest of the nucleus is shown to be substantially the same in all atoms. The quantum mechanical assumption that particles can pass through regions where their total energy would classically be less than their total energy affords an explanation of the experiments of Rutherford and Chadwick (cf. A., 1925, ii, 1109).

N. M. BLYTH.

Transmutation of elements. L. THOMASSEN (Physical Rev., 1929, [ii], 33, 229—238).—If transmutation is possible it might take place in an X-ray tube, where it could be detected in the X-ray spectrum. No lines other than those due to tungsten were found before or after working an X-ray tube with a tungsten target for 80 hrs. No transmutation of lead to mercury could be detected when the experiments of Smits and Karssen (cf. A., 1926, 106) with the lead arc were duplicated. Their experiments on a high-potential discharge between platinum electrodes in carbon disulphide (cf. A., 1927, 87) were repeated, as a trace of mercury in the residue from the electrodes is regarded as an impurity.

N. M. BLYTH.

Space required by atoms (ions) in crystals and the character of the lithosphere. V. M. GOLDSCHMIDT (Neues Jahrb. Min., 1928, A, 57, 1119—1130; Chem. Zentr., 1928, ii, 867—868).—A discussion. The influence of ionic size on molecular volume is examined; the density of space occupation of a compound AX of the sodium chloride type is greatest when $R_A : R_X = 0.41$, and least when Oxygen is the only important anion of the lithosphere; the whole lithosphere is regarded as an oxygen-

packing. The maximum density for spherical oxygen ions is 2.03, this value being modified by the cations.

A. A. ELDRIDGE.

Low-voltage sparks as spectroscopic sources. A. OCCHIALINI (Atti R. Accad. Lincei, 1928, [vi], 8, 389—393).—Low-voltage sparks suitable as spectroscopic sources may be obtained by using a cathode of incandescent carbon, forming part of an auxiliary arc, and a cold anode. A condenser of some microfarads capacity serves to store energy from the direct current source in the intervals of the sparks. Details are given of an electrolytic rectifier suitable for obtaining the necessary direct current.

F. G. TRYHORN.

Use of the under-water spark with the Hilger sector photometer in ultra-violet spectrophotometry. H. J. McNICHOLAS (Bur. Stand. J. Res., 1928, 1, 939—949).—Means for operating high-voltage under-water spark to produce a uniform continuous spectrum for quantitative spectrophotometric measurements are described. Spark terminals of tungsten are enclosed in an ebonite box, through which a stream of distilled water is circulated. External adjustments are provided for the length of the spark gap (about 16 mm.) and its position relative to the axis of the optical system. Methods of avoiding the wave-length dispersion in the Hilger sector photometer, and thus permitting the use of a shorter spark, are discussed.

C. J. SMITHELLS.

Elimination of stray radiations in an infra-red spectrometer. J. LECOMTE (Compt. rend., 1929, 188, 622—625).—The proportion d ($d < 1$) of stray radiation passing into the instrument at each point of the spectrum beyond 10μ is determined by the transparent-shutter method, and the gross transmission of the substance is then determined by the usual opaque-shutter method. The true transmission of the radiation above 10μ is given by the formula $T = (T' - d)/(1 - d)$, where T' is the gross transmission of the radiation in the presence and absence of the absorbent. The true absorption is given by $1 - T$. The variation of d with wave-length is usually a straight line.

R. BRIGHTMAN.

Absorption vessel for variable thicknesses of liquid. C. LEISS (Z. Physik, 1928, 52, 748—749).—A new form of absorption vessel is described, the distance between the windows of which can be set to within 0.05 mm. All possibility of contamination by metal, grease, etc. is avoided, the liquid coming into contact with glass only.

E. B. ROBERTSON.

Vacuum spark-gap. C. LEISS (Z. Physik, 1928, 52, 750—751).—A vacuum spark-gap is described which can be either attached to a vacuum spectrograph or placed on a stand directly in front of the slit.

E. B. ROBERTSON.

Experimental test of the combination principle for band spectra. E. BENGTSSON and E. HULTHÉN (Z. Physik, 1928, 52, 275—279).—The AIH band spectrum has been examined with a large concave grating (dispersion 2.4 \AA./mm.) and, in addition to the band systems $^1P \rightarrow ^1S$ and $^1S' \rightarrow ^1S$ already known, a new system given by $^1S' \rightarrow ^1P$ has been discovered and measured. This is therefore a case

in which all three transitions between three electronic terms are realised, and the measurements confirm Kronig's combination principle (that transitions take place only between primed and unprimed terms).

E. B. ROBERTSON.

Spectrum of H_2 : bands analogous to the orthohelium line spectrum. O. W. RICHARDSON and K. DAS (Proc. Roy. Soc., 1929, A, 122, 688—718).—A summary is given of Richardson's previous work on the structure in the secondary hydrogen spectrum (A., 1926, 873; 1927, 1). An examination of the wave-length tables of Gale, Monk, and Lee (A., 1928, 1166) confirms the series of systems of Q branches recorded, and the combinations are found to be exact to the accuracy of the new data. This applies to the bands which involve the electron transitions $3 \rightarrow 2$ (α), $4 \rightarrow 2$ (β), and $5 \rightarrow 2$ (γ), but the weak bands involving the $6 \rightarrow 2$ (δ) and higher transitions require reconsideration. By using the more exact final vibration intervals thus obtained it has been possible to identify the P and R branches accompanying the Q branches previously studied. There are found to be only three branches, P' , Q , and R' , the initial levels for the P' and R' branches being different from those for the Q branches. There is a final level in the R' branches lower than any present in the Q branches. The lines of the P' , Q , and R' branches of the H_2 bands are tabulated, using the wave-numbers and intensities of Gale, Monk, and Lee. The bad agreement given by the older infrared data for the Q branches has entirely disappeared. The existence of all the states, both initial and final, with vibration numbers between 0 and 7 is securely established, and there is some evidence for the occurrence of $n'=8$ and 9 and $n''=8$. The usual expression for the vibrational energy which includes only terms as high as n^2 is shown to be inadequate, but the function can be completely expressed by adding terms in n^3 and n^4 . The Q branches of the H_2 band system are also tabulated. The existence of the levels up to $n'=5$ and $n''=5$ is now certain. The P' and R' branches, extremely weak except for the $0 \rightarrow 0$ bands, have very similar properties to those of the corresponding H_2 bands. There is the same alternation of intensity of the lines, and the maximum strength lies on or close to the diagonal sequence. The analysis has been extended to include the rotational structure of the band systems. The lines of the bands are single, and conclusive evidence is adduced that the bands are $2S-mP$. The system of bands ($2S-3S$) in the red and infra-red having the same final states as the $H_{2,\beta,\text{etc.}}$ bands is also discussed, and the lines, with the final and initial vibration and rotational term differences, are tabulated. These bands are characterised by the presence of P and R branches of about equal intensity and by the absence of Q branches.

L. L. BIRCUMSHAW.

Fulcher bands of hydrogen. I. SANDEMAN (Nature, 1929, 123, 410—411).—The terms of the bands fit the form $1) - \sigma^2$, provided j is given integral values, but a correction term in the fourth power of j or j_k is present. The tentative formula $F(j) = \sum X_n \{j(j+1) - \sigma^2\}^n$, $n=1, 2, \dots$, is adopted. For the hydrogen bands only the first

two terms need be taken into account. The constants of the Fulcher null band $0a_0$ are evaluated.

A. A. ELDRIDGE.

Existence of metastable molecules in active nitrogen. J. KAPLAN (Physical Rev., 1929, [ii], 33, 189—194; cf. this vol., 365).—The only basis for the existence of metastable nitrogen molecules has been that they afforded an explanation of the nitrogen afterglow. Experimental evidence of their existence is found in the excitation of the fourth positive group of bands of the nitrogen molecule by a mild discharge simultaneously with the quenching of the afterglow. The main spectroscopic characteristics of a condensed discharge have been reproduced simply by introducing active nitrogen into a weak discharge. The relation of these phenomena to the structure of the nitrogen molecule is discussed. N. M. BLICK.

Band spectrum of chlorine or hydrogen chloride. E. B. LUDLAM (Nature, 1929, 123, 414).—The bands previously recorded (this vol., 118) were caused by the presence of traces of sulphur.

A. A. ELDRIDGE.

Band absorption spectrum of iodine in an extreme ultra-violet region. M. KIMURA and M. MIYANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 33—42).—Oldenburg (A., 1923, ii, 708) has shown that iodine emits equally-spaced resonance lines in the region 1860—2173 Å. when exposed to monochromatic light in the region 1900 Å. The absorption thus disclosed has now been studied in detail, the iodine vapour being at 35—120° with vapour pressures corresponding with 35—60°. At 35°, the absorption extended from 1950 to 2064 Å., and as the temperature was slowly raised to 120°, the bands in the above region gradually disappeared and new bands with wider spacing progressively appeared until at 120° the spectrum extended from 2066 to 2145 Å. The bands were usually most intense in the middle of the spectrum. The interval 210 cm^{-1} appears in several series, and attention is directed to the agreement between this constant and the intervals between levels for iodine molecules in the normal state, and also the intervals of the resonance lines recorded by Oldenburg. The formula $\nu = 52800 + 78n' - n'^2 - 210n$ cm^{-1} expresses approximately the wave numbers of the observed band edges.

R. A. MORTON.

Diffuse bands and predissociation of iodine monochloride. G. E. GIBSON and O. K. RICE (Nature, 1929, 123, 347—348).—Evidence that the convergence limit of the group of bands (I^*), of which Gibson and Ramsperger observed the members 17446 and 17570 cm^{-1} , corresponds with dissociation of iodine monochloride into normal chlorine and excited iodine atoms has been obtained. A second continuum probably corresponds with the same process. The band 17446 cm^{-1} clearly shows fine structure, but the next following bands are diffuse. The effect is probably of the same nature as Henri's "predissociation." The diffuseness is probably due to interaction between the Cl^* band group continuum and the discrete states of group I^* . A. A. ELDRIDGE.

Spectra excited by active nitrogen. J. H. FINDLAY (Trans. Roy. Soc. Canada, 1928, [iii], 22,

III, 341—352).—A comparison was made of the spectrum of the exciting discharge when the nitrogen afterglow was present and when it was absent. The differences between the two are, in the first place, the presence of the first positive nitrogen bands in the spectrum of the discharge with no afterglow and the absence of them from the glow-producing discharge, and, in the second place, a more intense spectrum in the latter case. The main problem attacked was the excitation of spark lines of elements with low ionisation potentials, *e.g.*, calcium, strontium, and barium, by means of active nitrogen. Although sodium and potassium lines were present in the afterglow spectrum no calcium lines were present. This is probably due to the formation of stable calcium nitride. The work of Ruark and of Okubo and Hamada on the excitation of the mercury spectrum by active nitrogen was repeated. The results agree with those of the latter authors, *viz.*, the highest level of excitation was the 4^3D level, corresponding with an excitation potential of 9.51 volts. The temperature to which mercury had to be heated in order to produce the blue glow of mercury in the tube was found, and hence the vapour pressure of the mercury. The relative concentrations of mercury vapour and active nitrogen would not preclude the possibility of chemiluminescence being the origin of spectra excited by active nitrogen. It was not found possible to excite the spectrum of indium by active nitrogen in spite of its low ionisation potential (5.76 volts). This may be due to the fact that it does not combine with nitrogen. A. J. MEE.

Ultra-violet absorption spectrum of nitrogen peroxide. M. LAMBREY (Compt. rend., 1929, 188, 251—252).—The wave-lengths of the apparent absorption maxima of the NO_2 molecule and the intensities of the lines are tabulated for 2083—4009 Å., with an accuracy of 1 Å. Liquid nitrogen dioxide at -20° (1 mm. layer) shows a single spectrum with intense absorption for wave-lengths below 3975 Å., whilst the gas shows two spectra. That due to N_2O_4 has two large structureless bands at about 3400 and 2400 Å., whilst the bands due to NO_2 are complex in structure and extend from the yellow to 2900 Å., and from 2490 Å. to the limit of the spectrum. The absorption coefficient is a minimum at about 3020 Å., but is never zero. J. GRANT.

Quantum analysis of the beryllium oxide bands. (Miss) J. E. ROSENTHAL and F. A. JENKINS (Physical Rev., 1929, [ii], 33, 163—168).—New measurements of the lines in six bands of the visible BeO system are reported. Each band has *P* and *R* branches of almost equal intensity, and the agreement among the bands of the combination relations between the two branches is shown graphically. The rotational terms are investigated by the combination principle. An equation is deduced for the null lines. Some of the principal molecular constants are evaluated from rotational term-differences, using the new quantum mechanics. N. M. BLIGH.

Ultra-violet spectrum of magnesium hydride. I. Band at 2430 Å. R. W. B. PEARSE (Proc. Roy. Soc., 1929, A, 122, 442—455; cf. Watson and Rudnick, A., 1926, 657; 1927, 395).—Besides the well-known visible (α) band system in the spectrum

of MgH , two others (β and γ) are found in the ultra-violet. The β -system is represented by a strong band at 2430 Å., whilst the γ -system covers the range 5500—2430 Å. The 2430 Å. band has been measured and found to resemble the 0,0 band 5211 Å. of the α -system in possessing *P*, *Q*, and *R* branches, of which the *Q* are much the strongest. Each is composed of lines which are apparently single, but are probably double. The doubling appears to be similar to that of the 5211 Å. band in decreasing rapidly in separation with increasing *m*, but to be on a smaller scale. A curious feature of the band is the rapid decline of intensity in the *P* and *R* branches after passing the maximum value. A comparison of the combination differences relating to the final and initial states of the 2430 and 5211 Å. bands indicates that the final level of the 2430 Å. band is the same as that of the 5211 Å. band, and that the initial state is of the same type as that of the α -system, $2P$. The α -system is the MgH analogue of the "*D*" lines of Na, the "comparable atom," whilst the β -system corresponds with the second member of the $2P \rightarrow S^2$ series of Na. The 2430 Å. band is the 0,0 band of the β -system. The *Q*-heads of three neighbouring bands of the same system have been detected and measured under low dispersion, and values of the initial and final vibrational quantum numbers n' , n'' assigned.

L. L. BIRCUMSHAW.

Complexity of the $K\beta'$ line of X-ray spectra. V. DOLEJSEK and H. FILČAKOVA (Nature, 1929, 123, 412—413).—A study of various manganese compounds has not revealed any relationship between the state of chemical combination and the breadth or displacement of the line $K\beta'$. The intensity ratio $K\beta_1 : K\beta'$ is greater for oxides than for the free elements. For the elements of atomic number 24—27 the width of the line $K\beta'$ increases with decrease of atomic number; in the lower elements the line is composed of two unresolved doublet lines which in the higher elements are superimposed. The two lines cannot both be due to the transition $K \rightarrow M_{III}$. A. A. ELDRIDGE.

Absorption of X-rays from 0.63 to 2 Å. I. BACKHURST (Phil. Mag., 1929, [vii], 7, 353—373).—An X-ray tube suitable for absorption measurements with homogeneous radiation in the region of 1 Å. is described. The results of absorption measurements on silver, aluminium, platinum, gold, and copper for wave-lengths 0.63—2 Å. are given. The relationship between absorption and wave-length was found to conform approximately to the law recently found by Jonsson (Uppsala Univ., Årsskrift, 1928). The *K*-absorption jump for copper and the *L*-absorption jumps for gold and platinum have been measured and the values are found to be in closer agreement with Jonsson's theory than with others.

A. E. MITCHELL.

Fluorescence of mercury vapour under low excitation. [LORD] RAYLEIGH (Nature, 1929, 123, 127).—When the exciting source consists of radiation from which wave-lengths < 3360 Å. have been cut off, fine structure in the band at wave-length 3130—3650 Å. can still not be observed.

A. A. ELDRIDGE.

Absorption spectra and molecular structure of the dihalogen derivatives of benzene. J. ERRERA and V. HENRI (J. Phys. Radium, 1928, [vii], 9, 205—224, 249—264).—The ultra-violet absorption spectra of some dihalogen derivatives of benzene, in the vapour state, have been investigated up to 400° and at pressures of from 10 to 100 mm. The source of illumination was a high-frequency condensed spark between electrodes of copper or aluminium under water and an iron spark was used for comparison. The minimum concentration of vapour necessary for the production of each band was found to be within 5—10%, and the bands were thereby classified according to their intensities. The absorption spectra of dichloro- and dibromobenzene contain many bands and fine lines in the ultra-violet between 2850 and 2500 Å., whilst the three di-iodobenzenes give continuous spectra from about 3000 to 3100 Å., the absorption becoming more intense towards the ultra-violet. The dichloro- and dibromo-benzenes give spectra similar to all the mono- and di-derivatives of benzene, which are also characteristic of all aromatic substances, there being two regions, corresponding with two states of electronic activation. In the first of these regions are five or six groups of bands, at intervals of 80—60 Å. corresponding with atomic vibrations. Between the principal groups are secondary and tertiary groups. At very low pressures only the groups nearest to the red are obtained, more bands appearing as the pressure is raised. There is also a second region of continuous absorption beginning at about 2350 Å. From these bands the energies of dissociation of dichloro- and dibromo-benzene are deduced to be at least 124,000 g.-cal./mol., whilst for the di-iodo-derivative it is about 95,000 g.-cal./mol. The difference in moment of inertia between the activated and unactivated molecule has been calculated from the rotation spectra.

A formula is given showing the distribution of bands in the absorption spectrum of *p*-dichlorobenzene. The spectrum, like those of the *o*- and *m*-derivatives, is composed of doublets, but in this case the separation is more feeble, also the distribution of bands corresponds with three, not with two, intramolecular vibration frequencies. The formula for *p*-dibromobenzene is also given. Its absorption spectrum is very similar to that of the *p*-dichloro-derivative, but the vibration frequencies are less pronounced.

These spectra are discussed from the point of view of molecular structure. From the data obtained, the energies of activation and of dissociation of these molecules have been calculated. Both the dichloro- and dibromo-derivatives show two states of activation, the second state corresponding with dissociation of the molecule, whilst the di-iodo-derivative shows only one, its energy being less than for the others. This is due to the di-iodo-derivatives being more labile so that they dissociate at the first stage of activation. By comparison with benzene it is shown that the introduction of chlorine into this molecule progressively displaces the spectrum towards the red and lowers the energy of activation. By analogy with atomic spectra it is concluded that these deriv-

atives possess an electron which is less firmly held than the others, and it is this electron which, under the influence of ultra-violet light, produces doublets by moving to an orbit of a higher energy level.

J. L. BUCHAN.

Theory of sensitised fluorescence. A. CARELLI (Atti R. Accad. Lincei, 1928, [vi], 8, 495—500).—A mathematical treatment based on wave mechanics.

F. G. TRYHORN.

Fluorescence excited in oxygen and nitrogen by ultra-violet light of short wave-length. J. C. McLENNAN, R. RUEDY, and F. H. CLEMENTS (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 253—255).—The question whether ultra-violet light of short wave-length (1100 Å.) from a spark gives rise to any fluorescence in the surrounding air is studied experimentally. The light source was placed in the gas itself. Spectrograms were taken and it was found that the most intense bands of the first negative system and of the second positive system of nitrogen were present. Atomic oxygen lines also appeared, but no lines of molecular oxygen. This demonstrates the great stability of the nitrogen atom, and the fact that the oxygen molecule readily breaks down into atoms under the influence of light of short wave-length. There was no trace of the green auroral line of oxygen, λ 5577 Å., the absence of which is explained by the fact that at the comparatively high pressures used collisions of the second kind would be so numerous that atoms in the metastable state would lose their energy through these collisions instead of by the spontaneous emission of radiation. A method of obtaining light of the wave-length 5577 Å. (oxygen auroral green line) is suggested. The pressure used must make collisions of the second kind very infrequent, and the gas must be irradiated with light of wave-lengths slightly longer than those which would cause nitrogen molecules to emit any light of their second, and possibly of their first, positive band system.

A. J. MEE.

Luminous discharge in gases at low pressure. H. PETTERSSON (Nature, 1929, 123, 346).—By the use of oscillations of frequency 10^8 cycles per sec., a luminous discharge was maintained in tubes only 5 mm. wide under extremely low pressure. The gas showed a faint blue luminosity; the silica tube showed a strong fluorescence in the blue or blue-green, although some tubes showed a brilliant fluorescence in the red. Thermo-luminescence and after-glow of the silica were also observed. Under the influence of the ultra-violet light of very short wave-length generated by the discharge, the silica appears to decompose, releasing oxygen. The spectrum from the white light of the self-generated gas represents the band spectrum of ozone, with some lines of elementary oxygen superimposed.

A. A. ELDRIDGE.

Origin of the luminescent light of phosphorus. A. PETRIKALN (Z. Physik, 1928, 51, 395—409; cf. A., 1924, ii, 289; Emeleus and Purcell, A., 1927, 497).—Investigations have been carried out on the emission and absorption spectra of phosphorus pentoxide and phosphorus trioxide. On electronic excitation of phosphorus pentoxide in the gaseous

phase the spectrum of oxygen only is produced. The pentoxide vapour shows no absorption in the quartz ultra-violet region; its emission spectrum appears to lie in the Schumann region. On the other hand, phosphorus trioxide vapour on electronic excitation shows a band spectrum which is completely identical with the phosphorus luminescence spectrum. The trioxide gives a continuous spectrum in the visible region and a band spectrum built up of two band systems, *A* and *B*, of which the former, the longer-wave system, has been partly analysed and the latter completely analysed and classified. It is concluded that the continuous spectrum is to be attributed to solid phosphorus pentoxide. The conditions of excitation of the phosphorus trioxide in the oxidation of phosphorus are discussed. J. W. SMITH.

Luminescence associated with electrolysis. R. T. DUFFORD (J. Opt. Soc. Amer., 1929, 18, 17—28).—Investigations of the luminescence frequently found during electrolysis, its extent, brightness, efficiency, and the influence on the last two of voltage changes, concentration, nature of the solution and impurities, have been carried out. The brightness and efficiency at first increase with the applied voltage and subsequently decrease; the effects of differences in concentration are relatively small, and are comparable for chemically similar solutions. Impurities generally have a small effect on the brightness and efficiency. The chief solutions studied were sodium hydrogen carbonate and phosphates, and ethereal solutions of Grignard reagents.

N. M. BLYTH.
Nitrogen afterglow. J. C. McLENNAN, R. RUEDY, and J. M. ANDERSON (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 303—321).—To discover how far chemiluminescence may contribute to the excitation of spectra by active nitrogen, the afterglow was allowed to act on an inert gas. If spectral lines are observed when these gases are mixed with activated nitrogen they must be due to direct excitation by the afterglow itself. If the available energy of active nitrogen is about 11.5 volts, as predicted from its spectrum, practically the whole spectrum of xenon should be excited in the afterglow, since the lowest excitation potential of xenon is 8.3 volts. Also several lower levels of krypton should be excited. It was found, however, that xenon when mixed with active nitrogen was not excited. The lines emitted by metallic vapours when acted on by active nitrogen are probably not due to the simple transfer to the metal atoms of the heat of recombination of nitrogen atoms produced by the discharge. Chemiluminescence probably plays a part when the spectra of foreign substances are excited. The result obtained with xenon is in agreement with evidence derived from a study of the decay of the nitrogen afterglow at different pressures. If it is assumed that a simple transfer of energy is responsible for the afterglow itself, the kinetics of the process do not agree with experiments. The effect of inert gases on the afterglow was studied and it was found that they all modify it in the same way, apart from minor details. The emission starts from the tenth, ninth, eighth, or seventh level, instead of from the eleventh level, as

the amount of inert gas present is increased. The effect is probably due to pressure, since it is the same for all the gases. The bands observed can be accounted for on the theory of intensity distribution in a band system which is applied to the first positive bands.

A. J. MEE.

Raman effect in quartz. M. CZERNY (Z. Physik, 1929, 53, 317—325).—A more detailed account of work already published (this vol., 240).

Secondary radiations in light diffused by quartz. J. CABANNES (Compt. rend., 1929, 188, 249—250).—An attempt is made to verify the author's hypothesis that the action of light on a molecule depends on its orientation, by the study of the Daure diffusion spectra and the polarisation of the secondary radiations produced by quartz crystals in which the molecules are oriented in a small number of fixed directions. The Daure spectra always comprise the same radiations, whatever the orientation of the crystal. J. GRANT.

Theory of light scattering in liquids. C. V. RAMAN (Phil. Mag., 1929, [vii], 7, 160—161).—A reply to comments by Rocard on the work of Raman and Krishnan (A., 1928, 461).

A. E. MITCHELL.

Raman spectra of scattered radiation. W. W. COBLENTZ (Phil. Mag., 1929, [vii], 7, 203—204).—The calculated infra-red absorption bands of calcite and benzene (Wood, A., 1928, 1306) are shown to be in very good agreement with the observations of Coblenz and Nyswander and to afford a striking confirmation of Raman's discovery of the relation between infra-red bands and the frequency change of the scattered light.

A. E. MITCHELL.

Raman lines from gaseous hydrogen chloride. R. W. WOOD (Nature, 1929, 123, 166).—The modified lines of gaseous hydrogen chloride at atmospheric pressure corresponding with the vibration-rotation absorption band at 3.46 μ have been observed.

A. A. ELDRIDGE.

Raman effect with liquid oxygen and with liquid nitrogen. J. C. McLENNAN and J. H. McLEOD (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 413—416).—An attempt was made to see if the Raman effect could be obtained with liquid oxygen or nitrogen. At least six Raman lines were found. The primary vibration frequencies appear to be involved in the production of four of these lines, the other two being produced by absorptions corresponding with the frequencies of the second vibration states of the elements. These would appear to be the first examples of homopolar molecules having the power to absorb light having frequencies equal to those of fundamental vibrations of their nuclei. A. J. MEE.

Raman effect with liquid oxygen, nitrogen, and hydrogen. J. C. McLENNAN and J. H. McLEOD (Nature, 1929, 123, 160).—The spectrum of the scattered light contained the following lines not included in that of the irradiating light from a mercury arc: liquid oxygen, 4317.7, 4674.3, 5026.5 Å.; liquid nitrogen, 4468.9, 4849.3, 4980.3 Å.; liquid hydrogen, 4426.6, 4473.1, 4863.5 Å. Mean vibration frequencies involved in the Raman effect with oxygen

and nitrogen, respectively, are 1551.5 cm^{-1} and 2328.5 cm^{-1} , suggesting that primary vibration frequencies are involved in the production of four of the lines, the other two lines being produced by absorptions corresponding with the frequencies of the second vibration states of the two elements. The Raman effects with hydrogen are due to $0 \rightarrow 2$ and $1 \rightarrow 3$ rotational transitions and a $0 \rightarrow 1$ vibrational transition for hydrogen molecules in the zero vibrational state. Thus it is shown that Raman effects can be obtained with homopolar molecules, that part of the energy of light quanta can be taken up directly as rotational energy, the balances appearing as quanta degraded in frequency, and that two-quantum rotational transitions can be demonstrated in connexion with light-scattering phenomena. In accord with Dennison's view, liquid hydrogen contains some molecules in the zero vibrational and zero rotational states, and others in the zero vibrational and first rotational states, the proportion being about 1 : 2.

A. A. ELDRIDGE.

Raman and infra-red spectra of carbon dioxide. C. R. BAILEY (Nature, 1929, 123, 410).—A study of the concordance observed by Rasetti (this vol., 241) shows that there is a close connexion between the deduced values and the observed spectrum. The wave-number differences between the band centres in the double doublets and those in the "undoubled" bands are of the same order as the deduced frequencies, whilst with the double doublets themselves the agreement is exact; moreover, the frequency difference between the undoubled bands is a simple fraction of one of these frequencies. These facts are considered in relation to the results of Bailey and Lih (A., 1928, 687) for the emission spectrum, which can be represented in a simple manner.

A. A. ELDRIDGE.

Incoherent scattering. R. M. LANGER (Nature, 1929, 123, 345).—The observations of Raman and Krishnan and others are accounted for much more successfully by the correspondence principle of Kramer and Heisenberg and by Schrodinger's wave mechanics than by Smekal's theory.

A. A. ELDRIDGE.

Apparent Mie effect and its possible role in atmospheric optics. G. I. POKROVSKI (Z. Physik, 1929, 53, 67—71).—The interference of light scattered from various centres is discussed. It is shown that under fixed conditions the greater portion of the light is only slightly deviated from the initial direction. The theoretical deductions are confirmed by comparison with the atmospheric light scattering and other observations.

J. W. SMITH.

Influence of temperature on the absorption [of light] by tourmaline. P. LE ROUX (J. Phys. Radium, 1928, [vii], 9, 365—376; cf. A., 1928, 934).—By means of the apparatus previously described, measurements have been made on the absorption by tourmaline of the mercury arc lines $5790\text{--}3655\text{ \AA}$. at various temperatures. Two sections of tourmaline were cut from the same crystal, parallel and perpendicular, respectively, to the crystal axis. From the ordinary temperature up to about 250° the absorption is a linear function of the temperature and reversible. The slope of the straight lines

obtained in this way decreases with increase in the wave-length, and depends also on the directions of vibration and propagation of the light. Measurements carried out up to 658° show that above a certain temperature (between 250° and 327°) the absorption ceases to be reversible. For these higher temperatures the tourmaline acquires a definite state depending on the temperature to which it has been heated.

O. J. WALKER.

Simultaneous energy transfers by collision and radiation. O. OLDENBERG (Z. Physik, 1928, 51, 605—612).—Arguments are advanced to show that evidence for the transfer of energy to a chemically inactive molecule by simultaneous collision and absorption of radiation in an atmosphere of excited molecules might be sought in the fluorescence of mercury vapour when mixed with helium. Experiment shows that under such conditions a continuum exists in the neighbourhood of the resonance line 2537 \AA . extending in the direction of lower frequencies. This is regarded as affording the necessary evidence.

R. W. LUNT.

Dissociation of hydrogen by collisions of the second kind. J. KAPLAN (Nature, 1929, 123, 162—163).—As an alternative interpretation of Cario and Franck's experiment on the dissociation of molecular hydrogen in a mixture of hydrogen and excited mercury atoms in the 2^3P_1 state, it is suggested that the result of a collision between an excited mercury atom and a normal hydrogen molecule is the excitation of the molecule from the 1^1S to the new 1^3S level, an unstable state, followed by immediate dissociation. The probability of such a transition is considered.

A. A. ELDRIDGE.

Change that a gaseous molecule may undergo between successive collisions. R. D. KLEEMAN (Phil. Mag., 1929, [vii], 7, 53—63).—It is shown that the function ξ in the equation $pv = \xi MRT$ (cf. A., 1928, 955) decreases as v increases. This is interpreted as signifying a decrease in the average velocity of translation of the molecules with an increase of v . It is concluded that the velocity of a molecule gradually decreases after a collision and that the subsequent collision increases it again to its initial value, whence the average velocity of the molecules will decrease with increase of volume.

A. E. MITCHELL.

Ionisation by slow electron impact of ammonia and hydrogen sulphide. J. H. BARTLETT, jun. (Physical Rev., 1929, [ii], 33, 169—174).—Positive-ray analysis showed the occurrence, in the case of ammonia, of three principal types of ion at $m/e = 15$, 16, and 17, respectively, and interpreted as having the compositions $(\text{NH})^+$, $(\text{NH}_2)^+$, and $(\text{NH}_3)^+$, with ionisation potentials of 11.2 ± 1.5 , 12.0 ± 1.5 , and 11.2 ± 1.5 volts, respectively. In the case of hydrogen sulphide, three principal types of ions occurred at $m/e = 32$, 33, and 34, and are interpreted as having the compositions $(\text{S})^+$, $(\text{HS})^+$, and $(\text{H}_2\text{S})^+$, with ionisation potentials of approximately 10.4, 16.9, and 15.8 volts, respectively. The mechanism of ionisation is discussed for the two substances.

N. M. BLYTH.

Dielectric anisotropy of liquid crystals in a magnetic field. M. JEZEWSKI (Z. Physik, 1928,

52, 268—274).—Using an improved form of resonance method the dielectric constants of *p*-azoxyanisole and *p*-azoxyphenetole in the nematic phase have been determined with the substances in a magnetic field using condensers of different forms and different plate spacings. It was shown that a magnetic field parallel to the electric lines of force in the condenser caused a decrease in the dielectric constant and a magnetic field at right angles to them an increase. The negative results previously obtained with a perpendicular field are explained on the grounds that with the condenser plates close together the orientation action of the walls was considerable, whilst with more widely spaced plates the edge effect was quite large.
J. W. SMITH.

Dielectric properties of liquid crystals in simultaneous magnetic and electrostatic fields. M. JEZEWSKI (Z. Physik, 1929, 52, 878—881; cf. A., 1927, 92; this vol., 12).—The influence of the simultaneous application of magnetic and electrostatic fields on the capacity of a condenser filled with *p*-azoxyanisole and *p*-azoxyphenetole has been investigated, both with the fields parallel and at right angles. An electrostatic field of less than about 400 volts per cm. caused no appreciable change in the capacity of a condenser in a magnetic field of 4000 gauss, although such an electrostatic field alone produced a considerable diminution in the capacity. A stronger electrostatic field parallel to the magnetic field caused an increase in the dielectric constant, whereas when the fields were at right angles a diminution occurred.
J. W. SMITH.

Change of the dielectric constants of air and carbon dioxide with wave-length in the range 600—60 metres. (FRL.) M. FORRÓ (Z. Physik, 1928, 51, 374—377).—Both air and carbon dioxide show a slight increase in dielectric constant with increasing frequency over the wave-length range 600—60 metres.
J. W. SMITH.

Variation of dielectric constants of gases and vapours with temperature. II. Ethyl ether, methyl ether, ethylene oxide, and acetone. H. A. STUART (Z. Physik, 1928, 51, 490—510).—A description is given of the apparatus with which the temperature variation of the dielectric constant of methyl and ethyl ethers, ethylene oxide, and acetone in the temperature range 20—180° was measured in the gaseous state. The electrical measurements were carried out with the apparatus previously described (A., 1928, 460). A Spindler-Hoger standard air condenser calibrated at the P.T.R. was used as a capacity standard. Accurate values of the vapour densities of the compounds have been determined. The electric moments are: ethyl ether 1.14×10^{-18} , methyl ether 1.29×10^{-18} , ethylene oxide 1.88×10^{-18} , acetone 2.84×10^{-18} . The electric moment of the water molecule is calculated from the results of Zahn as 1.79×10^{-18} . The results are compared with those of other authors and the molecular models of methyl and ethyl ethers discussed, together with the connexion between the electrical distribution of the charge of the molecules, association, and the van der Waals constant.
G. E. WENTWORTH.

Dielectric constants of liquid hydrogen fluoride. K. FREDENHAGEN and J. DAHMLOS (Z. anorg. Chem., 1929, 178, 272—274).—The dielectric constant of hydrogen fluoride decreases from 174.8 at -73° to 83.6 at 0°. Hydrogen fluoride therefore belongs, like water and hydrogen cyanide, to the group of solvents which have an abnormally high dielectric constant.
A. R. POWELL.

Dielectric constants and absorption indices of several alcohols for short electric waves. S. MIZUSHIMA (Proc. Imp. Acad. Tokyo, 1929, 5, 15—16).—Dielectric constants and absorption indices of methyl, propyl, isobutyl, and amyl alcohols are given together with those of glycerol for a wavelength of about 60 cm. over a range of temperatures. Comparison with earlier measurements (A., 1928, 934) indicates the existence of anomalous dispersion. Calculation of the molecular radii from the Debye theory gives the following values: methyl 1.7×10^{-8} , propyl 2.3×10^{-8} , isobutyl 2.3×10^{-8} , and amyl alcohol 2.5×10^{-8} cm. These values accord well with those obtained from critical data.
F. J. WILKINS.

Dielectric constants of some organic solvents. Y. MATSUIKE (Proc. Imp. Acad. Tokyo, 1929, 5, 29—31).—The dielectric constants of benzene, toluene, carbon disulphide, carbon tetrachloride, ethyl ether, and chloroform have been measured at various temperatures between their b. p. and f. p. with a probable error of about 0.2%.
F. J. WILKINS.

Electric moment of primary alcohols. P. N. GHOSH (Nature, 1929, 123, 413—414).—Since the primary alcohols have practically the same dipole moment, it is inferred that the dipole moment is due to the polarisation of the oxygen atom by the hydrogen atom on one hand and by the carbon atom on the other. Hence the binding forces acting on the carbon atom reacting with the oxygen are the same whether the chain is long or short, open or closed. *iso*Alcohols give differing values. A. A. ELDRIDGE.

Refraction of beams of molecules. I. I. RABI (Nature, 1929, 123, 163—164).—The refraction of beams of molecules in magnetic or electric fields is considered in analogy to optical refraction.

A. A. ELDRIDGE.

Refractivity of gaseous compounds. G. W. BRINDLEY (Nature, 1929, 123, 165).—If $(\mu-1)_R$ is the refractivity of the substance R in the gaseous state, under normal conditions as defined by Cuthbertson, where μ is the refractive index, then $(\mu-1)_{HCl} = \frac{1}{2}(\mu-1)_{CH_4}$, $(\mu-1)_{HBr} = \frac{1}{2}(\mu-1)_{CH_4}$, $(\mu-1)_{CCl_4} = \frac{1}{2}(\mu-1)_{CH_4}$, $(\mu-1)_{CBr_4} = \frac{1}{2}(\mu-1)_{CH_4}$, $(\mu-1)_{CS_2} = \frac{1}{2}(\mu-1)_{CH_4}$. The fractions are closely related to the number of loosely bound electrons. In general, such simple relations do not appear to hold.
A. A. ELDRIDGE.

Stability and molecular volume of organic groups in molecular compounds. E. HERTEL [with E. RISSEL and F. RIEDEL] (Z. anorg. Chem., 1929, 178, 202—212).—Freshly-precipitated nickel cyanide reacts with ammonia, primary aliphatic amines, dimethylamine, and trimethylamine, yielding co-ordination complexes containing 1 mol. of ammonia or amine. Anhydrous nickel cyanide obtained by heating any of the above compounds to constant

weight reacts with the evolution of heat with the anhydrous amines mentioned above and with aniline to form complexes containing 2 mols. of the amine. The mol. vol. of the primary amines in the complexes containing 1 mol. of amine is always greater than its zero volume (cf. Lorenz, A., 1916, ii, 311), the difference increasing with the length of the carbon chain; the zero volume increases by about 15 c.c. for every methylene group in the chain. The logarithm of the vapour pressure of these compounds is directly proportional to the reciprocal of the temperature and the stability of the primary amine complexes decreases with increasing mol. wt. of the amine. On the other hand, the benzylamine compound, $\text{Ni}(\text{CN})_2 \cdot \text{CH}_3\text{Ph} \cdot \text{NH}_2$, is less stable than the ω -phenylethylamine compound, $\text{Ni}(\text{CN})_2 \cdot \text{CH}_3\text{Ph} \cdot \text{CH}_2 \cdot \text{NH}_2$. This may be explained on the assumption that in the latter case the nickel atom is co-ordinatively quadrivalent, the third co-ordination valency being attached to the amino-group and the fourth to the phenyl nucleus. The correctness of this view is borne out by the fact that a second group, e.g., H_2O or NMe_3 , may be introduced easily into the benzylamine compound, whereas this cannot be done in the case of the ω -phenylethylamine compound. A. R. POWELL.

Molecular diameters in gas reactions. R. C. TOLMAN, D. M. YOST, and R. G. DICKINSON (Science, 1928, 67, 241).—Previous conclusions (A., 1927, 604) are not greatly affected by the discovery of a numerical error. A. A. ELDRIDGE.

Derivation of grating forces, grating energies, ionic dimensions, and compressibilities of simple salts by wave mechanics. H. BRUCK (Z. Physik, 1928, 51, 707—727).—Mathematical.

R. W. LUNT.

Liquid drops on the same liquid surface. J. SETHI, C. ANAND, and L. D. MAHAJAN (Phil. Mag., 1929, [vii], 7, 247—253).—Drops of liquid on the surface of the same liquid are divided into two classes. Primary drops arise from the introduction of liquid from an external source and represent the portions which do not mix immediately with the main body of the liquid. Secondary drops are those which arise from the splashing of liquid from the main body. Various methods for the production of such drops are described. The formation of primary drops appears to be easiest with a liquid having a surface tension 20—80 dynes/cm., a viscosity up to 0.25 c.g.s. unit, and a density about unity. For the production of secondary drops best results are obtained with different liquids, depending on the method of production. The best primary drop formation with a phenol solution was obtained with a concentration of 30% and with a Boys soap solution at a concentration of 15%. Both these solutions exhibit a sudden small rise in surface tension at the concentrations given.

A. E. MITCHELL.

Superficial properties of mercury. E. PERUCCA (Phil. Mag., 1929, [vii], 7, 418—419).—Previous work by the author (Atti Accad. Sci. Torino, 1921, 57, 81, etc.) offered experimental support of the deductions of Oliphant and of Bircumshaw that in the surface of liquid mercury there is a superficial molecular or atomic orientation. A. E. MITCHELL.

Surface tension of liquid sulphur dioxide. V. M. STOWE (J. Amer. Chem. Soc., 1929, 51, 410—415).—The surface tensions (capillary-tube method) and densities of liquid sulphur dioxide are recorded for the range -79° to 50° . Between -20° and 50° the equation γ (dynes/cm.) = $0.061534(157.5 - t)^{1.2}$ holds to within 5%; the results indicate that the liquid is practically unassociated over this temperature range. Sulphur dioxide comes between chloroform and benzene in Hildebrand's solubility table.

S. K. TWEEDY.

Surface tension of insulating liquids under the influence of an electric field. M. J. BICKERMAN (J. Phys. Radium, 1928, [vii], 9, 386—389).—Theoretical. It has been calculated that the lowering of the surface tension of a liquid, produced by an electric field normal to its surface, is given by $-\Delta\gamma - \delta E^2/8\pi\epsilon$, where $\Delta\gamma$ is the change in surface tension, δ the thickness of the surface layer, E the field strength (measured in the air), and ϵ the specific inductive capacity of the liquid. It is pointed out that even for high values of E , $\Delta\gamma$ will be very small. It is suggested that those authors who have failed to detect any alteration in the surface tension due to the influence of an electric field were not using sufficiently delicate methods. J. L. BUCHAN.

Interpretation of X-ray crystal photographs. I. Use of photographic grids. W. H. GEORGE (Phil. Mag., 1929, [vii], 7, 373—384).—The photographic plate or film is supported in the X-ray camera entirely by geometric constraints. A printing frame similarly fitted with geometric constraints is employed, with a light exposure, to obtain on the X-ray photograph an image of some network suitable for the interpretation of the particular type of X-ray photograph. A single calibration photograph serves to fix accurately the geometric constraints of the printing frame and any subsequent X-ray photograph contains both the photograph required and an accurately aligned reference grid. Various applications to X-ray and other types of research are discussed. A. E. MITCHELL.

Adsorption and crystal form. C. H. SAYLOR (Fifth Colloid Symposium Monograph, 1927, 49—54).—A general discussion of the effect on the crystal form of substances which crystallise in more than one modification or habit produced by adsorption of ions on certain faces or habits. CHEMICAL ABSTRACTS.

Spiral markings on carborundum crystals. A. W. C. MENZIES and C. A. SLOAT (Nature, 1929, 123, 348—349).—A photograph and a description of spiral markings on the smooth hexagonal, basal pinakoid, surfaces of carborundum crystals are given.

A. A. ELDRIDGE.

Isomorphous mixtures in the calcite group. G. BLIHIN (Mem. Soc. Russe Min., 1927, 56, 3—36; Chem. Zentr., 1928, ii, 975).

Atomic spacing in gypsum crystals. J. NAGY (Z. Physik, 1928, 51, 410—412).—The distances between corresponding planes in gypsum crystals from different sources are not quite constant, the greatest differences observed being about 2.5 per mille. J. W. SMITH.

Systematic arrangement of neptunite and babingtonite. B. GOSSNER and F. MUSSGUG (Zentr. Min. Geol., 1928, A, 274—281; Chem. Zentr., 1928, ii, 1198).—Neptunite has a 16.54, b 12.64, c 10.04 Å., $\beta=115^\circ 38'$, with 8 mols. in the unit cell; the space-group may be C_{2h}^3 or C_{2h}^2 ; the formula $\text{FeNa}_2\text{Si}_2\text{O}_6\text{Si}_2\text{TiO}_6$ is suggested. Babingtonite, the formula of which is preferably written $\text{CaFeSi}_2\text{O}_6\text{SiO}_3$, has a 7.54, b 12.43, c 6.73 Å., α $93^\circ 48'$, β $86^\circ 9'$, γ $112^\circ 22'$; the axial ratio is computed to be $a:b:c=0.607:1:0.541$. A. A. ELDRIDGE.

Crystal structure of solid mercury. M. WOLF (Z. Physik, 1929, 53, 72—79).—A thermostatic X-ray spectrograph is described, by means of which investigations of crystal structure may be carried out at various temperatures. With this apparatus the crystal structure of mercury at -80° has been investigated and a simple rhombohedral structure found, in agreement with the observations of McKeehan and Cioffi (A., 1923, ii, 864) and Terrey and Wright (this vol., 16). It was found that the preparation obtained from small drops of mercury (mean diameter 10μ) persisted in a supercooled state even at -80° and was very difficult to crystallise out. J. W. SMITH.

Physical purity and powder-rontgenogram. N. H. KOLKMEIJER (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 1028—1029).—Polemical against Levi (cf. A., 1928, 1079) concerning the crystallographic identity of the two forms of mercuric oxide. N. M. Blich.

X-Ray levels of the rare earths, and the deviations from Moseley's laws. G. PICCARDI (Atti R. Accad. Lincei, 1928, [vi], 8, 414—418).—The regularities in the X-ray levels of the elements of the rare earths have been made the basis of a comparison of the corresponding levels of other elements of the periodic system. Using the values of the X-ray levels of the rare earths as the basis of the calculation of the constants in Moseley's law, the deviations of the levels for other atoms from the values obtained from this law have been plotted against atomic number. The irregular curves so obtained present certain regularities on analysis. The deviations for elements before the rare earths decrease (from positive to negative) on passing from the K level through the levels L_1 , L_2 , L_3 , etc., to the O level. For elements after the rare earths the corresponding deviations are all positive, but do not exhibit the same regularities. Within a given set of X-ray levels a certain regularity is shown: for example, the deviations for the L series increase in the order L_3 , L_2 , L_1 . But whereas the curves for different sets of X-ray levels for the earlier elements are separated, for the heavier elements considerable overlapping occurs among the curves for the different series. The deviations for all levels are of the same order of magnitude, reaching maximum values of about 4 in the case of the lighter elements, when the levels are expressed as $\sqrt{\nu}/R$, where ν is the frequency and R the Rydberg constant.

F. G. TRYHORN.

Influence of X-rays on the structure of bismuth and tellurium. III. E. ADINOLFI (Atti R. Accad. Lincei, 1928, [vi], 8, 381—388).—The specific heat of bismuth is increased by about 14% and that of

tellurium by about 8% by the exposure of these metals to X-rays. This result is attributed to a change of structure of the metals. Indications of this change were obtained in the case of bismuth by measuring the changes of resistance during solidification of spirals of bismuth before and after exposure to X-rays. F. G. TRYHORN.

Crystal structure of nickel. L. MAZZA and A. G. NASINI (Phil. Mag., 1929, [vii], 7, 301—311).—X-Ray examination of nickel produced by electrolytic deposition, separation from the carbonyl, and by reduction of the oxide has shown the metal to be crystallised in face-centred cubes, the mean value for the edge of the elementary cell being 3.514 ± 0.002 Å., in close agreement with those of Wever (B., 1922, 359A), McKeehan (Physical Rev., 1923, 21, 402), and of Lange (A., 1923, ii, 402). No confirmation of Hull's observation (Physical Rev., 1919, 14, 540) of the existence of body-centred cubes was obtained. Annealed cold-drawn nickel shows no recrystallisation up to 940° . Characteristic recrystallisation structures are obtained by annealing at 1000° and above. Prolonged annealing at 1200° gives a recrystallisation into irregularly oriented coarse grains. Quenching produces no changes in the nickel lattice. A. E. MITCHELL.

Direct determination of Thomson coefficients in single-crystal zinc rods. L. A. WARE (Proc. Iowa Acad. Sci., 1927, 34, 282).

CHEMICAL ABSTRACTS.

Crystal structure of rhenium. V. M. GOLDSCHMIDT (Naturwiss., 1929, 17, 134—135).—Using the Debye-Scherrer method it was found that rhenium has a hexagonal close-packed structure, $a=2.752 \pm 0.001$, $c=4.448 \pm 0.002$ Å. The crystalline structure of rhenium resembles that of osmium, whilst tungsten, the element immediately preceding rhenium in the periodic table, has a body-centred cubic structure. The atomic radius of rhenium is calculated from the mean distance between the atoms in the crystal. It lies between those of tungsten and osmium, being 1.371 Å. From the lattice constants and the at. wt., the density of rhenium can be calculated. The specimen used, which contained 0.3% of molybdenum, gave 21.33. After making a small correction for the molybdenum the density of the pure element is found to be 21.40 ± 0.06 . This lies between the values for tungsten and osmium, and is in agreement with the value obtained by other methods. A. J. MEE.

Determination by X-rays of density and axial ratio of hexagonal silver iodide. N. H. KOLKMEIJER, W. J. D. VAN DOBBENBURGH, and H. A. BOEKENOOGEN (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 1014—1027).—X-Ray investigations were made of a specimen of silver iodide of d 5.68, supposed to be physically and chemically pure. Powder photographs were made of this specimen, and also of one of d 5.49, and evidence of cubic structure for the former and hexagonal structure for the latter specimen was obtained. By spectrographic means it is concluded that this evidence as to structure is correct, and the axial ratio is determined as 1.633(4). N. M. Blich.

Reflexion of soft X-rays. S. D. GEHMAN (Physical Rev., 1929, [ii], 33, 141—144).—The relation between the wave-length of soft X-rays and the reflecting power of a metal mirror was investigated; the latter was measured by a photo-electric method, as a function of the voltage for a given angle of incidence and as a function of the angle for a given voltage. Mirrors of aluminium, carbon, and platinum were employed. The reflecting power-plate voltage curves for the light elements aluminium and carbon show a maximum related to a critical potential.

N. M. BLYTH.

Soft X-rays from crystal faces. O. W. RICHARDSON and U. ANDREWES (Nature, 1929, 123, 344).—An attempt to extend earlier experiments (A., 1928, 692) to diamond failed on account of the immeasurably high resistance of the material. With graphite, however, between 70 and 320 volts 17 discontinuities have been observed, each agreeing with a value, or with the mean of two values a few volts apart, previously found with carbon. Fifteen discontinuities observed with the carbon target were absent with the graphite target, *i.e.*, the number of discontinuities from a single crystal surface is smaller than from a polycrystalline surface. A. A. ELDRIDGE.

Soft X-rays from a single-nickel crystal. S. R. RAO (Nature, 1929, 123, 344—345).—The results (cf. preceding abstract) suggest that if an ideal crystal surface were employed inflexions would appear at 63.8, 72.2, 106.2, and 116.0 volts. The former two values can be associated with transitions from the $M_{II,III}$ level in the nickel atom, and the latter two with transitions from the M_I level. Surface alteration of the non-crystalline metallic target on electronic bombardment may account for the large number of inflexions which have been reported.

A. A. ELDRIDGE.

X-Ray examination of some salts of the fatty acids. S. H. PIPER (J.C.S., 1929, 234—239).—The spacing between the crystal planes in the potassium salts of the fatty acids from formic up to lignoceric acid has been measured. Since salts of long-chain compounds of this type crystallise with these planes separated by the lengths of two molecules placed end to end with like groups in contact, the spacing measured may be regarded as twice the effective length of the molecule. The spacing increases linearly with increase in the number of carbon atoms for the normal potassium salts. A similar linear increase in spacing, but with a lower rate of increase, is shown by the potassium hydrogen salts of these acids. The chain in this type of salt cannot be accounted for by a normal tetrahedral angle of $109^\circ 28'$ between the lines joining the centres of successive carbon atoms. A minimum angle of $111^\circ 46'$ is required.

F. G. TRYHORN.

X-Ray contributions to the problem of polymerisation. G. L. CLARK (Ind. Eng. Chem., 1929, 21, 128—133).—The X-ray method of investigating crystal structure is discussed and its application in the study of polymerised substances such as rubber, cellulose, proteins, and resins is explained in outline. The observation that the unit cell of these substances is very much smaller than would be anticipated on

physico-chemical grounds and contains only a few simple chemical molecules is discussed.

H. INGLESON.

Deformation of fibrous materials. R. O. HERZOG and W. JANKE (Z. Physik, 1929, 52, 755—758).—By taking X-ray diagrams both parallel and at right angles to the direction of stress, it has been shown that both mercerised cellulose and natural silk on rolling or pressing yield a structure of the anisotropic class IV.

J. W. SMITH.

Supermolecular state of polymerised substances in relation to thin films and interfaces. S. E. SHEPPARD, A. H. NIETZ, and R. L. KEENAN (Ind. Eng. Chem., 1929, 21, 126—127).—A discussion of the theories of the molecular constitution of rubber, cellulose, and proteins advanced by Hess and Pringsheim and by Staudinger.

H. INGLESON.

Separation of the Faraday effect into two phenomena of different origin. Diamagnetic and paramagnetic rotatory polarisation. Law of magnetisation of a crystal. Bohr's magneton. J. BECQUEREL and W. J. DE HAAS (J. Phys. Radium, 1928, [vii], 9, 346—356, and Z. Physik, 1928, 52, 678—694).—In order to obtain evidence for the view that the large magnetic rotatory power of certain minerals which contain rare-earth elements is of paramagnetic origin, the variation of the rotatory power of tysonite with the intensity of the magnetic field has been investigated. At very low temperatures it is to be expected that the rotation will cease to be proportional to the field. Experiments made at the low temperatures obtainable by means of liquid helium show that this is the case. The following hyperbolic tangent relation is found to hold between the paramagnetic rotation ρ and the field H : $\rho = \rho_s \tanh(\Sigma H/RT)$. ρ_s is the saturation magnetisation per g.-mol. and has almost exactly the value of the Bohr magneton. This expression is derived from the theoretical views of Lenz and of Ehrenfest concerning the magnetisation of a crystal along its principal axis, on the assumption that the magnetic rotation is proportional to the magnetising effect producing it, which appears probable. The existence of paramagnetic rotatory polarisation is therefore proved.

O. J. WALKER.

Piezo-electric amorphous and crystalline substances in an electric field. A. V. SCHUBNIKOV and B. K. BRUNOVSKI (Bull. Acad. Sci. U.R.S.S., 1928, 367—374).—Experimental results are given which indicate that every dielectric, when placed in an electric field, owing to orientation of its molecules or other structural units, becomes more or less markedly piezo-electric. When such dielectric is subjected to shock, it assumes a state of vibration, that is, of periodic compression and expansion, the result being the establishment of an internal subsidiary electric field, which changes its direction during the vibration and so alternately strengthens and weakens the original electric field.

T. H. POPE.

High-frequency hysteresis loss in steels. W. NEUMANN (Z. Physik, 1928, 51, 355—373).—Data are given for the hysteresis loss and remanence of two varieties of Swedish bar steel and of an iron alloy

containing 50% Ni at 500, 1500, and 2550 cycles per sec. R. W. LUNT.

Electrical conductivity in relation with mechanical stress in rock salt. Z. GYULAI and D. HARTLY (Z. Physik, 1928, 51, 378—387).—The conductivity of rock salt suddenly compressed between one pair of crystal faces increases and then, the compression remaining constant, decreases to the initial value in approximately 20 min. The crystal is then in a hardened state, and considerable increase in mechanical stress is required to produce a further increase in conductivity. Crystals of various thickness were examined in the stress range 20—200 kg./cm.² R. W. LUNT.

Hall effect and other properties of the copper-antimony series of alloys. E. STEPHENS and E. J. EVANS (Phil. Mag., 1929, [vii], 7, 161—176).—The temperature coefficient of resistance, thermo-electric power, Hall effect, specific heat, and density of fully annealed copper-antimony alloys have been measured. Singular points corresponding with both Cu₂Sb and Cu₃Sb were obtained in each of the curves showing the relation between all these constants and the concentration of one metal in the alloy. No evidence of the formation of Cu₂Sb and Cu₃Sb was obtained from the change of the temperature coefficient of the resistance with the antimony concentration. The electrical properties of Cu₃Sb were strongly modified by annealing, whilst those of Cu₂Sb remained practically unchanged. A. E. MITCHELL.

Magnetic susceptibilities of some amalgams and binary alloys. W. G. DAVIES and E. S. KEEPLING (Phil. Mag., 1929, [vii], 7, 145—153).—The relative magnetic susceptibilities of dilute amalgams of gold, tin, indium, and gallium with respect to that of mercury have been determined. The diamagnetic susceptibility of the amalgams increases as the concentration of the solute metal increases. The atomic effect of the dissolved metal on the susceptibility of mercury is greatest in the case of indium. Similar measurements have been made with copper-magnesium and copper-antimony alloys. In the first series the susceptibility-composition curve shows maxima corresponding with eutectics and minima corresponding with compounds indicated by the equilibrium diagram. In the second series of alloys annealing increases the susceptibility, particularly over the region 20—60% Cu. Maxima on the susceptibility-composition curve again correspond with eutectics, but the only compound definitely indicated for the unannealed alloy is Cu₃Sb₂ and for the annealed alloy Cu₂Sb corresponding with the change of phase to be expected, from the equilibrium diagram, on annealing. A. E. MITCHELL.

Conductivity and cold-working. M. MASIMA and G. SACHS (Z. Physik, 1928, 51, 321—327).—Experiments are described dealing with the dependence of the electrical resistance of brass on the extension of the crystals, the degree of hardening of the metal, annealing, and temperature. Curves are given showing the relation between the resistance, the tensile strength, and compressibility. The temperature coefficient of the conductivity of the metal is shown to be independent of mechanical strains. D. W. BANDEY.

Magnetostriction. L. W. MCKEEHAN (Z. Physik, 1928, 52, 752—754).—Polemical against Schulze (A., 1928, 1314). G. E. WENTWORTH.

Initial conductivity of gypsum and rock salt. N. A. SALESSKY (Z. Physik, 1928, 52, 695—707).—The initial conductivities of gypsum and rock salt were observed at intervals of 0.01—0.06 sec. after the application of potential, and the impossibility of extrapolation was demonstrated. Ohm's law is obeyed by both substances. The applicability of the superposition principle, and the errors due to a previous passage of current, were confirmed. The temperature variation of the initial conductivity of gypsum is probably represented by an exponential function; that of rock salt, however, depends on the time period at which the measurements were made. G. E. WENTWORTH.

Initial current in quartz. A. D. GOLDHAMMER (Z. Physik, 1928, 52, 708—725).—A photographic method is used for the study of the initial current in two types of quartz. The dependence on time of the initial current in the first 4 to 17×10^{-2} sec. is given by $i - at^{-n}$, where the letters have their usual significance. The potential-current graph is not a straight line; it changes its sign with alteration in the time period. The superposition principle is inapplicable, the reason being that passage of current diminishes the conductivity in the direction of the current and increases it in the opposite direction. If the crystal is earthed for some time the unipolarity changes sign. G. E. WENTWORTH.

Recrystallisation of aluminium. II. A. E. VAN ARKEL and M. G. VAN BRUGGEN (Z. Physik, 1928, 51, 520—533).—Strong deformation of a crystalline body such as aluminium produces very small crystals which act as a nucleus for recrystallisation. These small nuclei are formed by the stresses acting within the lattice. The second crystallisation is not only proportional to the amount of cold working but, in contradistinction to the idea of recrystallisation by cold turning, is largely dependent on the initial state of the material. The surface recrystallisation of pure aluminium is much greater than in technical aluminium. Numerous etchings are shown and the results are compared with those of Smithells in the recrystallisation of pure tungsten. G. E. WENTWORTH.

Recrystallisation of single aluminium crystals. I. The orientation of crystals produced by cold turning, the deformation being small. W. G. BURGERS and J. C. M. BASART (Z. Physik, 1928, 51, 545—556).—An attempt is made to elucidate the problem of the orientation of crystals produced by the cold turning of aluminium when the deformation is relatively small (10—15% extension). These crystals appear to be connected on the average with the position of the mother crystal, but they are widely scattered, although the mother crystal must exert some influence. Experimental results show that the direction of deformation has a small influence, but the scattering is so large as to make any method of estimation difficult. G. E. WENTWORTH.

Measurements of ultrasonic velocities in liquids. R. W. BOYLE, J. F. LEHMANN, and S. C.

MORGAN (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 371—378).—The determination of the velocity of ultrasonic waves in liquids by modifications of the method of stationary waves is described. Methods are also given for use when a moderate quantity of liquid is available. The change of velocity in sodium chloride solution with small changes of concentration at a constant temperature of 17° was investigated. The velocity was found to increase slightly as the concentration is increased. Experiments were also carried out to measure the change in velocity with change in temperature from 0° to 20° in water and in sodium chloride solution. In both cases the velocity increases with rise of temperature.

A. J. MEE.

Electromotive potential and electrokinetic potential of graphite [and other elements]. N. THON (Compt. rend., 1929, 188, 253—254).—A relation between the electromotive (ϕ) and electrokinetic (ζ) potentials analogous to that found for gold (A., 1928, 953) has been established for graphite, but in this case ϕ becomes more positive with an increase in the concentration of the electrolyte, whilst which is negative, decreases in value. This explains the action of graphite as a "borrowing electrode" and its electromotive behaviour as the metal of the ions in the solution. Platinum, silver, mercury, and copper behave similarly to gold.

J. GRANT.

Theory of electrical rectification. R. DE L. KRONIG (Nature, 1929, 123, 314).

Superconductors. W. J. DE HAAS (Nature, 1929, 123, 130—131).—Combinations of non-superconducting with superconducting metals (copper, silver, or antimony with tin; bismuth with thallium) have been studied. Combinations of antimony (but not copper) with tin and of bismuth with thallium become superconductors. Although neither gold nor bismuth is a superconductor at 1.5° Abs., their eutectic alloy is a superconductor.

A. A. ELDRIDGE.

Measurement of the thermo-electric Thomson effect down to the temperature of liquid hydrogen. G. BORELIUS, W. H. KEESOM, and C. H. JOHANSSON (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 1046—1058).—In view of its bearing on the electron theory of metals the temperature dependence of the Thomson effect below the temperature of liquid air was investigated, using wires of copper and silver alloyed with small quantities of gold, and also pure copper wire. The alloys were used for the lowest temperatures to minimise errors due to the variation of heat conductivity of pure metals with temperature; steps were also taken to avoid errors due to the Peltier effect. The specific heat-conductivity was measured and plotted against temperature. The measurements and calculations of the Thomson effect for a number of temperatures are tabulated and plotted. The thermo-electromotive forces of couples formed by the wires investigated and also with lead were measured for various temperatures, tabulated, and thence calculated per degree.

N. M. BIGH.

Theory of Heusler alloys. O. VON AUWERS and H. WEINOLDT (Z. Physik, 1928, 51, 754—756).—Polemical.

R. W. LUNT.

Theory of Heusler alloys. A. KUSSMAN and B. SCHARNOW (Z. Physik, 1928, 51, 757—758).—Polemical.

R. W. LUNT.

Birefringence and dichroism of thin layers of iron obtained by distillation. M. CAU (Compt. rend., 1929, 188, 246—249).—The formulæ hitherto obtained by the author (this vol., 251) are valid only to a first approximation. Exact formulæ are deduced representing the effect on a rectilinear vibration of simultaneous rectilinear birefringence and dichroism having the same principal directions. Formulæ valid to a second approximation are then obtained, and a good agreement is shown to exist between the observed and calculated results.

J. GRANT.

Platinum thermometer temperature scale. F. E. HOARE (Phil. Mag., 1929, [vii], 7, 384—386).—A simplified method for finding the correction, to a platinum thermometer, for any value of the difference coefficient in the equation $X = (t - 100)t$ is given. At temperatures as high as 1200° the correction is shown to give temperatures accurate to 0.1°.

A. E. MITCHELL.

Thermal conductivity of solid and liquid sulphur. G. W. C. KAYE and W. F. HIGGINS (Proc. Roy. Soc., 1929, A, 122, 633—646).—An investigation has been made of the thermal conductivity of solid and liquid sulphur over the temperature range 20—210°, a region embracing the transition point from rhombic to monoclinic sulphur (95°), the "natural" m. p. of monoclinic sulphur (115°), and the change point of liquid sulphur (160°). In the case of solid sulphur, measurements were made on the rhombic and monoclinic varieties, each in the form of crystalline aggregates, and on the plastic modification. The progressive change in thermal conductivity was followed during the slow transition at the ordinary temperature from the unstable plastic to the stable rhombic form, and the influence of temperature on the rate of transformation was studied. The experiments demonstrate the effect of the previous thermal history on the velocities of the various transformations. The measurements were made by means of a "plate" method similar to that previously described (A., 1928, 114), using a small temperature drop, usually from 3° to 5°, across the test specimen. For the measurements on solid sulphur, it was necessary to employ glycerin films between the test layer and the surfaces of the hot and cold blocks. The following values were obtained: rhombic aggregate, 0.00065 (20°), 0.00061 (40°), 0.00058 (60°), 0.00055 (80°), 0.00054 (95°, change point); monoclinic aggregate, 0.00037—0.00040 (100°); liquid, 0.00031 (115°, m. p.), 0.00031 (120°), 0.00032 (140°), 0.00033 (160°), 0.00033 (165°), 0.00034 (170°, change-point region 160—170°), 0.00036 (190°), 0.00037 (210°); plastic, 0.0002 (20°).

L. L. BIRCUMSHAW.

Thermal conductivity of lead and of single- and poly-crystal zinc. C. C. BIDWELL and E. J. LEWIS (Physical Rev., 1929, [ii], 33, 249—251).—Determinations were made over the range —250° to 100°, using an adaptation of the Forbes bar method (cf. Bidwell, A., 1926, 1087). The thermal conductivity increases as the temperature is lowered, but

shows no great increase at very low temperatures as was found for lithium. Conductivity is about 18% better for single- than for poly-crystal zinc, and is about 7% poorer for a sample cast in air than for one prepared in a vacuum.

N. M. BLIGH.

General formulæ for calculating the atomic or molecular heat and the specific heat of elements in the solid state. J. MAYDEL (Z. anorg. Chem., 1929, 178, 113—145).—The true atomic heat (u) of any element at any temperature (t) is given by the equation $u = \gamma - \alpha/(t + \beta)$, where β and γ are constant parameters for that element and α is a constant for all elements and equals 939.8. The values of β and γ for all the elements have been calculated and are shown to be periodic functions of the atomic number; when their values are plotted against one another for all the elements two intersecting curves are obtained, both of which are hyperbolas identical with the curve for μ given by the above equation. The elements may therefore be divided into two classes according to the line on which the point represented by their β and α values falls. For class I the equation to the curve is $\beta = B_1 - \alpha(\gamma - G_1)$, and for class II $\gamma = G + \alpha/(\beta + B)$. Hence the constants G_1 and B_1 and G and B are the origins of a system of co-ordinate axes which are asymptotic to the curves for class II and class I, respectively. The calculated values for these constants are $G = 6.05$ kg.-cal., $B = 0^\circ$, $G_1 = -0.242$ kg.-cal., and $B_1 = 492.3^\circ$. Hence for elements of class II the atomic heat at 0° is 6.05 kg.-cal., which agrees with the value according to Dulong and Petit's law. To this class belong the elements of group 0, the four elements which succeed and the three elements which precede each of these in atomic number, but there are several exceptions; all the other elements belong to the first class except iodine and mercury, the β, γ points of which apparently do not fall on either curve. The atomic heat of elements of the first class may be calculated from the equation $u_1 = 0.242 + \alpha(t + 2\beta - 492.3)/(t + \beta)(492.3 - \beta)$. As every element has its own value for β , there is obviously no temperature at which the second expression on the right-hand side becomes zero or the same for all elements of this class, and hence these elements show more or less deviation from Dulong and Petit's law according as to whether their β, γ points lie remote from or near to the intersection of the two curves. Equations are given for calculating the true and mean specific heats of the elements of both classes, the mean atomic heat, and the heat required to raise 1 g.-atom from t_1 to t_2 , and the effect of allotropic transformations on the atomic heat is discussed. Tables are given showing the values of β and γ for all the elements, and the atomic heats at various temperatures calculated from these values are compared with those obtained experimentally by various authors; in general, the agreement between calculated and observed values is very good.

A. R. POWELL.

Specific heat of tungsten between 90° and 2600° Abs. C. ZWIKKER (Z. Physik, 1928, 52, 668—677).—The inconsistency in the published values of the specific heat of tungsten has led the author to a redetermination over a wide temperature range. A description of the experimental method is given for

the high-temperature determinations, for which C_p increases linearly with rising temperature, whilst C_v falls, remaining below 8 g.-cal. per g.-atom.

G. E. WENTWORTH.

Specific heat of molybdenum from 250° to -40° . D. COOPER and G. O. LANGSTROTH (Physical Rev., 1929, [ii], 33, 243—248).—Existing data for the specific heat of molybdenum being untrustworthy, experiments were made with a slightly modified Richards adiabatic calorimeter, by which values from high temperatures could be obtained. Values accurate to about 1% are given for the range -30° to 300° by the equation $C_p = 0.0593 + 0.000013(T' + 40) - 0.0265/(T' + 40)^{1.06}$. Stern's equation is linear (cf. A., 1928, 1083) and agrees with the values given between 50° and 300° . Below 50° the curve shows a decided bend.

N. M. BLIGH.

Specific heat of manganese phosphide. B. G. WHITMORE (Phil. Mag., 1929, [vii], 7, 125—129).—The specific heat of manganese phosphide shows an increase at 16° . This is of the order required by the Weiss theory of ferromagnetism, but the temperature is just below the magnetic critical temperature at which, according to the theory, the phenomenon should occur.

A. E. MITCHELL.

Specific heats of acetone, methyl, ethyl, and *n*-propyl alcohols at low temperatures. S. MITSUKURI and K. HARA (Proc. Imp. Acad. Tokyo, 1929, 5, 27—28).—The specific heats of acetone, methyl, ethyl, and *n*-propyl alcohols have been measured over the temperature range 170 — 270° Abs.

F. J. WILKINS.

Heats of fusion and specific heats of calcium and magnesium. E. ZALESINSKI and R. ZULINSKI (Bull. Acad. Polonaise, 1928, A, 479—505).—The specific heats of calcium (99.13% Ca) and of magnesium (98.68% Mg) over a range of temperature have been determined in a silver-plated brass calorimeter furnished with a lid of iron, the only metal that does not react with calcium and magnesium at high temperatures. The mean specific heats found were: (a) Calcium, between 20° and 304° , 0.1610; 20 — 504° , 0.1764; 22 — 520° , 0.1768; 20 — 697° , 0.1887; 21 — 755° , 0.1927; 22 — 785° , 0.1901; 22 — 785° , 0.1724; 22 — 802° , 0.1724; 810 — 930° (liquid), 0.2670. The lower values were obtained when the specimen was first heated at about 800° and the specific heats determined on cooling and are due to the presence of two allotropic modifications of calcium. (b) Magnesium, between 22° and 625° , 0.2823; 650 — 775° (liquid), 0.2880. The heats of fusion were also determined in an electrically heated silica vacuum oven in an atmosphere of argon, the heat of fusion being calculated from the duration of crystallisation by Tammann's formula; the transition point of the two forms of calcium was about 800° . The results obtained were: (a) from duration of crystallisation; calcium, 74.0 g.-cal./g., heat of transition, 5.75 g.-cal./g.; magnesium, 46.0 g.-cal./g.; (b) calorimetrically; calcium 78.5 g.-cal./g., magnesium, 55.5 g.-cal./g.

A. I. VOGEL.

M.p.-pressure curves. F. SIMON and G. GLATZEL (Z. anorg. Chem., 1929, 178, 309—316).—Tammann's equation ("Aggregatzustände," Leipzig,

1922) connecting the m. p. of a substance with the pressure is shown to give results for high pressures which are much too low; the p - T curve bends backwards. A much more accurate expression, derived from van der Waals' vapour-pressure equation, is the following: $\log(a+p) = c \log T + b$, where a , b , and c are constants, the values of which have been calculated for 19 substances. Using these constants, the deviations of the calculated values of the m. p. for pressures up to 12,000 atm. from the observed values are less than 5%.

A. R. POWELL.

Melting curve of hydrogen to 245 kg./cm.² W. VAN GULIK and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1928, **31**, 1059—1060; cf. A., 1927, 301).—Continuing previous work, the curve is examined over the range of pressure 94—237 atm., corresponding with a temperature range 16.31—20.34° Abs., and gives results which combine with the previous ones for a smooth curve.

N. M. BLIGH.

Densities of *n*-propyl and isobutyl alcohols at low temperatures. S. MITSUKURI and Y. KITANO (Proc. Imp. Acad. Tokyo, 1929, **5**, 21—22).—The densities of *n*-propyl and isobutyl alcohols have been measured over a range of about -10° to -110° . The results may be expressed by the formulæ, $D = 0.8193 - 0.00006749t + 0.000001351t^2$ and $D = 0.8169 - 0.0007055t + 0.000000684t^2$, respectively.

F. J. WILKINS.

Vapour pressures at low temperatures. N. VON KOLOSOVSKI (J. Russ. Phys. Chem. Soc., 1928, **60**, 1403—1416).—It is shown that even at temperatures above the absolute zero the vapour pressure of a substance must be infinitesimally small and practically zero; also that at those temperatures any change in the temperature of the walls of the containing vessel will have no effect on the slight vapour pressure. Hence it is concluded that there can be no equation for the vapour-pressure curve, say, in the form $\log_e p = A - B/T - C \log_e T + DT$. The criticism by Golitschuch (this vol., 398) is answered.

A. FREIMAN.

Lowering of the vapour pressure of liquid argon by active substances. G. F. HUTTIG and R. JUZA (Z. anorg. Chem., 1928, **177**, 313—322).—Active calcium, nickel sulphide, and powdered cassiterite do not influence the vapour pressure of liquid argon. The depressions produced by various proportions of active carbon, active silica, antimony trioxide, and stannic acid have been measured at temperatures in the neighbourhood of 85° Abs. The system silica-argon closely resembles the systems silica-water-ethyl alcohol and -benzene; the other systems investigated exhibit more or less graded differences from that containing silica, but nevertheless the cause of the depression of vapour pressure by active carbon does not appear to be the same as in the case of silica.

H. F. GILLBE.

Vapour density and pressure of ammonium iodide. R. H. PURCELL and W. DE LANGE (J.C.S., 1929, 275—279).—A static method has been used for the redetermination of the vapour pressure and vapour density of ammonium iodide at temperatures between 299.1° and 426°. The results agree with those obtained

by the isotenoscope method. Ammonium iodide is completely dissociated at all temperatures up to 400°.

F. G. TRYHORN.

Vapour-pressure chart for hydrocarbons. H. B. COATS and G. G. BROWN (Dept. Eng. Res. Univ. Michigan, 1928, No. 2, 1—17).—A new method of constructing vapour-pressure graphs is described, and curves are given for propane, isobutane, butane, dimethylbutane, pentane, diisopropyl, dimethylpentane, hexane, hexamethylene, benzene, dimethylhexane, and heptane from -150° to 280° . The accuracy claimed for the chart is $\pm 0.5^{\circ}$ in most cases.

C. W. GIBBY.

Interpretation of the linear isotherms derived from the Wiedemann-Franz-Lorenz law of conductivity. E. GRUNEISEN (Z. Physik, 1928, **51**, 652—668).

Van der Waals' equation and thermodynamics. J. E. VERSCHAFFELT (Compt. rend., 1929, **188**, 312—313).—A criticism of Karpen's deductions (this vol., 138).

J. GRANT.

Equations of state and thermodynamics. V. KARPEN (Compt. rend., 1929, **188**, 496—498).—Polemical against Verschaffelt (preceding abstract).

J. GRANT.

Viscosities of ethyl, *n*-propyl, and isobutyl alcohols at low temperatures. S. MITSUKURI and T. TONOMURA (Proc. Imp. Acad. Tokyo, 1929, **5**, 23—26).—The viscosities of ethyl, *n*-propyl, and isobutyl alcohols have been measured over the temperature range of 0° to -100° . The results may be expressed by an equation of the form $\log \eta = -A + B/(T - C)$, where A , B , and C are constants.

F. J. WILKINS.

Tube correction in measurements of the velocity of sound in gases. R. E. CORNISH and E. D. EASTMAN (Physical Rev., 1929, [ii], **33**, 258—259; cf. this vol., 253).—A reply to Shilling and Partington (this vol., 128).

N. M. BLIGH.

Thermal diffusion of rare constituents in gas mixtures. S. CHAPMAN (Phil. Mag., 1929, [vii], **7**, 1—16).—A mathematical examination of the effects and magnitude of the results of thermal diffusion in gases and the changes in concentration to be expected therefrom.

A. E. MITCHELL.

Molecular association. II. Relation between the viscosity of binary liquid mixtures and the polarity of the constituent molecules. J. ERRERA (Z. physikal. Chem., 1929, **140**, 273—280; cf. A., 1928, 1316).—The viscosity-concentration curves are considered with reference to the polarity of the molecules. The curves are found to be concave to the concentration axis if the molecules of one or both components are non-polar and convex if the molecules of both components are dipolar. Gases dissolved in liquids also follow this rule. A theoretical interpretation of this regularity is given.

R. N. KERR.

Viscosity formula for binary mixtures. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1929, **4**, 5—15).—A formula is given for the viscosity η of a binary mixture $\eta = \eta_1 + (\eta_2 - \eta_1)k_1 a_1 Z_m / \{k_1 a_1 (1 - Z_m) + k_2 a_2 Z_m\}$, where a_1 and a_2 are the degrees of association in the two liquids of viscosity η_1 and η_2 , Z_m is the molar

fraction of the second liquid, and k_2 are constants.

C. W. GIBBY.

Hardness and magnetic properties of iron-copper alloys and their relation to the equilibrium. A. KUSSMANN and B. SCHARNOV (*Z. anorg. Chem.*, 1929, 178, 317—324).—Alloys of iron with 0.5 and 1% Cu which is retained in solid solution show no change in the hardness or coercivity after quenching. Addition of more copper increases the hardness and decreases the coercivity after quenching from above the A3 point, showing that the solubility of copper in iron is greater at high temperatures than at the ordinary temperature. Quenching from above the A2 point but below the A3 point causes no sudden change in the hardness or coercivity, contrary to the results obtained by Ishihara (*B.*, 1922, 941A).

A. R. POWELL.

Influence of rate of cooling on the structure of eutectics. G. TAMMANN and A. A. BOTSCHWAR (*Z. anorg. Chem.*, 1929, 178, 325—328).—Very slow cooling of the lead-bismuth eutectic alloy from just above to just below the m. p. results in considerable segregation, the upper part of the alloy being enriched in bismuth, the excess of which beyond the eutectic composition crystallises in large cubes, and the lower part in lead, the excess of which crystallises in long dendrites in a ground mass of fine-grained eutectic. In the middle portion of the ingot both dendrites and cubes are found together in the eutectic ground mass. Similar results are obtained by slowly cooling eutectic alloys of bismuth-tin, bismuth-cadmium, and lead-antimony. On overheating the eutectic iron-carbon alloy and then cooling it slowly through the m. p. large graphite needles separate, especially at the top and round the sides of the ingot.

A. R. POWELL.

Crystal form in the formation of solid solutions. III. Thermal analysis of the systems $\text{MnCl}_2\text{--CoCl}_2$, $\text{CdCl}_2\text{--CoCl}_2$ and $\text{MgCl}_2\text{--CoCl}_2$. A. FERRARI and A. INGANNI (*Atti R. Accad. Lincei*, 1928, [vi], 8, 238—243).—These three systems show complete series of solid solutions of which the m. p. are in all cases intermediate between those of the pure components and show neither maxima nor minima.

F. G. TRYHORN.

Equilibrium between two liquid phases. V. System aniline-propionic acid-water. VI. System *o*-toluidine-propionic acid-water. E. ANGELESCU (*Bul. Soc. Chim. Romania*, 1928, 10, 160—169, 183—191; cf. *A.*, 1927, 1030).—V. Measurements of the solubility of aniline in aqueous solutions of propionic acid of various concentrations give no indication of the existence of lower critical points, so that the existence of such points in the system aniline-acetic acid-water (*A.*, 1925, ii, 854) cannot be attributed solely to hydrolysis of the amine salt. The binodal curves for the ternary system at 0° and 20° have also been determined. The ratio of the concentration of acid in the aqueous phase to that in the other conjugate at 20° first decreases with increasing concentration, then passes through a minimum, and ultimately rises again, tending to the value 1 as the critical point is approached. The effect of lactic, acetic, and propionic acids in increasing the miscibility

and depressing the critical solution temperature diminishes in this order, as does also the dissociation constant.

VI. Similar determinations have been made with the system *o*-toluidine-propionic acid-water. Here, however, there is evidence that at low temperatures closed solubility curves would be obtained, and it is therefore suggested that even the binary system possesses a lower critical point, and that the acid raises the critical solution temperature very considerably. The effect of propionic acid on the upper critical solution temperature is greater than that of acetic acid, the molecular depression increasing with increasing concentration in each case.

R. CUTHILL.

Solubility of magnesium hydroxide at high temperatures. A. TRAVERS and NOUVEL (*Compt. rend.*, 1929, 188, 499—501; cf. Gjaldbaeck, *A.*, 1925, ii, 653).—The solubility of magnesium hydroxide determined by electrometric or colorimetric titration (using phenol-red as indicator) in the absence of carbon dioxide decreases with time, and approximately linearly with temperature. It is not appreciable at 178° and is increased by salts such as sodium chloride or sulphate. Such determinations should be carried out in copper or paraffined glass vessels.

J. GRANT.

Solubility of calcium hydroxide. L. B. MILLER and J. C. WITT (*J. Physical Chem.*, 1929, 33, 285—289).—The solubility of calcium hydroxide in water at 30° has been determined, the approach to equilibrium being followed by means of measurements of the conductance of the solutions. Mean values for calcium oxide prepared by ignition of Iceland spar and by ignition of the carbonate precipitated from solutions of the nitrate by ammonium carbonate are 1.199 and 1.197 g. of calcium oxide per 1000 c.c. of saturated solution, respectively.

L. S. THEOBALD.

Solubility of calcium sulphate from 0° to 200°. E. P. PARTRIDGE and A. H. WHITE (*J. Amer. Chem. Soc.*, 1929, 51, 360—370).—The solubilities of anhydrite and hemihydrate are recorded for the range 100—200°. The values for anhydrite agree with those found by Melcher and the hemihydrate values agree with those previously recorded for "soluble anhydrite" (e.g., Hall, Robb, and Coleman, *B.*, 1926, 391). The "soluble anhydrite" curve above 100° is merely a continuation of the hemihydrate curve below 100°, thus supporting the view that the crystal structures of these two compounds are identical (cf. Jung, *A.*, 1925, ii, 367). A provisional diagram is given for the calcium sulphate-water equilibrium which indicates that gypsum is converted into anhydrite at 38—39° and into hemihydrate at 98°. Hemihydrate is metastable in the approximate range 90—130°, showing decreasing stability with falling temperature below 90° and with rising temperature above 130°.

S. K. TWEEDY.

Distribution law. I. Ideal distribution law expressed in molar fractions. II. Distribution law for condensed systems. R. LORENZ (*Z. anorg. Chem.*, 1929, 178, 346—352, 366—370).—I. If molar fractions are substituted for volume concentrations, the distribution law is readily established by the method of thermodynamic potential without any

assumption other than the validity of an equation of state for "ideal" solutions.

II. Using the same method, an equation for the distribution ratio for "condensed" systems may be derived.

R. CUTHILL.

Partition coefficient of infinitely soluble substances. S. G. MOKRUSCHIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1633—1639).—Perschke (cf. A., 1926, 345) showed that for infinitely soluble substances the partition coefficient between two immiscible solvents should be unity. Partition coefficients calculated from the data of different workers prove them to vary between 0.5 and 2.1. These values are explained by the use of the kinetic theory, Langmuir's conception of molecules as "dipoles," Langmuir's "principle of independent surface action," and lastly Langmuir's idea of molecules reacting only when certain definite parts of their surfaces come close together. Deviations from the values of 0.5, 1, or 2 are explained by introducing a fresh conception of the reactivity of molecules being confined to strictly limited parts of their surface, a so-called "polypolar" structure for molecules; influences on the part of the solute molecules on the mutual miscibility of the two solvents are also assumed, and finally changes in the state of the solute molecule itself, *e.g.*, dissociation, association, solvation, etc.

A. FREIMAN.

Adsorption of iodine, bromine, and some halogen salts by carbon from different organic liquids. J. TRIVIDIC (Rev. gen. Colloid., 1929, 7, 14—24).—A general introduction to the research. Contrary to the results of Davis (J.C.S., 1907, 91, 1666), the adsorption of iodine by activated carbon from organic liquids is complete after 30 min.

R. N. KERR.

Adsorption. W. KALBERER and H. MARK (Z. physikal. Chem., 1928, 139, 151—162).—The simplest formula deduced for the adsorption of a gas on a solid assumes that the phase concentration and the adsorption potential are independent of the surface density of film, and that the energy of polyatomic molecules which are adsorbed is represented by the same equations as in the gaseous state. The adsorption isotherms for argon on a given silicic acid were compared with those of the triatomic carbon dioxide on the same acid. Both gases give straight lines passing through the origin. There is no essential difference in behaviour. Other silicic acids show steep slopes for small increases in the film density, finally becoming straight lines. The heat of adsorption over the linear part of the curve is for argon 2500 g.-cal. and for carbon dioxide 6200 g.-cal. Similar relationships are found for the adsorption of carbon dioxide on aluminium and other foils; the adsorption isotherms for many temperatures are given and the thickness of the adsorbed layer appears to be of the order of magnitude 1.5×10^{-8} cm.

G. E. WENTWORTH.

Adsorption phenomena in solutions. XVII. Modifications of active carbon. M. DUBININ (Z. physikal. Chem., 1929, 140, 81—88).—Sugar charcoal activated at 550° adsorbs inorganic acids from aqueous solution to an extent which increases with the basicity of the acid, whilst the adsorption of

organic acids forms a series conforming to Traube's rule; activation of the charcoal at 800° results in the complete reversal of these series. The difference is ascribed to the formation of a surface layer of amorphous carbon on the one hand and of crystalline carbon on the other. In the absence of carbon dioxide neither modification is capable of adsorbing alkalis. By careful ignition of wood charcoal an active carbon is obtained which corresponds closely with the crystalline modification.

H. F. GILLBE.

Adsorption of acetic and propionic acids in presence of salts with a common anion. E. ANGELESCU and V. N. COMANESCU (Bul. Soc. Chim. Romania, 1928, 10, 170—182).—The amounts of acetic or propionic acid adsorbed by charcoal from aqueous solutions containing the corresponding sodium or potassium salt are somewhat less than when the salt is absent, but in both cases the Freundlich isotherm is applicable. It is also possible to represent the distribution of acetic acid between benzene and water by an equation of the same form as the adsorption isotherm, the result of adding potassium acetate being to displace the equilibrium in favour of the aqueous phase, whilst addition of sodium chloride has the opposite effect. Hence it may be concluded that the effect of the acetate on the adsorption is due to its increasing the tendency of the acid to dissolve in the water, whereas sodium chloride, acting in the reverse direction, promotes the adsorption (cf. Wiegner, Magasanik, and Virtanen, A., 1921, ii, 244).

R. CUTHILL.

Adsorption. XXII. Adsorption of alkali and of cupric salts in the precipitation of cupric hydroxide. M. R. MEHROTRA and N. R. DHAR (J. Physical Chem., 1929, 33, 216—225).—The factors affecting the gravimetric determination of copper by precipitation with sodium and potassium hydroxides have been investigated. Both hydroxides are adsorbed to a marked extent by the copper oxide precipitated from solutions of copper chloride and sulphate. The amount adsorbed is greater with the chloride than with the sulphate, and sodium hydroxide is adsorbed in larger quantities than potassium hydroxide. Adsorption quickly reaches a saturation limit. Copper can be precipitated completely from cupric salts by an amount of alkali slightly less than the equivalent amount, and, in the case of copper sulphate, the weight of copper oxide obtained on ignition is too great owing to adsorption of copper sulphate. With excess of alkali, however, the weight of oxide obtained approaches the theoretical value. Cupric and sulphate ions are adsorbed by the hydroxide in equivalent quantities; cupric chloride is also adsorbed, but volatilises on ignition. The existence of the basic salt $3\text{Cu}(\text{OH})_2 \cdot \text{CuSO}_4$ is supported.

L. S. THEOBALD.

Gas-solid equilibria. II. Pressure-concentration equilibria between benzene and (a) ferric oxide gel, (b) silica gel, directly determined under isothermal conditions. B. LAMBERT and A. M. CLARK (Proc. Roy. Soc., 1929, A, 122, 497—512; cf. A., 1928, 131).—The equilibrium of the system ferric oxide gel-benzene has been examined at 40°, 50°, and 60° in a special form of apparatus and

isothermals representing the pressure-concentration equilibria are given. Equilibrium pressures of benzene are plotted against concentration in grams of benzene per gram of gel. The adsorption and desorption isothermals are definitely coincident over the lower ranges of benzene concentration, but show great divergence, with the production of a hysteresis region, at intermediate concentrations, and become again coincident over the very steep portions of the curve obtained when the benzene concentrations approach the saturation value of the gel. The time taken for the establishment of equilibrium was about $\frac{1}{2}$ hr. over the coincidence ranges, but much longer (about 2 hrs.) over the intermediate range. Experiments were made at 40° to study the effect of interruptions in the "smooth" addition or withdrawal of benzene, and the effect on an established equilibrium of temporary alterations in the temperature of the system. It is shown that there are ranges of concentration—lower and higher—over which the pressure-concentration relations are reproducible and reversible, and also that intermediate ranges occur (the limits of which vary with the temperature) for which these relations are not reversible. In the latter circumstances results are reproducible only if the system is maintained at its constant temperature and the benzene "smoothly" added or withdrawn. The results obtained with the system silica gel-benzene at 15.25°, 40°, 50°, and 70° are, on the contrary, reproducible and reversible over the whole concentration range, from zero to saturation. Temporary cooling or heating of the system is without effect on the equilibrium pressure. Interruption of the "smooth" addition or withdrawal of benzene was also found to have no influence on the equilibrium state.

L. L. BIRCUMSHAW.

Adsorption on the surface of binary liquid mixtures. R. S. BRADLEY (Phil. Mag., 1929, [vii], 7, 142—145).—Previous considerations of surface phenomena in liquids have paid undue attention to the adsorption of one constituent without considering at the same time changes in the surface concentration of the other. Schofield and Rideal's (A., 1925, ii, 960) expression for the surface concentration of alcohol in alcohol-water mixtures $d\sigma/(-RTd \log a_1)$, where σ is the surface tension of the mixtures and a_1 the activity of the alcohol, is in reality not a measure of the surface concentration of the alcohol, but $\Gamma_1 - \Gamma_2 N_1/N_2$, where Γ_1 and Γ_2 are the Gibbs surface excesses and N_1 and N_2 the mol-fractions of alcohol and water, respectively. Γ_1 and Γ_2 have been evaluated by means of Frumkin's potential at the surface (A., 1925, ii, 109) and each surface concentration is shown to exhibit a maximum. From these figures the sectional area of oriented alcohol is shown to be 25.6 Å.

A. E. MITCHELL.

Adsorption at a water surface. I. B. W. CURRIE and T. ALTY (Proc. Roy. Soc., 1929, A, 122, 622—633; cf. Alty, A., 1926, 1096).—Measurements have been made of the velocity of air bubbles of various diameters in water and in sodium chloride solution, the bubble being introduced into a cylindrical silica cell with platinum end-pieces which served as electrodes. From the velocity under a known potential

gradient, the total charge on the bubble, E , is derived from the formula $XE = 6\pi\eta rv$. The results indicate that all bubbles, if they are not too small, have a charge which is independent of the radius and depends only on the rate of absorption; below a certain critical diameter, E ceases to be constant and decreases rapidly as the radius is still further decreased. The higher the rate of absorption the greater is E . The time taken for the surface to attain equilibrium is surprisingly long, being about 2000 sec. in the case of dilute sodium chloride solution. In very pure water ($\kappa = 0.7 \times 10^{-6}$ ohm⁻¹), however, there is no appreciable charging period. E is found to be 5.4×10^{-4} e.s.u., the critical radius in this case being 0.033 cm. The colour of the light used to illuminate the bubble appears to have no influence on the results.

L. L. BIRCUMSHAW.

Adsorption of ions and the physical character of precipitates. H. B. WEISER and G. E. CUNNINGHAM (J. Physical Chem., 1929, 33, 301—316).—The influence of the adsorption of ions on the physical character of a precipitate has been investigated for the case of a sulphur sol coagulated by the addition of certain chlorides. The sulphur sol was prepared by passing hydrogen sulphide and sulphur dioxide simultaneously into a saturated aqueous solution of the latter, and approximate uniformity of particle size was obtained by coagulation with sodium chloride, re-precipitation with water, and dialysis through cellophane membranes. The physical character of the sol varies almost continuously from gelatinous and reversible to plastic and irreversible when coagulated by a lyotropic series of ions from lithium to caesium and from magnesium to barium. Coagulation with a highly-hydrated, weakly-adsorbed ion, such as those of lithium and sodium, yields a reversible, gelatinous precipitate composed of individual micelles separated by a film of adsorbed water. Ions which are less hydrated and strongly adsorbed, e.g., those of barium, potassium, and caesium, yield plastic, irreversible precipitates. The rate of precipitation does not determine the character of the precipitate. Ultramicroscopic examination shows that replacement of a highly-hydrated ion from a gelatinous sulphur clump by one less hydrated and more strongly adsorbed is accompanied by a marked shrinkage due to loss of adsorbed water and coalescence of the particles, and ultramicroscopic convection currents become visible. When the sulphur sol is neutralised in the cell of a cardioid ultramicroscope so that the particles do not collide, the precipitation is reversible only when the adsorbed ion can be removed by washing. It is inferred that reversibility can be obtained in any sol when the conditions are such that coalescence is prevented by the intervention of a film of adsorbed solvent or by elimination of the opportunity to collide, provided that the adsorbed precipitating ion can be removed by washing. Further, the size and shape of a sulphur clump depend on the number and manner of chance collisions during the precipitation process. Von Weimarn's law of corresponding states for precipitation is discussed and shown to be often inapplicable and of little value in the prediction of the form of a precipitate.

L. S. THEOBALD.

Adsorption isotherms. A. BOUTARIC (Compt. rend., 1929, 188, 450—452).—The adsorption isotherms of J. Perrin and of Freundlich are compared after mathematical transformation with the symmetrical generalised form $dy/y^n = K \cdot dc/c^n$, where y is the concentration of the adsorbed substance in the adsorbing material, c the concentration in the medium, K a constant, and n is 1 and 2, respectively.

J. GRANT.

Equilibrium of heterogeneous systems including electrolytes. III. Effect of an electric field on the adsorption of organic molecules, and the interpretation of electrocapillary curves. J. A. V. BUTLER (Proc. Roy. Soc., 1929, A, 122, 399—416; cf. A., 1927, 112).—Starting with the electrostatic theorem, that the work done by an element of dielectric of volume ∂v , when it is moved from a place where the electric field is E to a place where it is 0, is $w - \partial v \cdot P dE$, where P is the polarisation per unit volume corresponding with the field strength E , an expression is derived for the variation of the amount of substance adsorbed from solution with the $P.D.$ at the interface. This is given by $\Gamma - \Gamma_0 e^{-aV/bV}$, where Γ is the excess amount of the substance adsorbed, Γ_0 is the amount adsorbed when $V=0$, V is the $P.D.$ at the interface, and a and b are constants. It is also shown that $\Delta\gamma = \Delta\gamma_0 \cdot f(V)$, where $\Delta\gamma$ is the depression of the surface tension produced by the substance and $\Delta\gamma_0$ is the depression produced when $V=0$. The variation with the $P.D.$ of the surface tension lowering produced by a number of organic substances at a mercury-aqueous solution interface has been determined. The values of the constants a and b , which have been calculated for numerous compounds, are discussed, and the main features of the electrocapillary curves of solutions containing organic substances, determined by Gouy, are interpreted. From a consideration of the effect of orientation at the interface, it is shown that the maximum of adsorption should occur when the $P.D.$ between the mercury and the solution is zero. The maxima of the adsorption curves should all occur at the same value of V . It is found, however, that whilst in nearly all cases these curves are of the same general form, the maximum is often displaced, sometimes considerably, to the right or left of the maximum of the primitive solution. Reasons for this are adduced.

L. L. BIRCUMSHAW.

Effect of the addition of protein on the surface tension of a sodium glycocholate solution. R. SUGINO (J. Biochem. Japan, 1928, 9, 353—381).—It is only at p_H values at which the protein exists as cation that it affects the surface activity of sodium glycocholate solutions, probably as a result of stoichiometric combination. An explanation is offered for the fact that the addition of protein to a dilute glycocholate solution increases the surface tension, whilst that to a more concentrated solution diminishes it.

CHEMICAL ABSTRACTS.

Orientation of organic compounds by cylindrical glass surfaces and superficial orientation of glass. Applications. J. J. TRILLAT (Compt. rend., 1929, 188, 555—556).—The author's X-ray spectrographic method (A., 1928, 938) is extended to deposits

on a glass cylinder of layers of palmitic acid less than 0.01 mm. thick deposited from light petroleum solution. Anisotropic orientation was found in the direction of the radius of the cylinder, corresponding with reflexion from planes 35.6 Å. apart, containing two fatty acid molecules. In the other directions the orientation was isotropic. The surface of the glass itself also showed anisotropic orientation with an intermolecular spacing of 3.3 Å.

J. GRANT.

Floating mercury on water. N. K. ADAM (Nature, 1929, 123, 413).—Finely-divided mercury may float on water, even when the surface tension is reduced to about 46 dynes per cm. by the addition of a drop of oleic acid. Since the tensions of clean mercury against air and against water differ by more than the surface tension of clean water, it would be impossible for clean mercury to float on clean water. Treatment of the mercury with sulphuric and chromic acids had apparently reduced the mercury-air tension by 100—200 dynes per cm.

A. A. ELDRIDGE.

Residual thermoelectricity of a mercury filament. T. TSUTSUI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 19—32).—Preliminary experiments on the effects of heating portions of capillary tubes containing filaments of mercury show that very small but measurable $E.M.F.$ may thereby be set up which vary in magnitude with the nature of the glass-mercury interface. Although the cause of these thermoelectric effects could not be elucidated, it is suggested that they may be due to the production of a state of strain through the unequal expansion of the mercury and the glass surfaces.

H. T. S. BRITTON.

Velocity of dissolution of comminuted solids.

I. W. JACEK (Rocz. Chem., 1929, 9, 19—40).—The process of dissolution is supposed to consist of two processes: one that of penetration of atoms, ions, or molecules of the solid into the solvent, and the other of deposition of solute on the surface of the solid. The velocity of the former process is, in the simplest case, constant, whilst that of the second is proportional to the concentration of solute at the given moment. An expression, $-dr/dt = (P/4\pi r^2) \cdot (\rho/a_1^3)(a_1^3 - a^3 + r^3)$, is derived for the velocity of dissolution of solids, where a is the radius of a sphere the mass of which is the same as that of the solid at the beginning, r that of the undissolved solid after time t , a_1 that of a sphere corresponding with the mass of solute present in a saturated solution, ρ the thickness of a layer of solid dissolved in unit time, and P the total surface of the solid. In the case of crystalline solids, ρ is, as a result of their anisotropy, a variable quantity, and a mean value has to be taken. Values calculated from the above expression are in good agreement with those found experimentally for cubes of sodium chloride in water.

R. TRUSZKOWSKI.

Reciprocal action of ions in diffusion processes. W. S. BUTKEWITSCH and W. W. BUTKEWITSCH (Biochem. Z., 1929, 204, 303—321).—From consideration of Donnan's theory of membrane equilibrium, it is shown that the rate of diffusion of the ions of an electrolyte should be altered by changes in the amount of undissociated electrolyte present; experimental proof is given in support of this view.

The rate of diffusion of potassium nitrate through a collodion membrane increases with the initial concentration. The increase is in direct proportion to the increase in the relative quantity of undissociated molecules as determined by conductivity measurements. The rates of diffusion of nitric acid and potassium and sodium nitrates at equal concentrations differ considerably, but the ratio of the change of diffusibility with the concentration to the change in the number of undissociated molecules is the same for these three electrolytes. The value of the above ratio is much smaller for calcium nitrate, due probably to the presence of the bivalent cation. The effect of adding acid and alkali on the diffusion of ammonium nitrate has been investigated. The ions diffuse in equivalent quantities at p_H 3, but if the acidity falls below this value the rate of diffusion of the nitrate ion decreases and that of the ammonium ion increases. The rates of diffusion of the phosphate ion from solutions of the acid and of the three sodium salts have been determined. The highest value is obtained from the free acid and the lowest from the normal salt.

R. N. KERR.

Osmosis of ternary liquids. VII—VIII.

F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 923—930; 1929, 32, 23—31).—Theoretical. A discussion of the relations between the influence of the membrane and the composition of the liquids on the diffusion type in osmosis, and of the nature of the isotonic and isentonic W -curves in different species of osmotic equilibria.

F. G. TRYHORN.

Permeability of dry collodion membranes.

II. J. H. NORTHRUP (J. Gen. Physiol., 1929, 12, 435—461; cf. A., 1928, 359).—The permeability of gases and dissolved solids with reference to dry collodion membranes indicates that the penetration is largely due to dissolution in the collodion, rather than to diffusion through the pores. The rate of penetration does not decrease regularly with increase in mol. wt.; hydrogen and carbon dioxide diffuse at the same rate whether the membrane is dry, wet, or immersed in water. At low concentrations, carbon dioxide, acetic acid, and phenol dissolve reversibly in collodion. Determination of the pore size from the rate of penetration of water gives a figure a hundred times as great as that determined by a vapour-pressure method.

E. BOYLAND.

Permeability of membranes. VII. Conductivity of electrolytes within the membrane.

A. A. GREEN, A. A. WEECH, and L. MICHAELIS.

VIII. Behaviour of dried collodion membrane towards bivalent cations. A. A. WEECH and L. MICHAELIS (J. Gen. Physiol., 1929, 12, 473—485, 487—493; cf. this vol., 87).—VII. The electrical resistance of dried collodion membranes in concentrated electrolyte solutions varies with the concentration of electrolyte, but on dilution a limiting value is reached, which is probably due to the membrane itself rather than the electrolyte. Different electrolytes give markedly different values, hydrochloric acid conducting much better than potassium chloride, which in turn has a higher conductivity than sodium chloride. Lithium chloride has a still lower con-

ductivity. These differences in conductivity of the alkali salts follow the electrolyte content of the membrane, but the high conductivity of hydrochloric acid is due to the high mobility of its ions within the membrane. Thus there are two factors concerned in the phenomenon.

VIII. The potential drop across a collodion membrane in calcium chloride solution is the same as that in a concentration chain. The resistance of this membrane is very high and the transport numbers of calcium and chloride ion are both about 0.5. These results are explained by the fact that very little calcium chloride penetrates into the membrane; the total electrolyte content of a membrane in equilibrium with a solution of calcium chloride was only 20% of that observed with a solution of lithium chloride.

E. BOYLAND.

Real concentration of solutions. M. LEVALIT-EZERSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 1391—1398).—Raoult's simple relation is replaced by the expression $(p-p')/p = K_{in}/(N+in)$, where $i = \Delta_i$ obs./ Δ_i calc. If E is the molecular depression of f. p. or elevation of b. p., then Δ_i calc. $= En$. By substitution and transformation, expressions are obtained for the "real concentration" of a solution, and for Δ_i obs. Using Tammann's data, values for Δ_i and n are calculated and compared for sodium chloride, potassium chloride, bromide, iodide, nitrate, and chlorate, and for barium chloride.

A. FREIMAN.

Synthesis and properties of colloidal aluminium and magnesium hydroxides. I. A. JAKOVLEV (J. Russ. Phys. Chem. Soc., 1928, 60, 1551—1555).—To carefully washed mercury protected from the action of carbon dioxide, air, and other gases was added a weighed quantity of aluminium or magnesium free from oxide and then distilled water (p_H 6.98). Sols were formed in the course of 6—12 hrs. A greater degree of dispersion of the aluminium sols is attained by peptisation with aluminium chloride. Experiments on the absorption of sodium d -tartrate from aqueous solution show that the aluminium sols have a smaller absorbing power than the sols prepared from aluminium chloride and ammonium carbonate.

A. FREIMAN.

Colloidal solutions of alumina and chromium oxide and their desiccation. P. BARY and J. V. RUBIO (Compt. rend., 1929, 188, 625—626).—The oxide obtained by drying colloidal aluminium oxide or chromium oxide at 60° is not homogeneous, and as in the case of the iron oxide (A., 1928, 1186) consists of two products, one more or less opaque tending to form more or less parallel with the liquid margin and the other a homogeneous gel. The differences observed in the three cases are probably due to differences in the relative amounts of the two products, and it is suggested that colloidal solutions of these oxides consist of a suspension of slightly hydrated oxide stabilised by a hydrate swelled with water, capable of giving gels on evaporation and behaving as a hydrophile.

R. BRIGHTMAN.

Structure of colloids. A. LUMIÈRE (Rev. gén. Colloid., 1929, 7, 1—8).—Kruyt's theory of colloids is not applicable to lyophile sols. The latter cannot

be regarded merely as hydrated lyophobic sols. The author's theory that colloids are divisible into two classes, in one of which the particles are molecular and in the other micellar, is more in accord with the facts.

R. N. KERR.

Colloidal structure in the solid state. J. DUCLAUX (Rev. gén. Colloid., 1929, 7, 9—14).—The variation of the structure of cellulose nitrate obtained from different solvents and by addition of various substances has been studied. Evaporation from an anhydrous solvent gives a product of the well-known "compact" form; the density of the flakes obtained varies with the solvent employed. A very porous product is obtained by evaporation of ordinary collodion to which antipyrine has been added. A product of a new structure is obtained by evaporation of an alcohol-ether solution of cellulose nitrate to which cinnamic acid has been added. The name "cellular" is suggested for this new structure, which is characterised by slow desiccation in air and in this way resembles certain living tissues. The incompletely dried flakes are soft and plastic. Addition of carbamide or urethane also produces this structure, but to a less marked degree.

R. N. KERR.

Flocculation of gold hydrosols. BOUTARIC and (MLLE.) M. DUPIN (Bull. Soc. chim., 1929, [iv], 45, 28—29).—Flocculation of gold sols is accompanied by a change of colour. The opacity in the red attains a maximum and then diminishes. By addition of small quantities of electrolyte all the gold is not precipitated; the amount precipitated increases with the concentration of electrolyte used and a certain minimum amount of electrolyte is necessary for complete precipitation. Further examples of periodic precipitation (A., 1927, 309) have been obtained by treatment of gold sols with aluminium, ferric, and thorium chlorides.

R. N. KERR.

Coagulation by electrolytes of non-spherical colloidal particles. I. **Rapid perikinetic coagulation.** II. **Slow perikinetic coagulation.** G. WIEGNER and C. E. MARSHALL (Z. physikal. Chem., 1929, 140, 1—38, 39—63).—I. Ultramicroscopical study of the coagulation by electrolytes of vanadium pentoxide and of benzopurpurin sols, in which the particles are non-spherical, indicates that this type of sol coagulates more rapidly than do sols having spherical particles. Benzopurpurin sols with approximately spherical particles exhibit the normal rate of coagulation calculated by Smoluchowski. The abnormal rate of coagulation of the non-spherical sol particles is independent of the chemical natures of the colloid and of the coagulant, and increases as the ratio length/breadth of the particles increases; the initial velocity increases also with the initial number of particles present. Coagulation of the first aggregates produced proceeds more slowly than does that of the single particles, and the rate diminishes as the aggregates increase in size until, when the process is nearing completion, the rate becomes the same as that for spherical sol particles. The rate of coagulation of the aggregates is influenced to a considerable degree by shaking, and the same holds, to a smaller extent, for the single particles.

II. The slow coagulation of benzopurpurin sol,

containing approximately spherical particles, follows Smoluchowski's law, and the rate is less influenced by shaking than in the case of rapid coagulation. The initial rate of the slow coagulation of sols having non-spherical particles, *e.g.*, vanadium pentoxide, may be greater than the rate of rapid coagulation of the spherical type, but the velocity decreases as the process approaches completion. The transition from rapid to slow coagulation at low concentrations of electrolyte is such that the retardation of the coagulation is greater for the non-spherical than for the spherical type. For a vanadium pentoxide sol having particles from 2 to 9 μ in length the relation between the number of particles remaining after a certain time and the concentration of coagulant is similar to that observed for lyophobic sols of the spherical type. A quantitative ultramicroscopical study has been made of the ageing and the slow and rapid coagulation of the non-spherical type of benzopurpurin sol in presence of various concentrations of electrolyte. The greater the aggregation velocity during the coagulation and the more nearly the particles approach the spherical form, the more nearly does the course of the coagulation agree with that calculated by Smoluchowski.

H. F. GILLBE.

Effect of non-electrolytes on the coagulation of colloids. III. **Copper ferrocyanide sol.** S. G. CHAUDHURY and N. P. CHATTERJEE (J. Physical Chem., 1929, 33, 244—249; cf. this vol., 135).—The effect of the addition of methyl or ethyl alcohol, carbamide, sucrose, gelatin, and acetic acid on the coagulating concentrations of hydrochloric, sulphuric, and citric acids, and of potassium, barium, and aluminium chloride for copper ferrocyanide sol, prepared from copper sulphate and potassium ferrocyanide, has been investigated. As in the case of ferric hydroxide sol (*loc. cit.*), but contrary to the finding of Mukherjee and others with arsenious oxide sol, methyl and ethyl alcohols have a uniform effect in sensitising the copper ferrocyanide sol against the electrolytes examined. Gelatin also has a similar effect except in the case of barium and aluminium chlorides, but with the other non-electrolytes examined the effects are specific, the valency of the coagulating ion giving no clue to the expected behaviour. This specific action is discussed, and it is emphasised that other changes, as well as changes in adsorbability and original charge, must be considered in the interpretation of coagulation phenomena.

L. S. THEOBALD.

Kinetics of the coagulation of gold sols. "Thermo-senesence effect" exhibited at elevated temperatures. (MISS) A. E. DAVIES (J. Physical Chem., 1929, 33, 274—284).—The effect of maintaining a gold sol at a temperature of 80° for 4—6 hrs. has been investigated, using barium chloride as coagulant. The change in behaviour brought about by such treatment is termed "thermo-senesence." The sol was prepared by dialysis of the ruby-red sols obtained by boiling an aqueous solution containing gold chloride, potassium carbonate, and acetone, and the extent of coagulation for a coagulation time of 20 sec. was measured colorimetrically. The pronounced thermo-senesence at 80° is made up of (i) a

primary effect which consists of a fall in the Smoluchowski coefficient β , with an increase in ageing period of the sol, to a minimum after 3 hrs., and (ii) a secondary effect, which shows itself by a subsequent rise in the value of β and practically disappears when evaporation is minimised. The primary effect is irreversible, and its nature is discussed. The ratio β_{80}/β_{25} varies between 1.5 and 3.3 for different sols, but would be 2.9 if the temperature effect was due to viscosity alone; this discrepancy is discussed. It is pointed out that variability in behaviour due to thermo-senescence should be eliminated before investigating colloidal systems at the ordinary temperature, a desideratum which is made possible by the irreversibility of the primary effect mentioned above.

L. S. THEOBALD.

Protective action of silicic acid sols and of tin hydroxide on silver sols. A. V. DUMANSKI and P. A. SCHERSCHNEV (J. Russ. Phys. Chem. Soc., 1928, 60, 1593—1600).—Alkaline solutions of the protecting sols were mixed with a few drops of 40% formaldehyde solution and the desired quantity of silver nitrate solution (dilution 1:5000) was then added. Differences in the colour of the protected and non-protected silver sols have been investigated by means of the spectral photometer. The curves obtained by plotting the percentage adsorption against the wavelength are very similar in character, both showing a maximum in the violet, although for the protected sol the maximum is farther in the violet, and both curves slope toward the red.

A. FREIMAN.

Action of ionising radiations on colloids. J. A. CROWTHER (Phil. Mag., 1929, [vii], 7, 86—98).—Previous work of Crowther and Fairbrother has been extended by an investigation of the effects of X-rays and β -rays on ceric hydroxide sol and a Bredig copper sol. In both cases there is a constant ratio between the quantity of X-radiation and β -radiation required to produce a given amount of coagulation, an exposure of 1 hr. to β -rays being equivalent to a dose of 0.4 m.c. of X-radiation. Within the limits of the experimental error these two doses are found to represent the same relative energy. It is therefore suggested that the coagulation is due to the ionising effect which the two types of radiation possess in common, followed by the discharge of the colloidal particles as previously suggested by Crowther and Fairbrother. (Cf. A., 1921, 935; 1928, 1091.)

A. E. MITCHELL.

Cellulose nitrate diffusion experiments. R. O. HERZOG and D. KRUGER (J. Physical Chem., 1929, 33, 179—189).—Diffusion data for various commercial cellulose nitrates in acetone and in methyl ethyl ketone as solvents are recorded for solutions in which the heterodispersity of the solution may be disregarded. When referred to the diffusion coefficient in water at 20°, the values of these diffusion coefficients lie between 0.015 and 0.021. Other experiments show that the diffusion coefficient depends on the raw material employed and on the conditions of nitration, and in the majority of cases Fick's law is not followed. This is attributed to heterodispersity and to a disaggregation of the larger particles of cellulose nitrate during diffusion.

L. S. THEOBALD.

Effect of temperature on viscosity and ease of precipitation of sols of cellulose acetate and rubber. G. S. WHITBY and W. GALLAY (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 1—6).—Experimental results are given for the relative viscosity (i.e., the viscosity referred to the viscosity of the pure solvent at the same temperature) and the percentage volume occupied by the disperse phase (calculated from Hatschek's equation for the viscosity of emulsoids) of a rubber sol in benzene and of sols of cellulose acetate in phenylethyl alcohol, benzyl alcohol, acetone, and cyclohexanone. The rubber sol showed only a small change in relative viscosity with change of temperature. The measurements with cellulose acetate were carried out on sols of different concentrations and it was found that, for sols with a relative viscosity of 4 or less, temperature had a comparatively small effect on the viscosity relative to the viscosity of the solvent at the same temperature. With sols of greater relative viscosity, the effect of temperature was more considerable. This conclusion is in accord with some data recorded by Mardles (J.C.S., 1923, 123, 1951) for sols in triacetin and in benzyl alcohol. The viscosity of the sols is most markedly affected by temperature when the volume occupied by the disperse phase (cellulose acetate+bound solvent) is high, and especially when it is equal to or higher than the volume corresponding with close packing of the micelles. The ease of precipitation of sols of cellulose acetate by the addition of a non-solvent is affected by temperature to a much greater extent than is the relative viscosity, and the higher the concentration (and therefore the smaller the proportion of unbound solvent) the smaller is the volume of precipitant required to produce separation. It is concluded that precipitation by a non-swelling agent is not a trustworthy method of comparing the degree of solvation at different temperatures.

E. S. HEDGES.

Influence of proteins on the solubility of sparingly soluble calcium salts. The carbonic acid compounds of proteins. W. PAULI and T. STENZINGER (Biochem. Z., 1929, 205, 71—103).—The solubility of calcium sulphate increases in the presence of serum-albumin, pseudoglobulin, and haemoglobin (the effect increases in this order). This depends on an equivalent inactivation of calcium and sulphate ions determinable by the decrease in conductivity, multivalent ions being formed with the protein. The absorption of calcium by the proteins on shaking with calcium carbonate as solid phase must be regarded as the result of the formation of calcium proteinate, calcium carbonate in saturated aqueous solution being 66% hydrolysed. The effect is accompanied by increased conductivity, strong anodic migration, and decreased coagulability by heat and alcohol.

P. W. CLUTTERBUCK.

Mutual influencing of the solubilities of proteins. G. ETTISCH, W. EWIG, and H. SACHSSE (Biochem. Z., 1928, 203, 147—158).—Part of the protein precipitated by one third saturation of serum with ammonium sulphate goes again into solution by washing with the same medium. This effect depends only in part on changes of concentration of electro-

lytes. The protein remaining in solution must, therefore, by its presence cause a portion of protein to precipitate which in its absence redissolves. The redissolution may be avoided by washing with sulphate containing protein. This influence of protein increases with its concentration and depends on the nature of the protein, serum-albumin being especially active. P. W. CLUTTERBUCK.

Equilibrium of halogen ions. I. Combination of egg-albumin with halogen ions. K. ITO (J. Biochem. Japan, 1928, 9, 17—43).—The halogen-ion activity in potassium, sodium, or lithium chloride, and in sodium bromide or iodide, as measured with the silver halide electrode, diminishes on addition of egg-albumin. The effect is attributed to adsorption of the halogen ions. CHEMICAL ABSTRACTS.

Mechanism of the specific action of ions on proteins. Degree of activity of different myogen salts. P. RONA and H. H. WEBER (Biochem. Z., 1928, 203, 429—451).—The distribution of diffusible ions between an inner protein-containing and an outer protein-free solution follows the Donnan law providing the "activity" of the ions is taken into account. It is possible therefore to measure the relative activity of different salts with the same protein. The activity of myogen salts decreases rapidly from myogen phosphate, chloride, bromide, nitrate, thiocyanate, to sulphate. The osmotic pressure runs parallel with the activity. The specific action of anions increases in the same order as the activity of their myogen salts decreases. The viscosity of the myogen in solution is smaller the smaller is the activity of the myogen salt. The specific action of anions with myogen depends on the activity of the salts which they form with this protein. P. W. CLUTTERBUCK.

Mutual influencing [of flocculation] of cholesterol and cholesteryl ester in colloidal solution. R. STERN (Biochem. Z., 1928, 203, 313—322).—Further experiments (cf. A., 1926, 576; 1927, 1025) are described on the flocculation of cholesterol and cholesteryl ester sols in acetate and tartrate buffers with addition of serum- and egg-albumin at varying p_H . Cholesterol sol is much more sensitive to change of p_H than cholesteryl ester sol, flocculation occurring at p_H 4.7—5, whereas with the ester sol there is no flocculation at p_H 3 after 24 hrs. Small amounts of serum-albumin and of crystallised egg-albumin sensitise both sols. Cholesteryl ester sol is able to inhibit the flocculation of cholesterol sol, the protective action being readily shown by plotting the flocculation p_H (decreasing) against the quotient ester concentration ÷ cholesterol concentration, when a rapidly rising curve is obtained. P. W. CLUTTERBUCK.

Independence of protein hydration and protein ionisation. H. H. WEBER and D. NACHMANN SOHN (Biochem. Z., 1929, 204, 215—252).—The non-solvent space of ionised and electro-neutral protein is found to be independent of the degree of ionisation, the value for albumin being 1 c.c. per g. and for globulin 1.3 c.c. per g. Measurements of osmotic pressure and viscosity show that these depend on the degree of ionisation. One g. of albumin has a viscosity volume increasing from 2.0 c.c. at isoelectric point to about 15 c.c. at the acid-swelling maximum.

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The change in the total volume gives a measure of the dependence of the forces of hydration on protein ionisation. In the ionisation of various proteins and amino-acids there is no contraction but an increase in total volume. The value of the equivalent expansion when ionised by acids is 7—9 c.c. and by alkalis 16—22 c.c. according to the nature of the ampholyte. The difference between protein and amino-acid is scarcely greater than between individual proteins. Deionisation, whether by acid or alkali, leads to a total increase in volume of 22 c.c.

All the measurements point to virtual independence of protein hydration and protein ionisation.

J. H. BIRKINSHAW.

Reactions between colloids. I. Dyes and proteins. W. PAULI and E. WEISS (Biochem. Z., 1928, 203, 103—141).—The preparation by electro-dialysis of pure Congo-blue sol from Congo-red is described. This sol can be kept unchanged only in Jena glass vessels, and its p_H is determined by conductivity titration and not by use of the gas cell. The titratable hydrogen ions are completely dissociated only in dilute solution. The conductivity temperature coefficient of the blue sol is higher than for a typical electrolyte; at higher temperatures the colour becomes red, but returns to blue on cooling. Precipitation of the sol by a number of weak organic acids and by electrolytes is described. Filter-paper coloured blue by the sol becomes red on drying. Congorubin blue sol behaves similarly, but in aqueous solution there is always an equilibrium between red and blue phases, dilution favouring displacement to the blue. The precipitation of these sols with egg- and serum-albumin, gluten, pseudoglobulin, stannic acid, aluminium hydroxide sols, and a number of negative colloids, e.g., neutral sodium caseinate, starch, silicic acid, colloidal gold, are quantitatively investigated. The concentration of protein just precipitated by Congo-blue sol decreases in the following order: egg-albumin, serum-albumin, gluten, pseudoglobulin. The presence of carbon dioxide in these experiments causes an increase of the free positive charges in the protein solution, and also an increase of sensitivity to precipitation. These reactions, therefore, permit the differentiation of the proteins, and the precipitation in presence of carbon dioxide is perhaps the most sensitive protein reaction. The highly sensitive colour change of the blue sol detects minute amounts of alkali, e.g., of glass (except Jena), and filter paper, and after slight bacterial decomposition.

P. W. CLUTTERBUCK.

Hydrodynamics and the kinetic theory of gases. Y. ROCARD (Compt. rend., 1929, 188, 553—554).—The limits of validity of classical hydrodynamics (e.g., from the point of Stokes' law) are discussed. It is assumed that if a fluid is defined as obeying Maxwell's rule for the distribution of molecular velocities, then a gas or liquid is no longer a fluid in the neighbourhood of the walls of the containing vessel where its pressure is dependent on the orientation of the surface. J. GRANT.

Constant of mass action. R. F. GOLDSTEIN (Phil. Mag., 1929, [vii], 7, 205—206).—In his treatment of the constant of mass action Kleeman (A.,

1928, 239) has not considered the decrease in free energy in the dissociation of his "sepro-stable" molecules, this being independent of the path chosen for a given initial and final state. When this is done the expression for the mass action constant reduces to the usual van 't Hoff form. Furthermore, the kinetic evidence adduced in support of Kleeman's new constant of mass action is substantially the deduction of the mass action law on the kinetic theory, and the correction factor introduced is not a correction to the velocity of reaction, but is the activity coefficient of the concentration term.

A. E. MITCHELL.

Constant of mass action. R. D. KLEEMAN (Phil. Mag., 1929, [vii], 7, 206—208).—A reply to Goldstein (cf. preceding abstract). In the usual van 't Hoff cycle, it is generally supposed that no change in the partial pressure of the molecules in a reservoir takes place when a small fraction is removed and that this holds for the pressure in the cylinder used for removing them independently of dissociation. Hence the free energy remains constant and does not decrease, as claimed by Goldstein. A fresh deduction of the mass action constant is made by equating to zero the external work done during the cycle. It is shown that the factor introduced in the kinetic deduction of the new mass action constant is not the activity coefficient of the concentration term.

A. E. MITCHELL.

Relation between stationary state and equilibrium. E. BAUR (Z. physikal. Chem., 1929, 140, 194—198).—Theoretical. The breaks in the Δk curves found in certain equilibrium reactions (see A., 1928, 1329) are not in disagreement with the equation connecting the equilibrium constant with the velocity coefficients.

R. N. KERR.

Optical measurement of small degrees of dissociation of the vapours of metallic salts. I. WYNEKEN (Z. physikal. Chem., 1929, 140, 78—80; cf. A., 1928, 1093).—An incorrect value for the heat of reaction was employed in the original paper; substitution of the correct figure causes the observed degree of dissociation to differ widely from the theoretical, but the discrepancy is attributed to traces of mercurous chloride in the mercuric chloride used.

H. F. GILLBE.

Calculation of the water-gas equilibrium by means of the exact form of Nernst's heat equation. E. MAURER and W. BISCHOF (Z. anorg. Chem., 1929, 178, 371—380).—From existing specific heat data, the relation between the heat effect in the formation of water-gas and the temperature has been calculated. By application of the method of least squares to the resulting expression, the coefficients for the Nernst heat equation have then been derived. The values for K_p obtained from the equation are in good agreement with the published experimental figures.

R. CUTHILL.

Thermal decomposition of water vapour into hydrogen and free hydroxyl. K. F. BONHOEFFER and H. REICHARDT (Z. physikal. Chem., 1928, 139, 75—97).—Spectroscopic evidence for the thermal dissociation of water vapour into hydrogen and free hydroxyl has been obtained at temperatures above

1300°. The dissociation constant of the reaction has been calculated in the following way. A consideration of the reaction $4\text{OH} = 2\text{H}_2\text{O} + \text{O}_2 + W_0$ shows that z_1/z_2 can be expressed as a simple function of v_1/v_2 provided that z is small, where z denotes p_{OH} , v denotes the ratio $(2p_{\text{H}_2\text{O}} + p_{\text{OH}})/(p_{\text{H}_2\text{O}} + 2p_{\text{O}_2} + p_{\text{OH}})$, and the suffixes correspond with temperatures T_1 and T_2 . The hydroxyl absorption of three oxygen-rich mixtures of water vapour and oxygen was determined at 1590° (T_1), and three corresponding temperatures, T_2 , were then found at which the absorptions observed were respectively equal to that of a mixture weak in oxygen. Hence three values of z_1/z_2 are obtained; and, provided z is small, $k_1/k_2 = z_1^4/z_2^4$, where k_1 and k_2 are the equilibrium constants of the reaction $4\text{OH} = 2\text{H}_2\text{O} + \text{O}_2 + W_0$ and T_2 , respectively. W_T may therefore be calculated from the equation: $W_T = (4.571T_1T_2 \log k_1/k_2)/(T_1 - T_2)$. The mean of the three values for W_T is 146,000 g.-cal., corresponding with $W_0 = 142,000$ g.-cal. Hence it follows that $\text{H}_2 + 2\text{OH} = 2\text{H}_2\text{O} + U_0$, where $U_0 = 128,000$ g.-cal. The dissociation constant of this reaction is then given by: $\log K_{\text{OH}} = -U_0/4.571T + \Sigma C_{p_0} \log T/1.986 + (1/4.571) \int_0^T (1/T^2) dT \int_0^T \Sigma C_{p_T} dT + \Sigma i$, where the symbols have their usual connotation. The chemical constants were calculated from the Sackur-Tetrode equation, the moments of inertia being derived from spectroscopic data: $\Sigma i = 2i_{\text{OH}} - i_{\text{H}_2} - i_{\text{O}_2} = -0.82 + 3.36 - 0.53 = +2.01$. Classical values for diatomic molecules were assumed for C_{p_0} terms; and the C_{p_T} terms were calculated from $(v/T) = R(h\nu/kT)^2 e^{h\nu/T}$, in which to v the following values were assigned for hydrogen, oxygen, and hydroxyl, respectively: 5000, 3600, and 5100. The hydroxyl value was obtained by adopting that corresponding with the vibrational energy in the OH band spectrum, $\nu = 3570$ cm.⁻¹. The values of K_{OH} so calculated differ but slightly from the accepted values of K for the reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$. The most intense absorption in the experiments recorded corresponds with a partial pressure of hydroxyl of 8 mm. at 1600°.

R. W. LUNT.

Ebullioscopic determination of equilibrium constants. W. SWIENTOSŁAWSKI, Z. BŁASZKOWSKA, and E. JÓZEFOWICZ (Rocz. Chem., 1929, 9, 1—18).—Two mixtures are prepared containing ethyl alcohol, acetic acid, ethyl acetate, and water in such proportions that in one mixture the reaction is one of hydrolysis, whilst in the other it is one of esterification, and the mixtures are kept at boiling temperature in an atmosphere of nitrogen, until the b. p. of the two mixtures are identical (76.32°), indicating that equilibrium has been attained. Knowing the temperature coefficient of vapour pressure of such equimolecular systems (27.21), and the latent heat of vaporisation (8.76 kg.-cal./mol.), the equilibrium constant is derived from the b. p., and is found to be 3.76 for the above system.

R. TRUSKOWSKI.

Ebullioscopic measurements on resorcinol in lithium chloride solutions. F. BOURION and E. ROUYER (Compt. rend., 1929, 188, 626—628; cf. A., 1928, 477).—In lithium chloride solutions resorcinol exists only as single or triple molecules; the equilibria observed in water or in potassium or

sodium chloride solution between single and double molecules have not been observed in lithium chloride solutions even at low temperatures. The ebullioscopic constant increases with the concentration of the lithium chloride solution and, at constant alkali chloride concentration, decreases with the at. wt., whilst the equilibrium constant increases. In the series 1.225*M*-lithium chloride-water, for concentrations of resorcinol greater than 1.75*M* equilibrium appears to exist between single and quadruple molecules. These results are reconciled with earlier observations indicating that solutions of resorcinol in alkali chlorides have the properties of ideal solutions (A., 1927, 515) by assuming hydration of the alkali salt, the degree of hydration varying with the ionic activity of the salt. R. BRIGHTMAN.

Influence of sucrose on the dissociation constant of weak acids in aqueous solution. I. M. KOLTHOFF (Rec. trav. chim., 1929, 48, 220—226).—The influence of sucrose on the p_H values of a series of buffer solutions has been determined, and has been found to be slight, confirming the inference that the addition of sucrose up to a concentration of 1.5*M* is practically without effect on the dissociation constants of acetic and citric acids. From measurements of the conductance of aqueous solutions of succinic, tartaric, acetic, and salicylic acids, and of similar solutions containing 20% of sucrose, it would seem that the dissociation constants of these acids may be regarded as unaltered by the presence of the sucrose if the concentration of the acid is expressed as the molal fraction with regard to the free water, and a hydration number of eight is accepted for sucrose in 20% solution. F. G. TRYHORN.

Dissociation constants of adenosinephosphoric acid of muscle and of inosinic acid. H. WASSERMEYER (Z. physiol. Chem., 1928, 179, 238—242).—By electrometric titration the following dissociation constants were obtained: for adenosinephosphoric acid: $pK_1=3.8$, $pK_2=6.2$; for inosinic acid $pK_1=2.4$, $pK_2=6.3-6.5$. J. H. BIRKINSHAW.

Dissociation constants of amino-acids. P. L. KIRK and C. L. A. SCHMIDT (J. Biol. Chem., 1929, 81, 237—248).—Valine has $K'_a 2.40 \times 10^{-10}$, $K'_b 2.09 \times 10^{-12}$; *D*-isoleucine, $K'_a 2.09 \times 10^{-10}$, $K'_b 2.29 \times 10^{-12}$; *nor*leucine $K'_a 1.72 \times 10^{-10}$, $K'_b 2.46 \times 10^{-12}$; glutamic acid $K'_a 5.62 \times 10^{-5}$ and 2.19×10^{-10} , $K'_b 1.55 \times 10^{-12}$; β -hydroxyglutamic acid $K'_a 5.82 \times 10^{-5}$ and 2.76×10^{-10} , $K'_b 2.12 \times 10^{-12}$; serine $K'_a 7.08 \times 10^{-10}$, $K'_b 1.62 \times 10^{-12}$; oxyproline $K'_a 1.86 \times 10^{-10}$, $K'_b 8.32 \times 10^{-13}$. Introduction of a hydroxyl group into an amino-acid thus increases the acid dissociation constant. The isoelectric points of glutamic and β -hydroxyglutamic acids lie at p_H 3.22 and 3.28, respectively; the other amino-acids show an extended isoelectric zone. C. R. HARRINGTON.

Dissociation constants of ornithine. W. SCHMIDT, P. L. KIRK, and C. L. A. SCHMIDT (J. Biol. Chem., 1929, 81, 249—250).—Ornithine has $K'_a 1.74 \times 10^{-11}$, $K'_b 4.46 \times 10^{-6}$, $K'_{ba} 8.70 \times 10^{-13}$; the isoelectric point is at p_H 9.7. C. R. HARRINGTON.

Mutual displacement of benzoic acid and salicylic acid from their compounds with *m*-

phenylenediamine. G. K. GLININ (J. Russ. Phys. Chem. Soc., 1928, 60, 1641—1653).—The nature of the systems formed by benzoic acid with salicylic acid, by benzoic acid with the compound of salicylic acid with *m*-phenylenediamine, by salicylic acid with the compound of benzoic acid with *m*-phenylenediamine, and lastly by the two compounds with each other was investigated by the method of thermal analysis. The results of Kremann, Weber, and Zechner (A., 1926, 393) for the systems salicylic acid-*m*-phenylenediamine and benzoic acid-*m*-phenylenediamine have been recalculated so as to be expressed in the same terms as the author's other results and the thermal diagrams for these systems have been drawn. A rectangular diagram has been constructed, each corner of the diagram representing salicylic acid or benzoic acid or the compound of either acid with *m*-phenylenediamine. The fields occupied on the diagram by the four components differ both in size and character, that for the compound of salicylic acid with *m*-phenylenediamine is the largest and that for the other compound the smallest. One of the two diagonals represents a stable section and the other a metastable section. The stable section is represented by the section of the binary system benzoic acid-compound of salicylic acid with *m*-phenylenediamine. On this section there is practically no indication of any replacement of the salicylic acid by the benzoic acid from its compound with *m*-phenylenediamine. The section of the binary system salicylic acid-compound of benzoic acid with *m*-phenylenediamine represents the metastable section, and on it are clear indications of the salicylic acid displacing the benzoic acid from the compound of the latter with *m*-phenylenediamine to a large extent. A. FREIMAN.

Electrolytic solution forces and the condition of electrolytic ions. IV. Calculation and comparison of the energies of solution and solvation. Are electrolytic ions solvated gas ions? K. FREDENHAGEN (Z. physikal. Chem., 1929, 140, 65—77).—The electrolytic solution energy and the solvation energy associated with the production of electrolytic ions from gaseous ions have been calculated for a number of uni- and bi-valent elements by regarding the solvation energy (solute ion \rightarrow gaseous ion) as the sum of the solution energy (solute ion \rightarrow gaseous atom) and the ionisation energy (gaseous atom \rightarrow gaseous ion). The solution energy, which involves specific interaction between solvent and solute, is smaller than the energies of solvation and ionisation. The partition coefficients of the ions between the gaseous and liquid phases differ widely from the theoretical values based on the dielectric constants of the media; from this and other observations the conclusion is reached that electrolytic dissociation is not a simple process of electrostatic partition of charged particles between two media having different dielectric constants.

H. F. GILLBE.
Ionic radius and osmotic activity. G. B. BONINO and V. VAGLIO (Gazzetta, 1929, 59, 49—56).—The conception of deformability of ions is applied to the Debye-Hückel theory, and the following expression is derived connecting the deformability, d , the

"osmotic" radius, a , and the effective radius, r , of an ion in 0.1*N*-solution: $a = 0.6z[(r/d) \times 10^{16} + 4.67] \times 10^{-8}$, where z is the valency of the ion. Using the ionic deformabilities given by Born (A., 1924, ii, 434) and the effective radii by Grimm and Wolff (A., 1926, 664), the values of a for the alkali and alkaline-earth metal ions in solutions of the chlorides have been calculated. These values can be used to calculate the depression of the f. p. in solutions of these chlorides, and the agreement with the experimental results recorded in the literature is good. It is therefore possible to calculate the osmotic properties of dilute solutions from physical constants of the ions without the introduction of an empirical constant depending on the nature of the ion.

O. J. WALKER.

Generalisation of the third law of thermodynamics. J. G. GOLITSCHUCH (J. Russ. Phys. Chem. Soc., 1928, 60, 1399—1401).—Polemical against Kolosovski (*ibid.*, 1927, 59, 741). A. FREIMAN.

Equilibrium of a liquid with its vapour and the connexion with the thermodynamic potential. J. W. DEKKER (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 973—977).—Boltzmann's condition $v_b e^{-\epsilon_{\text{mol}}/kT}$ for the equilibrium between liquid and vapour requires that the value of $2\epsilon_{\text{pot}} - RT \cdot \log v_b$ shall be the same for the two phases. It is shown that the latter expression should be $\epsilon_{\text{pot}} - (\partial \epsilon_{\text{pot}} / \partial v) v - RT \cdot \log v_b$, where v_b is per g.-mol. the space available for a last molecule centre among the molecules already present, ϵ the potential energy of one molecule in relation to the others, and kT is twice the mean kinetic energy per degree of freedom.

F. G. TRYHORN.

Heat capacities in aqueous salt solutions. M. RANDALL and F. D. ROSSINI (J. Amer. Chem. Soc., 1929, 51, 323—345).—The precision of the differential method of measuring apparent molal heat capacities of salts in solution previously recorded (A., 1927, 208) has been improved and the method used to carry out measurements at 25° on the chloride, bromide, iodide, nitrate, and sulphate of sodium and potassium in solutions up to 0.6, 1, 1.5, or 2.5 molal. The partial molal heat capacities of the solute (which rise to remarkably high values as the concentration of the solution increases), the partial molal heat capacities of the water, and the specific heats of the solutions are calculated from the results. The partial molal heat capacity of the potassium ion is more negative than that of sodium ion; the negativity increases for the anions in the order nitrate, chloride, bromide, iodide, sulphate. An equation is derived, on the basis of the Debye-Hückel theory, for the partial molal heat capacity of the solute, to which the experimental results for dilute solutions conform very well. A review of previously published data shows that in any given group of elements the partial molal heat capacity at infinite dilution becomes more negative as the atomic number increases, and becomes more negative in any given period of elements as the ion charge increases. The hydrogen ion does not fall in the regular order of the univalent positive ions, perhaps because of the formation of the oxonium ion, H_3O^+ . The results are discussed with reference

to hydration of ions and the temperature coefficient of the heat of dissolution of a strong electrolyte in a large amount of water.

S. K. TWEEDY.

Activities of molten alloys of thallium with tin and with lead. J. H. HILDEBRAND and J. N. SHARMA (J. Amer. Chem. Soc., 1929, 51, 462—471).—The *E.M.F.* of cells of the type $Tl|$ fused mass containing 3 parts LiCl and 2 parts KCl|alloy were measured at 352°, 414°, and 478°. The activity coefficients, a_1 , of thallium in the tin alloys are given by $\log a_1/N_1 = (1.0763 - 0.001017)N_1^2$, where N_1 is the mol.-fraction of thallium. Other thermodynamic quantities are calculated. The calculated heats of transfer of thallium from an ideal solution to a tin solution of the same mol.-fraction do not agree with the free energies calculated for the same process. The solution, therefore, is regular with respect to composition changes, but not with respect to temperature changes. The alloys exhibit a slight positive deviation from Raoult's law. Similar experiments were carried out on the thallium-lead system, which, although it does not deviate much from Raoult's law, exhibits complications attributable to the presence of $PbTl_2$.

S. K. TWEEDY.

Heat of combustion and dissolution of dihydroxyacetone. M. KOBEL and W. A. ROTH (Biochem. Z., 1928, 203, 159—163).—The heat of combustion of freshly prepared dihydroxyacetone is 343.1 g.-cal. per mol., that of two molecules being 12.2—16.0 g.-cal. greater than that of the hexoses. The heat of dissolution is 3.98 g.-cal. per mol. P. W. CLUTTERBUCK.

System magnesium-zinc. W. HUME-ROTHERY and E. O. ROUNSEFELL (Inst. Metals, March, 1929, advance copy, 20 pp.).—The equilibrium diagram of the system magnesium-zinc has been investigated by thermal and microscopical methods in the range 0—70 at.-% magnesium. The solubility of magnesium in solid zinc increases from about 0.15 at.-% at 200° to 0.3 at.-% at 364°, which is the temperature of the Zn-MgZn₅ eutectic. The compound MgZn₅ discovered by Chadwick (B., 1928, 268) is confirmed, but the solid solution in this compound which was claimed by Chadwick is shown not to exist; the compound is formed at 381° by a peritectic reaction between MgZn₂ and liquid. The compound MgZn₂ melts at 590°, but does not form solid solutions. A new compound, MgZn, which is also of fixed composition, is formed at 354° by a peritectic reaction between MgZn₂ and liquid. The compounds MgZn and MgZn₂ are distinguished by etching with Benedicks' reagent, which stains MgZn brown. The equilibrium diagrams of the systems magnesium-cadmium and magnesium-zinc are compared, and the wide range of solid solutions in the former is shown to coincide with approximately equal atomic volumes. In elektron metal and similar alloys, any zinc which is present in excess of that in solid solution in magnesium exists as the new compound MgZn and not, as previously supposed, as MgZn₂.

W. HUME-ROTHERY.

Constitution of the cadmium-rich alloys of the system cadmium-gold. P. J. DURRANT (Inst. Metals, March, 1929, advance copy, 33 pp.).—The system cadmium-gold has been investigated in the range 0—48 at.-% gold by thermal and microscopical

analysis. From pure cadmium the liquidus falls to a eutectic point at 7.95 at.-% (309°), rises to a flat maximum at 28.6 (500°), and then falls to a second eutectic at 30.0 (496°). From this point the liquidus continues to rise with a break at 540°, corresponding with a peritectic reaction at which a solid solution denoted III is formed. At 309° the solubility of gold in cadmium is 3.5 at.-%, but falls to 2.1 at 240°. The maximum at 500° corresponds with a solid solution denoted II, the solubility limits of which have been determined. The solid solution III was not detected by Saldau (*J. Inst. Metals*, 1923, **30**, 351); it extends from 32.5 to 40 at.-% Au, and undergoes two transformations into forms denoted III' and III''. The solubility limits diminish with falling temperature, until at 200° the range of solid solutions extends only from 37.5 to 38.5 at.-% Au. There is no evidence of the existence of a compound AuCd_3 at the liquidus, but there may be compounds Au_2Cd_5 and Au_2Cd_3 , both being much dissociated at higher temperatures.

W. HUME-ROTHERY.

Silver-copper eutectic. J. A. A. LEROUX and E. RAUB (*Z. anorg. Chem.*, 1929, **178**, 257—271).—The formation of primary silver- and copper-rich mixed crystals simultaneously with eutectic in the cooling of silver-copper alloys containing 68—75% Ag is not always due to supercooling, nor is it caused by separation of two liquid phases in the molten alloy. The true explanation appears to lie in the greater rate of crystallisation of the copper-rich crystals as compared with the silver-rich crystals. This is especially marked in alloys which deviate by a few per cent. from the eutectic composition, the silver-rich alloys having a great tendency towards supercooling, whereas the copper-rich alloys have no such tendency. For these reasons the determination of the true eutectic composition is a matter of great difficulty and no trustworthy results have yet been obtained. The microstructure of eutectiferous alloys of this system has been studied both before and after homogenisation. In the cast alloys the eutectic colony is identical with the crystal grain, or several colonies may coalesce to form a grain the shape of which is therefore always dependent on the configuration of the colony; this in turn depends on the greater rate of growth of the copper-rich solution. The whole mechanism of the crystallisation of these alloys is therefore determined by the behaviour of this phase and is only relatively slightly affected by the properties of the silver-rich phase.

A. R. POWELL.

Equilibria in the systems cobalt-sulphur-oxygen and nickel-sulphur-oxygen. R. SCHENCK and E. RAUB (*Z. anorg. Chem.*, 1929, **178**, 225—251).—Cobalt powder obtained by reduction of the formate with hydrogen reacts readily with sulphur dioxide yielding cobalt sulphide and oxide, and the reaction is irreversible, at least below 1050°. The reaction $\text{CoSO}_4 + 4\text{Co} = 4\text{CoO} + \text{CoS}$ proceeds to completion at 525° and is also irreversible, but the reaction $3\text{CoSO}_4 + \text{CoS} = 4\text{CoO} + 4\text{SO}_2$ is reversible provided that the solid reactants are in an extremely fine state of subdivision. The decomposition of cobalt sulphate by heat first becomes appreciable at about 900° and is complete after prolonged heating at 970°. Nickel

reacts rapidly with sulphur dioxide at 550°, but equilibrium is established only after many days, complete conversion into nickel oxide and mono-sulphide being effected. The equilibrium is univariant, as there are three solid phases, but by removing part of the sulphur dioxide one of these disappears and the equilibrium becomes bivariant. From a consideration of the equilibrium diagram and from measurements of the sulphur dioxide pressure the three phases appear to be nickel oxide, nickel sulphide, and the γ solid solution; with low pressures of sulphur dioxide the nickel sulphide phase disappears. The reverse reaction with the formation of nickel from nickel oxide and sulphide proceeds only as far as the solid solution phase below the m. p. (about 1400°); bundles of fine hair crystals of this phase, or possibly of Ni_3S_2 , can be seen throughout the reacting mass in the early stages of this reaction. The sulphate reactions in the case of nickel are similar to those with cobalt, except that the temperature at which the gas pressure reaches 1 atm. is 475° instead of 525°. The heats of formation of cobalt and nickel sulphates have been calculated from the data obtained in this investigation as 228,800 and 232,000 g.-cal., respectively.

A. R. POWELL.

Equilibria in the system calcium-sulphur-oxygen. I. R. SCHENCK and K. JORDAN (*Z. anorg. Chem.*, 1929, **178**, 389—399).—The reaction of calcium oxide with sulphur dioxide at high temperatures may be represented by the equations $4\text{CaO} + 4\text{SO}_2 = 3\text{CaSO}_4 + \text{CaS}$, and $\text{CaSO}_4 + \text{S}_2 \rightleftharpoons \text{CaS} + 2\text{SO}_2$. The gas pressures corresponding with the univariant equilibrium calcium oxide-calcium sulphate-calcium sulphide-gas (sulphur dioxide+sulphur vapour) are: 27 mm. at 850°, 34 mm. at 900°, and 46.5 mm. at 950°.

R. CUTHILL.

Two correlated space models for representing the equilibria in the system iron-carbon-oxygen. E. JANECKE (*Z. anorg. Chem.*, 1929, **178**, 73—96).—The equilibria in the iron-carbon-oxygen system may be represented by two space models, one showing the relation between temperature and composition without reference to the gas pressure and the other the relation between the temperature and pressure with respect to the composition of the gas phase in equilibrium with the solid phase. The former model is a triangular prism and the latter a rectangular prism. In the construction of both models the invariant and univariant equilibria in the system are of considerable importance, especially the invariant point at which ferrous oxide first appears in the solid phase and the invariant equilibria at the temperatures at which martensite appears for the first time in the solid phase. In the first case the constituents present are iron, ferrous oxide, ferrosiferrous oxide, and gas with carbon or cementite (metastable), and in the second case martensite, iron, ferrous oxide, and gas with carbon or cementite. With cementite the equilibrium is metastable and occurs at a relatively low temperature. The construction of the models is shown by diagrams and the equilibria in various sections are discussed fully.

A. R. POWELL.

Two forms of crystalline beryllium hydroxide, and the system $\text{BeO}-\text{Na}_2\text{O}-\text{H}_2\text{O}$. R. FRICKE and

H. HUMME (Z. anorg. Chem., 1929, 178, 400—410).—If the crystalline variety of beryllium hydroxide which is obtained by heating the precipitated amorphous hydroxide with an aqueous solution of ammonia is left in contact with a 20—35% aqueous solution of sodium hydroxide at 30°, the crystalline form slowly changes, and ultimately becomes identical with that of the hydroxide prepared by slow hydrolysis of an alkali beryllate solution. The solubility of the stable form in the hydroxide solution increases with the sodium hydroxide concentration until the concentration of alkali hydroxide is about 35%; at this point the solubility curve shows a discontinuous maximum, owing to the solid phase undergoing transformation into monosodium beryllate, $\text{BeO} \cdot \text{NaOH} \cdot \text{H}_2\text{O}$. The solubility increases with rise in temperature.

R. CUTHILL.

Ammonium sulphite and hydrogen sulphite.
II. System ammonium sulphite-ammonium sulphate-water. F. ISHIKAWA and H. MUROOKA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 75—88; cf. this vol., 141).—The solubility of ammonium sulphate in water (per 100 c.c. of solution) between the cryohydric point (−18.5°) and b. p. (108.5°) is given by the expression $(41.22 + 0.09t)$. The system ammonium sulphite-ammonium sulphate-water has been studied in detail at 15° and 30°. Between the cryohydric point (−21.5°) and 100° there is no evidence of the formation of compounds or solid solutions.

J. GRANT.

Equilibrium between water, sodium nitrate, and sodium chloride. A. CHRÉTIEN and E. CORNEC (Compt. rend., 1929, 188, 628—631).—The equilibrium diagram is analogous to that for the system water-potassium chloride-sodium chloride. A warm saturated solution of the two salts deposits only the nitrate. The transition temperature, $\text{NaCl} + 2\text{H}_2\text{O}$

$\text{NaCl} \cdot 2\text{H}_2\text{O}$, is lowered by successive additions of nitrate from 0.2° to −5.85°, at which point the saturated solution is in equilibrium with NaCl , $\text{NaCl} \cdot 2\text{H}_2\text{O}$, and NaNO_3 . The ternary eutectic point, −24.3°, is in equilibrium with ice, $\text{NaCl} \cdot 2\text{H}_2\text{O}$, and NaNO_3 .

R. BRIGHTMAN.

System mercuric iodide-potassium iodide-acetone. (Mlle.) M. PERNOT (Compt. rend., 1929, 188, 635—637).—The compound $\text{Me}_2\text{CO} \cdot 4\text{KI} \cdot 4\text{HgI}_2$ is obtained by isothermal evaporation at 34°. When the crystallisation is effected by cooling, the compound $\text{HgI}_2 \cdot 2\text{KI}$ and four supposedly isomeric compounds $\text{Me}_2\text{CO} \cdot 4\text{KI} \cdot \text{HgI}_2$ are said to be formed (cf. A., 1926, 695). The compound, $2\text{HgI}_2 \cdot 3\text{KI}$, found at 56°, is not obtained at 34°.

R. BRIGHTMAN.

Equilibria between molten metals and salts.
Displacement of the equilibrium in the reaction $\text{Cd} + \text{PbCl}_2 \rightleftharpoons \text{Pb} + \text{CdCl}_2$ by additions to (XIII) the salt phase and (XIV) both phases simultaneously. R. LORENZ and M. HERING (Z. anorg. Chem., 1929, 178, 33—39, 40—48; cf. this vol., 266).—XIII. Addition of the eutectic sodium-potassium chloride mixture to the salt phase in the reaction $\text{Cd} + \text{PbCl}_2 \rightleftharpoons \text{Pb} + \text{CdCl}_2$ displaces the equilibrium from left to right, i.e., lead becomes more noble with respect to cadmium.

XIV. Simultaneous addition of antimony to the

metal phase in equimolecular proportion to the salt added to the salt phase first displaces the equilibrium from left to right, but larger additions have the reverse effect. At the same time the displaced isotherms approach more closely to those corresponding with the ideal mass action law.

A. R. POWELL.

Equilibria between metals and salts in the molten state. XV. Displacement of the equilibrium point in the equilibrium $\text{Cd} + \text{PbCl}_2 \rightleftharpoons \text{Pb} + \text{CdCl}_2$. R. LORENZ and M. HERING (Z. anorg. Chem., 1929, 178, 337—345; cf. preceding abstract).—The effect of the simultaneous addition of an equimolecular mixture of sodium and potassium chlorides to the salt phase and antimony or bismuth to the metal phase has been investigated. With increase in the amount of substance added the displacement of the equilibrium tends to a limiting value. When both salts and a metal have been added, addition of more salts has a greater effect than the addition of an equimolecular amount of metal. From the data obtained, it is possible to calculate the amounts of metal and salts which must be added for the net displacement to be zero.

R. CUTHILL.

Reduction of fused silicates by carbon monoxide. Copper silicates. B. BOGITCH (Compt. rend., 1929, 188, 633—635).—In presence of an atmosphere containing more than 2% of carbon monoxide at 1350—1400° fused blue copper silicate (stable in an oxidising atmosphere) is partly reduced to metallic copper, reduction being almost complete when the proportion of carbon monoxide exceeds 25%. Simultaneously with this reduction, the blue silicate is converted successively into other silicates as the proportion of carbon monoxide is increased: 2.5—4% green, 9% white, 10.5—12.5% opaque brick-red, 20—22.5% transparent blood-red.

R. BRIGHTMAN.

Quaternary system lead acetate-lead chloride-acetic acid-water at 25°. K. SANDVED (J.C.S., 1929, 337—344; cf. A., 1928, 131).—The systems lead acetate-lead chloride-water and lead chloride-acetic acid-water have been studied at 25°, and the former also at 35°. In combination with the data for the system lead acetate-acetic acid-water the results are applied to the quaternary system. In the first system two invariant points occur at 1.46% PbCl_2 , 37.43% $\text{Pb}(\text{OAc})_2$, and 4.48% PbCl_2 , 21.25% $\text{Pb}(\text{OAc})_2$, respectively. The solubility of lead acetate in pure water at 25° is 35.53%, and that of lead chloride 1.06%. At 35° the invariant points occur at 2.17% PbCl_2 , 49.53% $\text{Pb}(\text{OAc})_2$, and 7.72% PbCl_2 , 31.90% $\text{Pb}(\text{OAc})_2$, respectively. The solubilities of lead acetate and of lead chloride are 47.40 and 1.30%, respectively. The study of the quaternary system shows the existence of the compounds $\text{PbCl} \cdot \text{OAc}$, $\text{Pb}(\text{OAc})_2 \cdot 0.5\text{HOAc}$ and $(\text{PbCl} \cdot \text{OAc})_2 \cdot \text{HOAc}$.

F. G. TRYHORN.

System NaNO_3 - Na_2SO_4 - MgCl_2 - H_2O in the neighbourhood of 0°, 10°, 25°, 75°, and 100°. G. LEIMBACH and A. PFEIFFENBERGER (Caliche, 1929, 10, 447—468).—A detailed study has been made of the system at 0°, 10°, and 25°, and the results have been compared with those of other observers.

H. F. GILLBE.

Chemical equilibria between solid salts. C. TUBANDT and H. REINHOLD (Z. physikal. Chem., 1929, 140, 291—308).—Interaction in pairs between the solid sulphides, selenides, tellurides, and halides of silver and of univalent copper leads to a definite state of equilibrium. The diffusion which takes place when the solids are brought into contact can be followed by the change in weight and the equilibrium composition derived. It is shown that the law of mass action is applicable to the reactions $\text{Ag}_2\text{S} + 2\text{CuI} \rightleftharpoons \text{Cu}_2\text{S} + 2\text{AgI}$ and $\text{Ag}_2\text{S} + \text{Cu}_2\text{Se} \rightleftharpoons \text{Cu}_2\text{S} + \text{Ag}_2\text{Se}$. The equilibrium constants have been determined at more than one temperature and the heats of reaction have been calculated. The values found, 12.7 and 8.77 kg.-cal., respectively, are in good agreement with values calculated by other methods. The difference in mechanism between these reactions and ordinary diffusion in solid salts is discussed.

R. N. KERR.

Hydrocarbons as solvents. I. Conductivity of binary salts in ethylene chloride. P. WALDEN and G. BUSCH (Z. physikal. Chem., 1929, 140, 89—123).—The conductivities of the following salts have been determined at 25° at dilutions up to 400,000 litres: tetraethylammonium chloride, perchlorate, and iodide, tetramethylammonium picrate, tetrapropylammonium picrate, perchlorate, and iodide, tetraisoamylammonium picrate and perchlorate, triethylammonium picrate and chloride, diethylammonium picrate and chloride, tripropylammonium picrate, dipropylammonium picrate, monopropylammonium picrate, and, at 0°, 25°, and 50°, tetraethylammonium picrate. The densities of the solvent and salts have also been determined. The Kohlrausch-Debye-Hückel square-root law is valid for ethylene chloride solutions at high dilutions. The nature of the salt has a well-defined influence on the value of the conductivity and on the classical degree of ionisation α . The tetra-alkylated ammonium salts behave as strong electrolytes, in contradistinction to the corresponding mono-, di-, and tri-alkylated compounds, the degree of ionisation of the strong electrolytes diminishing in the order $\text{N}(\text{C}_5\text{H}_{11})_4$, NPr_4 , NEt_4 , NMe_4 . The causes of the difference of behaviour of the two classes are considered, and the relationships between the free bases in aqueous solution and their picrates in the fused state are discussed. Kohlrausch's law of the additivity of conductivities is completely valid for ethylene chloride solutions. The Walden constant

has for tetraethylammonium picrate in ethylene chloride solution from 0° to 50° the value 0.563, in agreement with the value for water, methyl alcohol, ethyl alcohol, and acetone solutions. The individual ionic mobilities have been calculated.

H. F. GILLBE.

Conductivity of solutions of some aliphatic organic acids in water and ethyl alcohol. H. HUNT and H. T. BRISCOE (J. Physical Chem., 1929, 33, 190—199).—The specific conductances of the fatty acids from acetic to valeric acid and of their substituted derivatives, chiefly halogen, have been determined in water and in ethyl alcohol at 30°. In all cases the molecular conductance in alcohol is much less than that in water, and the rate of increase for successive dilutions is approximately twice as great

in alcohol as in water. The order of conductance in the two solvents is not the same, e.g., acetic acid is the 15th in the alcohol series and 8th in the water series, whilst β -bromopropionic acid is the poorest conductor in alcoholic solution, but stands above eight other acids in the water series. With the exception of isovaleric acid in water and hexoic acid in alcohol, the molecular conductance decreases with an increase in the number of carbon atoms for an homologous series. In alcohol, the *iso*-acids have a lower conductance than the corresponding normal acids, but in water the *iso*-acid may have a higher or lower conductance than the normal acid. The data do not show agreement in all cases with the Stark-Lewis theory of the effect of substituent groupings. The curves obtained by plotting the logarithm of the volume against conductance are in agreement with the mass action law at high dilutions.

L. S. THEOBALD.

High mobility of hydrogen and hydroxyl ions in aqueous solutions. M. S. SKANAVI-GRIGORIEVA (J. Russ. Phys. Chem. Soc., 1928, 60, 1459—1475).—In order to ascertain the cause of the high mobility of the hydrogen and hydroxyl ions in aqueous solutions the molecular conductivities, viscosities, and densities of aqueous solutions of potassium chloride, hydrochloric acid, and sodium hydroxide containing different amounts (10, 20, 40, and 50%) of glycerol have been determined. The percentage changes in the molecular conductivities when compared with the changes in viscosity are found to be nearly the same for all three electrolytes. From this it is inferred that the high mobility of the hydrogen and hydroxyl ion is not due to the Grotthuss-Danneel effect.

A. FREIMAN.

Influence of a high-potential direct current on the conductivity of an electrolyte. J. A. H. LEECH-PORTER and T. ALTY (Phil. Mag., 1929, [vii], 7, 153—159).—Direct-current potentials up to 600 volts have been applied to very dilute solutions of electrolytes in the measurement of their conductivities and have been shown to cause large variations in the conductivities in certain narrow ranges of concentrations. The effect is most marked in the case of hydrogen chloride solutions when the specific conductivity is about 2×10^{-4} ohm⁻¹, when the conductivity can vary as much as 600%. The results are explained on the view that the high potential causes a segregation of the ions towards the electrodes, where they remain until on reversing the potential each of the segregations moves across to the opposite electrode as a unit. Rough measurements of the velocity of this unit give a value of 74×10^{-5} cm./sec./volt/cm. for the mobility of the chlorine ion. This is in fair agreement with the accepted value of 68×10^{-5} , and indicates the possible application of the phenomenon in the determination of ionic mobilities.

A. E. MITCHELL.

Voltage effect in electrolytic conductance with very high fields. M. WIEN (Ann. Physik, 1929, [v], 1, 400—416).—The limiting value for the voltage effect (A., 1928, 244; this vol., 32) for various electrolytes is in harmony with the concentration effect, and also shows close agreement with the values given by the

Debye-Onsager theory provided the valencies of the ions are small. With ions of higher valency, the theoretical values are lower than those obtained from the limiting voltage effect and the concentration effect. According to Debye and Falkenhagen, the influence of ionic forces should become vanishingly small with sufficiently strong fields. When association occurs, the limiting voltage effect should fall more markedly than the concentration effect. Inasmuch as the two phenomena run parallel, even with solutions containing ions of high valency, association can scarcely occur in the very dilute solutions of strong electrolytes which have been studied. R. A. MORTON.

Potential of the nickel electrode. M. M. HARING and E. G. V. BOSCHÉ (J. Physical Chem., 1929, 33, 161—178).—Measurements at $25 \pm 0.5^\circ$ of the *E.M.F.* of cells of the type $\text{Ni}|\text{NiSO}_4|\text{Hg}_2\text{SO}_4|\text{Hg}$, using nickel and nickel sulphate prepared in various ways and from different sources, gave a mean value for E_0 equal to 0.852 volt, and using the value of Lewis and Randall for the electrode $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{SO}_4^{--}$, this gives for the standard potential of nickel at 25° the value -0.231 ± 0.002 volt. Nickel prepared by electrolysis at high current densities is the most satisfactory for this type of work. Owing to hydrolysis of the nickel chloride, cells of the type $\text{Ni}|\text{NiCl}_2(0.05 \text{ molal})|\text{Hg}_2\text{Cl}_2|\text{Hg}$ could not be used. The necessity for excluding oxygen and hydrogen in such measurements is re-emphasised. Previous data are summarised and discussed. L. S. THEOBALD.

P.D. of dilute solutions. II. M. PLANCK (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 9—11; cf. A., 1928, 481).—A formula applicable to simplified systems is deduced for the previously observed difference between the values found by Henderson and by the author for the diffusion potential between two dilute solutions of different electrolytes. An experimental arrangement is suggested which, according to this formula, is suitable for testing the two theoretical values for the potential. R. N. KERR.

Dialuric acid-alloxan equilibrium. G. M. RICHARDSON and R. K. CANNAN (Biochem. J., 1929, 23, 68—77).—Equilibrium potentials for the reversible oxidation-reduction system dialuric acid-alloxan have been determined for the p_{H} range 1—6 and related to the equilibrium potentials of alloxantin observed by Biilmann and Lund (A., 1923, ii, 605). Above p_{H} 6 approximate equilibrium potentials have been derived from the range p_{H} 6—12 on the assumption that over this range there is a slow isomeric change of alloxan to alloxanic acid. The first acidic constants of dialuric acid ($K' = 1.48 \times 10^{-3}$) and of alloxan ($K'_1 = 6.31 \times 10^{-8}$) have been determined. A value has also been found for the second acidic constant of alloxan ($K'_2 = 1.0 \times 10^{-10}$). The association constant of alloxantin ($K = 39$) has also been derived. Observations have also been made on the connexion between p_{H} and the rates of the isomeric change of alloxan and of the autoxidation of dialuric acid. S. S. ZILVA.

"Natural" P.D. at the boundary, cell-electrolyte. G. ETTISON (Z. physikal. Chem., 1928, 139, 516—528).—Measurements made on *Amoeba terricola* in a cell of the type $\text{Hg}, \text{HgCl}, 0.1N\text{-KCl}|\text{buffer soln.}|$

amoeba $|\text{Hg}, \text{HgCl}, 0.1N\text{-KCl}$ show that such a cell assumes a state of minimum free energy. The *E.M.F.* measured is zero, but by altering the concentration of the buffer solution during the measurement, by introducing a small crystal of sodium chloride, a temporary *E.M.F.* is produced. In a very short time the reading recedes to the null-point again. At the boundary cell-electrolyte some phase boundary force must appear, the so-called "natural" *P.D.*, the living *amoeba* setting up a state of equilibrium which is very quickly adjusted when disturbed by variation in concentration. G. E. WENTWORTH.

Nature of Kucera's electrocapillary curve anomalies. K. TEIGE (Chem. Listy, 1929, 23, 54—58).—The maxima shown by Kucera (Ann. Phys., 1903, II, 568) to occur in electrocapillary curves are due to the displacement of non-electrolytes by electrolytes from the surface of the cathode, within certain limits of *E.M.F.* R. TRUSZKOWSKI.

Hydrogen overvoltage of alloys. M. G. RAEDER and D. ERFJESTAD (Z. physikal. Chem., 1929, 140, 124—132).—The hydrogen overvoltage of alloy cathodes has been studied by reference to potential-current density curves. Previous results (A., 1928, 597) have been confirmed. Mixed crystal formation sometimes has but little influence on the overvoltage curve (mercury-cadmium), but in other cases a peaked curve is produced (tin-lead, copper-tin, silver-zinc). A sharp drop in the overvoltage has not so far been observed. Formation of eutectics or of compounds has no marked influence on the curve.

H. F. GILBE.
Theory of passivity. IV. Dependence of specific passivating time for iron on the concentration and nature of electrolytes. W. J. MÜLLER and O. LÖWY (Monatsh., 1929, 51, 73—85).—The relation between initial current strength and passivation time has been studied with sulphuric acid over the range $N/16$ — $13N$. The results confirm the validity of the formula $\log t_p = \log B + n \log (i_0/F_0)$ (cf. A., 1928, 714), where B is the specific passivation time when the current density is unity. Small acid concentrations give small specific passivating times. A maximum is reached at $2N$, and above this concentration there is a fall in the time. In N -sulphuric acid the passivation time increases with rise of temperature over the range $(20\text{—}60^\circ)$ studied. With varying amounts of ferrous and ferric sulphates in N -sulphuric acid the values of n remain constant, but those of B decrease with increasing concentration of added salts. A rise of temperature is in this case associated with an increase in the value of B , but with saturated solutions of ferrous sulphate in N -sulphuric acid the values at 20° and 40° are the same. The results confirm the theory that the first stage of the passivation of iron consists in the deposition of a salt layer (cf. A., 1928, 247, 714). H. BURTON.

Theory of physico-chemical periodicity. N. VON RASCHEVSKY (Z. Physik, 1928, 52, 372—381).—Theoretical arguments are put forward indicating that when a sequence of reactions occurs which gives rise to a heterogeneous, cell-like structure it may occur in a periodic manner. J. W. SMITH.

Velocity of combination of hydrogen atoms. Z. BAY and W. STEINER (Z. physikal. Chem., 1929, B, 2, 146—147).—Atomic hydrogen was obtained by the usual method, and the amount of combination determined by means of diffusion columns. It was found that if the concentration of atomic hydrogen were plotted against time, at low pressures a straight line was obtained, whilst at higher pressures curves were found. From the experiments at higher pressures (0.2 mm.), for a concentration of 35% of hydrogen atoms, the mean life (half-value period) was about 1 sec. This agrees with Bonhoeffer's value obtained by chemical methods. The half-value period obtained is the value expected on the assumption that there are triple collisions. A. J. MEE.

Mechanism of the homogeneous combination of hydrogen and oxygen. H. W. THOMPSON and C. N. HINSHELWOOD (Proc. Roy. Soc., 1929, A, 122, 610—621).—The chain theory of chemical reaction in gases is briefly reviewed, and it is shown that the velocity of a chain reaction can be expressed by the formula $v = F(c)/\{f(c,s) + A(1-\alpha)\}$, where $F(c)$ is a function of the concentrations of the reacting substances, to which the number chains starting in unit time is proportional; $f(c,s)$ is another function of the concentrations, governing the rate of breaking of the chains; A is a constant in reactions where only one kind of molecule is involved, but is a function of the concentration in reactions between two kinds of molecules; and α is a fraction measuring the average number of activated molecules produced in each act of transformation. Two types of chain reaction are possible, one leading to a "stationary" condition (identified with slow reaction) and the other where this condition is impossible (explosive reaction). The combination of hydrogen and oxygen between 500° and 600° has previously been shown to be a chain reaction, the rate increasing rapidly with the pressure (cf. A., 1928, 483, 960). It is now found that, as the pressure is decreased, the chains become "non-stationary" and the reaction explosive over a certain region of falling pressure, after which, with still further falling pressure, the reaction again becomes slow. A detailed investigation of the upper and lower pressure limits of the explosive region shows that, with regard to the upper critical pressure, (a) at a given temperature it is slightly lowered by an increase in the ratio of the H_2/O_2 mixture; (b) it is somewhat lowered by the presence of argon; (c) at any temperature over a wide range it is almost, if not quite, independent of the nature and extent of the surface of the reaction vessel; it diminishes rapidly as the temperature falls. The temperature at which ignition ceases completely will obviously be that at which the upper and lower pressure limits coincide. In an unpacked silica bulb this is about 450°, from which it is deduced that the lower limit will be approximately 8 mm. The theory of these phenomena is discussed, and a hypothesis of two simultaneously operating mechanisms is advanced. At high pressures the chains are initiated by the termolecular process $2H_2 + O_2 = 2H_2O$, but at low pressures it is assumed that the termolecular process is to a large extent superseded by a chain of bimole-

cular process, $H_2 + O_2 = H_2O_2$, $H_2O_2 + H_2 = 2H_2O$, etc. For a given condition of temperature and pressure there will be a small stationary concentration of hydrogen peroxide in the gas, regulated by the thermal equilibrium $H_2 + O_2 \rightleftharpoons H_2O_2$. This concentration will increase with pressure, and the upper and lower pressure limits will correspond with two limiting concentrations of hydrogen peroxide. This hypothesis accounts for the facts concerning the critical pressure limits, and also suggests an explanation of the influence of traces of nitrogen peroxide on the reaction.

L. L. BIRCHMISHAW.

Spark ignition of hydrogen-air mixture. K. YUMOTO (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 131—142).—Variations in the nature of the spark used for the ignition of a mixture of air and 5.5% of hydrogen indicate that the flame formed in a static electric field between parallel plate electrodes is attracted to the metallic cathode of the field, a considerable amount of heat then being lost by conduction so that the flame is eventually extinguished. Whether the flame is extinguished or further propagated, in the absence of a static field it is always propagated initially towards the cathode of the ignition spark gap. J. GRANT.

Firedamp explosions within closed vessels; "pressure piling." C. S. W. GRICE and R. V. WHEELER.—See B., 1929, 193.

Inflammation of mixtures of olefines and air in a closed spherical vessel. G. B. MAXWELL and R. V. WHEELER (J.C.S., 1929, 245—251).—Experiments parallel to those already described (A., 1927, 1036) on the inflammation of mixtures of the paraffins and air have been made with ethylene, propylene, and butylene. The results for the olefines are similar to those obtained with the paraffins. There is a marked "displacement" of the observed maximum pressure mixture, from the theoretical for complete combustion, towards excess of hydrocarbon. This displacement is attributed to dissociation. The amounts of "lost pressure" are higher than with the paraffins. In accord with the results of the experiments with paraffins, a close correspondence between observed values for maximum speed mixtures and calculated values for the maximum temperature mixtures was found, indicating that flame temperature is the controlling factor in determining the mean rate of development of pressure. F. J. WILKINS.

Active nitrogen. V (amended). **Decay of the nitrogen after-glow.** E. J. B. WILLEY (J.C.S., 1929, 228—231; cf. A., 1928, 961).—An arithmetical error in an earlier paper is corrected and its influence on the theoretical discussion contained in it pointed out. It is now suggested that the decay process is of the third instead of the fifth order. The analysis is complicated by the existence of a surface action. F. J. WILKINS.

Explosion regions of some gas and vapour mixtures in which carbon monoxide is the only or principal inflammable gas. J. H. A. P. LANGEN VAN DER VALK (Rec. trav. chim., 1929, 48, 201—219; cf. A., 1925, ii, 874).—Under certain experimental conditions the upper and lower explosion limits of carbon monoxide in air were 72.75 and 15.35%,

respectively. The effect of saturating the carbon monoxide at 14° with the vapours of various organic liquids has been determined. The explosion limits were brought closer together by trichloroethylene. For dichloroethylene and air the explosion limits were 3.25% and 15%. The lower limit decreases linearly with admixture of carbon monoxide, but the upper limit is little affected. Admixture of perchloroethylene, tetrachloroethane, or pentachloroethane brings closer together the explosion limits of carbon monoxide-air mixtures. The presence of little more than 1% of carbon tetrachloride vapour completely inhibits the explosion of carbon monoxide-air mixtures. For mixtures containing 3% and 2% of chloroform vapour the explosion limits were, respectively, 25.5–38.5%, and 22.5–45.5%. Of methylene dichloride 20% was necessary to inhibit explosion, the limits separating to 13.15 and 35.45% for mixtures containing 10% of this substance. Methyl chloride, of which the explosion limits in air are 16.3 and 24.4%, widens the limits of explosion of carbon monoxide-air mixtures. The investigation was extended to the quaternary system carbon monoxide-air-methane-chloroform, and an unsuccessful search was made for a closed explosion region in the system methylene dichloride-methylene dibromide-oxygen-nitrogen. F. G. TRYHORN.

Decomposition of nitrous oxide in the silent electric discharge. II. S. S. JOSHI (Trans. Faraday Soc., 1929, 25, 108–117; cf. A., 1927, 635).—In a previous paper (cf. A., 1927, 212) an equation was derived for the velocity of a chemical reaction in the silent electric discharge. In order to test the applicability of this equation to the initial stages of the decomposition of nitrous oxide the percentage decomposition of nitrous oxide (θ) has been determined under different conditions of gas pressure, applied potential, and duration of exposure. It is found that θ decreases with increase of initial pressure and increases with increase of potential applied to the ozoniser. The diminution of $\log \theta$ with respect to the pressure is linear, as required by the velocity equation. From this equation the critical energy for the decomposition of nitrous oxide by an ionic collision is calculated, and the values from several experiments with different reaction vessels and applied voltage and a wide range of time intervals all lie between 0.7 and 1.0 volt. This value corresponds with the partial decomposition of nitrous oxide into the peroxide and nitrogen, and is smaller than the value of the critical energy of the reaction in which nitrous oxide changes completely into nitrogen and oxygen. O. J. WALKER.

Decomposition of nitrous oxide in the silent electric discharge. III. Variation of the current and power during the reaction. S. S. JOSHI (Trans. Faraday Soc., 1929, 25, 118–128; cf. preceding abstract).—The decomposition of nitrous oxide has been examined with particular reference to the composition of the gaseous mixture at different stages of the reaction in order to determine to what extent the substances characteristic of the intermediate and final stages are responsible for the changes in the power and current, which were previously found to

occur during the course of the reaction (cf. A., 1927, 635). These changes have been confirmed by more exact measurements of the power consumed in the ozoniser. The results are in good agreement with the mechanism of the reaction previously suggested. The first stage consists of the conversion of nitrous oxide into nitrogen peroxide and nitrogen. During this stage both the current and the power consumed in the ozoniser diminish from large initial values to a minimum at approximately the same time that the proportion of the peroxide reaches a maximum. The decomposition of the peroxide into nitrogen and oxygen is the main reaction in the intermediate and final stages. During the intermediate stage the values of the current, of the power consumed, and of the reaction rate are relatively low and practically constant. In the final stage, which is characterised by a sudden increase of pressure, the reaction becomes more rapid, and during this period the current and power increase appreciably up to a constant value corresponding with the completion of the decomposition. O. J. WALKER.

Interference of characteristic vibrations as cause of energy fluctuations and chemical changes. M. PÓLANYI and E. WIGNER (Z. physikal. Chem., 1928, 139, 439–452).—The velocity coefficient of unimolecular reactions in solution and in the gaseous state contains in addition to an exponential term a quantity which is always of about the same order of magnitude, 10^{14} . In order to explain this, it is suggested that the atoms in molecules fluctuate about equilibrium positions and therefore give rise to characteristic vibrations. If, by interference, the amplitude for a certain band increases beyond a critical amount chemical change occurs. The expression for the velocity coefficient is $ve^{-Q/RT}$, where v is the frequency of atomic vibrations. Calculations are given showing that this frequency is of approximately the required order of magnitude, 5×10^{12} – 5×10^{13} sec.⁻¹ R. N. KERR.

Oxidation by air of stannous chloride in sulphuric acid solution, and the dissolution velocity of oxygen in sulphuric acid solutions. S. MIYAMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 7–17, and Bull. Chem. Soc. Japan, 1929, 4, 48–56).—The rate of oxidation of stannous chloride in sulphuric acid solutions by the passage through them of air at a definite speed at 20°, 30°, and 40°, when calculated as a zero-order reaction, increased slowly as the acid concentration was increased up to 0.8*N*, after which it assumed a constant rate. Calculations from the data obtained of the volumes of oxygen dissolved per min. revealed that they were nearly the same as those utilised in the oxidation in hydrochloric acid solutions under the same conditions. Temperature had a negligible effect when the concentration of sulphuric acid was greater than 0.8*N*. H. T. S. BRITTON.

Influence of the polarity of the solvent on the velocity of a reaction. R. N. KERR (J.C.S., 1929, 239–242).—The reaction between allyl bromide and pyridine has been studied in a series of disubstituted benzene derivatives. The results for chlorobenzene and the dichlorobenzenes, anisole, and the tolyl methyl

ethers may be interpreted on the basis of variations in the electric moments of the solvent molecules. In other cases, such as the nitrobenzenes, variations occur in the reaction velocities which cannot be explained only in terms of the influence of the dipole moment of the solvent molecules.

F. J. WILKINS.

Kinetics of the hydrolysis of certain glucosides.

II. Trehalose, α -methylglucoside, and tetramethyl- α -methylglucoside. E. A. MOELWYN-HUGHES (Trans. Faraday Soc., 1929, 25, 81—92; cf. A., 1928, 374).—The rates of hydrolysis of the above three substances by means of *N*-hydrochloric acid have been determined polarimetrically at two temperatures and the corresponding critical increments calculated. The critical increments furnish a more trustworthy guide in the comparison of structural stability than the velocity coefficients, which are only of qualitative value, since the ratio of velocity coefficients varies with the temperature except in particular cases. The lability of sucrose towards acids cannot be associated with the grouping

—O·C·O·C·O— and is more probably due to the γ -fructose half. Evidence is advanced for the view that the process of mutarotation does not involve the rupture of the oxide ring. It is attempted to reconcile the data for glucoside hydrolysis with Hinshelwood's velocity equation (A., 1927, 26) based on a collision theory of unimolecular reactions. The idea that internal degrees of freedom of the "hydrolyst" molecule can contribute to the energy of activation can be used as a means of differentiating between enzymic and non-enzymic hydrolyses. It is suggested that the function of an enzyme is to allow a greater number of internal degrees of freedom to come into play in the process of activation than is possible in its absence.

O. J. WALKER.

Atmospheric oxidation, or dealkylation, of aqueous solutions of methylene-blue. W. C. HOLMES and E. F. SNYDER (Stain Tech., 1929, 4, 7—10).—At about 25° dilute solutions of methylene-blue are stable below p_H 9·5. Oxidation begins between p_H 9·5 and 9·8 and increases with increasing alkalinity. Below p_H 11 the rate is slow and the amount of oxidation limited, but at p_H 12 oxidation is rapid and complete in a few days.

Trimethylthionine is less stable than methylene-blue to atmospheric oxidation. H. W. DUDLEY.

Steric hindrance. S. C. J. OLIVIER (Rec. trav. chim., 1929, 48, 227—236).—Hydrolysis velocity coefficients for a number of halogen-substituted benzoyl and benzyl chlorides were determined. The observed rates of hydrolysis of *o*-, *m*-, and *p*-bromo-, 2:6-, 2:4-, and 3:5-dibromo-benzoyl chlorides were (benzoyl chloride=1) 1·35, 1·69, 0·92, 0·0112, 2·19, 13·5, respectively, showing the considerable steric hindrance effect operative with the 2:6-compound. The author considers that in the case of hydrolysis of acid chlorides the reaction measured is addition of water: $\text{ClR}\cdot\text{C}\cdot\text{O} + \text{H}_2\text{O} \longrightarrow \text{ClR}\cdot\text{C}(\text{OH})_2$. No steric effects were observed in similar experiments with corresponding halogenated benzyl chlorides, for which the figures were (benzyl chloride=1) 0·280, 0·202, 0·51, 0·120, 0·207, 0·070, respectively. Reaction

velocities were determined in 50 vol.-% acetone-water mixtures.

R. J. W. LE FEVRE.

Rate of oxidation of porcelain and ball clays.

H. M. KRANER and E. H. FRITZ.—See B., 1929, 208.

Corrosion of steel at high temperatures. L. LOSANA and G. REGGIANI.—See B., 1929, 210.

Action of atomic hydrogen on hydrocarbons.

H. VON WARTENBERG and G. SCHULTZE (Z. physikal. Chem., 1929, B, 2, 1—9).—A method is described for measuring the heat evolved when methane, ethane, ethylene, and acetylene respectively are mixed with atomic hydrogen. The products of the reactions were also investigated. Methane remained practically unchanged, but brought about a little catalytic combination of the hydrogen atoms to form molecules. Acetylene and ethane were also unaffected, but brought about some catalytic combination of the atoms. Ethylene was converted into ethane and also catalysed the combination of hydrogen atoms, obviously through the action of the ethane formed. Some acetylene was also produced. An attempt is made to explain the catalytic activity of acetylene and ethane. Probably the reaction is represented by the equations: $\text{C}_2\text{H}_6 + \text{H} = \text{C}_2\text{H}_5 + \text{H}_2$; $\text{C}_2\text{H}_5 + \text{H} = \text{C}_2\text{H}_6$.

A. J. MEE.

[Oxidative catalytic activity of iron.] H. HANDOVSKY (Biochem. Z., 1928, 202, 157—158).—The author's theory of the mechanism of the oxidative catalytic action of iron (A., 1928, 718) is maintained against Warburg's criticisms (*ibid.*, 1195).

P. W. CLUTTERBUCK.

Action of carbon monoxide and hydrogen cyanide on catalysis by hæmatin.

H. A. KREBS (Biochem. Z., 1929, 204, 322—342).—Experiments on the catalytic oxidation of cysteine to cystine by hæmatin and by some of its derivatives show that the compound of hæmatin with pyridine is particularly active. At 20° an amount of this compound equivalent to 1 mg. of iron transfers 100,000 c.c. of oxygen per hr. to cysteine, the tervalent iron of the hæmatin compound being first reduced in the process to the bivalent iron of pyridine-hæmochromogen and then reoxidised by molecular oxygen. The tervalent iron of pyridine-hæmatin does not react with the thiol group of cysteine. Carbon monoxide and hydrocyanic acid (but not hydrogen sulphide) check the oxidation process. Carbon monoxide combines in the dark with the bivalent iron of the hæmochromogen and so interferes with the reaction between the iron and oxygen, but on illumination the carbon monoxide-hæmochromogen compound is dissociated and the catalytic process proceeds as before. Hydrocyanic acid, on the other hand, reacts with the tervalent iron of the pyridine-hæmatin compound. The reactions of the hæmin compounds are also the characteristic reactions of the respiratory enzyme.

W. MCCARTNEY.

Biological oxidation-reduction systems. II. Reducing effect of cysteine induced by free metals.

L. MICHAELIS and E. S. G. BARRON (J. Biol. Chem., 1929, 81, 29—40).—Mercury, platinum, especially in the form of platinum-black, and gold deposited on platinum accelerate the uptake of oxygen by a solution of cysteine, the effect being maximal

at p_H 12.8. Salts of the above metals have no such effect; cyanides have no influence in the case of mercury, but inhibit the effect of platinum. Mercury and platinum also accelerate the reduction of methylene-blue by cysteine. Silver has no effect on either reaction whether in the metallic state or as a salt.

C. R. HARRINGTON.

Action of heavy metals on the autoxidation of alkali sulphides and of hydrogen sulphide. H. A. KREBS (Biochem. Z., 1929, 204, 343—346).—The rate of oxidation of alkali sulphide is enormously increased by the presence of minute quantities of heavy metals. Manganese and nickel are the most active metals; the presence of the former in amounts of the order 10^{-9} g. or of the latter in amounts of the order 10^{-8} g. doubles the velocity of oxidation. Solutions of hydrogen sulphide require much greater amounts (10,000—100,000 times) of heavy metals to produce the same results. For aqueous solutions of hydrogen sulphide nickel is the most active catalyst; for solutions of hydrogen sulphide in *N*-hydrochloric acid a mixture of manganese and iron. The so-called autoxidation of solutions of sulphides is probably due to the presence of traces of heavy metals.

W. MCCARTNEY.

Thermal decomposition of methane. T. KUSANA and Y. UNO.—See B., 1929, 193.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. III. *X*-Ray examination of methyl alcohol catalysts composed of copper and zinc. P. K. FROLICH, R. L. DAVIDSON, and M. R. FENSKE (Ind. Eng. Chem., 1929, 21, 109—111; cf. A., 1928, 1112; this vol., 153).—Zinc oxide is partly reducible at 200—220° in a stream of methyl alcohol vapour particularly when in admixture with copper oxide. The exothermic reduction of the latter oxide may furnish the necessary energy for the partial reduction of the zinc oxide. An attempt has been made to ascertain by *X*-ray examination if the zinc oxide is reduced to the metallic state. It has not been possible to prove the presence of metallic zinc, although there are indications that it is present. The complete series of zinc oxide-copper catalysts studied (from pure zinc oxide to pure copper) all possess the characteristic crystal structure of the two components. The cell unit sizes of both copper and zinc oxide are markedly influenced by the presence of the other constituent. The selective activity of these catalysts appears to be related in some way to the distances separating the atoms of their constituents.

H. INGLESON.

Catalysis by metals of the platinum group. G. R. LEVI (Atti R. Accad. Lincei, 1928, [vi], 8, 409—414; cf. A., 1926, 365).—From measurements of the decomposition of hydrogen peroxide by preparations of pure platinum, and of platinum containing 10% respectively of palladium, osmium, ruthenium, iridium, and rhodium, supported in each case on an inert base, it has been found that the catalytic activity of the platinum is lowered by the presence of the other metals, except in the case of osmium. The inhibiting effects of these metals were in the order rhodium, palladium, and iridium. Ruthenium was almost without effect, whilst the

presence of 10% of osmium roughly doubled the catalytic activity of the platinum. Except in this last case, the results are analogous to those obtained with the same catalysts in the formation of sulphur trioxide.

F. G. TRYHORN.

Formation of hydrazine from ammonia by electrical discharges. G. BREDIG, A. KOENIG, and O. H. WAGNER (Z. physikal. Chem., 1928, 139, 211—223).—Ammonia is decomposed partly into hydrazine at pressures of the order of 100 mm. by an ozoniser discharge excited by alternating potentials of frequency 50, and by streaming the gas through a high-tension cooled arc excited by continuous or alternating potentials. By using streaming velocities of the order of 400 mg. per min. a yield of hydrazine corresponding with about 1 g. per kw.-hr. may be obtained.

R. W. LUNT.

Quantitative electrolytic reduction. II. Reduction of nitric acid. E. NIETZ (J. pr. chem., 1929, [ii], 121, 27—55).—The various errors involved in the quantitative electrolytic reduction of a nitrate to ammonia have been studied in detail. With a spongy copper cathode, which is the most efficient for this reduction, the main causes of error are: (1) the evolution of a small amount of nitrogen, probably as oxides of nitrogen formed by anodic oxidation, a source of error which it was not found possible to remove either by cooling, by use of a gauze anode, or by using a soluble anode; (2) dissolution of traces of copper from the cathode during the reduction and subsequent washing. This source of error is almost eliminated by neutralising the reduced solution before stopping the current. Another important source of error, which, however, is negligible when the reduction proceeds normally, is the formation of hydroxylamine, since this is not reduced under the conditions of current density employed, but requires a much higher current density which causes a greater evolution of hydrogen, and is oxidised at the anode to nitrate. Incomplete reduction of the nitrate to ammonia from this cause arises if the cathode surface is not completely spongy, or if the path of the current is not symmetrical, since the cathode current density is then not uniform and a greater evolution of hydrogen occurs. Such is the case if the distance between the cell-wall and the cathode is too small. Rotation of the anode has no effect, since efficient mixing is brought about by the oxygen evolved at the anode. The degree of acidity is also unimportant, providing it is not reduced to a value approaching the theoretical quantity. Measurements of the electrode potentials show that the course of the reduction is conditioned by a large increase in the depolarisation of the spongy copper electrode due to the catalytic action of the copper surface. The depolarising effect of the nitrate ions occurs only above a certain minimal concentration, which is smaller for a spongy copper cathode than for one of polished copper. A considerable quantity of hydroxylamine is produced if the cathode potential goes beyond a certain negative value which varies with the other electrolysis conditions.

J. W. BAKER.

Quantitative electrolytic reduction. I. Reduction of tervalent to bivalent iron. E. NIETZ

(J. pr. Chem., 1929, [ii], 121, 1—26).—The various sources of error in the quantitative electrolytic reduction of tervalent iron have been studied. When either a porous pot or a collodion diaphragm is used a small quantity of iron always diffuses back against the current into the anode compartment, the quantity not being appreciably influenced by the period of electrolysis, the current strength, or the temperature. This back diffusion is not prevented by an increase in hydrostatic pressure in the anode compartment. If the same pot diaphragm is repeatedly used with only air drying intermediately, the quantity of iron in the anode compartment gradually decreases until finally no colour can be obtained with potassium thiocyanate, since a quantity of iron approximately proportional to the period of electrolysis and the original concentration of iron gets back through the cell-wall by an "interchange-absorption" mechanism. The reduction is never quite complete owing to the diffusion of persulphate ions through the diaphragm into the cathode department. The influence of various factors on the optimum period of reduction was investigated. When the quantity of iron is varied from 0.1 to 0.3 g. the optimum reduction period changes from 30—40 to 80—90 min., after which further electrolysis causes a small decrease in the amount of ferrous iron, due either to absorption by the diaphragm or to an increased amount of persulphate consequent on the increased concentration of sulphate ions in the anode compartment. The optimum concentration of acid is 5—10% of free sulphuric acid. Rise of temperature to 96° or use of a rotating anode shortens the period of reduction. The current strength must not fall below 1 amp. These results were tested in the quantitative electrolytic reduction of iron using a diaphragm and stationary platinum electrodes, by Hostetter's method (A., 1913, ii, 1078) and Allen's methods (A., 1914, ii, 581) using a closed cell with a soluble (amalgamated zinc) anode and a rotating copper cathode, and the errors of the various methods compared.

J. W. BAKER.

Electrolysis of cyanogen halides. R. H. CLARK and H. R. L. STREIGHT (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 323—329).—An attempt was made to isolate and identify the products of electrolysis of the cyanogen halides employing various solvents, in the hope of obtaining definite proof of the deposition of halogen on the cathode. In all cases, however, it was found that the halogen travels to the anode with the exception of iodine from iodocyanogen in pyridine, which goes to the cathode. It would appear that iodocyanogen acts as an electromeride $\dot{\text{I}}\cdot\text{CN} \leftarrow \text{I}\cdot\text{CN}$. The iodine reacts negatively in electrolysis in most solvents, but positively in pyridine solution.

A. J. MEE.

Effect of different electrolytes in the electro-deposition of copper. A. JULIARD and J. LEDRUT.—See B., 1929, 177.

Electrolysis of nickel. B. BOGITCH.—See B., 1929, 213.

Measurement of the strength of sunlight. H. H. BAGNALL (Analyst, 1929, 54, 101—103).—

Solutions of potassium iodide are acidified with sulphuric acid and exposed to the action of the light in presence of air. The amount of iodine liberated is a measure of the chemical activity of the light received. Tables illustrating the seasonal variations in the activity of the sunlight are given. J. S. CARTER.

X-Ray photolysis of hydrogen peroxide. O. RISSE (Z. physikal. Chem., 1929, 140, 133—157).—The conditions governing the X-ray photolysis of aqueous hydrogen peroxide solutions have been studied over the concentration range 0.001—0.25*M*. At very low concentrations the quantity decomposed bears a linear relationship to the product It , where I is the intensity of the incident rays and t the time of exposure; the decomposition velocity is practically independent of the concentration, whilst at the higher concentrations, and down to about 0.05*M*, the process conforms tolerably well to the law for unimolecular reactions. Since the observed values do not satisfy the equation for second- or third-order reactions a complex process is postulated. Investigation of the action of X-rays on conductivity water shows that dissolved oxygen is converted quantitatively into hydrogen peroxide and that even in absence of dissolved oxygen the conductivity and acidity increase. Irradiation of conductivity water by a quartz-mercury lamp results in a greater increase of acidity, but no hydrogen peroxide is produced unless a photocatalyst such as zinc oxide is present. Activation of the oxygen is thus a necessary condition for the production of hydrogen peroxide from water and oxygen. During the decomposition of hydrogen peroxide by X-rays an inflammable gas is produced in quantity equal to about 1.5—2% of the volume of oxygen liberated. The temperature coefficient of the reaction in about *M*/600-solution is unity at temperatures from 2° to 50°. Strong acids and alkalis retard the decomposition. From energy considerations it is demonstrated that the energy necessary for the complete decomposition of one molecule of hydrogen peroxide, which in *M*/600-solution is 70 kg.-cal., decreases with increase of the hydrogen peroxide concentration.

H. F. GILBE.

Action of light and X-rays on ammonium thiocyanate. C. G. PATTEN and H. D. SMITH (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 221—224).—When a concentrated aqueous solution of ammonium thiocyanate is exposed to sunlight for 1 min. it turns bright red, but the colour disappears in the dark after 2 min. This is not due either to the formation of sub-microscopic particles of sulphur, or to the dissociation of the salt into ammonia and thiocyanic acid, as has been supposed, but to the fact that minute traces of iron in the salt are oxidised by a photo-reaction and then form the red ferric thiocyanate, the process being reversed in the dark. The wave-lengths effective in this reaction extend from the middle of the visible spectrum well into the ultra-violet. X-Rays are equally effective as sunlight. The importance of this photo-reaction with iron in the explanation of the coloration and change in optical transparency produced in many glasses by X-rays and intense sources of ultra-violet light is being investigated.

A. J. MEE.

Action of X-rays on ferrous sulphate solutions. H. FRICKE and S. MORSE (Phil. Mag., 1929, [vii], 7, 129—141).—The action of different X-ray doses on $0.01\text{--}4 \times 10^{-5}M$ -solutions of ferrous sulphate in $0.8N$ -sulphuric acid saturated with air has been investigated. With $0.00878M$ -, $0.000337M$ -, and $0.001M$ -solutions the rate of decomposition is linear up to the same X-ray dosage. For increased dosages the decomposition is still linear, but the rate is halved. With a $0.0000406M$ -solution the rate of decomposition has a linear relationship to the X-ray dosage until decomposition is practically complete. With increased doses the concentration of ferrous sulphate is gradually restored to an equilibrium value about 50% of the initial one. In the first cases the change in the rate of decomposition is shown to take place at the point where all the dissolved oxygen in the solutions has been used up. It is concluded that in the later stages of the decomposition the transformation of the ferrous ions is a secondary effect due to activated water molecules produced by secondary X-ray electrons. The apparent reversal of the reaction in the last case is attributed to the presence in the solution of a reducing substance (perhaps hydrogen peroxide) which would interfere with the analysis, which was carried out by an oxidation-reduction potential method. A. E. MITCHELL.

Production of colour in glass and in gems by X-rays and radium rays. M. C. REINHARD and B. F. SCHREINER.—See B., 1929, 208.

Lattice energies and photochemical decomposition of the silver halides. S. E. SHEPPARD and W. VANSELOW (J. Physical Chem., 1929, 33, 250—273).—Theoretical. The energy changes accompanying the decomposition of the silver halides are discussed in relation to the lattice energies of the crystals concerned. The lattice energies of silver chloride, bromide, and iodide are first evaluated using the thermochemical cycle of Born (A., 1920, ii, 156) after a consideration from the results of previous investigators of the best values for the terms to be taken. By this method the lattice energies have the values 212, 205, and 201.5 kg.-cal., respectively, as compared with the values 184, 178, and 150 calculated from the electrostatic theory. It follows that the quantum required to overcome electron affinity is greater than that actually found by experiment to be necessary. The relation of lattice energy to photochemical change is discussed in the light of these results and of other evidence, and it appears that lattice loosening and electron liberation and transfer are closely connected with any photochemical change in solids. A discussion of lattice disorientation and of ionic deformation in the light of the work of von Hevesy and Fajans, respectively, leads to the conclusion that both photochemical and photo-electric effects take place primarily in such disoriented parts of the lattice that the initial work can be supplied by the quanta available, a view which receives support from the fact that photochemical decomposition commences locally on the surface of crystals. The preliminary overcoming of lattice energy which is necessary before absorbed radiation can loosen an electron is analogous to energy of activation in

chemical reactions, and it is concluded that the photochemical decomposition of the silver halides can be regarded as a typical case of heterogeneous catalysis at an interface. Internal disorientation and photo-conductance, photo-electric effects, and orientation at interfaces are also discussed. L. S. THEOBALD.

Intermediate regressions. LUPPO-CRAMER (Z. wiss. Phot., 1929, 26, 295—299).—If a negative which has been treated with a sodium nitrite solution is exposed under the Eder-Hecht scale under conditions which would cause solarisation in an untreated plate, solarisation is hindered except under the red strip. Since the ordinary Herschel effect cannot be obtained with this red filter, it is suggested that the red rays exert a protective influence on the silver halide, preventing blackening when the silver nuclei are nascent, as in the present experiments, but not when, owing to previous exposure, they have become larger and less reactive. R. CUTHILL.

Limiting short wave-length for the Herschel effect. E. MAUZ (Z. wiss. Phot., 1929, 26, 289—294).—On exposure to yellowish-orange light of "Satrox" paper which has previously been blackened by exposure to white light, the blackening at first diminishes, i.e., the Herschel effect appears, but later increases again. In explanation it is suggested that one part of the orange light causes bleaching, and the other part blackening, and that when the time of exposure is increased beyond a certain point the blackening effect predominates. By photographing a spectrum on paper previously exposed to white light, it is found that light of wave-length shorter than about $600 m\mu$ will not cause the Herschel effect. R. CUTHILL.

Photo-decomposition of ethyl iodide. T. IRDALE (J. Physical Chem., 1929, 33, 290—295).—Measurements of the photo-decomposition of ethyl iodide at the ordinary temperature by light of the region $365 m\mu$ from a quartz-mercury vapour lamp indicate that this is a simple process (cf. Job and Emschwiller, A., 1924, i, 929) in which one quantum effects the detachment of an atom of iodine from one molecule of the iodide. Preliminary experiments indicate that, contrary to Stobbe and Schmitt (A., 1921, ii, 76), oxygen is not necessary for the decomposition. L. S. THEOBALD.

Photosynthesis of naturally occurring compounds. IV. Temperature coefficient of the photosynthesis of carbohydrates from carbonic acid. E. C. C. BALY and N. R. HOOD (Proc. Roy. Soc., 1929, A, 122, 393—398; cf. A., 1927, 1040, 1041).—Nickel carbonate, free from every trace of adsorbed salts, may be prepared by the electrolysis of pure conductivity water, saturated with carbon dioxide, with nickel electrodes. The carbonate is dried at 100° , heated at 140° for 30 min., passed through a 100-mesh sieve, and activated by exposure to light. Nickel carbonate thus prepared gives very constant yields of carbohydrates if the temperature, light intensity, and relation between volume of water and weight of powder are kept constant. If the yield of carbohydrates (weight of photosynthesised organic matter soluble in absolute methyl alcohol) obtained with 50 g. of the carbonate suspended in

1500 c.c. of water is plotted against the temperature, the relation is found to be a linear one between 5° and 31° (maximum yield, 0.0783 g.), after which there is a rapid decrease in yield. The values of the temperature coefficient for 10° are in good agreement with those found by Warburg with the unicellular alga *Chlorella* under constant illumination (Biochem. Z., 1919, 100, 258). The close analogy shown between the photosynthetic process *in vitro* and *in vivo* is discussed, with special reference to the work of Matthaei on the assimilation of carbon dioxide at various temperatures (Phil. Trans., 1905, B, 197, 47), and to the fact that the process, both in the living leaf and in the laboratory, has an upper and a lower temperature limit. The results recorded support the view previously expressed (*loc. cit.*), that the complete activation of the carbonic acid takes place in two stages, *i.e.*, partial activation by adsorption on the surface of the catalyst and a further activation by the action of visible light on the adsorbed layer.

L. L. BIRCUMSHAW.

Photochemical decomposition of benzaldehyde. A. DE HEMPTINNE (Ann. Soc. Sci. Bruxelles, 1928, 48, B, 98—100).—It is concluded that the photolysis of benzaldehyde by light of wave-lengths less than 2600 Å., which was previously observed (A., 1928, 720), takes place as follows: $C_6H_5 \cdot CHO = C_6H_5 + H + CO$, the hydrogen then reacting with the phenyl group to form benzene. The energy necessary for this decomposition is calculated to be 115,780 g.-cal., corresponding with light of wave-length 2461 Å. This is the wave-length at which the total absorption band of the benzaldehyde spectrum begins. For benzaldehyde there is a complete parallelism between the appearance of total absorption and the possibility of photochemical decomposition.

O. J. WALKER.

Photochemical decomposition of benzaldehyde vapour. A. DE HEMPTINNE (J. Phys. Radium, 1928, [vi], 9, 357—364; cf. preceding abstract).—The decomposition by ultra-violet light of benzaldehyde vapour at 0.2 mm. has been investigated. Only those wave-lengths corresponding with the "total absorption" portions of the benzaldehyde spectrum are effective in the photochemical decomposition. With rise of temperature the intensities of the bands gradually decrease until at 200° a continuous spectrum results, which in turn disappears at 400°. Below this temperature the photolysis is reversible. Between 400° and 500° benzaldehyde begins to decompose thermally and irreversibly. The decrease in the light energy necessary for decomposition at the higher temperatures is of the same order of magnitude as the increase in the vibration energy of the benzaldehyde molecule, as calculated from the variation of the specific heat with the temperature. The theory of absorption spectra and photochemical decomposition is discussed.

O. J. WALKER.

Relations between the photochemical reactivity and the fluorescence of organic compounds. Qualitative fundamental law. G. KÖGEL (Z. wiss. Phot., 1929, 26, 311—319).—Theoretical. From the fact that by opening the rings of fluorescent closed-chain compounds and introducing unsaturated

groups at the point of fission, if such groups are not already present there, compounds which are very sensitive to light are obtained, it is concluded that fluorescence is a criterion of photochemical activity. If, however, owing to structural or physical conditions reaction is not possible, the fluorescence represents only potential activity. The principal groups giving rise to photochemical sensitivity are: $\cdot CH:CH \cdot$, $\cdot CH:N \cdot$, $>C:O$, $\cdot NO_2 \cdot$, $\cdot NCl:N$, and $\cdot N:N$. Substituents for the hydrogen atoms in the benzene ring will enhance the fluorescence or promote chemical action according as they oppose or facilitate, respectively, the opening of the ring. The groups Me and OMe and the halogens increase the reactivity of the sensitive groups, whilst the nitro-group has the opposite effect.

R. CUTHILL.

Physico-chemical investigations of irradiated proteins. V. Changes in serum-albumin produced by radium rays and their relation to coagulation by heat and light. A. FERNAU and M. SPIEGEL-ADOLF (Biochem. Z., 1929, 204, 14—27).—Freshly electro dialysed serum-albumin kept under toluene loses its power of coagulation by exposure to radium owing to the formation of traces of ammonia. To prevent visible changes under radium irradiation, small amounts of acid or alkali are effective. Even when visible changes are prevented by hydrochloric acid there is almost complete denaturation. The period of coagulation is practically independent of the concentration of the serum-albumin. Coagulation is prevented by high concentrations of neutral salts. Radium coagulates are not rendered soluble by the action of alkali. Hydrogen peroxide coagulates show properties similar to those produced by radium.

J. H. BIRKINSHAW.

Reaction of monatomic hydrogen with hydrocarbons. K. F. BONHOEFFER and P. HARTECK (Z. physikal. Chem., 1928, 139, 64—74).—When hydrocarbon vapours, methane excepted, are allowed to mix with a stream of monatomic hydrogen a greenish-blue light, resembling that of the inner cone of a Bunsen flame, is emitted. The products of reaction have been examined for the following substances: ethane, pentane, ethylene, acetylene, and benzene. No change takes place in the case of methane, but the evidence indicates that this gas facilitates the recombination of monatomic hydrogen according to the equations: $CH_4 + H = CH_3 + H_2$, $CH_3 + H = CH_2 \cdot$. Ethane gives small quantities of ethylene and acetylene and some methane, but is mostly unchanged. Pentane gives the same products as ethane with propane in addition. Ethylene yields acetylene, but acetylene, although giving a strong light emission, gives only traces of ethane and ethylene and remains practically unchanged. In the case of benzene the ring is broken, and methane, together with some ethylene and acetylene, is formed. The results therefore show that monatomic hydrogen may hydrogenate and dehydrogenate hydrocarbons, and may rupture very stable rings.

R. W. LUNT.

Formation of acid lithium aluminate. D. PROCHV (J. Czechoslov. Chem. Comm., 1929, 1, 95—103).—The solution obtained by the dissolution of aluminium amalgam in aqueous lithium hydroxide

which exhibits "supersaturation" (cf. Allen and Rogers, A., 1900, ii, 727) has been investigated by conductance and cryoscopic methods and it is concluded that the aluminium in the solution exists mainly as the normal aluminate, $\text{Al}(\text{OH})_4'$, before spontaneous precipitation. The solubility of acid lithium aluminate, $\text{Li}[\text{Al}_2(\text{OH})_7] \cdot 2\text{H}_2\text{O}$ or $\text{Li}_2\text{Al}_4\text{O}_7 \cdot 11\text{H}_2\text{O}$, deduced from the conductance measurements is 1.2×10^{-4} and 3.3×10^{-4} g.-equiv. per litre at 25° and 80° , respectively. The separation of the acid lithium aluminate takes place according to the equation, $2\text{Al}(\text{OH})_4' \rightleftharpoons \text{Al}_2(\text{OH})_7' + \text{OH}'$, the mass action constant of which is about 1×10^4 . A method for the determination of lithium based on its precipitation as the acid aluminate in sodium or potassium hydroxide solutions is described.

A. I. VOGEL.

Combination of alkali metals with carbon. II. K. FREDENHAGEN and H. SUCK (Z. anorg. Chem., 1929, 178, 353—365).—The investigation previously described (A., 1927, 218) has been continued with improved apparatus. When heated at 400° in potassium vapour at a given pressure, both graphite and lampblack take up the same amount of metal, but with lampblack equilibrium is reached only after a considerable time. A curve constructed with the pressures of vapour as abscissæ and the amounts of metal taken up as ordinates consists of two almost vertical portions separated by a short flatter part; with further increase in pressure, the second and longer steep section is ultimately succeeded by a part which slopes much less. There is no evidence of the formation of K_2C_2 , and the most satisfactory explanation of the form of the curve seems to be that adsorption occurs in two stages. Neither sodium nor potassium reacts with diamond at 500° .

R. CUTHILL.

Displacement of copper from neutral and acidic copper sulphate solutions by hydrogen under pressure. V. IPATIEV and V. IPATIEV, jun. (Ber., 1929, 62, [B], 386—390).—The experiments are performed in an Ipatiev high-pressure autoclave containing the solution in a glass tube. Under all conditions cuprous and cupric salt and metallic copper are present at the close of the experiment. Copper cannot be displaced without the simultaneous presence of cuprous and cupric ions in the solution, the latter frequently in very small amount. Precipitation of copper is never quantitative, a portion of the metal remaining ionised in solution no matter how long the experiment is continued. It appears that the following reactions proceed simultaneously: $2\text{CuSO}_4 + \text{H}_2 = \text{Cu}_2\text{SO}_4 + \text{H}_2\text{SO}_4$; $\text{Cu}_2\text{SO}_4 + \text{H}_2 = 2\text{Cu} + \text{H}_2\text{SO}_4$; $\text{CuSO}_4 + \text{Cu} = \text{Cu}_2\text{SO}_4$. With increasing acidity of the solution, the conditions become more favourable for a high concentration of cuprous ions; in some cases, this increase is effected at the expense of the precipitated copper. At a constant pressure of hydrogen, the influence of added acid becomes less marked with increasing concentration of the copper sulphate solution.

H. WREN.

Reaction of cupric salts with thiosulphate. J. HANUS and V. HOVORKA (J. Czechoslov. Chem. Comm., 1929, 1, 65—82).—A re-investigation of the

reaction between cupric salts and sodium thiosulphate in aqueous solution over a wide variety of conditions has been made. The resultant precipitate was analysed as follows: sulphur, by extraction with nitrobenzene at 100° ; cuprous sulphide, by treatment with silver sulphate solution which converts the cuprous sulphide into cupric sulphate, silver sulphate, and an equivalent quantity of silver (cf. Posnjak, A., 1915, ii, 24), the last-named being removed by dissolution in 6% ferric nitrate solution at about 80° and the silver determined by Volhard's method. The precipitate consisted of a mixture of cuprous and cupric sulphides and free sulphur in varying proportions, the composition depending on the duration of boiling, the amount of thiosulphate, and the acidity of the solution. The maximum amount of cuprous sulphide in the precipitate was obtained from solutions in which the ratio was 1 g.-at. of copper to 2.5—3 mols. of thiosulphate. Further increase of the thiosulphate content resulted in a decrease of the amount of cuprous sulphide until with a very large excess (1:15—30) the precipitate consisted largely of cupric sulphide and free sulphur. The composition of the precipitate formed in acid solutions according to the analytical methods of Carnot (A., 1886, ii, 580) and Girard (Ann. Chim. anal., 1899, 4, 382) (copper:thiosulphate about 1:4—5) was 8% $\text{Cu}_2\text{S} + 92\%$ CuS .

A. I. VOGEL.

Constitution of silver subfluoride. C. DEL FRESNO (Anal. Fis. Quím., 1928, 26, 407—416).—See A., 1928, 694.

Action of water on calcium aluminates. L. S. WELLS.—See B., 1929, 173.

Carbon sulphidoselenide. H. V. A. BRISCOE, J. B. PEEL, and P. L. ROBINSON (J.C.S., 1929, 56—60).—Carbon sulphidoselenide (cf. Stock and Willfroth, A., 1914, ii, 200), a yellow oil, b. p. $83.90\text{—}83.95^\circ/749.2\text{ mm.}$, has been prepared by treating ferrous selenide with carbon disulphide vapour at 650° , and repeatedly fractionating the product. The mol. wt., determined by vapour density and by cryoscopic measurement, is normal. The surface tension $\gamma = 40.44$ dynes/cm.² at 20° , hence the molecular parachor is 156.4. If the constitution S-C-Se be assumed for the sulphidoselenide, the atomic parachor of selenium is 58.7 (cf. Briscoe and Peel, A., 1928, 1021).

Carbon sulphidoselenide is reduced by zinc and hydrochloric acid to hydrogen sulphide and hydrogen selenide. It reacts with ammonia, but the products are ill-defined. With phenylhydrazine in alcoholic solution it yields the compound $(\text{NHPh} \cdot \text{NH}_2)_2\text{CSSe}$, m. p. 98° , which is unstable and decomposes when kept; under similar conditions aniline yields a compound, $(\text{NHPh})_4\text{CSSe}$, m. p. 164° , which is somewhat more stable in air.

C. W. SHOPPEE.

[Silicic acids.] H. STAUDINGER (Ber., 1929, 62, [B], 442).—The conception of the relationship between fibrous structure and molecular size, attributed by Diltthey and Holterhoff (this vol., 280) to Meyer, has been enunciated previously by the author.

H. WREN.

Reactions between colloidal silica and lime. P. JOILBOIS and L. CHASSEVENT (Compt. rend., 1929,

188, 452—454).—It is concluded from electrometric determinations of the amounts of lime present in the precipitate produced in solutions containing various concentrations of lime and silica mixed at 30° that the reactions are due to (1) coagulation of silica by lime, (2) fixation of lime by silica to form a hydrated calcium silicate, and (3) adsorption of lime which may continue for several months in concentrated solutions.

J. GRANT.

Action of silica, alumina, and kaolin on barium sulphate. (Mlle.) G. MARCHAL (Compt. rend., 1928, 188, 399—402).—Earlier experiments (this vol., 266) have been extended to various mixtures of barium sulphate and silica, alumina, or dehydrated kaolin heated at 1300°, and have resulted in each case in a reaction which is rapid at first and then very slow. They indicate an advantage in replacing barium carbonate by the sulphate in certain manufactures, e.g., of glass.

J. GRANT.

Dissolution of metals in fused salts. II. W. EITEL and B. LANGE (Z. anorg. Chem., 1929, 178, 108—112; cf. A., 1928, 700).—From thermodynamical considerations based on the work of Lorenz and Adler (A., 1928, 945), and from their own experiments, the authors show that the dissolution of lead and cadmium in their respective fused chlorides is a chemical process involving the formation of a lower chloride. The reaction is reversible, the metal being precipitated in a highly dispersed, colloidal form when the fused mass solidifies.

A. R. POWELL.

Acid phosphates of thorium. J. D'ANS and W. DAWIDL (Z. anorg. Chem., 1929, 178, 252—256).—Addition of thorium phosphate to a 40% solution of phosphoric acid results in the slow crystallisation of the compound $\text{Th}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. From solutions of thorium hydrogen phosphate in sulphuric and phosphoric acids crystalline compounds having the composition $\text{Th}(\text{SO}_4)(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$ and $\text{Th}_2\text{SO}_4 \cdot (\text{H}_2\text{PO}_4)_6 \cdot 8\text{H}_2\text{O}$ have been obtained.

A. R. POWELL.

Reaction mechanism in the sulphuric acid contact process and the action of promoters. B. NEUMANN.—See B., 1929, 205.

Nitrosylsulphuric acid. II. C. W. H. JONES, W. J. PRICE, and H. W. WEBB (J.C.S., 1929, 312—315; cf. A., 1926, 811).—Attempts to synthesise dinitrosyl sulphate, $\text{SO}_2(\text{O}\cdot\text{NO})_2$, have been unsuccessful. The methods of preparation of nitrosylsulphuric anhydride suggest that it has the structure $\text{O}\cdot\text{NO}\cdot\text{SO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{NO}$. When heated it suffers partial decomposition to form the substance $2(\text{2SO}_3\cdot\text{N}_2\text{O}_3)\cdot\text{SO}_3$.

F. J. WILKINS.

Metallic chromates. S. H. C. BRIGGS (J.C.S., 1929, 242—245; cf. Britton, A., 1926, 247).—The author has confirmed the existence of a normal zinc chromate (cf. Schulze, A., 1896, ii, 24; Briggs, A., 1908, ii, 113), and has isolated the following compounds: $9\text{ZrO}_2\cdot 5\text{CrO}_3\cdot 12\text{H}_2\text{O}$; $3\text{Al}_2\text{O}_3\cdot 2\text{CrO}_3\cdot 6\text{H}_2\text{O}$; $2\text{Fe}_2\text{O}_3\cdot 4\text{CrO}_3\cdot \text{H}_2\text{O}$; $3\text{Sb}_2\text{O}_3\cdot 2\text{CrO}_3$; $2\text{Sb}_2\text{O}_3\cdot \text{Cr}_2\text{O}_3$; $3\text{Bi}_2\text{O}_3\cdot 2\text{Cr}_2\text{O}_3$. Sodium chromate with a large excess of a very concentrated solution of the corresponding dichromate gives the normal chromates of copper, cobalt, and cadmium in the

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hydrated forms $\text{CuCrO}_4\cdot 2\text{H}_2\text{O}$, $\text{CoCrO}_4\cdot 2\text{H}_2\text{O}$, and $\text{CdCrO}_4\cdot \text{H}_2\text{O}$. Corresponding zinc and nickel compounds could not be prepared.

F. J. WILKINS.

Preparation and electrical conductivity of pure hydrogen fluoride. K. FREDENHAGEN and G. CADENBACH (Z. anorg. Chem., 1929, 178, 289—299).—When potassium hydrogen fluoride is heated, one third of its content of hydrogen fluoride is evolved slowly with rising temperature up to 504°, at which the remainder is steadily evolved. For the preparation of pure hydrogen fluoride not only must the salt used be perfectly anhydrous but all traces of moisture must be rigorously excluded from the apparatus and the first distillate should be redistilled very slowly. Working in this way hydrogen fluoride with a specific electrical conductivity of only 14×10^{-6} has been obtained. Although this value is about 0.0005 of that usually accepted it is believed still to be much too high owing to the presence of minute traces of water.

A. R. POWELL.

Bromine chloride. S. BARRATT and C. P. STEIN (Proc. Roy. Soc., 1929, A, 122, 582—588).—The fact, first observed by Balard (Ann. Chim. Phys., 1826, 32, 371), that a marked diminution takes place in the colour of bromine on mixing with chlorine, is a strong argument in favour of the formation of a compound between the halogens, more transparent than bromine in the visible region of the spectrum. The results of spectrophotometric observations on the colour changes on mixing carbon tetrachloride solutions of bromine and chlorine can be accounted for quantitatively on the basis of the formation of a compound BrCl , and that in equimolecular mixtures this compound is formed to the extent of approximately 50%. The conclusions are based on the assumption that the intensity of the bromine absorption band in the visible forms a measure, in the mixtures, of the amount of bromine left uncombined with the chlorine. It was found to be impossible to measure the chlorine left in the free state by similar observations on the ultra-violet bands, owing to the overlapping of the various spectra concerned. The formation of a chemical compound is further indicated by the appearance of a new ultra-violet absorption band, with the maximum at 3700 Å., peculiar to the mixtures, and by the fact that in carbon tetrachloride solutions an appreciable time-lag is detected in the colour change. The formula suggested agrees with the observation that the volume change on mixing chlorine and bromine in the gaseous state, if existent, is very small.

L. L. BIRCUMSHAW.

Action of bromine on phosphorus trichloride. T. MIŁOBĘDZKI and S. KRAKOWIECKI (Rocz. Chem., 1928, 8, 563—567).—Crystalline phosphorus tetrachlorobromide is produced by the action of bromine on phosphorus trichloride, or of bromine with phosphorus pentabromide on phosphorus pentachloride. The compound PCl_3Br_2 could not be prepared. A number of crystalline products of the general type PCl_2Br_n and PCl_3Br_n , where n is 2—10, are obtained by the action of bromine vapour on phosphorus trichloride vapour.

R. TRUSZKOWSKI.

Oxygen compounds of rhenium. I. NODDACK and W. NODDACK (Naturwiss., 1929, 17, 93—94).—

White rhenium peroxide, Re_2O_7 , is obtained as a "snow" by heating the metal or lower oxides in a stream of oxygen below 150° . It melts near 150° and is rapidly converted into a yellow oxide. The peroxide is readily soluble, the aqueous solution being very weakly acid. Hitherto the oxide has been regarded as Re_2O_7 , but this view is mistaken, not only because the analysis corresponds with $\text{Re}/\text{O}=1/4$, but also because the substance reacts as a peroxide.

The yellow oxide obtained in hexagonal plates as a result of the interaction of rhenium and oxygen above 150° melts to a yellow liquid at 200° and boils at 450° , distilling without decomposition in an atmosphere of oxygen or nitrogen. The oxide is Re_2O_7 and not ReO_3 as was thought earlier; it deliquesces in air and the aqueous solution is colourless and strongly acid. The following salts have been prepared as white crystals and their solubilities determined: NH_4ReO_4 , NaReO_4 , and $\text{Ba}(\text{ReO}_4)_2$. By heating the two salts first named in a current of hydrogen at 400° , rhenium dioxide is formed as a black solid. When the dioxide is dissolved in dilute nitric acid, the solution is at first bright orange, but when heated or kept becomes colourless. If the yellow solution is treated with sodium hydroxide the colour persists and by adding calcium or barium hydroxide a yellow precipitate is formed which is stable only for a brief period even in alkaline media. The barium salt analyses to BaReO_4 (rhenate). The yellow solution first obtained therefore contains ReO_3 , which is oxidised to Re_2O_7 by keeping or heating. By the action of sulphur dioxide on dry Re_2O_7 or Re_2O_3 , blue and violet oxides of variable composition are formed. When sulphur dioxide is led into a sulphuric acid solution of the heptoxide, a deep violet colour appears. The blue oxide corresponds approximately with Re_2O_8 , and the violet and blue oxides are compounds of ReO_2 with ReO_3 or Re_2O_7 . The black oxide, ReO_2 , results after sodium per-rhenate has been fused in hydrogen. It is readily reduced to the metal at 800° . R. A. MORTON.

Oxidation of iron in water by the action of oxygen and carbon dioxide. N. M. GAVRILOV, S. K. MEL, and P. K. MEL.—See B., 1929, 210.

Corroding action of solutions of various chlorides on cast iron and lead. B. K. PERSHIKE and G. I. CHUFAROV.—See B., 1929, 210.

[Iron carbonyls containing pyridine.] W. HIEBER and F. SONNEKALB (Ber., 1929, 62, [B], 422; cf. A., 1928, 511; this vol., 41).—The method described for the preparation of iron carbonyls containing pyridine should be deleted from the literature. Further investigation of the system iron carbonyl-pyridine has shown that oxidised products are formed which, when treated with acid, evolve carbon dioxide in addition to carbon monoxide and hydrogen.

H. WREN.

Action of mercury salts on iron pentacarbonyl. II. H. HOCK and H. STUHLMANN (Ber., 1929, 62, [B], 431–437, cf. A., 1928, 1344).—Iron pentacarbonyl reacts with a solution of 1 mol. of mercuric sulphate in about 10% sulphuric acid, giving carbon dioxide, sulphuric acid, and a compound, $\text{Fe}(\text{CO})_4\text{Hg}$, designated "mercury iron tetracarbonyl." When

heated at about 150° , it decomposes quantitatively into mercury, iron, and carbon monoxide. The compound is also derived from iron pentacarbonyl and mercurous sulphate, metallic mercury being precipitated. It does not give a precipitate of mercury sulphide when its solution in dilute sulphuric acid is treated with hydrogen sulphide. When treated with iodine in ether, pyridine, or carbon disulphide, it gives mercuric iodide and the compound $\text{Fe}(\text{CO})_4\text{I}_2$. A similar change is effected by bromine in light petroleum, but is accompanied by partial decomposition of the compound $\text{Fe}(\text{CO})_4\text{Br}_2$. The analogous change with chlorine is best effected by passing the dry gas over the substance. Iron tetracarbonyl does not appear to be produced by the interaction of mercury iron tetracarbonyl and the substance $\text{Fe}(\text{CO})_4\text{I}_2$. Hydrogen peroxide and potassium permanganate in acetone readily attack mercury iron tetracarbonyl, whereas it is indifferent towards boiling pyridine. Iron pentacarbonyl and cupric chloride in acetone give a transitory reddish-yellow precipitate and, ultimately, cuprous chloride, ferrous chloride, and carbon monoxide; a precisely analogous change occurs with mercury iron tetracarbonyl. When mercury iron tetracarbonyl is shaken with a feebly acid, aqueous solution of mercuric sulphate or when the pentacarbonyl is treated with an excess of mercuric sulphate, the compound $\text{Fe}(\text{CO})_4\text{Hg}, \text{HgSO}_4$ separates in rhombic crystals. It is rapidly decomposed by boiling water into ferrous sulphate, mercury, and carbon monoxide and transformed by iron pentacarbonyl into mercury iron tetracarbonyl. Prolonged agitation of mercury iron tetracarbonyl with a solution of mercuric bromide in methyl alcohol gives the compound $\text{Fe}(\text{CO})_4\text{Hg}, \text{HgBr}_2$; the substance $\text{Fe}(\text{CO})_4\text{Hg}, \text{HgI}_2$ is analogously prepared, whereas mercuric chloride in aqueous solution yields the compound $\text{Fe}(\text{CO})_4\text{Hg}, \text{HgCl}_2$. In contrast with the substance $\text{Fe}(\text{CO})_4\text{Hg}, \text{HgSO}_4$, these compounds, when suspended in water, do not react with hydrogen sulphide. Iron pentacarbonyl and mercuric acetate afford mercury iron tetracarbonyl and the additive compound $\text{Fe}(\text{CO})_4\text{Hg}, \text{Hg}(\text{OAc})_2$. H. WREN.

Univalent iron, cobalt, and nickel, and nitroso-sulpho-salts. L. CAMBI (Gazzetta, 1929, 59, 56–59).—A reply to Manchot's criticism (A., 1928, 1344) of the author's previous work. The formation of hyponitrite in the decomposition of Roussin salts by silver nitrate cannot be due to the reduction of the silver salt, since a similar reaction occurs with silver salts in general. The largest yields of hyponitrite are obtained using silver perchlorate. The reactions between metallic mercaptides and nitric oxide are discussed. O. J. WALKER.

Quantitative analysis with the spectrograph. C. C. NICKIE (Ind. Eng. Chem. [Anal.], 1929, 1, 1–7).—The spectrum of the sample is compared with a graded series of standards photographed under similar conditions. Determinations usually agree within 10%. The choice of lines for comparison depends only on the concentration, the weakest lines that are clearly defined being selected. Magnesium and some other metals can be detected at a concentration of less than 1 in 10^6 , but arsenic at

l in 10^4 . It is essential that the standards shall have nearly the same composition as the sample, so that a considerable number of standards is needed. An arc between carbon electrodes is preferred as a source of light, but the impurities in the carbon must be known. The sample should be obtained from a solution, as 20–50 mg. only are required and uniformity cannot be certain if it is prepared direct from the solid. A drop of solution is placed in a cavity of the lower arc carbon. C. IRWIN.

Quantitative emission spectrum analysis. I. Principles of quantitative spectrum analysis. H. THURNWALD and G. F. HUTTIG (*Z. anal. Chem.*, 1929, 76, 260–272).—A lecture. A. R. POWELL.

Micro-electroanalysis. R. KELLER (*Naturwiss.*, 1929, 17, 100–103).—A general account is given of the application of micro-electrical methods to physiological problems with inhomogeneous materials, special reference being made to the transport of sugar in the organism. R. A. MORTON.

Derivation of reference values for the calomel electrode used in p_H determinations. D. H. CAMERON (*J. Amer. Leather Chem. Assoc.*, 1929, 24, 80–87).—Assuming that a hypothetical normal hydrogen electrode has zero potential at 25°, that 0.1N-hydrochloric acid at 25° contains 0.0816 g.-mol. per litre of free hydrogen ions, and that for the temperature range 15–30° the hydrogen-ion concentration of 0.1N-hydrochloric acid remains constant, the author has derived a series of reference values for the saturated potassium chloride-calomel half cell for each degree from 15° to 30°. The reference value of the calomel electrode is equal to its true value at a particular temperature minus the true value of a hypothetical normal hydrogen electrode at that temperature. The true temperature coefficient of the saturated potassium chloride-calomel electrode is less than that of the 0.1N-potassium chloride-calomel electrode, but the change in reference value of the latter is less than for the saturated.

D. WOODROFFE.

Simplified methods of potentiometric and conductometric analysis and their industrial application. T. CALLAN and S. HORROBIN.—See B., 1929, 154.

Simple reference electrode for potentiometric titrations. H. H. WILLARD and A. W. BOLDYREFF (*J. Amer. Chem. Soc.*, 1929, 51, 471–474).—A platinum wire is sealed in the lengthened tip of the burette. Such an electrode exhibits constant potential in oxidation-reduction, neutralisation, and precipitation reactions. S. K. TWEEDY.

[Colorimetric] determination of hydrogen-ion concentration of salt solutions. A. NEUMANN (*Pharm.-Ztg.*, 1929, 74, 278–280).

Universal indicator giving spectrum colours for the p_H range 2–12. H. W. VAN URK (*Pharm. Weekblad*, 1929, 66, 157–162; cf. this vol., 162).—A modified indicator mixture, giving sharper colour changes than that formerly proposed, is suggested. S. I. LEVY.

Possible indicators to determine the p_H of alkaline solutions. F. R. MCCRUMB and W. R.

KENNY (*Ind. Eng. Chem. [Anal.]*, 1929, 1, 44–46).—Most of the dyes sold for the purpose of p_H studies over the range 10.0–14.0 are unsatisfactory. About five can be used for hydrogen-ion work: α -naphtholbenzein, which is, however, low in tinctorial power; Clayton-yellow, alizarin-yellow GR and R (the last gives misleading lemon-yellow shades in solutions containing lime); tropaeolin O, which gives quite marked readings but has been reputed to have rather a large salt error; and azo-blue, which gives good colour changes in the p_H range 10.0–11.0 but is not entirely satisfactory above or below. None of these, however, is as satisfactory in this range as the sulphonphthaleins of Clark and Lubs, and of Cohen at lower ranges. D. G. HEWER.

Colorimetric hydrogen-ion determination. D. H. CAMERON (*J. Amer. Leather Chem. Assoc.*, 1929, 24, 76–80).—To 25 c.c. of the solution in a 50 c.c. Nessler tube 1.6 cm. in diam. 1 c.c. of a suitable indicator solution (0.004% or 0.008%) followed by distilled water to 50 c.c. is added. 25 c.c. of a solution containing 0.1M-potassium hydrogen phthalate, potassium dihydrogen phosphate, or boric acid for p_H values 4–6, 6–8, or 8–10, respectively, are pipetted into a similar Nessler glass, 1 c.c. of the same indicator solution is added, and 0.2N-sodium hydroxide added from a burette until the colour produced matches that in the first glass. The volume of buffer solution is made up to 50 c.c. before the final comparison of the colour is made. The p_H value is obtained from the composition of the buffer mixture in the second tube (cf. W. M. Clark, "Determination of Hydrogen Ions," 1922).

D. WOODROFFE.

Oxidation-reduction indicators. J. GILLIS (*Natuurwetensch. Tijds.*, 1929, 11, 15–20).—A short account of the commoner oxidation-reduction indicators, with special reference to the transition range potentials. Curves are given for electrometric titration of ferrous chloride in acid buffered solution by means of potassium dichromate, and of zinc by potassium ferrocyanide containing a trace of ferricyanide. S. I. LEVY.

Detection of bromide and iodide. E. MURMANN (*Oesterr. Chem.-Ztg.*, 1929, 32, 36–37).—The solution is treated with 0.1 g. of ammonium persulphate or potassium permanganate and a current of air is passed through the liquid, the issuing gases passing along a narrow-bore delivery tube. To test for bromine a piece of cotton wool soaked in fluorescein is placed at the end of this tube; a red colour appears with as little as 1×10^{-6} g. of bromine. Iodine is tested for in a similar manner using cotton wool soaked in a solution of starch in 50% glycerol; the sensitivity is the same as that of the bromine test.

A. R. POWELL.

Determination of traces of iodine. II. Iodine in vegetables. J. F. MCCLENDON and R. E. REMINGTON (*J. Amer. Chem. Soc.*, 1929, 51, 394–399).—A modification of the method previously described (A., 1928, 607). The vegetables are moulded into rods, which are fed into a strongly heated silica tube through which oxygen is passing, the feeding being regulated so that combustion

proceeds without the separation of carbon and tarry matter. After washing, the oxygen is passed to a Cottrell precipitator. The ashing may also be carried out in boats, or by prolonged heating below 450° in an open dish. The ash must not be allowed to fuse and calcium lactate and sodium carbonate must be added if the vegetable yields an acid ash.

S. K. TWEEDY.

Micro-determination of iodine in organic materials. J. F. REITH (Rec. trav. chim., 1929, 48, 254—262).—Details are given of a simplified combustion method for the determination of minute amounts of iodine in organic substances. The apparatus is much simpler than that hitherto employed, and the accuracy of the determination is increased by the adoption of a colorimetric method which renders possible the use of less material than is usually necessary.

F. G. TRYHORN.

Critical examination of the determination of nitrous oxide by gasometric methods. H. MENZEL and W. KRETZSCHMAR (Z. angew. Chem., 1929, 42, 148—156).—Nitrous oxide from the thermal decomposition of ammonium nitrate was carefully purified by chemical means, then by fractional distillation after liquefaction, and four methods of determining it in gas mixtures were thoroughly tested. In Winkler's method involving thermal decomposition on the surface of a glowing platinum spiral results correct to ± 0.2 c.c. were obtained for nitrous oxide in gas mixtures containing less than 10% N₂O; with higher percentages nitrogen peroxide is formed and reacts with the mercury in the gas apparatus. Explosion with hydrogen-oxygen mixtures gives fair results when the gas mixture contains less than 5% N₂O. Explosion with a limited supply of moist hydrogen (Bunsen) or reduction by hydrogen in a heated quartz capillary tube containing a platinum spiral gives results accurate to ± 0.1 c.c. with mixtures containing 0.4—100% N₂O. Oxygen can be determined in mixtures containing nitrous oxide by absorption with slightly damp phosphorus over mercury, and nitrous oxide in the residual gas is then determined by either of the last-named methods.

A. R. POWELL.

Dimethyl- α -naphthylamine for determination of nitrite ion. F. G. GERMUTH (Ind. Eng. Chem. [Anal.], 1929, 1, 28—29).—Dimethyl- α -naphthylamine can be advantageously used in place of α -naphthylamine in nitrite determinations. Whilst with the latter the colour begins to fade in about 30 min., with the former it is unchanged for 60 days. Permanent standards can be prepared, obviating the use of fuchsin. The dimethyl derivative is also less affected by hydrogen sulphide.

C. IRWIN.

Acidimetry of phosphorous acid in presence of indicators. T. MŁOBEDEZKI and K. BORATYNSKI (Rocz. Chem., 1928, 8, 554—562).—Pure phosphorous acid is prepared by the action of concentrated hydrochloric acid on phosphorus trichloride; the product, 480 g. of which can be dissolved at 20° in 100 g. of water, is obtained free from hydrogen chloride after five recrystallisations. The neutralisation of the first hydrogen atom using sodium hydroxide solution is best indicated using bromo-

phenol-blue, whilst α -naphtholphthalein is most suitable for the second hydrogen atom.

R. TRUSZKOWSKI.

Sensitive test for silicic acid. F. OBERHAUSER and J. SCHORMULLER (Z. anorg. Chem., 1929, 178, 381—388).—As little as 1 part in 10⁶ of silicon in a solution of a silicate may be detected by the blue colour produced by adding an excess of a neutral 10% solution of ammonium molybdate, acidifying slightly, and then adding in the cold a stannite solution, freshly prepared by adding a large excess of sodium hydroxide to stannous chloride solution. The silicon forms with the molybdic acid a heteropoly-acid (cf. Parmentier, A., 1882, 702), which is reduced by the stannite to a blue lower oxide of molybdenum. Silicon as fluosilicic acid also gives the reaction. Arsenates and phosphates, if present in large amount, interfere.

R. CUTHILL.

Apparatus for the determination of silica in steel and iron by the chlorine method. P. DICKENS.—See B., 1929, 210.

Determination of cyanides and basic cyanides of mercury. A. IONESCO-MATIU and (MILEA) A. CARALE (Bul. Soc. Chim. Romania, 1928, 10, 127—130).—See A., 1928, 1230.

Colorimetric determination of carbon disulphide in gas. G. G. DESY.—See B., 1929, 194.

Determination and separation of rare metals from other metals. XII. Separation of lithium from potassium, sodium, and magnesium. L. MOSER and K. SCHUTT (Monatsh., 1929, 51, 23—42).—A detailed investigation of the various methods for the quantitative separation of lithium from sodium, potassium, and magnesium is described. Two main sources of error are (1) the hygroscopic nature of lithium chloride, (2) the small amounts of organic solvents which remain adhering to the walls of the vessels. The first is avoided by drying the lithium chloride at 120—150° and storing over concentrated sulphuric acid (Winkler's contention [A., 1913, ii, 877] that lithium chloride is unaltered by heating at 180° is confirmed) and the second by the use of mechanical filtration and washing in a specially designed apparatus which is described. The following methods for the quantitative separation of lithium from sodium and potassium are found to be untrustworthy; Gintl (Polyt. J., 1881, 240, 83), Richard (A., 1905, ii, 653; this method is completely worthless), Murmann (A., 1911, ii, 334), Kahlenberg and Krauskopf (A., 1908, ii, 777), and Smith and Ross (A., 1925, ii, 601). Very satisfactory results are obtained by slight modification of Winkler's method (*loc. cit.*). By improved drying of the isobutyl alcohol by repeated refluxing with barium oxide the correction for the solubility of sodium and potassium chlorides, when three 10 c.c. extractions with this solvent are used, is reduced to -0.5 mg. of mixed sulphates, and by use of mechanical filtration extremely accurate results both for lithium and sodium+potassium are obtained. Berzelius' method (Jahresber., 1842, 21, 142) for the separation of lithium from magnesium is vitiated by the fact that magnesium chloride cannot be completely converted into the oxide by heating with yellow

mercuric oxide. Even less complete conversion occurs with the sulphate, bromide, or iodide. In Gooch and Eddy's method (A., 1908, ii, 632), although magnesium is quantitatively precipitated by addition of an alcoholic ammonium carbonate solution, some lithium is always adsorbed by the precipitated magnesium ammonium carbonate. Satisfactory results are obtained by Berg's method (A., 1927, 639), the precipitated $\text{Mg}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$ being almost free from lithium by spectroscopic examination. On the basis of the above results lithium is quantitatively separated from sodium, potassium, and magnesium by first precipitating the magnesium with 8-hydroxyquinoline, and separation of the lithium from sodium and potassium in the filtrate by means of isobutyl alcohol. J. W. BAKER.

Spectroscopic determination of small quantities of strontium, barium, and caesium in minerals, rocks, mineral waters, etc. F. ZAMBONINI and V. CAGLIOTI (Atti R. Accad. Lincei, 1928, [vi], 8, 268—273).—A spectroscopic method is described by which small traces of elements (strontium, barium, caesium) in minerals and waters may be determined with a degree of accuracy much higher than is usually obtained. Absolute originality is not claimed, but the method has been used with considerable success by the authors, results from this and other methods agreeing well. Dealing separately with solutions of the alkaline earths, the effect of dilution and addition of comparatively large quantities of the other alkaline-earth salts on the intensity of characteristic lines is shown, with considerable data. For the determination of barium and strontium the solution must contain no free acid. G. E. WENTWORTH.

Decomposition of barium sulphate by solutions of sodium carbonate. E. WOLESENSKY (Ind. Eng. Chem. [Anal.], 1929, 1, 29—31).—If precipitated barium sulphate is boiled for 1 hr. with fourteen times its equivalent of sodium carbonate solution, at least 99% of the sulphate is brought into solution. Natural barium sulphate requires boiling for 2 hrs. The procedure can therefore be substituted for alkali fusion in the determination of sulphur in rubber compounds in conjunction with the acid oxidation method. C. IRWIN.

New metallic complexes [co-ordination compounds] of nitrosophenylhydroxylamine and their application in microchemical analysis. A. MARTINI (Anal. Assoc. Quím. Argentina, 1928, 16, 117—124).—See this vol., 164.

Determination and separation of rare metals from other metals. XIII. Gravimetric analysis of vanadium and two new methods for its determination. L. MOSER and O. BRANDL. XIV. Separation of beryllium from the alkaline-earth metals and the metals of the ammonium sulphide and arsenic groups. L. MOSER and F. LIST (Monatsh., 1929, 51, 169—180, 181—189).—XIII. Previous methods for the detection and determination of vanadium are reviewed. The error in the determination as silver pyrovanadate is large. When alkali vanadates are treated with sodium acetate and a small amount of ammonia (to neutralise the liberated acetic acid), and then with silver nitrate,

silver orthovanadate is precipitated quantitatively. When an alkali vanadate is treated with lead nitrate solution the salt $\text{Pb}_2\text{V}_6\text{O}_{17}$ is first formed. This is converted by lead nitrate into lead pyrovanadate provided the hydrogen-ion concentration of the solution is lowered by the addition of potassium bromide and bromate. The method is useful, but not so accurate as the silver orthovanadate precipitation. The method for the determination of vanadium with mercurous nitrate is improved by precipitating in presence of hydrogen peroxide. This gives a mixture of insoluble mercurous pyro- and ortho-vanadates, whilst in its absence the essential product is the soluble mercurous hexavanadate, $\text{Hg}_4\text{V}_6\text{O}_{17}$.

XIV. Beryllium is separated from calcium, strontium, or magnesium by precipitation as hydroxide with ammonium nitrite (A., 1928, 146). Since the nitrite invariably contains sulphate it is impracticable to use the same method for separating beryllium from barium. The barium is first precipitated as sulphate and the beryllium obtained from the filtrate by the action of tannic acid (*loc. cit.*). Separation from zinc is effected by precipitating the zinc as sulphide in presence of sulphosalicylic acid and subsequent nitrite treatment. Cadmium is removed as sulphide in sulphuric acid solution, and the beryllium obtained with tannin. The nitrite method can be used in the first place, with subsequent determination of cadmium. Nickel is separated with dimethylglyoxime from an ammoniacal solution in presence of either tartaric or sulphosalicylic acid. After removal of this last acid as tribromophenol, precipitation with tannin is employed. It is more convenient to separate the beryllium by the nitrite method and determine the nickel in the filtrate with dimethylglyoxime. Separation from cobalt and manganese can be accomplished by the nitrite method, or manganese is precipitated as the dioxide with ammonium persulphate and sulphuric acid, and the beryllium subsequently with tannin. The nitrite method is also used to separate beryllium from thallium (which is then determined as chromate [cf. A., 1927, 436] provided neutralisation is effected with sodium carbonate). Arsenic is removed either as sulphide or volatile chloride (cf. A., 1922, ii, 315); antimony as sulphide. The beryllium is then precipitated with tannin. To separate beryllium and tin, the latter is precipitated from a hot solution in concentrated hydrochloric acid by treatment with 10% tannin solution, solid ammonium acetate, and solid ammonium nitrate. The resulting tin-tannic acid complex is incinerated and the tin weighed as oxide. After neutralisation of the filtrate with ammonia the beryllium is precipitated with tannin. The precipitation of tungsten with tannin in presence of acetic acid (A., 1928, 145) is incomplete; if the filtrate is warmed with a 15% antipyrine solution the remainder of the tungsten is precipitated with the tannin. H. BURTON.

Applications of recent analytical methods. J. J. Fox (J. Oil and Col. Chem. Assoc., 1929, 12, 38—45).—The use of 8-hydroxyquinoline as an analytical reagent is illustrated by its application to the determination of magnesium and its separation from aluminium, and to the titration of the acid

radical of salts of aluminium, zinc, etc. The determination of metals, *e.g.*, cobalt, copper, zinc, etc., by forming their pyridine-thiocyanate complexes, according to Spacu's method, is discussed. The potentiometric titration method is briefly described and the results of four typical titrations are tabulated.

S. S. WOOLF.

Titration of thallous salts with permanganate in hydrochloric acid solutions. A. JILEK and J. LUKAS (*J. Czechoslov. Chem. Comm.*, 1929, **1**, 82—94).—The empirical nature of the volumetric determination of thallium in hydrochloric acid solutions by titration with potassium permanganate, which is due largely to the hydrolysis of the thallic chloride produced, has been overcome by the addition of potassium chloride, when a double salt, probably $3\text{KCl} \cdot \text{TlCl}_3$, is formed. The latter is not hydrolysed in strongly acid (hydrochloric) solutions.

A. I. VOGEL.

Detection and determination of mercury as the complex ammonium iodide compound. E. H. VOGELENZANG (*Pharm. Weekblad*, 1929, **66**, 65—67).—A colorimetric method is based on the Nessler reaction, by interaction between the mercury salt, an iodide, and ammonium chloride in alkaline solution. The molecular concentration of iodide must be between 3 and 16 times that of the mercury salt; preliminary determination of the amount of iodide required is therefore necessary. The solution must be at least 0.02*N* in respect of alkali hydroxide; the proportion of ammonium salt added has no influence. The test will detect about 2.2 mg. of mercury per litre, and is suitable for concentrations up to 50 mg. per litre.

S. I. LEVY.

Rapid determination of mercury. G. SPACU and J. DICK (*Z. anal. Chem.*, 1929, **76**, 273—277).—The solution (150 c.c.) containing not more than 0.3 g. of mercury is treated with 2 g. of powdered ammonium dichromate and, when that has dissolved, with 1 c.c. of pyridine. After stirring for 10 min. the mercury is completely precipitated as the compound $\text{HgCr}_2\text{O}_7 \cdot 2\text{C}_5\text{H}_5\text{N}$, a coarsely crystalline, orange precipitate which filters readily on a porous porcelain crucible; it is washed first with water containing dichromate and pyridine, then with 80% alcohol, and finally with absolute alcohol containing a trace of pyridine, dried in a vacuum desiccator, and weighed. It contains 34.90% Hg. Ammonium chloride must be removed by evaporation with nitric acid.

A. R. POWELL.

Potentiometric titration of gallium. S. ATO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1929, **10**, 1—5).—The formula, $\text{Ga}_4[\text{Fe}(\text{CN})_6]_3$, assigned by Kirschman and Ramsey (*A.*, 1928, 861) to the precipitate obtained in the potentiometric titration of gallium in slightly acid solutions with potassium ferrocyanide has been confirmed when the concentration of hydrochloric acid in 1% gallium chloride solution was between 0.005*N* and 0.0025*N*. For other acid concentrations the gallium contents of the precipitates were slightly lower than that demanded by the formula. The concentration of acid had, moreover, a marked effect on the change in potential at the end-point; in concentrations lower than

0.0005*N* the end-point could not be accurately detected. Concentrations of hydrochloric acid between 0.05*N* and 0.0025*N* enabled satisfactory titrations to be made.

H. T. S. BRITTON.

Comparative colorimetric investigations. R. WASMUHT (*Z. angew. Chem.*, 1929, **42**, 133—134).—Determination of iron as ferrocyanide with a dipping colorimeter gave results in good agreement with the titration method of Zimmermann and Reinhardt. For the colorimetric determination of manganese using potassium permanganate as standard, lead peroxide is more satisfactory as the oxidising agent than ammonium persulphate, since the colour given by the latter inclines to a rose shade and can be matched with the purplish tint of the permanganate only by the use of a compensating colorimeter.

F. R. ENNOS.

Volumetric determination of sodium and potassium ferrocyanides, using zinc sulphate solution. AZOT CHEMICAL FACTORY, JAWORZNO (*Przemysł Chem.*, 1929, **13**, 65—66).—Ferrocyanide solutions are titrated with 0.2*N*-zinc sulphate solution, the end-point being ascertained by observing when drops of the solution fail to give a blue coloration on ash-free filter-paper wetted with ferrous ammonium sulphate. The equivalent value of the zinc sulphate solution has previously to be determined separately for sodium and for potassium ferrocyanides.

R. TRUSZKOWSKI.

Diphenylamine as oxidation-reduction indicator for indirect titration of cobalt. J. GILLIS and V. CUVELIER (*Natuurwetensch. Tijds.*, 1929, **11**, 20—24).—The method of Willard and Hall (*A.*, 1922, ii, 875) has been modified, after examination by potentiometric methods, to permit of the use of diphenylamine as internal indicator. The alkaline solution, after oxidation by means of sodium perborate, and removal of the excess by boiling, is reduced by a known excess of stannous chloride, and this excess, together with the ferrous salt formed from any iron present, is determined by means of potassium dichromate in presence of the indicator. The parallel potentiometric titrations show that the minimum quantity of indicator must be used, and must be added only towards the end of the titration, and a small correction must be made. With these precautions, accurate results are obtained in the presence of nickel, and of considerable proportions of iron.

S. I. LEVY.

Volumetric determination of cobalt. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1928, [vi], **8**, 405—408).—In the green liquids which result from the decomposition of cobaltinitrites by means of hot sodium hydrogen carbonate (*A.*, 1928, 973), all the nitro-groups of the original cobaltinitroso-complex are present as alkali nitrite, whilst the tervalent cobalt exists as cobalticarbonate, to which the green colour is due. When the green liquid is added to permanganate solution acidified with sulphuric acid, the nitrous acid is oxidised quantitatively in the cold to nitric acid and the tervalent cobalt is reduced to the bivalent form, eleven equivalents of the permanganate oxygen being consumed for each molecule of the cobaltinitrite. This reaction forms the basis

of volumetric determinations of potassium (*Ind. saccharifera ital.*, 1928, **21**, 387) and of cobalt, the details of the procedure in the latter case being now described.

T. H. POPE.

Reactions of molybdates, nitrophosphomolybdates, tungstates, and phosphotungstates. T. GASPAR Y ARNAL (*Anal. Fis. Quím.*, 1928, **26**, 435—445).—The precipitation reactions are given in tabular form of solutions of sodium molybdate, ammonium molybdate, sodium nitrophosphomolybdate, sodium tungstate, and sodium phosphotungstate with lithium, sodium, ammonium, potassium, cupric, rubidium, silver, cesium, beryllium, magnesium, calcium, zinc, strontium, cadmium, barium, mercurous, mercuric, aluminium, thallium, lead, thorium, bismuth, uranyl, manganous, ferric, nickel, and cobalt salts in aqueous solution and, in some cases, in aqueous-alcoholic solution. The results are discussed, particularly from the point of view of the possibility of separation of metals by the use of these reagents.

R. K. CALLOW.

Gravimetric micro-determination of molybdenum. J. B. NIEDERL and (Miss) E. P. SILBERT (*J. Amer. Chem. Soc.*, 1929, **51**, 376—377).—Pregl's method for the micro-determination of metals in organic substances may be used in principle for the gravimetric micro-determination of molybdenum as trioxide in substances containing no other non-combustible or non-volatile constituents.

S. K. TWEEDY.

Potentiometric determination of titanium in the presence of other metals, especially iron. H. BRINTZINGER and W. SCHIEFERDECKER (*Z. anal. Chem.*, 1929, **76**, 277—280).—The solution is treated with 20 g. of calcium chloride crystals (or 12 g. of sodium chloride) and 10—20 c.c. of concentrated hydrochloric acid, diluted to 100 c.c., and titrated in an atmosphere of carbon dioxide at 90° with chromous chloride. Ferric chloride is reduced first, then cupric to cuprous chloride, and finally titanous to titanous chloride, the end-point being marked in all cases by an appreciable potential fall.

A. R. POWELL.

Determination of traces of antimony in copper and its alloys. S. G. CLARKE and B. S. EVANS.—See B., 1929, 175.

Solubility of Reinsch antimony films in water. S. G. CLARKE (*Analyst*, 1929, **54**, 99—101).—If washing of the film with water is unduly prolonged appreciable amounts of antimony are removed, the solubility being due to the presence of dissolved oxygen. Ordinary distilled water may safely be used provided the washing occupies a few seconds only.

J. S. CARTER.

Determination of the platinum metals in ores and concentrates. H. R. ADAM.—See B., 1929, 212.

Methods and apparatus used in the cryogenic laboratory. XX. High-vacuum pump. W. GAEDE and W. H. KEESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1928, **31**, 985—988).—Details are given of a mercury diffusion pump with an exhausting capacity at 0.15 mm. pressure of 130 litres/sec. for air, and 420 litres/sec. for helium. F. G. TRYHORN.

Gas density balance. A. STOCK (*Z. physikal. Chem.*, 1928, **139**, 47—52).—An improved form of density balance is described in which the beam containing a small piece of soft iron is controlled by means of an external electromagnet. An ammeter may then be conveniently calibrated to read gas densities.

R. W. LUNT.

Determination of refractive indices of materials, especially of fused mixtures, used in the Becke immersion method. A. GOOSSENS (*Natuurwetensch. Tijds.*, 1929, **11**, 1—5).—The method of the Duke of Chaulnes, in which the apparent depth of a layer of liquid of known refractive index, and that of a layer of the liquid to be examined, of the same thickness, are determined by means of a vertically moving microscope, is modified for measurements with transparent solids.

S. I. LEVY.

Extraction apparatus. S. J. GASPERÍK (*Chem. Listy*, 1929, **23**, 58—59).—A modification of Soxhlet's extraction apparatus is described.

R. TRUSZKOWSKI.

Continuous laboratory extractor for liquids. A. W. FRANCIS (*Ind. Eng. Chem. [Anal.]*, 1929, **1**, 15).—The sample is drawn into a pipette bulb packed with glass beads and the condensed vapour of the extracting liquid allowed to bubble up or down according as it is lighter or heavier than the sample.

C. IRWIN.

Extraction apparatus for liquids. II. J. FRIEDRICHS (*Chem. Fabr.*, 1929, 90—91; cf. A., 1928, 389).—The comparative rates of extraction of 0.01*N*-aqueous benzoic acid by chloroform, carbon disulphide, and carbon tetrachloride in various types of extractor were determined. A glass spiral to prevent the extracting liquid taking the shortest path, or a condenser with serrated edges, was less efficient than a distributor consisting of fine hollow points dipping into the solution, and this in turn less than the porous glass frits designed by the author.

C. IRWIN.

Micro-extraction method. J. B. NIEDERL (*J. Amer. Chem. Soc.*, 1929, **51**, 474—475).—One drop of the liquid and one drop of extraction medium are repeatedly centrifuged in a sealed capillary tube so that the layer of higher density is forced through the layer of lower density. The tube is then separated under a microscope at the boundary of the two liquids.

S. K. TWEEDY.

Haughton-Hanson thermostat. Method of fine adjustment. P. J. DURRANT (*Inst. Metals*, March, 1929, advance copy, 4 pp.).—In a method by which the temperature of the Haughton-Hanson thermostat can be adjusted to within 0.1° over a range of 5°, the "cold bulb" is placed in a small toluene thermostat, and the temperature of this is controlled by a movable wire in a mercury U-tube. The temperature of the thermostat depends on that of the "cold bulb," which in turn depends on the level of the wire. Preliminary experiments enable a scale to be drawn by the side of the wire.

W. HUME-ROTHERY.

Apparatus for vapour-pressure determinations. O. A. PICKETT (*Ind. Eng. Chem. [Anal.]*, 1929, **1**, 36—38).—Ramsay and Young's vapour-

pressure apparatus is modified by the insertion of a reflux condenser after the boiling tube. A mercury thermometer is used for approximate readings and a platinum resistance thermometer for precision, each being fitted with a cotton wick. By the use of different bath-liquids data over the temperature range 10—220° can be obtained in 2—4 hrs. with an accuracy of 0.5%.
C. IRWIN.

Pressure regulator for vacuum distillations. H. L. COX (Ind. Eng. Chem. [Anal.], 1929, 1, 7—8).—A closed-arm mercury manometer contains an adjustable contact in the open side and a fixed contact in the top of the same side. These are connected in series to a battery and a relay operating the motor vacuum pump. Any desired pressure between 2 mm. and atmosphere can be maintained to within 0.1 mm.
C. IRWIN.

Sublimation mercury still. K. HICKMAN (J. Opt. Soc. Amer., 1929, 18, 62—68).—An improved type of electrically heated glass still is described. A number of units can be worked in series, condensed mercury which ordinarily falls back into the mother-liquor being passed on to the next still. The still works automatically, and an advantage claimed is that the need for frequent chemical treatment of the mercury before distillation is avoided.
N. M. BLYTH.

Automatic mercury still. F. L. ROBESON (J. Opt. Soc. Amer., 1929, 18, 72—74).—An easily constructed glass still is described employing two barometric columns to maintain the vacuum. The still starts and stops automatically, and needs little attention. The power required is 90 watts for an output of 100 g./hr. of mercury.
N. M. BLYTH.

Still for liquids of high b. p. K. HICKMAN (J. Opt. Soc. Amer., 1929, 18, 69—71).—The apparatus is in the form of an alembic, and works on the principle that distillation can take place rapidly under very low pressures if the evaporating and condensing surfaces are large and close together. It is intended for liquids that oxidise or decompose when distilled in air.
N. M. BLYTH.

Distilling apparatus for the chemical engineering laboratory. W. L. BEUSCHLEIN (Ind. Eng. Chem. [Anal.], 1929, 1, 43—44).—An apparatus which combines the batch and continuous-type fractionating equipment, and gives constant conditions, consists of a 30-gallon still, plate column, and condenser of the usual type, with thermometers in the hand-hole covers of each plate, and in the vapour of the kettle. Piping from condenser to kettle converts into a continuous process, and the condensate passes through two Venturi meters (one for the reflux and one for the net output), of the two-liquid multiplying type. The reflux ratio is obtained and regulated by a valve, an open vent eliminating siphoning. In operation the condensate composition is built up by returning all as reflux to the kettle, after which a portion is allowed to flow continuously through the sight gravity jar into the kettle, and readings of the Venturi manometers, kettle thermometer, and condensate hydrometer are taken. By directing a fraction of the condensate through a cock to the storage vessel, concentration may be changed and a new set of conditions established.
D. H. HEWER.

Application of the vacuum tube in the falling-ball method [of determining viscosity] for dark-coloured solutions. E. M. SYMMES and E. A. LANTZ (Ind. Eng. Chem. [Anal.], 1929, 1, 35—36).—A steel ball is used and the coils of an oscillating circuit are wound in two slots corresponding with the graduation marks of the viscosity tube. The change in note due to the change in frequency of the oscillations marks the passage of the ball through the coils.
C. IRWIN.

Brine circulator for cooling condensers. H. T. GERRY (J. Amer. Chem. Soc., 1929, 51, 475).—An easily constructed laboratory adaptation of the air-lift pumps used in sulphuric plants is described.
S. K. TWEEDY.

Colorimeter for determination of hydrogen-concentration. J. J. BEAVER (J. Opt. Soc. Amer., 1929, 18, 41—49).—The apparatus described avoids the use of standardised buffer solutions. It has an additional cup and plunger and the total depth of liquid in the light path is kept constant irrespective of what this depth or the ratio of the depths of liquid in the two cups may be. The method is rapid and accurate, and it can be used for coloured or turbid solutions if the colour is not too deep. The apparatus can easily be adapted for use as an ordinary colorimeter.
N. M. BLYTH.

Suction as a filtering aid. G. L. HOCKENYOS (Chemist Analyst, 1928, 17, No. 4, 18).—A pressure regulator, consisting of a tube containing a variable amount of water, and fitted with a stopper carrying a tube to the suction flask and another tube from the water upwards into the air, is recommended.
CHEMICAL ABSTRACTS.

Porous filter crucibles. S. GERICKE (Chem.-Ztg., 1929, 53, 119).—Porous filter crucibles have a limited application only. Untrustworthy results are obtained when such crucibles are used in the determination of phosphoric acid as magnesium pyrophosphate or as phosphomolybdate, and the determination of nickel as the dimethylglyoxime compound. Calcium oxalate and barium sulphate pass through most porous crucibles and filtration of gelatinous precipitates is slow.
J. S. CARTER.

Ebullioscopic apparatus for high-pressure researches. W. SWIENTOSLAWSKI (Compt. rend., 1929, 188, 392—395).—The author's differential ebullioscope (this vol., 255) may be adapted for work at pressures up to 25 atm. by the use of compressed nitrogen, the apparatus being placed in gas-tight, steel protecting vessels. Electrical heating and temperature-measuring devices are used, and the pressure is determined from the b. p. of water, which is used as a control, or from the amount of nitrogen in a tube attached to the source of pressure and maintained at a constant temperature (cf. following abstract).
J. GRANT.

Modification of [Swientoslawski's] ebullioscope for high pressures. A. ZMACZYNSKI (Compt. rend., 1929, 188, 395—396; cf. preceding abstract).—A reservoir supplied with a siphon is connected to the portion of the apparatus containing the boiling liquid

and serves to maintain a constant liquid level over wide ranges of pressure, and to compensate for the effect of thermal dilatation. J. GRANT.

Stirrer from [motor-car] windscreen wiper. A. V. MOTSINGER (Ind. Eng. Chem., 1929, 21, 192).—A suction-operated windscreen wiper with a piece of wire attached is used as a stirrer. C. IRWIN.

Collapsing temperatures of various kinds of laboratory glass tubing. A. W. LAUBENGAYER (Ind. Eng. Chem., 1929, 21, 174).—The collapsing temperatures of glass tubing with a diameter of 13 mm. were found to range from 700° for soft soda-lime glass to 860° for Jena or Bohemian combustion tubing. Evacuated tubes collapse at temperatures 50–150° lower. C. IRWIN.

Geochemistry.

Influence of temperature on the composition of the upper layers of the atmosphere. HELGE-PETERSEN (Physikal. Z., 1928, 29, 879–884).—The hypothesis of a stationary streaming state as against that of a static diffusional equilibrium provides a plausible explanation of the absence of helium at great heights, *e.g.*, at 200 km., as evidenced by the lack of helium lines in the northern light spectrum. R. A. MORTON.

Amount of ozone in the earth's atmosphere and its relation to other geophysical conditions. III. G. M. B. DOBSON, D. N. HARRISON, and J. LAWRENCE (Proc. Roy. Soc., 1929, A, 122, 456–486; cf. A., 1926, 493; 1927, 439).—Observations have been made at seven stations in N.-W. Europe and the accuracy of the measurements is discussed. A study of the monthly means of the ozone values shows that the autumn minimum value is roughly the same for all stations, whereas the spring maximum is much greater at the northern stations. The results suggest that in the Arctic the ozone values are high in spring, but relatively low in the late summer. The tendency for days with much ozone to be associated with magnetically disturbed conditions is again indicated. The distribution of ozone in typical cyclones and anticyclones is discussed at length, and a series of maps is constructed to show the changes in the ozone distribution for typical pressure distributions. The 1927 observations entirely confirm the close connexion between the amount of ozone and the pressure distribution observed previously. The measurements give evidence that the great polar and tropical air currents extend to a great height and bring their own stratosphere with them. The amount of ozone appears to be uninfluenced by pressure surges or Föhn conditions. The results of the present observations make it almost certain that the chief cause of the formation of atmospheric ozone is not the action of the sun's ultra-violet radiation of wave-length about 1600 Å., as hitherto supposed, but that, on the contrary, the effect of sunlight is mainly to decompose the ozone already present. L. L. BIRCUMSHAW.

Altitude of the ozone layer. J. C. McLENNAN, R. RUEDY, and V. KROTKOV (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 293–301).—An account of attempts to determine the height of the ozone layer over Toronto is given. A series of spectrograms of the zenith of a clear sky were taken, and the intensities of the Huggins bands (absorption bands in the ultra-violet due to ozone) were determined by means of a photomicrometer. The observations are employed to determine the height of the ozone layer. Values

varying from 47.55 to 57 km. are obtained for different days and times. The average of the results is slightly higher than that of those previously obtained by Cabannes and Dufay. The thickness of the ozone layer is only 3 mm. on the average. A. J. MEE.

Measurements of ozone in the higher atmosphere in 1928. H. BUISSON (Compt. rend., 1929, 188, 647–648).—Diurnal determinations of ozone in the higher atmosphere during 1928 by the method previously described (A., 1928, 611) have confirmed the observations made in 1927, the maximum (spring), 3.75 mm., and minimum (autumn), 2.25 mm., being slightly less pronounced. The irregular variations are strongest at the beginning and end of the year and disappear in summer. The measurements are in agreement with those made at Arosa (Switzerland) at 1800 m. and for the period January to October the figures at each station are 0.16 mm. lower than those of 1927. R. BRIGHTMAN.

γ -Rays of potassium. A. SALMONY (Chem.-Ztg., 1929, 53, 137).—Radiations from potassium are believed to be responsible for the radioactivity of certain mineral deposits and to play an essential part in the re-activation, under the influence of radiation from radioactive substances, of hearts removed from the body. J. S. CARTER.

Dolomitisation of Palaeozoic limestones in Manitoba. D. J. BIRSE (Trans. Roy. Soc. Canada, 1928, [iii], 22, IV, 215–221).—The fossiliferous limestone presents a mottled appearance with darker dendritic forms in a lighter ground. It has been thought that these forms are of fucoidal origin. They can be etched out with dilute acids, and analyses of the dark and light portions show that the former are richer in magnesium carbonate. The forms are therefore due to a selective dolomitisation of the limestone. L. J. SPENCER.

Keweenawan sill-rocks of Sudbury and Cobalt, Ontario. T. C. PHENISTER (Trans. Roy. Soc. Canada, 1928, [iii], 22, IV, 121–197).—Detailed petrographical descriptions are given of the quartz-diorite occurring as large intrusive sills in rocks of Keweenawan age in these two mining areas. The quartz forms a micrographic intergrowth with an acid plagioclase, and as this increases in amount the rock grades into a micropegmatite. Analyses are given of the rocks and of the constituent pyroxenes. L. J. SPENCER.

Cyanite as found in Western North Carolina. A. H. FESSLER and W. J. McCAUGHEY.—See B 1929, 209.

Approximate gallium content of green kaolin from Tanokami. Existence of gallium in the solar chromosphere. S. IMORI (Suppl. to Sci. Papers Inst. Phys. Chem. Res., 1929, 10, No. 8, 1—4; cf. A., 1928, 42).—Spectrographical examination suggests that the gallium content of the green kaolin from Tanokami is of the order 0.0004—0.004%. It is suggested that certain of the solar lines are those of gallium. J. S. CARTER.

Pink kaolin, and ruthenium as a minor constituent of the Tanokami kaolins. S. IMORI and J. YOSHIMURA (Bull. Chem. Soc. Japan., 1929, 4, 1—5).—An analysis is given of a pink kaolin from Tanokami. From measurements of the X-ray absorption spectrum it is considered that the pink colour is due to the presence of rhodium or ruthenium as a minor constituent. C. W. GIBBY.

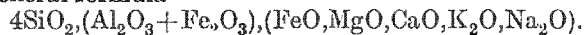
Prochlorite from Monte Rosso di Verra (Monte Rosa group). T. CARPANESE (Atti R. Accad. Lincei, 1929, [vi], 9, 77—83).—Analysis of this mineral gave: H_2O 13.13; SiO_2 29.20; Al_2O_3 21.32; Fe_2O_3 1.55; FeO 3.41; MgO 31.89; total 100.50%. Dehydration on heating follows a course closely resembling that observed with pennine from Zermatt and with clinocllore from Val Devero, the existence of a hydrate containing about 5% of water and stable at about 550—700° being indicated. Re-absorption of atmospheric moisture by the anhydrous mineral proceeds rapidly at first and then gradually ceases. Optical transformation occurs when the prochlorite is heated, the optic axial angle diminishing to zero and then becoming negative; later, the crystals become biaxial, still remaining negative but with the plane of the optic axis perpendicular to its original position. Comparison of the dehydration and re-absorption curves for the "noble" variety of serpentine and for antigorite indicates a sharp chemico-physical distinction between these two minerals.

T. H. POPE.

Baryta in the jurassic and cretaceous deposits of the Tschuvashki Republic. L. M. MIROPOLSKI (Bull. Acad. Sci. U.R.S.S., 1928, 425—441).—the different forms of baryta, which appears in these deposits both as concretion and as separate crystals of varying habit, are described. T. H. POPE.

Structure of leucite and of complex kaolinites. M. DOMINIKIEWICZ (Rocz. Chem., 1928, 8, 542—553).—Structural formulæ derived for leucite, andalusite, sillimanite, topaz, and beryl are shown to be in accordance with many of the observed properties of these minerals. R. TRUSZKOWSKI.

Chemical and mineralogical composition of red and green eocene schistous clay of the Eastern Carpathians. A. GAWEL (Bull. Acad. Polonaise, 1928, A, 523—537).—Chemical analyses are recorded of the portion of slate clay soluble in hydrochloric acid and these are expressed by the general formula



The red clay is characterised by the absence of combined ferric oxide but contains free ferric oxide, to which the colour is due, whilst in the green clay the iron oxide is combined with silica. A. I. VOGEL.

Relation between the increase in the magnetic susceptibility of certain rocks when heated and the modifications induced in certain of their mineral constituents. A. MICHEL-LEVY and G. GRENET (Compt. rend., 1929, 188, 640—642).—The increase in magnetic susceptibility of five specimens of rhyolite, containing varying amounts of biotite, chlorite, and titanite, a specimen of dacite and one of andesilabradorite produced by heating at 700° is connected with the dehydration of the chlorite surrounding titanite crystals and the formation of magnetite or titanomagnetite. R. BRIGHTMAN.

Calcareous soils of Bavaria. H. NIKLAS, R. PÜRCHKAUER, and H. POSCHENRIEDER (Z. Pflanz. Düng., 1929, 13A, 39—53).—The general classification of these calcareous soils is discussed from the point of view of chalk content and p_{H} value. Generally, poverty in phosphate is characteristic, but easily-soluble potash is present in satisfactory amounts. The growth of *Azotobacter* is not as satisfactory as the reaction and nutritive value would indicate. The catalytic power of these soils is also described.

A. G. POLLARD.

Weathering of sandstone, limestone, and basalt in red-earth areas. A. REIFENBERG (Z. Pflanz. Düng., 1929, 13A, 53—66).—The chemical and physical processes involved in the formation of some Palestine soils are examined and discussed. The soils are classified and their characteristic properties enumerated. A. G. POLLARD.

Etna and its lavas. A. RITTMANN (Naturwiss., 1929, 17, 94—100).—A general account of volcanic eruptions from Mt. Etna is given, together with chemical analyses of the lava of different periods of activity. The composition varies within fairly narrow limits. The geological interpretation of the changes is discussed. R. A. MORTON.

Constitution and classification of coal. A. C. FIELDNER.—See B., 1929, 155.

Organic Chemistry.

Purification of methyl fluoride. Quantitative gas analysis by high-dispersion infra-red spectroscopy. W. H. BENNETT (J. Amer. Chem. Soc., 1929, 51, 377—381).—Pure methyl fluoride may be prepared by heating 2 parts of anhydrous potassium fluoride with 5 parts of potassium methyl sulphate

at 140—200°, passing the gas successively through concentrated sulphuric acid (to remove methyl ether), concentrated potassium hydroxide solution, soda-lime, and calcium chloride, and finally condensing in liquid air. This gas is free from methyl ether and ethylene. The quantitative analysis of

methyl fluoride for these two impurities by high-dispersion measurements of the infra-red spectra of the gas is described. S. K. TWEEDY.

Catalytic activity of aluminium chloride. G. DOUGHERTY (J. Amer. Chem. Soc., 1929, **51**, 576—580).—The author's view that the catalytic activity of aluminium chloride is due to the formation of ionogenic additive products is confirmed by the observation that the halogens in mixtures of halogeno-paraffins are readily interchangeable in presence of a little aluminium chloride (cf. Walker, J.C.S., 1904, **105**, 1082). Thus, in equimolecular proportions, methyl iodide and ethyl bromide give methyl bromide and ethyl iodide, ethylene bromide and ethyl iodide give ethyl bromide (70% of theory), ethyl bromide and chloroform at the ordinary temperature give 35% of dichlorobromomethane, and ethylene chloride and bromide give an equilibrium mixture containing 50% of ethylene chlorobromide. The same mixture is obtained from ethylene chlorobromide

H. E. F. NOTTON.

Reactivity of carbinols. Walden inversion. P. A. LEVENE and A. ROTHEN (J. Biol. Chem., 1929, **81**, 359—368).—The velocity of substitution of Br for OH on heating a number of carbinols under standard conditions with hydrogen bromide was observed. The greatest difference was found between the rapidly reacting mixed aliphatic-aromatic carbinols and the slowly reacting aliphatic compounds. In the aliphatic series, the normal primary alcohols reacted more rapidly than those with branched chains, and the primary alcohols as a whole more rapidly than the secondary; methylcyclohexylcarbinol reacted much more slowly than any other compound studied. The unexpected fact that Walden inversion takes place principally in the mixed aliphatic-aromatic series in spite of the high speed of substitution may be accounted for by the great mobility of the groups in these compounds.

C. R. HARRINGTON.

Synthesis of methyl alcohol. E. AUDIBERT.—See B., 1929, 162.

Derivatives of aliphatic glycols. G. M. BENNETT and F. HEATHCOAT (J.C.S., 1929, 268—274).—Treatment of glycol monomethyl ether, in dimethylaniline solution, with thionyl chloride conveniently gave methyl β -chloroethyl ether, b. p. 90.5°/747 mm., d_4^{20} 1.031. An attempt to repeat Foran's preparation of bromodiethyl ether gave vinyl bromide as the only isolable product.

The reaction of sulphur monochloride on tri-, tetra-, and penta-methylene glycols has been examined. γ -Chloropropyl 3:5-dinitrobenzoate has m. p. 77°. Trimethylene glycol, by the successive interaction of acetic anhydride and sulphur chloride, gives γ -chloropropyl acetate, b. p. 66°/14 mm., in good yield. Treatment of the last substance with propyl mercaptan and aqueous-alcoholic sodium hydroxide leads to γ -hydroxydipropyl sulphide, b. p. 112°/16 mm., d_4^{20} (vac.) 0.9794, n_D^{20} 1.47789 (phenylurethane, p. 36°). β -Hydroxyethyl butyl sulphide yields the isomeric phenylurethane, m. p. 44.5°.

Tetramethylene glycol (corresponding di- α -naphthylurethane has m. p. 198°) gave, by treatment with

sulphur chloride, crude δ -chlorobutyl alcohol, b. p. 86°/15 mm. (decomp.), from which the α -naphthylurethane, m. p. 66°, was isolated. δ -Chlorobutyl acetate, b. p. 87°/17 mm., d_4^{20} (vac.) 1.0803, n_D^{20} 1.43811, was obtained either by heating tetramethylene glycol with sulphur chloride and acetylating the product or by the interaction of the glycol and acetyl chloride under pressure. δ -Chlorobutyl acetate reacted with ethyl mercaptan in methyl-alcoholic-aqueous solution, giving ethyl δ -hydroxybutyl sulphide, b. p. 120°/19 mm., d_4^{20} (vac.) 0.9794, n_D^{20} 1.48118 (phenylurethane, m. p. 37°); similar use of thiophenol led to phenyl δ -hydroxybutyl sulphide, m. p. 24° (phenylurethane, m. p. 68.5°).

Pentamethylene glycol (corresponding diphenylurethane and di- α -naphthylurethane, m. p. 174° and 147°, respectively) interacted with sulphur chloride to give crude ϵ -chloroamyl alcohol, b. p. 114°/16 mm. (α -naphthylurethane, m. p. 92°). ϵ -Chloroamyl acetate, b. p. 103°/18 mm., d_4^{20} (vac.) 1.0648, n_D^{20} 1.43791, was converted by methyl mercaptan and methyl-alcoholic-aqueous potassium hydroxide into methyl ϵ -hydroxyamyl sulphide, b. p. 121°/16 mm., d_4^{20} (vac.) 0.9846, n_D^{20} 1.488185 (phenylurethane, m. p. 43.5°). Phenyl ϵ -hydroxyamyl sulphide has m. p. 31.5° (phenylurethane, m. p. 59°).

Attention is directed to the general fact that an alternation of m. p. occurs in the diurethanes when the lengthening chain is terminated by large polar groups, whilst the m. p. fall with but slight alternation if the highly polar group is at one end only.

R. J. W. LE FEVRE.

Action between copper salts and glycerol. B. K. VAIDYA (Nature, 1929, **123**, 414).—When copper salts, except cupric chloride, are heated with glycerol at 150—200°, metallic copper and free acid (which may undergo further decomposition) are produced, together with ethyl alcohol, acetaldehyde, carbon dioxide, methane, and small quantities of carbon monoxide and hydrogen. Cupric chloride yields cuprous chloride quantitatively. Glycol, erythritol, and mannitol give analogous results. Probably the decomposition is catalysed by the copper, which is pure and finely divided.

A. A. ELDRIDGE.

Diacetylenic heterocyclic compound. LESPICHAU (Compt. rend., 1929, **188**, 502—503).—By condensation of dichloromethyl ether with magnesium acetylide the compound $O<CH^2\cdot C\equiv C\cdot CH^2>O$ is formed, m. p. (with deflagration) 180°. When heated slowly, it turns yellow, shrinks, and does not melt or deflagrate below 200°. It forms a precipitate with mercuric chloride, and absorbs 4 atoms of bromine from an ethereal solution.

B. W. ANDERSON.

Cyclic acetals. I. R. DWORZAK and T. M. LASCH (Monatsh., 1929, **51**, 59—72).—The formation of cyclic acetals by the interaction of a series of glycols with various aliphatic aldehydes is investigated. Contrary to experience in the case of cyclic benzylidene derivatives, the yields obtained are approximately the same whether the mixture is heated with concentrated hydrochloric acid in a sealed tube or condensed at 0° by the action of anhydrous hydrogen chloride. Contrary to Hibbert

and Timm's experience (A., 1924, i, 710), the yield of cyclic acetal increases with increasing mol. wt. of the aldehyde used. Acetals could be obtained only with $\alpha\beta$ - and $\alpha\gamma$ -glycols (yielding five- and six-membered rings) (cf. Franke and Gigerl, A., 1928, 759) and no definitely characterised, halogen-free compound could be isolated from the product of the action of isobutylaldehyde with pentane- $\alpha\delta$ -, octane- $\alpha\theta$ -, nonane- $\alpha\iota$ -, and decane- $\alpha\kappa$ -diols. By the above methods from the appropriate glycol and aldehyde are obtained the cyclic *methylene* derivatives of β -methyl- β -ethylpropane- $\alpha\gamma$ -diol, b. p. 150—152° (yield 30%); $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -diol (30%) (cf. Apel and Tollens, A., 1896, i, 115): the cyclic *ethylidene* derivatives of β -methyl- β -ethylpropane- $\alpha\gamma$ -diol, b. p. 156—160° (30%); the cyclic *isobutylidene* derivatives of $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -diol, b. p. 159—161° (67%); β -methylpentane- $\alpha\gamma$ -diol, b. p. 69—70°/12 mm. (69%); butane- $\alpha\gamma$ -diol, b. p. 42.5—43°/10 mm. (63%); $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol, b. p. 67—73°/21 mm. (25%); $\beta\gamma$ -dimethylbutane- $\beta\gamma$ -diol (pinacol), b. p. 59°/13 mm. (68%); and $\gamma\delta$ -dimethylhexane- $\gamma\delta$ -diol, b. p. 81—83°/10 mm. (66%); and the cyclic *heptylidene* derivative of $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -diol, b. p. 234—239° (78%).

J. W. BAKER.

Esters of phosphoric acid. I. Phosphates of cetyl alcohol, cholesterol, chloroethyl alcohol, and ethylene glycol. II. Action of ethyl metaphosphate on alcohols, ammonia, and some amino-compounds. R. H. A. PLIMMER and W. J. N. BURCH (J.C.S., 1929, 279—291, 292—300). —I. The interaction of phosphoryl chloride and cetyl alcohol in chloroform gave *barium monocetyl phosphate monohydrate* (from which monocetyl dihydrogen phosphate was isolated), *calcium monocetyl phosphate*, and *dicetylphosphoryl chloride* (hydrolysis of which yielded *barium dicetyl phosphate* and dicetyl hydrogen phosphate, softening at 46°). The action of 1 mol. of phosphoryl chloride on 1 mol. of cetyl alcohol at 100° gave cetene as the only isolable product. Tri-cetyl phosphate was obtained by the interaction of cetyl alcohol and phosphorus pentachloride and by boiling excess of cetyl alcohol with phosphoric oxide in presence of ether. It gave sodium dicetyl phosphate when boiled with aqueous sodium hydroxide.

The interaction of phosphoryl chloride and cholesterol in chloroform solution gave *barium monocholesteryl phosphate tetrahydrate* (from which *monocholesteryl dihydrogen phosphate* and its lead, silver, copper, and sodium salts were obtained) and *barium dicholesteryl phosphate* (whence *dicholesteryl hydrogen phosphate* was prepared). *Tricholesteryl phosphate* was obtained by treatment of cholesterol with phosphorus pentachloride.

Analogous reactions with phosphoryl chloride and ethylene chlorohydrin led to *tri- β -chloroethyl phosphate*, b. p. 140°/40 mm., *d* 1.39, barium β -hydroxyethyl phosphate, and *barium di- β -hydroxyethyl phosphate dihydrate*. The interaction of ethylene chlorohydrin and phosphoryl chloride in cold pyridine resulted in good yields of *barium chloroethyl phosphate monohydrate*; the corresponding *brucine salt* [$C_{23}H_{46}O_4N_2 \cdot (C_2H_4Cl)_2H_2PO_4 \cdot 4H_2O$] was converted into barium β -hydroxyethyl phosphate. Barium

chloroethyl phosphate was also obtained by the action of ethyl metaphosphate on ethylene chlorohydrin. Treatment of a saturated aqueous solution of trisodium phosphate with ethylene chlorohydrin resulted in the isolation of *disodium β -hydroxyethyl phosphate hexahydrate*, m. p. 61°. A very soluble salt, probably *sodium ethylene phosphate*, $C_2H_4O_2 \cdot PO \cdot ONa$, was formed by the action of phosphoryl chloride on the disodium derivative of ethylene glycol.

The various esters of phosphoric acid were completely hydrolysed by dilute acids. The mono- and di-esters of the aliphatic alcohols with phosphoric acid were not hydrolysed, and the triester was hydrolysed to the diester, by dilute alkali. The mono-, di-, and tri-phenyl phosphates were completely hydrolysed by dilute alkali. *Sodium dicetyl phosphate* is also described.

II. Ethyl metaphosphate and absolute ethyl alcohol interacted in chloroform solution to give *barium ethyl phosphate monohydrate* and *barium diethyl phosphate*. *n*-Propyl alcohol and ethyl metaphosphate similarly gave barium ethyl phosphate, *barium di-n-propyl phosphate*, and *barium dipropyl pyrophosphate* (whence *barium propyl phosphate* was obtained). Cetyl alcohol and ethyl metaphosphate yielded barium mono- and di-cetyl phosphates with barium mono- and di-ethyl phosphates. Phenol and ethyl metaphosphate formed barium ethyl phosphate, *barium phenyl phosphate*, barium diethyl phosphate, and *barium diphenyl phosphate tetrahydrate*. Similar treatment of cholesterol with ethyl metaphosphate gave barium ethyl phosphate and *barium cholesteryl phosphate tetrahydrate*, *cholesteryl ethyl ether*, b. p. 237°/20 mm., being also formed. Passage of anhydrous ammonia through a chloroform solution of ethyl metaphosphate gave ammonium ethyl hydrogen phosphate identical with the product obtained directly from ethyl alcohol and phosphoric oxide. *Diammonium ethyl phosphate* and *ammonium diethyl phosphate* were prepared by the action of ammonium sulphate on barium ethyl phosphate and barium diethyl phosphate, respectively.

The product of the interaction of ethyl metaphosphate and hydrazine (Strecker and Heuser, Ber., 1924, 57, 1364) is *hydrazine ethyl dihydrogen phosphate*, which reacted with copper sulphate to give *hydrazine copper sulphate* and copper ethyl phosphate. Similarly, ethyl metaphosphate formed with phenylhydrazine, alanine, and guanidine, respectively, phenylhydrazine ethyl dihydrogen phosphate, alanine ethyl pyrophosphate (which formed alanine ethyl dihydrogen phosphate on treatment with water), and *guanidine diethyl pyrophosphate*; in no case were any compounds isolated in which nitrogen is directly linked to phosphorus.

The use of ethyl metaphosphate for the preparation of phosphoric esters has no advantage over the alcohol-phosphoric oxide reaction.

R. J. W. LE FÈVRE.

Silver salts of esters of hexosemonophosphoric acids. F. WEINMANN (Biochem. Z., 1929, 204, 493—494).—The silver salt of Neuberg's hexosemonophosphoric ester, obtained in 81% yield from the barium salt, is a faintly yellow powder easily

soluble in cold water and, when prepared from satisfactory material, stable towards light. Its solution soon gives a silver mirror when heated. The silver salt of Robison's ester is, in solution, more sensitive than, but otherwise very similar to, the salt of the isomeric ester. W. MCCARTNEY.

Hexosemonophosphate (Robison). P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1929, **81**, 279—283).—The rate of hydrolysis by 0.1*N*. hydrochloric acid of the methyl glucoside of the hexosemonophosphate of Robison (A., 1923, i, 86) indicates that the latter has the structure of a γ -lactone; the phosphoric acid residue must therefore be attached to the ϵ -carbon atom. C. R. HARRINGTON.

β -Hydroxyethyl allyl sulphide and its derivatives. S. M. SCHERLIN and V. V. VASILEVSKI (J. pr. Chem., 1929, [ii], **121**, 173—176).—See this vol., 293.

Refractometric determination of formic acid in the presence of acetic acid. J. BULÍR (Chem. Listy, 1929, **23**, 25—26; cf. *ibid.*, 1920, **14**, 6, 45).—Objections raised against this method by Št'astný are shown to be unfounded, fairly accurate results (0.2 g. of formic acid per 100 c.c.) being attained provided that no substances other than the above acids and water are present in the solution. R. TRUSZKOWSKI.

Thorium formates. H. REIHLEN and M. DEBUS (Z. anorg. Chem., 1929, **178**, 157—176).—The compound $[\text{Th}_3(\text{HCO}_2)_6(\text{OH})_5]\text{SCN}, 7\text{H}_2\text{O}$ obtained by Weinland and Stark (A., 1926, 498) by the action of potassium thiocyanate on thorium formate is now shown to be *potassium hexaformiato-oxytetrahydroxythiocyanatotrithiorate*, $\text{K}[\text{SCN}(\text{OH})_4\text{O}(\text{HCO}_2)_6\text{Th}_3], 7\text{H}_2\text{O}$. In a vacuum it loses $7\text{H}_2\text{O}$ rapidly and a further $2\text{H}_2\text{O}$ after being heated for 24 hrs. at 61° , being converted into the *trioxy*-compound, $[\text{Th}_3(\text{HCO}_2)_6\text{O}_3\text{SCN}]\text{K}$. When thorium formate is added to a half-saturated solution of potassium thiocyanate until it ceases to dissolve, the compound

$3\text{K}[\text{SCN}(\text{OH})_4\text{O}(\text{HCO}_2)_6\text{Th}_3], 2\text{K}_2[(\text{SCN})_2(\text{OH})_5\text{O}(\text{HCO}_2)_6\text{Th}_3], 30\text{H}_2\text{O}$ crystallises on cooling to 0° . The following compounds have been obtained in a similar manner from thorium formate and solutions of alkali nitrate, chlorate, or perchlorate:

$\text{Na}[\text{Th}_3(\text{HCO}_2)_6\text{O}(\text{OH})_4\text{NO}_3], 10.5\text{H}_2\text{O};$
 $\text{Na}[\text{ClO}_3(\text{OH})_4\text{O}(\text{HCO}_2)_6\text{Th}_3], 13\text{H}_2\text{O};$
 $\text{Na}[\text{Th}_3(\text{HCO}_2)_6\text{O}(\text{OH})_4\text{ClO}_4], 9\text{H}_2\text{O};$
 $\text{Na}[\text{NO}_3(\text{OH})_4\text{O}(\text{HCO}_2)_6\text{Th}_3], [\text{NO}_3(\text{OH})_5(\text{HCO}_2)_6\text{Th}_3], 21\text{H}_2\text{O};$
 $2\text{K}[\text{NO}_3(\text{OH})_4\text{O}(\text{HCO}_2)_6\text{Th}_3], [\text{NO}_3(\text{OH})_5(\text{HCO}_2)_6\text{Th}_3], 30\text{H}_2\text{O};$
 $\text{K}[\text{ClO}_3(\text{OH})_4\text{O}(\text{HCO}_2)_6\text{Th}_3], 2[(\text{OH})_2\text{O}(\text{HCO}_2)_6\text{Th}_3], 29.5\text{H}_2\text{O}.$

Dissolution of thorium hydroxide in formic acid yields crystals of thorium formate; as this compound is not an electrolyte it should be formulated as $[\text{Th}_3(\text{HCO}_2)_{12}], 9\text{H}_2\text{O}$; when treated with pure formic acid on the water-bath the hydrate with $3.5\text{H}_2\text{O}$ is obtained, but with water under the same conditions hydrolysis ensues with separation of the complex $[\text{Th}_3(\text{HCO}_2)_6(\text{OH})_6], 4\text{H}_2\text{O}$. Interaction of aqueous solutions of thorium nitrate and sodium formate affords two *basic formates* which are most satisfac-

torily formulated as $[\text{Th}_3(\text{HCO}_2)_{10}(\text{OH})_2], 7\text{H}_2\text{O}$ and $[\text{Th}_3(\text{HCO}_2)_9(\text{OH})_3], 10\text{H}_2\text{O}$. Electrical conductivity measurements of solutions of the neutral formate $[\text{Th}_3(\text{HCO}_2)_{12}], 9\text{H}_2\text{O}$ show that the conductivity increases very rapidly with rise of temperature; this is ascribed to decomposition of the complex with the formation of the complex formate $[(\text{H}_2\text{O})_3\text{Th}(\text{HCO}_2)_3\text{Th}(\text{HCO}_2)_3\text{Th}(\text{H}_2\text{O})_3](\text{HCO}_2)_6$.

A. R. POWELL.

Products of partial hydrogenation of higher monoethylenic esters. T. P. HILDITCH and N. L. VIDYARTHI (Proc. Roy. Soc., 1929, A, **122**, 552—563).—Methyl oleate, palmitoleate, and erucate were treated with hydrogen at 114 — 220° in the presence of nickel mounted on kieselguhr (15% Ni), the concentration of metallic nickel present with respect to the ester being about 0.5%, until their iodine values were reduced by about 30%. The products of hydrogenation were examined by oxidation with potassium permanganate in hot acetone solution, with formation of free monocarboxylic acids and monomethyl ethers of dicarboxylic acids, together with neutral (non-oxidised) material of negligible iodine value. The evidence afforded by the identification of the dicarboxylic acids (and to a smaller extent of the monocarboxylic acids) indicates that the isomeric acids produced during hydrogenation consist in each case of a mixture of acids in which the ethylenic linking is adjacent to the position occupied in the original compound, and that these acids, together with the original position isomeric, are almost certainly present in both *cis*- and *trans*-forms in the hydrogenated products. The proportion of *iso*-acids formed appears to vary with the length of the carbon chain. The present results are in full accord with the view previously expressed by Armstrong and Hilditch (A., 1925, i, 355). L. L. BIRCUMSHAW.

Products of partial hydrogenation of some higher polyethylenic esters. T. P. HILDITCH and N. L. VIDYARTHI (Proc. Roy. Soc., 1929, A, **122**, 563—570; cf. preceding abstract).—In the case of higher polyethylenic esters the conclusions to be reached from the acids isolated as scission products from the oxidised esters are complicated by the facts that (a) the hydrogenation process is selective, not only as regards the degree of unsaturation present, but also to a considerable extent in that each ethylenic linking is not equally attacked, and (b) isomerisation occurs, as previously described (*loc. cit.*), although to a smaller degree. The utility and limitations of the procedure are illustrated by a description of experiments with methyl linoleate (from soya-bean and cotton-seed oil) and ethyl linolenate (from linseed oil). It can be deduced with certainty that the unsaturation in linoleic acid is in the Δ^1 - and Δ^6 -positions, whilst in linolenic acid the positions of the Δ^1 and Δ^6 linkings can be fixed, but it can only be indicated that the third double linking lies beyond the fourteenth carbon atom of the chain. L. L. BIRCUMSHAW.

ω -Hydroxyaliphatic acids; synthesis of sabinic acid. W. H. LYCAN and R. ADAMS (J. Amer. Chem. Soc., 1929, **51**, 625—629).— ω -Hydroxyaliphatic acids are conveniently prepared through their methyl esters, which are formed quantitatively

by hydrogenating ω -aldehydo-esters (cf. A., 1926, 712) in presence of platinum and ferrous sulphate. The following are described: *o*-hydroxynonoic acid, m. p. 53–54° (methyl ester, b. p. 137–139°/3 mm., d_{20}^{20} 0.9588, n_D 1.4438, and its phenylurethane, m. p. 53–54°), which gives at 220–230° a (?) dimeric intermolecular ester, m. p. 64–66°; *i*-hydroxydecoic acid, m. p. 75–76° (methyl ester, b. p. 145–147°/3 mm., d_{20}^{20} 0.9618, n_D 1.4471, and its phenylurethane, m. p. 54–55°); κ -hydroxyundecoic acid, m. p. 65.5–66° (methyl ester, b. p. 156–159°/3 mm., d_{20}^{20} 0.9542, n_D 1.4493, and its phenylurethane, m. p. 64.5–65.5°); λ -hydroxydodecoic acid, m. p. 83–84° (methyl ester, b. p. 164–166°/3 mm., m. p. 34–35°, and its phenylurethane, m. p. 64–65°), which is identical with naturally occurring sabinic acid (Bougault, A., 1909, i, 82; cf. Simonsen and others, A., 1928, 1355), and μ -hydroxytridecoic acid, m. p. 77–78° (methyl ester, b. p. 170–173°, m. p. 40.5–41.5°, and its phenylurethane, m. p. 73.5–74°) (cf. Ruzicka and Stoll, this vol., 68). Methyl hydroxy decane- $\alpha\kappa$ -dicarboxylate, m. p. 51.5–52°, is a by-product in the preparation of methyl κ -aldehydoundecoate (semicarbazone, m. p. 90–92°).
H. E. F. NOTTON.

Hydrogen peroxide as an oxidising agent in acid solution. IX. Oxidation of keto-acids. W. H. HATCHER and A. C. HILL (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 211–220).—The methods of analysis of pyruvic acid are studied and compared. Oxidation by means of alkaline hydrogen peroxide or acid permanganate is preferred. The oxidation of pyruvic and mesoxalic acids by acid permanganate was investigated with special reference to the effect of concentration of mineral acid. The oxidation of these acids with aqueous hydrogen peroxide was also investigated, the effects of temperature, concentration, alkali, and added mineral acid being given. In the case of pyruvic acid, the formation of a complex $\text{CH}_3\text{CO}\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}_2$ is assumed. This breaks down rapidly to give acetic and carbonic acids. With mesoxalic acid there is formed a complex, $\text{CO}(\text{CO}_2\text{H})_2\cdot 2\text{H}_2\text{O}_2$, which decomposes into carbonic acid. Mesoxalic acid is about one fifth as reactive towards hydrogen peroxide as pyruvic acid.

A. J. MEE.

Configurative relationship of β -hydroxy- and β -chlorobutyric acids, and of β -hydroxybutyric acid with methylpropylcarbinol. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, 425–433).—1- Δ^8 -Penten- δ -ol, $[\alpha]_D^{25}$ –6.1° in ether (hydrogen phthalate, $[\alpha]_D^{25}$ –4° in ether; α -naphthylcarbamate, m. p. 47–49°, $[\alpha]_D^{25}$ +1.37° in alcohol), gave with phosphorus pentachloride *d*- δ -chloro- Δ^8 -pentene, b. p. 95–97°, $[\alpha]_D^{25}$ +11.1° in ether; with ozone the latter yielded *d*- β -chlorobutyric acid, b. p. 67–70°/0.35 mm., $[\alpha]_D^{25}$ +11.5° in ether, $[\alpha]_D^{25}$ +21.5° in water (sodium salt, $[\alpha]_D^{25}$ +15.7° in water). When reduced with hydrogen and palladium, 1- Δ^8 -penten- β -ol gave 1-pentan- δ -ol, and when oxidised with ozone it yielded *l*- β -hydroxybutyric acid; the configurative relationship of the two last-mentioned compounds is thus confirmed (cf. A., 1927, 591) and hydroxybutyric acid is configuratively related to *d*- β -chlorobutyric acid.

C. R. HARRINGTON.

Hydrates of calcium oxalate. W. F. JAKÓB and E. ŁUCZAK (Rocz. Chem., 1929, 9, 41–48).— γ -Calcium oxalate, $\text{CaC}_2\text{O}_4\cdot 3\text{H}_2\text{O}$, is precipitated in rhombic plates or prisms on the gradual addition at 0° of 1% ammonium oxalate to 0.007*M*-calcium nitrate or chloride solutions containing 0.061*M*-normal sodium citrate. This modification is unstable at the ordinary temperature, and is rapidly converted into the monohydrate at 40°. The β -oxalate, erroneously supposed by Souhay and Lenfsen (Annalen, 1856, 100, 308) to possess 3 mols. of water of crystallisation, has in reality only 2.25 H_2O . It is prepared by the addition at 40–50° of 1% ammonium oxalate to a 0.024*M*-solution of calcium salt containing normal sodium citrate (0.061*M*). The crystals thus obtained are flattened octahedra, which lose 0.25 H_2O at 80°, but regain this when kept at the ordinary temperature. Above 100° a further molecule of water is irreversibly lost, the stable monohydrate being obtained.

R. TRUSZKOWSKI.

Ferric oxalate and ferric oxalate perchlorate. R. WEINLAND and K. REIN (Z. anorg. Chem., 1929, 178, 219–224).—On keeping a solution of ferric nitrate enneahydrate and oxalic acid in concentrated nitric acid in a desiccator over concentrated sulphuric acid a canary-yellow powder, $\text{Fe}_2(\text{C}_2\text{O}_4)_3\cdot 5\text{H}_2\text{O}$, is obtained. The compound dissolves slowly in water, but the solution gives no reaction for oxalic acid; it therefore appears to be a ferric salt of a ferrioxalic acid. When a solution of ferric chloride and oxalic acid in perchloric acid is evaporated on the water-bath a light green, microcrystalline, hygroscopic compound, $\text{Fe}_3\text{C}_2\text{O}_4(\text{C}_2\text{O}_4\text{H}_2)_2(\text{ClO}_4)_5\cdot 14\text{H}_2\text{O}$, separates. A solution of the compound in water gives reactions for perchloric but not for oxalic acid.

A. R. POWELL.

Mixed oxalato-fluoro- etc. -anions of tervalent chromium, iron, antimony, and bismuth. R. WEINLAND and W. HÜBNER (Z. anorg. Chem., 1929, 178, 275–288).—Evaporation of a solution of chromic nitrate, oxalic acid, and pyridine over sulphuric acid yields dark reddish-violet leaflets of pyridine tri-oxalatotrinitratedichromiate, $[\text{Cr}_2(\text{C}_2\text{O}_4)_3(\text{NO}_3)_3(\text{H}_2\text{O})_3]\text{H}_3(\text{C}_5\text{H}_5\text{N})_4$. Under the same conditions quinoline yields quinoline trioxalatotrinitratedichromiate, $[\text{Cr}_2(\text{C}_2\text{O}_4)_3\text{NO}_3(\text{H}_2\text{O})_4]\text{H}(\text{C}_9\text{H}_7\text{N})_4$. From a solution of chromic acid, oxalic acid, and pyridine hydrofluoride on evaporation minute satin-green crystals of pyridine dioxalatotrifluorodichromiate, $[\text{Cr}_2(\text{C}_2\text{O}_4)_2\text{F}_3]\text{H}(\text{C}_5\text{H}_5\text{N})_2\cdot 7\text{H}_2\text{O}$, are obtained, whereas from a solution of chromic fluoride, oxalic acid, and pyridine pyridine dioxalatopentafluorodichromiate, $[\text{Cr}_2(\text{C}_2\text{O}_4)_2\text{F}_5]\text{H}_3(\text{C}_5\text{H}_5\text{N})\cdot 5\text{H}_2\text{O}$, crystallises as a light green, microcrystalline powder. Addition of pyridine to a solution of ferric hydroxide in hydrofluoric and oxalic acids yields pyridine oxalatodifluorodiaquoferrate, $[\text{Fe}(\text{C}_2\text{O}_4)\text{F}_2(\text{H}_2\text{O})_2]\text{H}(\text{C}_5\text{H}_5\text{N})$, as a white, crystalline powder. Under the same conditions antimony oxide affords pyridine oxalatodifluoroantimoniate, $[\text{Sb}(\text{C}_2\text{O}_4)\text{F}_2]\text{H}(\text{C}_5\text{H}_5\text{N})$, in large, rectangular columns. Antimony and bismuth trichlorides yield with oxalic acid and pyridine large well-defined crystals of the complex compounds $\text{Sb}_4(\text{C}_2\text{O}_4)_5\text{Cl}_{12}\text{H}_{10}(\text{C}_5\text{H}_5\text{N})_8$ and $\text{Bi}_3(\text{C}_2\text{O}_4)_4\text{Cl}_{10}\text{H}_9(\text{C}_5\text{H}_5\text{N})_4\cdot 10\text{H}_2\text{O}$.
A. R. POWELL.

Autoracemisation. R. KUHN and T. WAGNER-JAUREGG (Naturwiss., 1929, 17, 103—104).—The autoracemisation of ethyl bromosuccinate is due to traces of hydrogen bromide which can be eliminated almost completely by repeated distillation in a high vacuum. The pure ester is very stable and the racemisation constants in different solvents do not apply. Not only does hydrobromic acid catalyse the racemisation in aqueous solution, but other bromides act similarly. The efficiency of a given catalyst varies enormously with the solvent, the merest trace of potassium bromide exerting a marked effect in acetone solutions, whereas in methyl alcohol the same effect is obtainable only when the bromide concentration is 0.5—1.0*N*. Animal charcoal, silver and lead bromides, lead oxide, and anhydrous copper sulphate strongly inhibit the racemisation, possibly through adsorption or combination with the catalyst. Chlorides and iodides in general catalyse the racemisation in acetone, but zinc bromide is exceptional in that it strongly inhibits the action of other bromides.

The racemisation of (+)-nitrodiphenic acid in cyclohexanone is much more rapid in glass than in quartz vessels, indicating apparently the catalytic activity of traces of alkali. R. A. MORTON.

Cleavage of ethyl $\alpha\delta$ -dibromoadipate by secondary amines. R. C. FUSON and R. L. BRADLEY (J. Amer. Chem. Soc., 1929, 51, 599—602).—Further evidence for the mechanism previously proposed for this reaction (A., 1928, 738) is afforded by the observation that, contrary to the results of von Braun (A., 1926, 1128; cf. A., 1928, 1115), ethyl *meso*-dibromoadipate yields with di-*n*-propylamine ethyl β -dipropylaminopropionate and with piperidine 75% of the theoretical of ethyl β -piperidinopropionate, b. p. 114—116°/22 mm., d_{20}^{20} 0.927 (methiodide, m. p. 100—102°), and only a little ethyl $\alpha\delta$ -dipiperidinoadipate. H. E. F. NOTTON.

Transformations of propino- $\alpha\gamma$ -dicarboxylic acid. F. MAKULEC, R. MAŁACHOWSKI, and L. MANITIUS (Rocz. Chem., 1928, 8, 576—582).—Methyl glutinate, b. p. 101°/6 mm., is prepared by the action of methyl sulphate on glutinic acid. Glutinic acid reacts with acetic anhydride to form 4-acetyl-4:6-dihydroxypyron; with hydrogen bromide it yields *cis*- β -bromoglutaconic acid, m. p. 140.5°, the anhydride, m. p. 148—149°, of which is prepared by the action of acetic anhydride. Direct bromination of glutinic acid yields *cis*- $\beta\gamma$ -dibromoglutaconic acid, m. p. 132° (anhydride, m. p. 93—96°), and *cis*- $\alpha\beta\gamma$ -tribromoglutaconic acid, m. p. 151°.

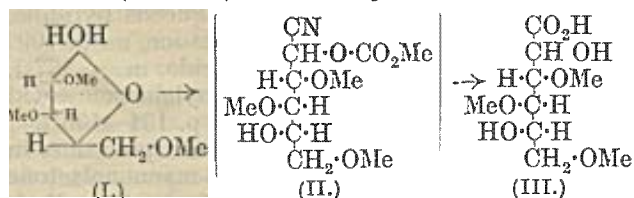
R. TRUSZKOWSKI.

Conjugated unsaturated compounds. VII. Determination of side-chains [methyl groups] in bixin and crocetin. R. KUHN, A. WINTERSTEIN, and L. KARLOVITZ (Helv. Chim. Acta, 1929, 12, 64—71).—The oxidation number (number of atoms of oxygen necessary to oxidise an unsaturated acid to carbon dioxide and any stable acid, such as acetic) has been determined for crotonic and sorbic acids, by oxidation with alkaline potassium permanganate. The best values, 4.91 for crotonic, 9.75 for sorbic (theory 5 and 10, respectively), are obtained by treating the acid with 0.4*N*-permanganate acidified

with phosphoric acid on the water-bath, cooling, making alkaline with 2*N*-sodium carbonate solution, and then heating for 30 min. at 90°. Application of the method to bixin and crocetin gives values of approximately 45 and 33, respectively, which are in agreement with those necessary for $\gamma\gamma\lambda\alpha$ -tetramethyloctadecanonaene- $\alpha\alpha$ -dicarboxylic acid and $\gamma\gamma\lambda$ -trimethyltetradecaheptaene- $\alpha\alpha$ -dicarboxylic acid, respectively (Kuhn and others, Karrer and Salomon, A., 1928, 869). Determination of the acetic acid produced during the oxidation shows that 4 mols. are obtained from bixin and 3 mols. from crocetin, thus affording further confirmation of the above formulæ. The paper also contains an analysis of Rinkes' results (A., 1917, i, 660; 1928, 1377) on the oxidation of methylbixin. H. BURTON.

Ultra-violet spectroscopic investigation of β -ketogluconic acid. P. NIEDERHOFF (Z. physiol. Chem., 1929, 181, 83—87).—The ultra-violet absorption spectrum of β -ketogluconic acid, m. p. 152°, $[\alpha]_D^{20}$ -70°, shows no selective absorption and hence favours the oxy-ring form (Ohle and Borend, A., 1927, 647) rather than the open-chain keto-form which contains two adjacent chromophoric groups. In alkaline solution, however, selective absorption occurs, a maximum at 2750 Å. (ϵ 60.2) being observed, the intensity of which depends on the concentration of the solution, temperature, and the proportion of alkali, and is assumed to be due to the $\beta\gamma$ -dienol form. After a time the alkaline solution becomes yellow, this colour being destroyed by addition of acids and reappearing on shaking. The absorption spectrum of the potassium salt in 0.2*N*-hydrochloric acid does not differ appreciably from that of the free acid in aqueous solution. J. W. BAKER.

Synthesis of 1-2:3:4:6-tetramethyl- δ -gluconolactone and of 1-2:3:4:6-tetramethyl- δ -mannonolactone from 1-2:3:5-trimethylarabofuranose. W. N. HAWORTH and S. PEAT (J.C.S., 1929, 350—357).—An improved method of ascent from pentose to hexose is described; e.g., 2:3:4-trimethylarabopyranose, dissolved in aqueous potassium cyanide, was treated with methyl chloroformate; the product contained both trimethylcarbomethoxymannono- and -glucono-nitriles. Similar treatment of 1-2:3:5-trimethylarabofuranose led to the two lactones (see title) of trimethylhexonic acid (III).



Hydrolysis of the mixture (II) of 1-3:4:6-trimethyl-2-carbomethoxy-glucono- and -mannono-nitriles was effected by the action of ethereal hydrogen chloride and gave 1-2-carbomethoxy-3:4:6-trimethylmannonic acid (III), m. p. 155°, a syrup. Treatment of the latter after removal of the carbomethoxy-residue by digestion with aqueous barium hydroxide and with phenylhydrazine gave a mixture of *phenylhydrazides*, m. p. 111—127°, resolved into the *phenylhydrazide*,

m. p. 137—139°, of trimethylmannonic acid, and the phenylhydrazide, m. p. 125°, of trimethylgluconic acid. Acid hydrolysis of the former phenylhydrazide afforded 1:3:4:6-trimethyl- δ -mannonolactone, m. p. 96—97° (constant), $[\alpha]_D^{20}$ -112.8°, whilst hydrolysis of the latter gave 1:3:4:6-trimethyl- δ -gluconolactone. A fourth methyl group was introduced into this pair of lactones by Purdie's method; the products yielded the phenylhydrazides of 1:2:3:4:6-tetramethyl-mannonic and -gluconic acids, m. p. 183—184°, $[\alpha]_D^{20}$ +22° (in chloroform), and m. p. 115°, $[\alpha]_D^{20}$ -50° (in ethyl alcohol), respectively, identical in all properties except optical rotation with the enantiomorphous compounds. Further, 1:2:3:4:6-tetramethyl- δ -mannonolactone (from the corresponding phenylhydrazide) had $[\alpha]_D^{20}$ -150° (initially) \rightarrow -58° (150 hrs.), whilst a specimen of the d -lactone from d -2:3:4:6-tetramethyl- d -mannose gave $[\alpha]_D^{20}$ +150° \rightarrow +63° (150 hrs.).

The constitution of trimethylarabofuranose, I, having been definitely settled previously, these syntheses confirm the conclusions previously stated in the constitutional studies of γ - and normal sugars inasmuch as it is shown that these stand in relation to one another as five-atom ring compounds to six-atom ring compounds. The furanose type has thus been transformed into the pyranose type by a procedure which admits only of the formation of a six-membered ring. R. J. W. LE FEVRE.

Conversion of tetramethyl- γ - and - δ -gluconolactones into corresponding mannonolactones and of trimethyl- γ - and - δ -xylonolactones into corresponding lyxonolactones. W. N. HAWORTH and C. W. LONG (J.C.S., 1929, 345—350).—Supplementary evidence to that previously adduced for the existence of two types of ring structure among sugars is given together with a correlation of a number of methylated lactones which have already been studied in their relation to the constitution of sugars. Epimerisation was accomplished in all cases by heating with dilute aqueous pyridine. It is suggested that epimerisation might proceed through an enolic lactone intermediate form rather than through an enolic acid (or salt), since the lactone which is less easily hydrolysed by water is found to be the one which predominates in the epimeric mixture.

I. Crystalline 2:3:5:6-tetramethyl- γ -gluconolactone gave, after digestion with aqueous pyridine, 2:3:5:6-tetramethyl- γ -mannonolactone, m. p. 109° (recognised also as the phenylhydrazide, m. p. 167°), together with 2:3:5:6-tetramethylgluconic acid (isolated as the phenylhydrazide, m. p. 134—136°).

II. [With E. H. GOODYEAR.] Similar procedure in the case of 2:3:5:6-tetramethyl- γ -mannonolactone led to a 30% formation of 2:3:5:6-tetramethyl- γ -gluconolactone.

III. 2:3:4:6-Tetramethyl- δ -gluconolactone epimerised to give, after treatment with phenylhydrazine, the phenylhydrazide of 2:3:4:6-tetramethylmannonic acid (90% conversion), m. p. 184—185°, together with the phenylhydrazide of 2:3:4:6-tetramethylgluconic acid, m. p. 115°.

IV. 2:3:4:6-Tetramethyl- δ -mannonolactone yielded the phenylhydrazides of 2:3:4:6-tetra-

methylmannonic and 2:3:4:6-tetramethylgluconic acids (conversion 8%).

V. The conversion of 2:3:4-trimethyl- δ -xylonolactone led abnormally to a 63% yield of furan-carboxylic acid together with the phenylhydrazide of 2:3:4-trimethyl-lyxononic acid (which was not identical with the phenylhydrazide of 2:3:4-trimethyl- δ -xylononic acid, m. p. 137—138.5°).

VI. 2:3:5-Trimethyl- γ -xylonolactone and hot aqueous pyridine led to the phenylhydrazide, m. p. 142°, of 2:3:5-trimethyl- γ -lyxonolactone (conversion 60%). R. J. W. LE FEVRE.

Selenocyanopropionic acid. I. A. FREDGA (J. pr. Chem., 1929, [ii], 121, 56—69).—Potassium selenocyanate reacts smoothly with potassium α -bromopropionate in aqueous solution at the ordinary temperature to give a 50—60% yield of the potassium salt, from which α -selenocyanopropionic acid, m. p. 69—70°, k 2.31×10^{-3} , is obtained (cf. Simon, A., 1905, i, 866). By fractional crystallisation of the strychnine salt is obtained an active acid, $[\alpha]_D^{20}$ +19°, but the acid regenerated from the quinine salt is inactive. Starting with d - α -bromopropionic acid was obtained potassium d -selenocyanopropionate, $[\alpha]_D^{20}$ +65°, which is probably pure. When the inactive acid (which need not be isolated) is heated with concentrated hydrochloric acid at 80—90° it is converted into diselenodi- α -propionic acid (I), which is isolated in two interconvertible forms, m. p. 70.5—72.5° (? meso), and m. p. 107—108° (? racemic). α -Selenocyanopropionic acid is stable in neutral solution, but with concentrated alkalis it is decomposed with separation of selenium, the main product being I. In acid solution it is smoothly decomposed in accordance with the scheme $2RSeCN = RSe-CN + (CN)_2$, $2RSe = RSe-SeR$, $2(CN) = (CN)_2$ ($R = CHMe \cdot CO_2H$). The reaction is followed polarimetrically and with N -hydrochloric acid gives a constant unimolecular velocity coefficient (9.37×10^{-5} min.⁻¹), only the first of the above reactions proceeding with a measurable velocity. β -Selenocyanopropionic acid, m. p. 58°, k 1.40×10^{-4} (potassium salt), is similarly prepared from β -chloropropionic acid. A method for the accurate determination of selenium is described.

J. W. BAKER.

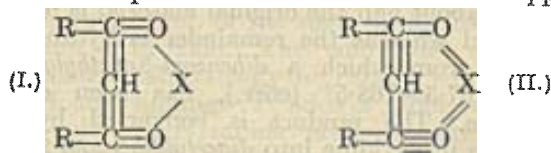
Carbohydrates and polysaccharides. XXI. Tendencies of saturated and unsaturated aldehydes towards acetal formation. H. HIBBERT, E. O. HOUGHTON, and K. A. TAYLOR (J. Amer. Chem. Soc., 1929, 51, 611—614).— Δ^1 -Unsaturated aldehydes show very little tendency to form cyclic acetals with ethylene glycol in presence of a trace of dilute sulphuric or phosphoric acid. Thus, cinnamaldehyde and crotonaldehyde give negligible yields of the corresponding acetals and α -methyl- β -ethylacraldehyde gives 10% of the theoretical yield of impure ethylene α -methyl- β -ethylacrylidene ether, b. p. 170—174°/12 mm. α -Chlorocinnamaldehyde, however, gives 22% of ethylene α -chlorocinnamylidene ether, m. p. 69—70°, and α -chlorocrotonaldehyde, 22% of ethylene α -chlorocrotonylidene ether, b. p. 76—80°/14 mm. $\beta\gamma$ -Dichloro- γ -phenylpropaldehyde gives 37% of ethylene $\beta\gamma$ -dichloro- γ -phenylpropylidene ether, b. p. 164—166°/8 mm., and $\beta\gamma$ -dichlorobutaldehyde,

50% of *ethylene β-dichlorobutylidene ether*, b. p. 100—105°/13—15 mm. H. E. F. NOTTON.

Structure of the higher carbohydrates. M. BERGMANN (Z. physikal. Chem., 1928, 133, 692—694).—The mechanism of the reduction of β-hydroxypropaldehyde and its acetyl derivative in relation to the structure of carbohydrates is discussed.

L. S. THEOBALD.

Parachor and chemical constitution. X. Singlet linkings in chelated co-ordination compounds. S. SUGDEN (J.C.S., 1929, 316—330).—Of the two possible formulæ (I and II) for chelated metallic derivatives of β-diketones I is preferred from a consideration of atomic neutralities. Measurements of the parachors of these substances support



this preference, since in every case the parachor anomaly associated with the presence in a compound of a singlet linking or linkings is found. Surface tensions were determined by the method of maximum bubble pressure. Parachors for six-membered chelate ring compounds were as follows: ethyl thalloacetate, $[P]=332.2$; dimethylthallium benzoylacetate, $[P]=523.7$; beryllium acetylacetate, $[P]=470.4$; beryllium propionylacetate, $[P]=539.0$; aluminium acetylacetate $[P]=680.5$; aluminium propionylacetate, $[P]=788.0$. From the values obtained in the cases of thallos ethoxide, formate, acetate, and nitrate, mercury diphenyl, lead tetraethyl, basic beryllium propionate, and boron acetylacetone difluoride (177.3, 150.3, 183.5, 177.3, 448.7, 456.6, 985.4, and 300.6, respectively) new atomic parachors (viz., thallium, 65.5; mercury, 68.7; lead, 76.2; beryllium, 38; aluminium, 39) have been extracted. Metallic mercury had $[P]=69.4$. In the cases of beryllium and aluminium duplet formulation of chelate derivatives leads to an inadmissible negative parachor. The formula $Al^{III}[AlBr_6]^{III}$ is excluded for aluminium bromide; the figure found, 457.6, agrees better with $Br_6 \triangleright Al < Br_6 \triangleright Al < Br_6$ (III). The following substances are evidently open-chain and not chelate rings: acetylacetone, $[P]=245.4$; propionylacetone, $[P]=279.7$; benzoylacetone, $[P]=382.4$; and stannic bisacetylacetone dichloride, $(C_5H_7O_2)_2SnCl_2$, $[P]=617.2$.

R. J. W. LE FÈVRE.

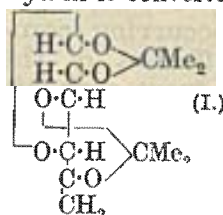
Degradation of *l*-arabinose. V. DEULOFEU and R. J. SELVA (J.C.S., 1929, 225—227).—Tetra-acetyl-arabonitrile, m. p. 119—120°, by treatment with a solution of sodium in methyl alcohol, gives a syrup containing erythrose and inorganic salts. A purer, nearly ashless, and dextrorotatory product is obtained by the action of barium hydroxide and silver carbonate on arabonitrile. Oxidation of the syrup isolated in the former experiment leads to a mixture of calcium oxalate and mesotartrate.

R. J. W. LE FÈVRE.

Acetone [isopropylidene] sugars. XVI. *l*-Altromethylose, chinovose, and digitoxose.

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System of the methylpentoses K. FREUDENBERG and K. RASCHIG (Ber., 1929, 62, [B], 373—383; cf. A., 1927, 858).—Diisopropylidenegalactose-ξ-iodohydrin is converted by sodium methoxide in methyl



alcohol at 125—130° into the unsaturated compound (I), b. p. 133°/15 mm., m. p. 86°, $[\alpha]_D^{20} -128^\circ$ in *s*-tetrachloroethane, which is hydrogenated in presence of spongy platinum to a mixture of diisopropylidene-methylpentoses, b. p. 128°/13 mm., $[\alpha]_D^{20} -60.6$ in substance, from which *d*-fucose is isolated after hydrolysis. The separation of the mixed methylpentoses is best effected by removal of the greater part of the *d*-fucose as the sparingly soluble *p*-toluenesulphonylhydrazide, m. p. 175°, $[\alpha]_D^{20} +17.1^\circ$ in pyridine (*l*-fucose-*p*-toluenesulphonylhydrazide, m. p. 174°, $[\alpha]_D^{20} -17.0^\circ$ in pyridine, is described), after which *l*-altromethylose is isolated as the *p*-bromophenylhydrazide, m. p. 178° (converted in boiling amyl alcohol into an isomeride, m. p. 155°). The new sugar is levorotatory, but has not been obtained crystalline. It gives a phenylosazone, m. p. 185°, $[\alpha]_D^{20}$ about $+75^\circ$ in pyridine-alcohol (2 : 3 vols.), a *p*-bromophenylosazone, m. p. 203°, and a freely-soluble phenylhydrazide, m. p. 132°, $[\alpha]_D^{20}$ about -1° in pyridine.

Chinovose, the sugar component of α- and β-chinovin, has been considered identical with allo- or altro-methylose, but this view is irreconcilable with the m. p. of the respective phenylosazones. β-Chinovin has therefore been converted into "ethyl-chinovoside," b. p. 136°/1 mm., $[\alpha]_D^{20} +106^\circ$ in alcohol, which on hydrolysis is found to give exclusively *d*-epirhamnose, identified by mixed m. p. and mutarotation as osazone and *p*-bromophenylosazone. The name "chinovose" should therefore be deleted from the literature.

Windaus and Schwarte (Nachr. Ges. Wiss. Göttingen, 1926) have obtained from the anhydride of digitoxose a methylpentose to which they assign the structure of *l*-altromethylose. The crystalline sugar does not induce solidification in the syrupy *l*-altromethylose and the compounds differ in optical activity. The *p*-bromophenylosazones are closely similar to one another in m. p. (and mixed m. p.), but their specific rotations are of opposite sign. The sugar cannot therefore be either *l*-altro- or *l*-allo-methylose and the configuration of digitoxose is rendered quite uncertain.

For the systematic nomenclature of the methylpentoses, it is proposed to follow Votocek's plan of suffixing the term "methylose" to the root syllable of the corresponding hexose, thus "manno-methylose," whilst retaining the terms "rhamnose, fucose, epirhamnose, epifucose." The expression "isorhamnose" should be abandoned in favour of epirhamnose. The name "rhodose" for the autipode of natural *l*-fucose is superfluous, as are all names dependent on it.

Three of the natural methylpentoses may be derived by disproportionation in the plant of two natural hexitols: sorbitol (*d*-epirhamnose) and dulcitol (*d*-fucose and *l*-fucose). For natural *l*-rhamnose an

explanation from natural mannitol is insufficient. A common explanation for the conversion of dextrose into the methylpentoses may be found in the fission of inositol and, possibly, quercitol. H. WREN.

Photosynthesis of naturally occurring compounds. IV. Temperature coefficient of the photosynthesis of carbohydrates from carbonic acid. E. C. C. BALY and N. R. HOOD.—See this vol., 408.

Acetylation of carbohydrates with acetic anhydride and alkali thiocyanates. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1929, 4, 21–23).—Starch is readily acetylated by acetic anhydride in presence of lithium, sodium, or calcium thiocyanate, and lithium or sodium iodide, but the product differs from that previously described (this vol., 175) since it disperses only slowly in organic media, forming highly viscous solutions. Hydrolysis of the acetyl derivative regenerates a product similar to the original starch. Acetylation of dextrose and galactose with acetic anhydride and dry sodium thiocyanate yields β -penta-acetylglucose, $[\alpha]_D^{25} +4.4^\circ$ in acetic acid, and β -penta-acetylgalactose, $[\alpha]_D^{25} +25.5^\circ$ in chloroform, respectively. Similar results are obtained using potassium thiocyanate.

H. BURTON.

Influence of hydrogen sulphite solutions on sugars at higher temperatures. E. HÄGGLUND (Ber., 1929, 62, [B], 437–440; cf. this vol., 297).—The possibility that dextrose is converted by sodium hydrogen sulphite solutions into non- or fully-reducing polymeric sugars is excluded, since the solutions when heated with hydrochloric acid directly or after fermentation do not exhibit an increase in reducing power. The presence of sorbitol in the solutions could not be established, but *d*-gluconic acid is produced. The hydrogen sulphite ion thus oxidises the sugar to the aldonic acid, whereby the thiosulphate ion is produced. The rate of reaction therefore increases with the concentration of hydrogen sulphite ion and sugar as previously established (*loc. cit.*).

H. WREN.

Quantitative determination of acetone groups. A. GRÜN (Ber., 1929, 62, [B], 473–474).—The application of the method described by Elsner (this vol., 50) to isopropylidene sugars has been indicated previously by the author (Grün and Limpächer, A., 1926, 632).

H. WREN.

Constitution of *l*-glucosan [β -glucosan]. K. JOSEPHSON (Ber., 1929, 62, [B], 313–316; cf. Pictet, A., 1920, i, 819; Irvine and Oldham, J.C.S., 1921, 119, 1744; Karrer and Smirnov, A., 1921, i, 766).—6-Triphenylmethyl- β -methylglucoside, m. p. about 105–110°, or, after solidification, m. p. about 148° (corr.) (cf. Helferich, A., 1924, i, 500), is converted by benzoyl chloride in cold pyridine into 2:3:4-tribenzoyl-6-triphenylmethyl- β -methylglucoside (+1MeOH), m. p. 99–101°. The product is very rapidly transformed by hydrogen bromide in glacial acetic acid in the presence of chloroform at 0° into 2:3:4-tribenzoyl- β -methylglucoside, transformed by acetic anhydride in pyridine at the atmospheric temperature into 6-acetyl-2:3:4-tribenzoyl- β -

methylglucoside, m. p. 150° (corr.), $[\alpha]_D^{20}$ yellow -6.9° in chloroform, identical with the product obtained by Bergmann and Koch (see below) from β -glucosan. Provided that an unknown change in the position of groups does not occur when β -glucosan is used as initial material, the presence of a 1:6-oxygen bridge is confirmed. H. WREN.

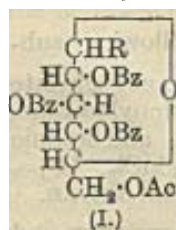
Acyl derivatives of glucose and β -methylglucoside from *l*-glucosan [β -glucosan]. K. JOSEPHSON (Ber., 1929, 62, [B], 317–321; cf. preceding abstract).—Attempts to remove only the 6-acyl group of 6-acetyl-2:3:4-tribenzoyl- β -methylglucoside (cf. Bergmann and Koch, following abstract) by means of 1 mol. or a slight excess of alkali show that the process cannot be carried out in this sense but that about half the original material is recovered unchanged whereas the remainder is hydrolysed to products from which a *dibenzoyl*- β -methylglucoside, m. p. 167.5–168.5° (corr.), has been obtained crystalline. The product is converted by acetic anhydride in pyridine into *diacetyldibenzoyl*- β -methylglucoside, m. p. 166°, and by benzoyl chloride in pyridine into *tetrabenzoyl*- β -methylglucoside, m. p. 160–161° (cf. Fischer and Helferich, A., 1911, i, 802). Tribenzoyl- β -glucosan is converted by successive treatment with hydrogen bromide in glacial acetic acid and silver benzoate into 6-acetyl-1:2:3:4-tetrabenzoylglucose, m. p. 183–184° (corr.), hydrolysed by mild treatment with aqueous sulphuric acid in the presence of acetone to a substance regarded as 2:3:4-tribenzoylglucose, m. p. 189–191° (corr.), on the assumption that acyl migration has not taken place during the change. It is converted by acetic anhydride and pyridine into *diacetyltribenzoylglucose*, m. p. 178–183° after softening at about 167°, which does not appear uniform.

H. WREN.

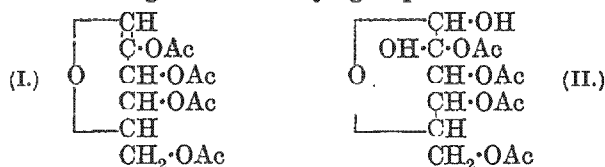
Preparation of mixed acetylated sugars. M. BERGMANN and F. K. V. KOCH (Ber., 1929, 62, [B], 311–313; cf. Ohle and Spencker, A., 1926, 1126).—Tribenzoyl- β -glucosan, m. p. 201–202° (corr.), dissolved in chloroform, is converted by a saturated solution of hydrogen bromide in glacial acetic acid into acetyltribenzoylglucose bromohydrin (I; R=Br), converted by methyl alcohol and silver carbonate into 6-acetyl-2:3:4-tribenzoyl- β -methylglucoside (I; R=OMe), m. p. 150–151° (corr.), $[\alpha]_D^{25} -5.15^\circ$ in *s*-tetrachloroethane, $[\alpha]_D^{25} -6.5^\circ$ in chloroform. With silver acetate the bromohydrin affords 1:6-diacetyl-2:3:4-tribenzoylglucose (I; R=OAc), m. p. 172–173° (corr.), $[\alpha]_D^{25} +24.75^\circ$ in *s*-tetrachloroethane.

H. WREN.

New, unsaturated anhydro-sugars. II. K. MAURER (Ber., 1929, 62, [B], 332–338; cf. A., 1927, 751).—The action of diethylamine on acetobromoglucose in the presence of benzene under somewhat modified conditions affords *tetra-acetylglucoseen* (I), m. p. 65–66°, $[\alpha]_D^{25} -20.71^\circ$ in ethyl alcohol, in 51% yield (for nomenclature cf. Helferich and Himmen, A., 1928, 1221). The constitution of the compound is established by its conversion into glucosazone by the restricted action of phenylhydrazine in boiling



50% acetic acid (whereby the loosening effect of the double linking on the acetyl groups is remarkable)



and by its oxidation by potassium permanganate to *potassium triacetyl-arabonate*, m. p. 214–215°, hydrolysed to potassium *d*-arabonate, which yields the phenylhydrazide of *d*-arabonic acid, m. p. 214°. The products obtained by hydrolysis of the tetra-acetyl-anhydro-sugar with methyl-alcoholic ammonia and sodium methoxide contain, respectively, nitrogen and sodium; 1 mol. of the sugar neutralises 5 mols. of sodium hydroxide. The compound cannot be hydrogenated catalytically or caused to add water at the double linking. It adds 2 atoms of halogen without giving crystalline products, since halogen hydride is subsequently eliminated. Successive treatment of the compound in anhydrous ether with chlorine until the colour of the gas just persists followed by silver carbonate and water gives a partly acetylated hydrate (II), m. p. 116–118°, $[\alpha]_D^{25} +14.2^\circ$ to $+54.45^\circ$ in 5 days in water, and a strongly halogenated syrup which retains chlorine very firmly. The hydrate reduces cold Fehling's solution and decolorises permanganate, but not bromine water. It does not react with phenylhydrazine in acetic acid, but, after pre-treatment with alkali, it affords glucosazone. Acetylation of the hydrate gives a crystalline substance of unknown constitution in the production of which acetyl groups are removed. Protracted chlorination of the anhydro-sugar gives a crystalline product apparently containing 3 atoms of halogen per sugar complex; these are so firmly retained that their removal or exchange with the usual reagents has not been found possible. If the tetra-acetyl-anhydro-sugar is warmed with aqueous sodium pyrophosphate solution, the amount of inorganic phosphate remaining in the solution diminishes with increasing amount of the sugar. Dextrose and tetra-acetylglucose do not produce this effect. H. WREN.

Preparation of α - and β -methylglucoside. T. S. PATTERSON and J. ROBERTSON (J.C.S., 1929, 300–302).—When a solution of pure anhydrous dextrose in twice its weight of dry methyl alcohol containing 3% of hydrogen chloride is boiled for 4–5 hrs. or longer at the ordinary pressure, α - (42.6%) and β -methylglucoside (2.5%) are obtained. If, after removal of α -methylglucoside, boiling be continued with further addition of hydrogen chloride, α -methylglucoside is produced at the expense of β -methylglucoside; a total yield of 75% may be obtained.

R. J. W. LE FÈVRE.

Structure of β -(para)glucochloralose. H. W. COLES, L. D. GOODHUE, and R. M. HIXON (J. Amer. Chem. Soc., 1929, 51, 519–524).—The constitution of this compound is discussed, a formula of the cyclic acetal type being preferred to those proposed by Pictet and Reichel (A., 1923, i, 755) and by Hanriot and Kling (A., 1913, i, 593). Its conversion into two dichloralglucoses and its reduction and subsequent

hydrolysis to dextrose and dichloroacetaldehyde are confirmed. With methyl sulphate and solid sodium hydroxide at 60° it yields *trimethylparachloralose*, m. p. 109–110° (optically inactive), which cannot be further methylated, but yields a monoacetyl derivative (to be described later) and reacts with magnesium methyl iodide. *Chloral- γ - ζ -trimethylglucose*, m. p. 120°, –29.01° in chloroform, from γ - ζ -trimethylglucose and chloral, does not contain an active hydrogen atom. Trimethylparachloralose is reduced by aluminium amalgam to *dichloroacetaldehydetrimethylglucose*, m. p. 68°, which yields dichloroacetaldehyde when hydrolysed with *N*-hydrochloric acid, and by sodium amalgam and water to *chloroacetaldehydetrimethylglucose*, b. p. 155–160°/4 mm., which, like the preceding compound, requires such concentrated acid for its hydrolysis that the methylated sugar obtained is rendered unidentifiable. H. E. F. NOTTON.

Carbohydrates. VI. Derivatives of 1-amino-glucose. P. BRIGL and H. KEPPLER (Z. physiol. Chem., 1929, 180, 38–63).—Acetylation of 1-amino-glucose (Ling and Nanji, J.C.S., 1922, 121, 1682) with pyridine and acetic anhydride yields a mixture of *penta-acetyl-1-aminoglucose*, m. p. 159–160° (decomp.), $[\alpha] +16^\circ$ (converted by the action of methyl-alcoholic ammonia at the ordinary temperature into α -*N*-acetylglucosidylamine, decomp. 257°, $[\alpha] -23.0^\circ$), and *octa-acetyl- α -diglucosidylamine*, m. p. 216–217° (decomp.), $[\alpha] +87^\circ$ (also obtained by acetylation, without isolation, of α -diglucosidylamine, which is obtained by the action of anhydrous dextrose on 1-aminoglucose in pyridine at 75–80°). Deacetylation of the latter product with methyl-alcoholic ammonia yields α -*diglucosidylamine*, decomp. 167–168°, initial $[\alpha] +85.1^\circ$, not identical with the compound obtained by Sjollem (A., 1899, i, 732), the latter being β -*diglucosidylamine*, decomp. 122–123° (*loc. cit.*, m. p. 132–134°), initial $[\alpha] -20^\circ$, which by acetylation yields β -*octa-acetyldiglucosidylamine*, sintering at 135–140°, clearing at 190–192°, partial conversion into the α -form taking place, $[\alpha] +7.6^\circ$. Under appropriate experimental conditions either the α - or β -octa-acetate can be obtained from both forms of the parent amine (which exhibits mutarotation) and they exhibit mutarotation, especially in the presence of acids (equilibrium 66% α -octa-acetate). Acetylation of either the α - or β -octa-acetate or of penta-acetyl-1-aminoglucose with acetic anhydride and zinc chloride yields *N*-acetylocta-acetyldiglucosidylamine, m. p. 192°, $[\alpha] -9.2^\circ$. By the action of nitrous gases on an ethereal solution of the α -octa-acetate is obtained the *nitrosoamine*, m. p. 204–205° (decomp.), $[\alpha] +80.4^\circ$, which is reconverted into its parent by hot alcohol, and by hydrolysis with methyl-alcoholic ammonia at the ordinary temperature yields α -*diglucosidylnitrosoamine*, which could not be obtained crystalline but was reacylated to the octa-acetylnitrosoamine, or converted by the Schotten-Baumann reaction into α -*octabenzoyldiglucosidyl-nitrosoamine*, m. p. 202–203° (decomp.), $[\alpha] +81.1^\circ$. By heating with acetic anhydride and zinc chloride this yields 1-acetyl-2:3:4:6-*tetrabenzoylglucose*, m. p. 159–160°, $[\alpha] +78.9^\circ$, whilst the corresponding octa-acetyl derivative yields penta-acetylglucose.

The corresponding β -octa-acetyldigluco-sidyl-nitroso-amine, m. p. 218–220° (decomp.), $[\alpha] +12.5^\circ$, is obtained similarly from the β -octa-acetate, or by the action of sodium nitrite on an acetic acid solution of the α -octa-acetate, which is partly converted into the β -form during the reaction. The supposed heptabenzoyl derivative of 1-aminoglucose, m. p. 91°, obtained by Schmuck (A., 1923, i, 1062) is shown to be a mixture from which a substance, m. p. 180–182°, $[\alpha] +16.7^\circ$, not a heptabenzoyl, can be isolated.

J. W. BAKER.

Constitution of nodakenin, a new glucoside from *Peucedanum decursivum*, Maxim. I. J. ARIMA (Bull. Chem. Soc. Japan, 1929, 4, 16–20).—Mainly an account of work already reviewed (A., 1927, 599). The following appears to be new. Nitration of nodakenin (*loc. cit.*) with warm nitric acid (*d* 1.2) gives a nitro-derivative, m. p. 206–207°, whilst fusion with potassium hydroxide and a small amount of water at 190–200° affords resorcinol, acetic acid, and a phenolic substance, $C_8H_8O_4$, m. p. 258–260°. When nodakenin is heated with aqueous-alcoholic potassium hydroxide isonodakenetic acid, $C_{14}H_{16}O_5$, m. p. 205–206° (decomp.) (silver salt), is obtained. This is methylated by diazomethane, forming dimethylisonodakenetic acid, m. p. 65–67°. It is concluded that nodakenin contains a $\cdot O \cdot C_6H_4 \cdot O \cdot CO \cdot$ (1 : 3) grouping.

H. BURTON.

Constitution of carthamin. I. (Miss) C. KURODA (Proc. Imp. Acad. Tokyo, 1929, 5, 32–33; cf. J.C.S., 1910, 97, 1415).—When crude carthamin is treated with cold dilute hydrochloric acid, dried, and crystallised from dilute methyl alcohol, isocarthamin, $C_{21}H_{20}O_{10}$, is obtained as the dihydrate, yellow needles, m. p. 228°, losing $1H_2O$ at 60° in a vacuum and $2H_2O$ at 100° in a vacuum. It is unstable and when exposed to air passes into a red, amorphous powder. isocarthamin is isomeric with, and is converted into, carthamin (red needles) when treated with pyridine; carthamin and isocarthamin are glucosides; hydrolysis with dilute mineral acid yields 1 mol. of dextrose.

C. W. SHOPPEE.

Lignin and cellulose. IX. Cellulose. K. FREUDENBERG (Ber., 1929, 62, [B], 383–386; cf. A., 1928, 1227).—The synthesis of trimethylglucose anhydride (Freudenberg and Braun, A., 1928, 399) is disproof of the hypothesis of Hess that cellulose is composed of monomeric glucose anhydride units, since the compound should be identical with the trimethylcellulose of his conception, whereas it shows completely different properties. It is considered that cellulose can be represented by a formula based on cellobiose linkings and that the usual doctrine of valency is adequate. Hess' more recent conception of cellobiosan as unit of cellulose (cf. A., 1928, 1225) is based mainly on the isolation of a biosan hexaacetate by the cautious acetolysis of cellulose. Preparations which have been precipitated with methyl alcohol give analytical values generally according with those required by a biosan hexa-acetate. After dissolution in acetone, precipitation with water, and careful desiccation, the percentage of acetyl is uniformly greater (45.8 instead of 44.8%) than that expected. The product is therefore not a biosan but

a polysaccharide with a mean chain length of 10–16 members. This view is confirmed by its reducing power towards Fehling's solution if the comparative reducing powers of cellobiose and dextrose are used as bases of comparison. The biosan cannot be regarded as the unit of cellulose and, contrary to Hess (*loc. cit.*), the yield of cellobiose is thoroughly significant in judging the constitution of cellulose.

Lignin, like cellulose, is built of main valency chains.

H. WREN.

Allylcelluloses. I. SAKURADA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 114–117).—By the action of allyl bromide on cotton cellulose suspended in 40–50% sodium hydroxide, di- and tri-allylcelluloses were prepared. The addition of bromine showed that the double linking remained intact. Diallylcellulose tetrabromide was obtained practically pure. Highly alkylated products were partly soluble in organic solvents. The purified ether was unchanged when heated at 210°.

R. K. CALLOW.

Celluloseglycollic acid. I. SAKURADA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 96–102).—It was found that celluloseglycollic acid was best prepared by soaking cellulose in 20% sodium hydroxide solution and then treating with concentrated cold sodium monochloroacetate solution. In this way a sodium salt was obtained which was soluble in water but precipitated by alcohol or acetone. Mineral acids precipitated the free acid in a finely-divided form which was flocculated by alcohol. The analysis of the products by electrometric and conductometric titration, titration of the acid with sodium hydroxide, and determination of ash indicated that no more than one glycollic acid residue per $C_6H_{10}O_5$ unit could be introduced. The celluloseglycollic acid was not hydrolysed by heating with acid or alkali. Barium, zinc, silver, and copper salts were prepared. The acid was readily dyed by basic dyes. The sodium salt was miscible with viscose.

R. K. CALLOW.

Cellulosexanthoacetic acid. T. NAKASHIMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 103–108; cf. Lilienfeld, B., 1925, 913).—When viscose, after purification by treatment with acetic acid, was treated with sodium chloroacetate, sodium cellulosexanthoacetate separated slowly as a jelly and was precipitated by alcohol or salt solution. Addition of dilute sulphuric acid to the aqueous solution precipitated cellulosexanthoacetic acid, which was stable at 105°, but decomposed slowly in alkaline solution. In contrast to cellulose xanthate, brief boiling with dilute sulphuric acid caused no decomposition. Analysis of the products obtained by the action of varying amounts of sodium chloroacetate was based on the determination of sulphur in the portions decomposable and non-decomposable in this way, total sulphur, and sodium, and the proportion of xanthoacetic acid formed was found to increase with the amount of sodium chloroacetate used. A product the composition of which approximated to $C_{12}H_{19}O_9 \cdot O \cdot CS \cdot S \cdot CH_2 \cdot CO_2Na$ was obtained when 2 mols. of chloroacetate were used.

R. K. CALLOW.

Cellulosexanthamides [thiourethanes]. T. NAKASHIMA (Bull. Inst. Phys. Chem. Res. Tokyo,

1929, 8, 109—113; cf. Lilienfeld, B., 1925, 913, 955, 985).—The reaction of ammonia or primary or secondary amines with solutions of sodium cellulose-xanthoacetate (cf. preceding abstract) slowly yielded gelatinous products the composition of which approximated to $C_{12}H_{19}O_9 \cdot O \cdot CS \cdot NRR'$. Cellulosethio-urethane was insoluble in water or the usual solvents. It dissolved in alkali hydroxide solution to give a viscous solution which decomposed slowly, regenerating cellulose. It was stable to dilute mineral acids and was unchanged by heating at 105° (cf. this vol., 300).
R. K. CALLOW.

Primary amines from Grignard reagents and chloroamine. H. G. H. COLEMAN and C. B. YAGER (J. Amer. Chem. Soc., 1929, 51, 567—569).—The yields of primary amines and ammonia obtained as previously described (A., 1928, 622) from chloroamine and a slight excess of the Grignard reagents from isopropyl, sec.-butyl, diethylmethyl, tert.-butyl, and tert.-amyl chlorides, bromides, and iodides are tabulated. They are similar to those obtained with primary alkyl halides. Benz-tert.-amylamide has m. p. 93—94°.
H. E. F. NOTTON.

Complex-chemical behaviour of lithium. I. System lithium halide-mono-, di-, and tri-methylamine. A. SIMON and R. GLAUNER (Z. anorg. Chem., 1929, 178, 177—201).—Lithium halides, dehydrated at 170° in a vacuum and loosened by treatment with liquid ammonia at -80° followed by removal of the ammonia in a vacuum, react with mono-, di-, and tri-methylamine to form series of additive compounds. Thermal analysis of the various systems shows the existence of the following compounds (decomposition temperature in parentheses): lithium chloride with 1 (16°), 2 (0°), 3 (-19°), and 4 (-47°) mols. of monomethylamine, 1 (3°), 2 (-15°), and 3 (-36°) mols. of dimethylamine and 1 (-15°) and 2 (-41°) mols. of trimethylamine; lithium bromide with 1 (63°), 2 (35°), 3 (28°), 4 (-32°), and 5 (-57°) mols. of monomethylamine, 0.5 (59°), 1 (44°), 2 (30°), 3 (-18°), 4 (-30°), and 5 (-57°) of dimethylamine, and 1 (23°) and 2 (-15°) mols. of trimethylamine; lithium iodide with 0.25 (200°), 0.5 (180°), 1 (100°), 2 (40°), 3 (-3°), and 3.5 (-55°) mols. of monomethylamine, 0.5 (140°), 1 (90°), 1.5 (51°), 2 (20°), 3 (5°), and 5 (-72°) of dimethylamine and 1 (67°), 1.5 (30°), and 2 (-16°) of trimethylamine. The valency isobars and thermochemistry of the various systems are discussed.
A. R. POWELL.

Catalytic racemisation of amino-acids and peptides. M. BERGMANN and L. ZERVAS (Biochem. Z., 1928, 203, 280—292).—When optically active amino-acids are treated in an anhydrous medium (acetic acid) with 1 mol. of acetic anhydride, an almost quantitative yield of an optically active mono-acetyl derivative is obtained, whereas with a small excess of anhydride the acetyl derivative is completely racemised, the anhydride acting catalytically, and with a large excess of anhydride it is also dehydrated, yielding an azlactone. Monoacetyl-*D*-arginine may be heated at 100° in acetic acid solution for an hour without decrease of rotation, but if a little acetic anhydride is added to the cold solution, complete racemisation rapidly occurs. The derivatives of *L*-tyros-

ine, *D*-glutamic acid, and *L*-histidine behave similarly. Racemisation is similarly obtained if the acetyl group is replaced by the benzoyl group. If, however, the acetyl derivative is esterified, the anhydride is no longer able to racemise. Diketopiperazine compounds of optically active amino-acids also are not racemised by acetic anhydride. *D*-isoValine is not racemised. Glycyl-*L*-leucine and *D*-phenylalanyl-*L*-tyrosine are readily racemised. A slower racemisation occurs when benzoic anhydride replaces acetic anhydride.
P. W. CLUTTERBUCK.

Separation of hexone bases by electrolysis. T. NOGUCHI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 152—155).—By electrolysis in a three-compartment cell with suitable membranes under certain conditions (cf. Bull. Agric. Chem. Soc. Japan, 1926, 2, 60), arginine, lysine, and histidine were isolated in the cathode compartment from the hydrolytic products of casein and ox-blood without the adjustment of the reaction of the centre compartment found necessary by Foster and Schmidt (A., 1923, i, 963).
R. K. CALLOW.

Ultra-violet absorption spectra of certain aromatic amino-acids, and of the serum-proteins. F. C. SMITH (Proc. Roy. Soc., 1929, B, 104, 198—205).—Spectrophotometric examination of the ultra-violet absorption of tyrosine shows the presence of new bands at $\lambda\lambda$ 2240.0 and 1940 Å. as well as the known one at λ 2750.0 Å. In the case of tryptophan the known bands at $\lambda\lambda$ 2790.0 and 2180.0 Å. were observed, whilst in the case of phenylalanine only a single simple absorption band was detected. The absorption of highly-purified serum-globulin and serum-albumin from horse and human sera has also been examined without disclosing any differences.
W. O. KERMAK.

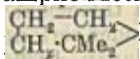
Synthesis of [calcium] cyanamide by combination of carbon and calcium nitride. KADLEC-FLECK (Compt. rend., 1929, 188, 561—563).—When 1 part of calcium cyanide finely powdered and well mixed with 5 parts of Acheson graphite was heated in soft steel tubes at 800—1100° the amount of nitrogen transformed according to the equation $Ca_3N_2 + 5C = CaCN_2 + 2CaC_2$ was found to increase from 33 to 91% with rise in temperature for a heating period of 3 hrs. Above 1000° small amounts of calcium cyanide were formed.
J. GRANT.

Mechanism of the reaction between organo-magnesium compounds and NN-disubstituted crotonamides. N. MAXIM (Bul. Soc. Chim. Romania, 1928, 10, 97—115).—Crotondiethylamide, b. p. 113°/23 mm., 224—225°/756 mm., is obtained in 95% yield by treatment of crotonyl chloride, b. p. 124—125°, with diethylamine in benzene. With magnesium ethyl bromide it yields quantitatively β -methylvalerdiethylamide, b. p. 123°/28 mm., 224°/760 mm.; with magnesium phenyl bromide are formed diphenyl and β -phenylbutyrdiethylamide, b. p. 184°/23 mm., also obtained from β -phenylbutyryl chloride and diethylamine. Neither amide could be hydrolysed to the corresponding acid. Crotondiphenylamide, m. p. 113—114°, prepared from crotonyl chloride and diphenylamine, when treated with magnesium ethyl bromide yields exclusively β -methylvalerdiphenylamide,

m. p. 55—56°, b. p. 270—280°/78 mm., hydrolysed by alcoholic potassium hydroxide to β -methylvaleric acid. With magnesium phenyl bromide the diphenylamide gives quantitatively β -phenylbutyrdiphenylamide, m. p. 76°, b. p. 267°/18 mm., also obtained from diphenylamine and β -phenylbutyryl chloride; hydrolysis with alcoholic potassium hydroxide regenerates β -phenylbutyric acid. These results are considered to exemplify 1:4-addition in agreement with the Thiele theory.

C. W. SHOPPEE.

Imide and amide chlorides of non-aromatic acids. III. J. VON BRAUN and A. HEYMONS (Ber., 1929, 62, [B], 409—413; cf. A., 1927, 231, 547).—Campholmethyylimide chloride,



$\text{Me}\cdot\text{CCl}\cdot\text{NMe}$, is converted by distillation under atmospheric pressure into campholonitrile, m. p. 70°; a similar behaviour is shown by the corresponding *ethylimide chloride* (obtained from *campholethylamide*, b. p. 160°/20 mm., m. p. 88°) and *isoamylimide chloride* (derived from *campholisoamylamide*, b. p. about 150°/1 mm., m. p. 42—43°). The gradual transition in behaviour by transition from the non-aromatic to the aromatic series is thus established.

Somewhat unexpectedly, *trichloroacetdiethylamide*, b. p. 108—112°/12 mm., and *campholdiethylamide*, b. p. 140—145°/12 mm., m. p. 29—30°, are unaffected by phosphorus pentachloride in the presence of benzene or chloroform. *Chloroacetdiethylamide*, b. p. 112—113°/10 mm., with phosphorus pentachloride gives products which decompose when distilled. *n-Butyrdiethylamide*, b. p. 92°/12 mm., is transformed when similarly treated into the amidochloride, which loses hydrogen chloride when distilled, yielding the compound (?) $\text{CHEt}\cdot\text{CCl}\cdot\text{NEt}_2$, b. p. 100—107°/13 mm. α -Methylbutyrdiethylamide, b. p. 84—86°/11 mm., is converted by the action of phosphorus pentachloride followed by distillation of the product into a mixture of the compound $\text{CMeEt}\cdot\text{CCl}\cdot\text{NEt}_2$, b. p. 76—85°/13 mm. (slowly decomposed by water), and α -methylbutyrdiethylamide chloride, instantaneously hydrolysed by water to the original amide and transformed by aniline in chloroform into the *amidine*, $\text{CHMeEt}\cdot\text{C}(\text{NPh})\cdot\text{NEt}_2$ (non-crystalline *picrate* and *hydrochloride*; *chloroplatinate*, decomp. 124—127°).

Aliphatic and fatty-aromatic imide chlorides (or bromides), in the form arising by displacement of hydrogen, add chlorine or bromine: $\text{R}\cdot\text{CH}\cdot\text{CCl}\cdot\text{NR}' \rightarrow \text{R}\cdot\text{CH}\cdot\text{CCl}\cdot\text{NHR}' \rightarrow \text{R}\cdot\text{CHBr}\cdot\text{CCl}(\text{Br})\cdot\text{NHR}' \rightarrow \text{R}\cdot\text{CHBr}\cdot\text{CCl}\cdot\text{NR}'(+\text{R}\cdot\text{CHBr}\cdot\text{CBr}\cdot\text{NR}') + \text{HBr}(+\text{HCl})$. Iodine does not behave similarly, so that α -iodo-acids cannot be prepared in this manner. If the acid residue contains an unsaturated linking, this can also be saturated; by using a suitable proportion of phosphorus pentachloride it is possible to achieve the production of the imide chloride, the exhaustive chlorination of the α -carbon atom, and the addition of chlorine to the double linking in a single operation. Thus Δ -undecenoethylamide, $\text{CH}_2\cdot\text{CH}(\text{CH}_2)_8\cdot\text{CO}\cdot\text{NHEt}$, m. p. 35°, is transformed by 5.2 mols. of phosphorus pentachloride and subsequent treatment with water into α,α,α -trichloro-undecenoethylamide, b. p. about 180°/0.2 mm.

H. WREN.

Organic catalysts. III. Formation of oxamide from dicyanogen in presence of aldehydes. W. LANGENBECK (Annalen, 1929, 469, 16—25).—The production of oxamide from cyanogen by the action of water in presence of acetaldehyde and propaldehyde at the ordinary temperature, followed by heating, is due to the aldehyde reacting in its enolic form. Acetaldehyde in presence of dilute acetic acid, formaldehyde, benzaldehyde, chloral hydrate, and dextrose does not promote the change. When a mixture of acetaldehyde, cyanogen, and water is allowed to remain at 15° for some days, and then evaporated at 30°/15—17 mm., the intermediate product, $\text{NH}_2\cdot\text{CO}\cdot\text{C}(\text{NH})\cdot\text{O}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{H}_2\text{O}$, m. p. 150° (decomp.) on rapid heating, is produced. This is decomposed by warming with dilute acid into oxamide, oxalic acid, and acetaldehyde, whilst decomposition with a few drops of 0.1N-sodium hydroxide causes immediate production of acetaldehyde and oxamide. When heated at 150° in a vacuum the above intermediate yields oxamide.

H. BURTON.

Hydrazide of κ -dihydroxystearic acid; s-bis-dihydroxyheptadecylcarbamide. C. BERNSTEIN and F. ULZER (Wiss. Mitt. Österr. Heilmittelstelle, 1928, xi—xiv; Chem. Zentr., 1928, ii, 1317).— κ -Dihydroxystearic hydrazide has m. p. 164° [*hydrochloride*, m. p. 194—195° (decomp.)]; *benzylidene derivative*, m. p. 143—144°; *piperonylidene derivative*, m. p. 153.5—154.5°. *s-Bis- κ -dihydroxystearic hydrazide*, from the monohydrazide and iodine in alcohol, has m. p. 202—204°. κ -Dihydroxystearic azide, from the hydrazine hydrochloride and nitrogen trioxide, m. p. 168—173°, when boiled with water affords *s-bis- κ -dihydroxyheptadecylcarbamide*, m. p. 187°.

A. A. ELDRIDGE.

Complex metallic cyanides. II. H. REIHLEN and U. VON KUMMER (Annalen, 1929, 469, 30—44).—Further support is deduced in favour of the polynuclear structure of complex metallic cyanides (cf. Reihlen and Zimmermann, A., 1927, 233). The complex salts, $[\text{Fe}(\text{CN})_6\text{Pb}(\text{H}_2\text{O})_2]\text{Ti}(\text{Cs})$ and $[\text{Co}(\text{CN})_6\text{Pb}(\text{H}_2\text{O})_2]\text{Ti}(\text{Cs})$, are obtained by the action of 1 mol. of thallium and caesium nitrates on 1 mol. of the complexes $\text{FePb}_2(\text{CN})_6\text{NO}_3\cdot 5.5\text{H}_2\text{O}$ (I) and $\text{CoPb}_2(\text{CN})_6\text{NO}_3\cdot 5\text{H}_2\text{O}$ (II). These salts have relatively high solubilities and at $v = 100$ litres per mol. the molecular conductivity is only about 60% of that of potassium ferricyanide. Further dilution causes an anomalous increase in the conductivity, presumably because of further dissociation of the complex ion into $[\text{Fe}(\text{CN})_6]^{---}$ and Pb^{++} . The compounds I and II are formulated with homopolar linkings in the complex. The salt $[(\text{NO}_3)_2\text{Pb}_2\text{Fe}(\text{CN})_6]\text{K}$ could not be obtained in the solid form, but the solubilities of potassium nitrate and I in presence of one another are much greater than for each salt alone. The salts $\text{FePbK}(\text{CN})_6\cdot 3\text{H}_2\text{O}$ and $\text{Fe}_2(\text{CN})_6\cdot 2\text{H}_2\text{O}$ are also described.

H. BURTON.

Electrolysis of organometallic compounds. W. H. RODEBUSH and J. M. PETERSON (J. Amer. Chem. Soc., 1929, 51, 638—639).—Electrolysis of magnesium ethyl bromide in ether with platinum electrodes (cf. Gaddum and French, A., 1927, 756) gives a crystalline adherent deposit of magnesium at

the cathode. Pure zinc diethyl is non-conducting, but in ether it is electrolysed and zinc is deposited at the cathode.

H. E. F. NOTTON.

Thermal decomposition of sodium ethyl. W. H. CAROTHERS and D. D. COFFMAN (J. Amer. Chem. Soc., 1929, 51, 588—593).—Sodium ethyl is quantitatively formed from mercury diethyl and sodium in a vacuum at the ordinary temperature. The product, containing sodium and mercury, decomposes rapidly at 90—100° into sodium hydride and a mixture of ethylene (85%) and ethane (15%), and slowly at the ordinary temperature, yielding ethylene (about 30%) and ethane (70%). The quantitative results indicate that the ethane is formed during the decomposition of the sodium ethyl through $C_2H_4Na_2$ and $C_2H_2Na_4$ into sodium carbide. No indication of a preliminary dissociation into sodium and the ethyl radical was found (cf. Schorigin, A., 1910, i, 547).

H. E. F. NOTTON.

Organomagnesium halides. H. GILMAN and J. M. PETERSON (Rec. trav. chim., 1929, 48, 247—250).—Magnesium ethyl bromide underwent no decomposition at 100° or 150°. At 200° the average percentage decomposition was 6·7, at 300°, 14·3 (times of heating 1 hr.). Heating at 300° for 2 hrs. caused 17·8% decomposition. A boiling cymene solution underwent no change during 45 min. It was stable to sunlight and to rays from a mercury arc lamp.

The interactions of the following substances with magnesium ethyl bromide were examined: boiling diphenylmethane (no reaction), boiling triphenylmethane (2% reaction), triphenylchloromethane (100% reaction), sodium hydrogen carbonate (no reaction), di- α -hydroxybenzyl-*p*-tolylarsine (no reaction), triphenylphosphine oxide (10% reaction), phenyl allyl ether (5% reaction), nitrous oxide (no reaction), *as*-diphenylethylene (no reaction).

R. J. W. LE FEVRE.

Zinc alkyls; preparation and use in synthesis of hydrocarbons. C. R. NOLLER (J. Amer. Chem. Soc., 1929, 51, 594—599).—Zinc diethyl, di-*n*-propyl, di-*n*-butyl, b. p. 81—82°/9 mm., and diisomyl have been prepared in high yield (cf. Lachman, A., 1900, i, 542) (a) by using an alloy of zinc with 5—8% of copper, (b) by using a suitable mixture of alkyl bromide and iodide instead of pure iodide, and (c) by vacuum-distilling the product. *sec*-Alkyl halides, cyclohexyl bromide, and ethyl sulphate yield mainly hydrocarbons. In hydrocarbon solvents the zinc alkyls do not inflame spontaneously and, when warmed with *tert*.-butyl and -amyl chlorides yield 24—51% of theory of tetra-alkylmethanes. In this way $\beta\beta$ -dimethylbutane, $\beta\beta$ -dimethylpentane, $\beta\beta$ -dimethylhexane, b. p. 106—107°, d_4^{20} 0·6967, n_D^{20} 1·3931; $\beta\beta$ -trimethylhexane, $\gamma\gamma$ -dimethylpentane, $\gamma\gamma$ -dimethylhexane, and $\gamma\gamma$ -dimethylheptane, b. p. 137—138°, d_4^{20} 0·7304, n_D^{20} 1·4095, are prepared.

H. E. F. NOTTON.

β -Substituted alkylarsinic acids and their derivatives. I. **β -Substituted ethylarsinic acids.** S. M. SCHERLIN and G. I. EPSTEIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1487—1492).—See A., 1928, 1231.

A. FREIMAN.

Alkylation of octacyanotungstic acid. F. HOLZL (Monatsh., 1929, 51, 1—22; cf. A., 1928, 279).

—When potassium octacyanotungstate (Olsson, A., 1914, i, 944) is treated in dilute sulphuric acid solution with silver nitrate it yields, in addition to the normal salt $Ag_4[W(CN)_8]$, the acid products $Ag_2H_2[W(CN)_8]$ and $Ag_3H[W(CN)_8]$. Methylation of these yields a series of complex salts of quadri- and quinque-valent tungsten by replacement of silver by a methyl group, some of the carbylamino-groups co-ordinating a molecule of water or alcohol to form the grouping $C(OH)\cdot NHMe$. Alkylation of all eight cyano-groups is not possible, only acidic or neutral complexes being obtained and never a salt containing tungsten in a complex cation. When the precipitated silver octacyanotungstate is treated with methyl iodide in the dark for 8 days and the ether-washed and dried solid residue is extracted with anhydrous methyl alcohol, the solution by evaporation yields a compound $[W(CN)_6\{C(OMe)\cdot NHMe\}_2]H_2$ (I), which reacts acidic in aqueous solution, neutral in alcoholic solution, yields carbylamine by treatment with alkali, and with methyl-alcoholic silver nitrate gives a yellow precipitate. This latter compound is also obtained by the action of methyl-alcoholic silver nitrate on the methyl-alcoholic solution of the product obtained when the original action of methyl iodide is extended for 28 days, and is assigned the structure $[(CN)_4(CNMe)\{C(OMe)\cdot NHMe\}W(CN)_2W\{C(OMe)\cdot NHMe\}(CNMe)(CN)_4]Ag_2$, formed by elimination of a molecule of alcohol from I and the union of two complexes by a doubly co-ordinated cyano-bridge. The residue, insoluble in methyl alcohol, after extraction of I is extracted with water and evaporation of the golden-yellow solution in a vacuum yields a brown, hygroscopic powder which after drying over phosphoric oxide has a composition corresponding with the compound $[(CN)_4(CNMe)_2\{C(OH)\cdot NHMe\}W(CN)W\{C(OH)\cdot NHMe\}(CNMe)_2(CN)_4]OH$ (II), and in agreement with this it is found to titrate as a monobasic acid. When dried over sulphuric acid one additional molecule of water remains. The residue, insoluble in methyl alcohol and water, from the extraction of I and II dissolves in dilute hydrochloric acid with separation of silver iodide. Complete evaporation of this solution in a vacuum and extraction of the crystalline residue with methyl alcohol yields the compound $[(CN)_5\{C(NHMe)\cdot O\}_2W(CN)W\{C(NHMe)\cdot O\}_3(CN)_4]H_5^+$ (III) (silver salt). The residue from the extraction of III is almost completely soluble in water. Concentration of the aqueous solution, which has an acid reaction and yields carbylamine with alkalis, yields the compound $[(CN)_4\{C(OH)\cdot NHMe\}_2W(CN)_2W\{C(OH)\cdot NHMe\}_2(CN)_4]$ containing a double co-ordinated cyano-bridge. The evidence on which these structures are based is discussed.

J. W. BAKER.

New type of complex platinum compounds. Ter- and quinque-valent platinum. P. C. RAY and K. C. B. RAY (Z. anorg. Chem., 1929, 178, 329—336).—Prolonged heating on the water-bath of a mixture of chloroplatinic acid and dibenzyl sulphide affords the compound $PtCl(CH_2Ph)_2S_2$ as a chocolate-coloured powder soluble in chloroform and benzene. Ebullioscopic determination of the mol. wt. in the former gives a value corresponding with five times and

cryoscopic determination in the latter a value corresponding with seven times the above formula. Treatment of the chloromercaptide $\text{Et}_2\text{S}_2\cdot\text{PtCl}$ (Ray, J.C.S., 1923, 123, 134) with ammonia at 0° yields the orange-yellow compound $\text{Pt}_3\text{Cl}\cdot 2\text{Et}_2\text{S}_2\cdot 2\text{NH}_3\cdot 6\text{H}_2\text{O}$, with piperidine the compound $\text{Pt}_2\text{Cl}\cdot 2\text{Et}_2\text{S}_2\cdot \text{C}_5\text{H}_{11}\text{N}$, with boiling anhydrous diethylamine the compound $\text{Pt}_5\text{Cl}\cdot 4\text{Et}_2\text{S}_2\cdot 2\text{NH}_4\text{Et}$, with boiling benzylamine the compound $\text{Pt}_5\text{Cl}\cdot 4\text{Et}_2\text{S}_2\cdot \text{CH}_2\text{Ph}\cdot \text{NH}_2$, with aniline at 100° the compound $\text{Pt}_5\text{Cl}\cdot 4\text{Et}_2\text{S}_2\cdot \text{PhNH}_2$, with hot ethylenediamine the compound $\text{Pt}_5\text{Cl}\cdot 4\text{Et}_2\text{S}_2\cdot 2\text{en}$, with alcoholic methylamine the compound $\text{Pt}_5\text{Cl}\cdot 4\text{Et}_2\text{S}_2\cdot 2\text{NH}_2\text{Me}$, with cold toluidine the compound $\text{Pt}_5\text{Cl}\cdot 4\text{Et}_2\text{S}_2\cdot \text{C}_6\text{H}_4\cdot \text{NH}_2$, with warm hydrazine hydrate the compound $\text{Pt}_5\text{Cl}\cdot 4\text{Et}_2\text{S}_2\cdot 4\text{N}_2\text{H}_4$, with propylamine the compound $\text{Pt}_7\text{Cl}\cdot 5\text{Et}_2\text{S}_2\cdot 2\text{NH}_2\text{Pr}$, with phenylhydrazine the compound $\text{Pt}_9\text{Cl}\cdot 7\text{Et}_2\text{S}_2\cdot 2\text{NHPh}\cdot \text{NH}_2$, and with 50% ethylamine the compound $\text{Pt}_{13}\text{Cl}\cdot 10\text{Et}_2\text{S}_2\cdot 2\text{NH}_2\text{Et}\cdot 8\text{H}_2\text{O}$. A second piperidine compound, $\text{Pt}_5\text{Cl}\cdot 4\text{Et}_2\text{S}_2\cdot \text{C}_5\text{H}_{11}\text{N}$, has also been prepared. The constitution of these compounds is discussed on the assumption that the quinquivalent platinum atom in the chloromercaptide becomes trivalent and that the diethyl sulphide radical behaves like an unsaturated compound with four latent valencies. A. R. POWELL.

***p*-Bromoethylenic benzenes and their magnesium organo-derivatives.** I. R. QUELET (Bull. Soc. chim., 1929, [iv], 45, 75—97; cf. A., 1927, 452).—The mono- and di-magnesium derivative of *p*-dibromobenzene (A., 1927, 890) with allyl bromide gives a mixture, b. p. $95\text{--}96^\circ/12\text{ mm.}$, of *p*-bromoallylbenzene, b. p. $96^\circ/12\text{ mm.}$, $222\text{--}223^\circ/730\text{ mm.}$, $d_4^{15}\text{ }1\cdot324$, $1\cdot559$, *p*-diallylbenzene, and unchanged *p*-dibromobenzene. The first-named is isolated by treating the mixture with bromine, distilling off the *p*-bromo- $\beta\gamma$ -dibromopropylbenzene (yield 60%), b. p. $178\text{--}180^\circ/11\text{ mm.}$, $d_4^{17}\text{ }1\cdot950$, $n_D^{20}\text{ }1\cdot622$, and treating this with zinc dust and acetic acid (yield 60%). Potassium hydroxide in amyl alcohol isomerises *p*-bromoallylbenzene to *p*-bromopropenylbenzene (yield 75%), m. p. 35° , b. p. $110^\circ/12\text{ mm.}$, $d_4^{25}\text{ }1\cdot332$, $n_D^{25}\text{ }1\cdot590$ (*p*-bromobenzene- $\alpha\beta$ -propylene oxide, yield 80%, has b. p. $123\text{--}124^\circ/11\text{ mm.}$, $d_4^{21}\text{ }1\cdot426$, $1\cdot570$), and perbenzoic acid in chloroform affords α -*p*-bromophenyl- $\beta\gamma$ -propylene oxide, b. p. $132^\circ/10\text{ mm.}$, $d_4^{10}\text{ }1\cdot430$, $n_D^{10}\text{ }1\cdot570$. Similarly from magnesium, *p*-bromobenzyl chloride and allyl bromide there are derived *p*-bromo- $\gamma\delta$ -dibromobutylbenzene, b. p. $190\text{--}191^\circ/12\text{ mm.}$, $d_4^{15}\text{ }1\cdot859$, $n_D^{15}\text{ }1\cdot610$, *p*-bromo- Δ^5 -butenylbenzene, b. p. $113^\circ/14\text{ mm.}$, $d_4^{15}\text{ }1\cdot275$, $n_D^{15}\text{ }1\cdot553$, and the corresponding oxide, b. p. $140\text{--}141^\circ/10\text{ mm.}$ *p*-Bromophenylmethylcarbinol, b. p. $130^\circ/12\text{ mm.}$, $d_4^{15}\text{ }1\cdot464$, $n_D^{15}\text{ }1\cdot574$ (phenylurethane, m. p. $103\text{--}104^\circ$), yield 95% from *p*-bromobenzaldehyde, 45—50% from acetaldehyde and magnesium *p*-dibromobenzene bromide, with phosphoric acid gives improved yields of *p*-bromostyrene, b. p. $87\text{--}88^\circ/12\text{ mm.}$, $d_4^{18}\text{ }1\cdot401$, $n_D^{18}\text{ }1\cdot599$ (cf. Ziegler and Tiemann, A., 1923, i, 30). Similarly, *p*-bromophenylethylcarbinol, b. p. $140\text{--}141^\circ/13\text{ mm.}$, $d_4^{18}\text{ }1\cdot405$, $n_D^{18}\text{ }1\cdot561$ (phenylurethane, m. p. 102°), yield 90% from *p*-bromobenzaldehyde, with phosphoric oxide gives 80% and with potassium hydrogen sulphate only 60% of *p*-bromopropenylbenzene. *p*-Bromophenylpropylcarbinol, b. p. $147^\circ/$

11 mm. , $d_4^{11}\text{ }1\cdot339$, $n_D^{11}\text{ }1\cdot558$ (phenylurethane, m. p. 83°), yield, 48% from *p*-dibromobenzene and 90% from *p*-bromobenzaldehyde, with potassium hydrogen sulphate gives 85% of *p*-bromo- Δ^5 -butenylbenzene, m. p. 30° , b. p. $126\text{--}127^\circ/14\text{ mm.}$, $d_4^{11}\text{ }1\cdot282$, $n_D^{11}\text{ }1\cdot580$, phosphoric oxide giving unsatisfactory results, apparently due to isomerisation to a product of lower b. p. *p*-Bromo- $\alpha\beta$ -dibromobutylbenzene has m. p. 78° , α -*p*-bromophenyl- $\alpha\beta$ -butylene oxide, b. p. $138^\circ/12\text{ mm.}$, $d_4^{16}\text{ }1\cdot362$, $n_D^{16}\text{ }1\cdot557$. *p*-Bromo- Δ^5 -butenylbenzene gives a magnesium derivative which is decomposed normally into Δ^5 -butenylbenzene, b. p. $80^\circ/12\text{ mm.}$ ($\alpha\beta$ -dibromobutylbenzene has m. p. 70°). The ethylenic derivatives with an $\alpha\beta$ -double linking are characterised by a higher m. p. and b. p. than the corresponding $\beta\gamma$ -derivatives, and by greater density and refractivity for light. *p*-Bromobenzaldehyde is obtained in 50% yield from *p*-bromobenzyl alcohol by Sommelet's reaction.

R. BRIGHTMAN.

Highly polymerised compounds. XVI. Polymerisation of α -methylstyrene. H. STAUDINGER and F. BREUSCH (Ber., 1929, 62, [B], 442—456; cf. this vol., 305, 306).— α -Methylstyrene is very violently polymerised by tin tetrachloride, yielding, in addition to Tiffeneau's dimeride, more complex, saturated compounds in small amount. Attempts to moderate the violence of the reaction by use of solvents cause essentially the formation of only the dimeride. Since the tendency towards polymerisation of α -methylstyrene is much less than that of styrene (*loc. cit.*) shorter chains are produced and ring closure takes place when only a few molecules have become attached to one another. A polymeric homologous series of polymethylstyrenes therefore results, extending from dimeric to octameric members. The presence of rings is established by the saturated nature of the products and the absence of other residues as terminal groups. The differences in properties between the individual members are sufficient to enable the separation of the simpler members by distillation in a vacuum and of the more complex substances by fractional dissolution and precipitation. As expected, the b. p. rises with increasing mol. wt., whereas the solubility diminishes greatly. The viscosity in benzene solution increases more rapidly than required by proportionality of mol. wt., so that it appears that with polymeric homologous compounds evidence as to the degree of polymerisation may be obtained by comparison of the viscosities of equally concentrated solutions (with respect to the unit molecule). Density and refractive index increase with degree of polymerisation. The molecular refraction of all polymerides agrees with that calculated for the saturated rings, showing that the mode of union of the unit molecule is the same. The dimeride and tetrameride have been obtained crystalline, whereas the other polymethylstyrenes are amorphous. The pentameride to octameride are white powders resembling externally the hemi-colloidal polystyrenes. Their temperature of liquefaction increases with the degree of polymerisation and is a criterion of the latter. With individual compounds mixtures of different polymerides soften far below the softening point of their components. The m. p. of the dimeride and tetrameride are far above the softening interval of the (undercooled) materials; the molecules in the crystall-

ine product are more firmly united by lattice forces than in the amorphous substance. Consequently, the density is greater.

It is remarkable that dimeric methylstyrene is a homogeneous compound, since four modifications are theoretically possible. Polymerisation proceeds therefore only in one direction, as observed with *cyclopentadiene*. Whether the more complex polymethylstyrenes are uniform or mixtures of isomerides cannot be established.

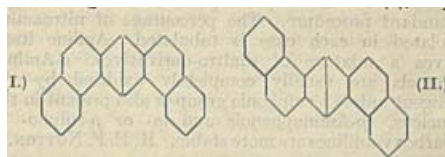
The presence of poly-membered rings in the polymethylstyrenes is firmly established, since the dimeride is already known and the similar constitution of the higher members is based on refractometric evidence. It is probable that eucolloidal polystyrene and caoutchouc are formed of extraordinarily large rings. This has a great effect on physical properties, since substances composed of thread molecules, such as guttapercha and cellulose, behave quite differently. Colloidal properties are not shown by the simpler members of the styrene series and appear only when their degree of polymerisation is great. Pummerer's conception of caoutchouc as an octameride of isoprene appears incorrect.

Dehydration of phenyldimethylcarbinol to α -methylstyrene is most conveniently effected by boiling acetic anhydride. The following polymerides are described: dimeride [1:3-diphenyl-1:3-dimethylcyclobutane], b. p. 118—120°/0.1 mm., m. p. 52°, softening temperature -32° to -24°, d^{20}_D (undercooled) 1.1183, n^{20}_D 1.5633; trimeride [1:3:5-trimethyl-1:3:5-triphenylcyclohexane], b. p. 172—178°/0.1 mm., softening temperature, -3° to +9°, d^{20}_D 1.0455, n^{20}_D 1.58429; tetrameride [1:3:5:7-tetraphenyl-1:3:5:7-tetramethylcyclooctane], b. p. 208—212°/0.1 mm., m. p. 127—129°, softening temperature, 38—48°, d^{20}_D (amorphous) 1.0594; d^{20}_D (crystalline) 1.1452; n^{20}_D 1.5934; pentameride [1:3:5:7:9-pentaphenyl-1:3:5:7:9-pentamethylcyclodecane], b. p. 240—244° (slight decomp.)/0.1 mm., softening temperature, 60—68°, d^{20}_D 1.0624, n^{20}_D 1.5960; hexameride, [1:3:5:7:9:11-hexaphenyl-1:3:5:7:9:11-hexamethylcyclododecane], b. p. 275—285° (partial decomp.)/0.1 mm., softening temperature, 98—108°, d^{20}_D 1.0657; n^{20}_D 1.6050; heptameride [1:3:5:7:9:11:13-heptaphenyl-1:3:5:7:9:11:13-heptamethylcyclotetradecane], b. p. 312—316° (partial decomp.)/0.1 mm., softening temperature, 125—133°, d^{20}_D 1.0671, n^{20}_D 1.6010; octameride [1:3:5:7:9:11:13:15-octaphenyl-1:3:5:7:9:11:13:15-octamethylcyclohexadecane], b. p. 345—360° (decomp.)/0.1 mm., softening temperature, 165—172°, d^{20}_D 1.0684, n^{20}_D 1.6120.

The polymerisation of α -methylstyrene by undiluted boron trichloride and titanium tetrachloride, by Florida earth, and by heating in an atmosphere of nitrogen at 250° is described; polymerisation does not occur at 180° or under the influence of ultra-violet light. All the polymerides are unsaturated. The following are described: *unsaturated dimeric α -methylstyrene*, b. p. 117—120°/1.0 mm., d^{20}_D 0.9889, n^{20}_D 1.5677 (non-crystalline dibromide); the trimeride, a viscous resin probably not homogeneous. H. WREN.

Polynuclear, aromatic hydrocarbons and their derivatives. I. Dibenzanthracene and its

quinones. E. CLAR (Ber., 1929, 62, [B], 350—359).—The action of α -naphthoyl chloride on β -methylnaphthalene in the presence of aluminium chloride and carbon disulphide affords 2-methyl-1:1'-dinaphthyl ketone, m. p. 140—141°, in about 90% yield. When heated at its b. p., the ketone loses water and gives 1:2:7:8-dibenzanthracene (I), m. p.



260—261° (picrate, m. p. 212°), oxidised by chromic acid in boiling glacial acetic acid to 1:2:7:8-dibenzanthraquinone, m. p. 243—244°. Similarly, β -naphthoyl chloride and β -methylnaphthalene afford successively 2-methyl-1:2'-dinaphthyl ketone, m. p. 170—171°, 1:2:5:6-dibenzanthracene (II), m. p. 262° (picrate, m. p. 214°), and 1:2:5:6-dibenzanthraquinone, m. p. 244—245° (cf. Weitzenböck and Klingler, A., 1918, i, 494). The hydrocarbons and their derivatives show unusually close resemblance to one another in their physical properties, but are differentiated by their behaviour towards ultra-violet light. The 1:2:7:8-dibenzanthracene prepared by Homer (J.C.S., 1910, 97, 1148) from naphthalene and *s*-tetrabromoethane differs widely from that described by the author. Re-examination of the product obtained by Honig by the action of concentrated sulphuric and anhydrous oxalic acid on α -naphthol and regarded as 1:2:7:8-dibenzanthraquinone discloses the presence of only one carbonyl group; although it does not appear identical with the compound so described in the literature, it is considered to be 1:2:7:8-dibenzanthrone, m. p. 297° (decomp.), and to be converted by magnesium phenyl bromide into 9-phenyl-1:2:7:8-dibenzanthrol (+1C₆H₅N), m. p. 195° after incipient decomp. 175°.

The product prepared by the action of *o*-toluyl chloride on phenanthrene in presence of aluminium chloride is not homogeneous, containing mainly *o*-tolyl 9-phenanthryl ketone mixed with isomerides. If the mixture of ketones is heated, the main and most soluble product is 1:2:3:4-dibenzanthracene, m. p. 196—197° (picrate, m. p. 207°), the structure of which appears confirmed by its oxidation (even with an excess of reagent) to 1:2:3:4-dibenzanthraquinone (9:10-phthaloylphenanthrene), m. p. 179°, whereas the isomerides of higher m. p. yield diquinones under like conditions. The phthaloylphenanthrene obtained by the action of phosphoric oxide on *o*-phenanthrolylbenzoic acid is a mixture of isomerides in which the 9:10-derivative probably predominates. H. WREN.

Decahydroquinoline and its derivatives. V. Synthesis of *trans*-*o*-dimethylaminopropylcyclohexane. S. FUJISE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 2).—By reduction of 2-propylcyclohexanoneoxime, followed by methylation, *trans*-2-dimethylaminopropylcyclohexane is obtained. Dehydration of 2-propylcyclohexanol yields Δ^1 -*n*-propylcyclohexene. B. W. ANDERSON.

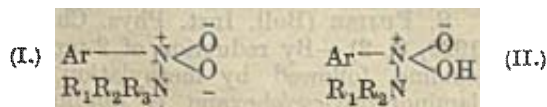
Nitration of substituted anilines. E. R. RIEGEL, H. W. POST, and E. E. REID (J. Amer. Chem. Soc., 1929, **51**, 505—508).—In order to compare the protective action of substituents, 14 derivatives of aniline containing hydroxyl, carboxyl, sulphonc acid, and nitro-groups have been nitrated at about 0° with sulphuric and nitric acids, using a standard procedure. The percentage of nitroamine isolated in each case is tabulated. Aniline itself gives a mixture of dinitro-derivatives. *o*-Aminophenols are usually completely oxidised by the reagent unless a sulphonc group is also present in the nucleus. *p*-Aminophenols and *m*- or *p*-sulpho- or -carboxy-anilines are more stable. H. E. F. NOTTON.

Introduction of the thiocyno-group into organic compounds. H. P. KAUFMANN (Ber., 1929, **62**, [B], 390—391; cf. A., 1926, 392).—Acetic or formic acid, as solvent, may be replaced by methyl alcohol, acetone, methyl or ethyl acetate. Methyl alcohol, saturated with the corresponding alkali halide as a protection against halogenation, is particularly suitable. Thus *p*-thiocynoaniline, m. p. 97°, is prepared in 97% yield by the addition of bromine in methyl alcohol saturated with sodium bromide to a methyl-alcoholic solution of aniline and sodium thiocyanate. H. WREN.

Monoarylguanidines. I. α -Phenylguanidine. G. B. L. SMITH (J. Amer. Chem. Soc., 1929, **51**, 476—479).—The sulphate of methylisothiocarbamide (cf. Phillips and Clarke, A., 1923, i, 903) yields with aniline a mixture of aniline and α -phenylguanidine sulphates, from which the latter may be precipitated as carbonate, m. p. 138—140°, after liberating the bases in aqueous solution. The optical properties of α -phenylguanidine and of its sulphate, m. p. 205°, hydrochloride, nitrate, picrate, and chloroplatinate (cf. Kampf, A., 1904, i, 534) are described.

H. E. F. NOTTON.

Structure of organic molecular compounds. G. M. BENNETT and G. H. WILLIS (J.C.S., 1929, 256—268).—The theory of the union of organic molecules by residual valency of a whole molecule or group is examined and rejected in favour of union through definite localised covalent linkings (cf. Lowry, Chem. and Ind., 1924, 218). The existence of organic molecular compounds in solution, often with occurrence of visible colour, supports the authors' theory, which also accounts for the general occurrence of a simple molecular ratio between the components of a complex. It is shown that the formation of the equimolecular compound of trinitrobenzene and quinoline (Sudborough and Beard, J.C.S., 1910, 97, 773) rather than a complex $[3C_6H_3(NO_2)_3, C_{10}H_7N]$ is to be anticipated. Union of polynitro-compounds and bases is considered to occur through a nitro-group (acceptor) and the basic nitrogen atom (donor) to yield complexes of type I, which if $R_3 = H$ may pass into form II (cf. Brewin and Turner, A., 1928, 402).



Examination of the *o*-, *m*-, and *p*-nitrobenzylalkylamines supports the mode of formulation I proposed;

the *o*-nitro-isomerides should exhibit intramolecular co-ordination and should therefore possess lower b. p. than, and differ in solubility from, their respective *m*- and *p*-isomerides in which any co-ordination must be intermolecular (cf. Sidgwick and Callow, A., 1924, i, 506). The *o*-, *m*-, and *p*-nitrobenzyl dimethylamines were prepared from the respective nitrobenzyl chlorides in 50—60% yield, using hexamethylenetetramine (cf. A., 1926, 1132), and also by means of dimethylamine hydrochloride and alkali in alcoholic solution; their b. p. determined (a) in the ordinary way, and (b) by the method of Smith and Menzies (A., 1910, ii, 687), are as follows (order *o*-, *m*-, *p*-): (a) 133°/16 mm., 144°/16 mm., 146°/16 mm.; (b) 116—117°/11 mm., 130—132°/10 mm., 131—133°/10 mm.; *o*-nitrobenzyl dimethylamine (hydrochloride, m. p. 215°; picrate, m. p. 143°) possesses a more intense yellow colour than either the *m*-isomeride (picrate, m. p. 217°) or the *p*-isomeride (picrate, m. p. 149°). The *o*-, *m*-, and *p*-nitrobenzyl diethylamines were prepared by the action of excess of diethylamine on the appropriate nitrobenzyl chlorides in 70—85% yield. The b. p. of the isomerides are: (a) 144°/13 mm., 158°/13 mm., 160°/13 mm.; (b) 124—127°/10 mm., 139—142°/10 mm., 146—148°/10 mm.; the *o*-isomeride is distinguished by its more intense yellow colour, and the *p*-isomeride yields a picrate, m. p. 151° (lit. m. p. 161°). The solubility of naphthalene in the nitrobenzyl diethylamines, and of the three nitroamines in trimethylene glycol were determined and in each case the *o*-isomeride differs to a small but definite extent from the *m*- and *p*-isomerides, which afford almost identical results.

Complexes between polynitro-compounds and hydrocarbons result from an ethylenic linking, which in the polarised form $-\text{CH}=\text{CH}-$, provides one covalency; the benzene nucleus provides one covalency only. Increased stability occurs when several nitro-groups are present, and it is shown that any group attracting electrons should stabilise these complexes. Thus methyl 5-nitroisophthalate forms with α -naphthylamine the compound $[C_6H_3(NO_2)(CO_2Me)_2, C_{10}H_7-NH_2]$, m. p. 82°, and 5-nitrobenzene-1 : 3-disulphonyl chloride, m. p. 97—98°, forms compounds with mesitylene, m. p. 68—70°, anisole, m. p. 55—60°, and naphthalene, m. p. 102—103°, in the molecular ratio 1 : 1.

Compounds of picric acid with bases and hydrocarbons are discussed, and an explanation of the red and yellow forms of various picrates is suggested; *s*-trichloroaniline picrate, m. p. 80—83°, forms deep red needles (cf. 2 : 4-dichloroaniline picrate, which is yellow).

Two compounds of benzoquinone with bases are described: a green compound with *pp'*-tetramethyldiaminodiphenylcarbinol $[C_6H_4O_2, 2C_{17}H_{22}ON_2]$, m. p. 169—170°, and with *pp'*-tetramethyldiaminodiphenylmethane a purple compound $[C_6H_4O_2, 2C_{17}H_{22}N_2]$, m. p. 71°. The halochromic effects displayed by quinones in the presence of sulphuric acid are due to complexes in which the quinone functions as the donor-molecule. Evidence in support of Pfeiffer's suggestion (A., 1925, i, 262) that the development of colour is connected with the appearance of positive unsaturation on a carbon atom owing to co-ordin-

ation has been obtained by a study of the halochromic effects produced by sulphuric acid with a series of substituted styrylquinoxalines. The preparation of 3-styryl-2-methylquinoxaline, m. p. 137°, is described.

Other types of complex formation are discussed, and many illustrative examples are given.

C. W. SHOPPEE.

Modified Curtius reaction. II. C. NAEGELI (Helv. Chim. Acta, 1929, 12, 205—207; cf. A., 1928, 881).—A reply to Lindemann (this vol., 78).

H. BURTON.

Action of methyl *p*-toluenesulphonate on α -naphthylamine. V. M. RODIONOV and W. E. VVEDENSKIY (Bull. Soc. chim., 1929, [iv], 45, 121—124; cf. A., 1926, 532).—When α -naphthylamine (1 mol.) is heated with 1 mol. of methyl *p*-toluenesulphonate at 155—160° for 5 hrs., 42% of dimethyl- α -naphthylamine is obtained, together with 5% of α -dinaphthylamine, 24% of α -naphthylamine, recovered as sulphate, and 23% of methyl- α -naphthylamine, separated as its acetyl derivative; with 2 mols. of ester a 90—97% yield of dimethyl- α -naphthylamine, b. p. 268—274°, is obtained. α -Naphthylmethylammonium *p*-toluenesulphonate, m. p. 163—164°, is obtained by heating methyl α -naphthylamine with *p*-toluenesulphonic acid in alcohol at 50°. α -Naphthyltrimethylammonium *p*-toluenesulphonate, m. p. 82—83°, obtained by heating dimethyl- α -naphthylamine with the ester at 153—160°, with potassium iodide yields the corresponding iodide, m. p. 163—164°, and is an excellent alkylating agent for phenols, especially aminophenols, at higher temperatures than are possible with phenyltrimethylammonium *p*-toluenesulphonate. R. BRIGHTMAN.

Methylated nitronaphthylamines. V. VESELY and A. VOJTECH (J. Czechoslov. Chem. Comm., 1929, 1, 104—118).—Methylation of 3-nitro- α -naphthylamine with methyl sulphate at 160° affords 3-nitro- α -naphthylmethylamine, m. p. 64—65° (picrate, m. p. 188—189°), and 4-nitro- β -naphthylamine under similar conditions gives 4-nitro- β -naphthylmethylamine, m. p. 65° (picrate, m. p. 194—196°). 4-Nitro- α -naphthylamine and methyl sulphate at 118° yield a mixture of 4-nitro- α -naphthylmethylamine, m. p. 184—185°, and 4-nitro- α -naphthylmethylamine, m. p. 65—66°, the latter in poor yield. 2-Nitro- α -naphthylamine cannot be methylated with methyl sulphate; treatment of 1:2-dinitronaphthalene with dimethylamine and alcohol gives 2-nitro- α -naphthylmethylamine, b. p. 182—184°/14 mm. (oriented by conversion into 2-nitro- α -naphthol, m. p. 127—128°, with alkali). Methyl sulphate with 5-nitro- α -naphthylamine gives 5-nitro- α -naphthylmethylamine, b. p. 194—196°/14 mm. (picrate, m. p. 165—166°), at 145°; with 8-nitro- α -naphthylamine, 8-nitro- α -naphthylmethylamine, m. p. 81°, at 140°; with 5-nitro- β -naphthylamine, 5-nitro- β -naphthylmethylamine, m. p. 74° (picrate, m. p. 176—177°), at 160°; with 8-nitro- β -naphthylamine, 8-nitro- β -naphthylmethylamine, m. p. 77° (picrate, m. p. 174—176°), at 135°; with 6-nitro- β -naphthylamine, a mixture of 6-nitro- β -naphthylmethylamine, m. p. 185—186° (picrate, m. p. 138—140°; acetyl derivative, m. p. 186—187°), and 6-nitro- β -naphthylmethylamine, m. p. 164° (picrate,

m. p. 158—160°) at 150°. Nitration of β -naphthylmethylamine with 86% nitric acid in glacial acetic acid solution gives a dinitro-compound, m. p. 157—158°, whilst nitration with fuming nitric acid and concentrated sulphuric acid yields a eutectic mixture, m. p. 52°, of two mononitro-compounds. Further nitration of the eutectic mixture with 86% nitric acid in glacial acetic acid solution affords an easily separable mixture of a dinitro-compound, m. p. 110°, identical with the product obtained by the nitration of 5-nitro- β -naphthylmethylamine, *i.e.*, 1:5-dinitro- β -naphthylmethylamine, together with an isomeric dinitro-compound, m. p. 176—177°, identical with the compound obtained by nitration of 8-nitro- β -naphthylmethylamine, *i.e.*, 1:8-dinitro- β -naphthylmethylamine. Nitration of α -naphthylmethylamine with nitric acid (*d* 1.525) in glacial acetic acid solution gives 2:4-dinitro- β -naphthylmethylamine, m. p. 88°, and a substance, m. p. 127—128°; nitration with fuming nitric acid and concentrated sulphuric acid yields a dinitronaphthylmethylamine, m. p. 137—138°, 5-nitro- α -naphthylmethylamine, b. p. 192—195°/14 mm. (picrate, m. p. 162—164°), and a small quantity of a mononitro-compound (picrate, m. p. 73°).

A. I. VOGEL.

Stereoisomerism of diphenyl compounds. II. Resolution of 3:3'-diaminodimesityl. W. W. MOYER and R. ADAMS (J. Amer. Chem. Soc., 1929, 51, 630—639).—Further evidence for the mechanical theory of the stereoisomerism of diphenyl compounds (cf. A., 1928, 1234) is afforded by the resolution of a derivative in which the 2-, 6-, 2', and 6'-substituents are identical. Dimesityl is more conveniently prepared from magnesium mesityl bromide and cupric chloride (cf. Sakellarios and Kyrimis, A., 1924, i, 381) than by Ullmann's method (A., 1904, i, 725). It is converted by nitric acid (*d* 1.50) into tetranitrodimesityl, m. p. 270—271°, which is reduced by alcoholic ammonium sulphide to a mixture of nitroamines and by zinc with hydrochloric and acetic acids to tetraaminodimesityl, m. p. above 360° (hydrochloride). Dimesityl gives with bromine in carbon tetrachloride 3:3'-dibromodimesityl, m. p. 112—113°, and with acetyl nitrate a dinitro-derivative, m. p. 162.5—163.5°, which is not further nitrated by this reagent and is, therefore, probably the 3:3'-derivative. It is reduced by zinc and acid to di-3:3'-aminodimesityl, m. p. 206—207° (diacetyl derivative, m. p. 303—304°), which is readily separated through the *d*-camphorsulphonate, m. p. 186—188° (indef.) (also +H₂O, m. p. 175—187°), [α]_D²⁰ +16.3°, into di-3:3'-diaminodimesityl, m. p. 203.5—204.5°, [α]_D²⁰ +42.3° (diacetyl derivative, m. p. 312—313°, shrinking from 307°, [α]_D²⁰ +30.8°), and the *l*-form, m. p. 203—204°, [α]_D²⁰ -41.5° (diacetyl derivative, m. p. 311—313°, [α]_D²⁰ -30.4°). The active amine is only slightly racemised by boiling with hydrochloric acid or alcoholic potassium hydroxide. The diazonium salt from nitroaminomesitylene (Kuster and Stallberg, A., 1894, i, 278) yields with potassium iodide iodonitro-*mesitylene*, m. p. 96—97°, which does not give 3:3'-dinitrodimesityl when heated with copper powder.

H. E. F. NOTTON.

Nitrophenylfluorenylamines. C. ANASTASI and L. GUGLIAMELLI (Anal. Asoc. Quím. Argentina,

1928, 16, 125—133).—2 : 4-Dinitrophenyl-2-fluorenylamine, m. p. 217°, is obtained in 56% yield by boiling a solution of 2 : 4-dinitrochlorobenzene and 2-fluorenylamine in absolute alcohol with anhydrous sodium acetate for 10 hrs. A preliminary account is given of the reduction of this compound by iron and acetic acid and by ammonium sulphide to the (?)diamino- and (?)nitroamino-derivatives, respectively, and its nitration to the (?)tetranitro-compound, m. p. 230° (decomp.), which has the properties of a ψ -acid.

R. K. CALLOW.

Manufacture of [new] substituted guanidines. I. G. FARBENIND. A.-G.—See B., 1929, 163.

Hexa-aminobenzene. B. FLURSCHEIM and E. L. HOLMES (J.C.S., 1929, 330—337).—Hexa-aminobenzene has been prepared by reduction of 2 : 4 : 6-trinitro-1 : 3 : 5-triaminobenzene with phenylhydrazine (cf. Walthers, A., 1896, i, 542); an attempt to employ stannous chloride in dry pyridine was unsuccessful. The base, m. p. 247—248° in hydrogen, forms light brown octahedra, the colour being due to surface oxidation, and is completely soluble in cold water; it may be crystallised from phenylhydrazine but is insoluble in all other media. Both the solid and the aqueous solution yield black oxidation products when kept in the air. The hexa-acetyl derivative, m. p. 356—357°, triplicate, no m. p., and the tetrahydrochloride, no m. p., are described; the last when treated with cold 50% aqueous potassium hydroxide yields a base (acetyl derivative, m. p. above 385°).

An attempt to reduce 2 : 4 : 6-trinitro-1-amino-3 : 5-dianilinobenzene, m. p. 264° (decomp.) (obtained from pentanitroaniline and aniline in acetone solution), with phenylhydrazine failed, but from 2 : 4 : 6-trinitro-1 : 3-diaminobenzene was obtained penta-aminobenzene, m. p. 228° in hydrogen, soluble in water with instantaneous decomposition and insoluble in organic solvents.

The stability of all known polyamino-derivatives of benzene, its homologues, and of anisole is discussed and it appears that (a) vicinally substituted compounds are more stable than their isomerides, and (b) vicinal as well as non-vicinal compounds become less stable as the number of amino-groups increases. The superior stability of hexa-aminobenzene as compared with penta-aminobenzene is accounted for on the theory of affinity demand. C. W. SHOPPEE.

Double salts of benzenediazonium iodide with mercuric iodide and the formation of diphenyliodonium salts by their decomposition. A. N. NESMEJANOV (Z. anorg. Chem., 1929, 178, 300—308).—A methyl-alcoholic solution of benzenediazonium chloride at -10° yields a yellow, crystalline precipitate of benzenediazonium tri-iodomercuriate, $C_6H_5N_2HgI_3$, m. p. 63—64° (decomp.), on addition of the requisite potassium and mercuric iodides in methyl-alcoholic solution. With a further quantity of potassium iodide in aqueous solution this compound yields the corresponding tetraiodomercuriate, $(C_6H_5N_2)_2HgI_4$, m. p. 59.5—60° (decomp.), as a canary-yellow powder. Both salts decompose when kept at the ordinary temperature chiefly with the production of iodobenzene and mercuric iodide, but

the first gives also a 10% and the second a 3% yield of diphenyliodonium tri-iodomercuriate, $[(C_6H_5)_2I]HgI_3$, light yellow crystals, m. p. 171.5°. The same substance is obtained by heating diphenyliodonium iodide, mercuric iodide, and acetone in a sealed tube at 100°.

A. R. POWELL.

Manufacture of new azo-dyes and intermediate products [2-anilino-8-hydroxy-6-naphthoic arylamides]. I. G. FARBENIND. A.-G.—See B., 1929, 165.

Manufacture of N- ω -aminoalkylamino-naphthoic acids. I. G. FARBENIND. A.-G.—See B., 1929, 200.

Influence of colloids on precipitation of salts. R. DICKINSON (J.C.S., 1929, 358—359).—The solubility of lead sozoiodolate (2 : 6-di-iodophenol-4-sulphonate) in water is 0.512 g. per 100 c.c. of solution. When the compound is prepared from lead acetate and sodium sozoiodolate in presence of 2% of gum acacia precipitation of more than half of the expected amount of lead salt is prevented: the solubility of lead sozoiodolate in 2% gum acacia solution is 1.116 g. per 100 c.c. of solution. Gelatin gives a white rubber-like precipitate with sodium sozoiodolate.

A. I. VOGEL.

3 : 5-Dichlorophenetidine. G. BARGELLINI and P. LEONE (Atti R. Accad. Lincei, 1928, [vi], 8, 399—404).—The compound, m. p. 46°, b. p. about 275°, obtained by Jaeger (A., 1875, 1260) by passing hydrogen chloride into an alcoholic solution of nitrosophenol may be either 3 : 5- or 2 : 6-dichlorophenetidine, but the latter has been prepared in another way (following abstract) and is found different. Treatment of 3 : 5-dichlorophenetidine with hydriodic acid gives the dichloroaminophenol obtained by passing hydrogen chloride through an ethereal solution of nitrosophenol (Jaeger, loc. cit.), so that this is 3 : 5-dichloro-4-aminophenol. Oxidation of the latter with dichromate and sulphuric acid yields 3 : 5-dichlorobenzoquinone (cf. Weselsky, Ber., 1870, 3, 646). 3 : 5-Dichlorophenetidine does not condense with aromatic aldehydes, carbon disulphide, phenylthiocarbimide, potassium thiocyanate, etc., but forms an acetyl derivative (3 : 5-dichlorophenacetin), m. p. 129—131°, a diacetyl derivative, m. p. 86—88°, and a benzoyl compound, m. p. 188°, and condenses with phthalic anhydride to give the compound, 193—194°, and with succinic anhydride to give a compound, m. p. 137°. On diazotisation and treatment with alkaline β -naphthol solution, it gives the azo-compound, $C_{18}H_{14}O_2N_7Cl_2$, m. p. 120°.

T. H. POPE.

2 : 6-Dichlorophenetidine. G. BARGELLINI (Atti R. Accad. Lincei, 1928, [vi], 8, 505—511; cf. preceding abstract).—2 : 6-Dichloro-4-aminophenol condenses with carbon disulphide to give 3 : 5 : 3' : 5'-tetracloro-4 : 4' - dihydroxydiphenylthiocarbamide, softening at 200°, m. p. 210° (decomp.); with phenylthiocarbimide, s. 3 : 5-dichloro-4-hydroxydiphenylthiocarbamide, m. p. 138—140°; with 1-chloro-2 : 4-dinitrobenzene, 3 : 5-dichloro-2' : 4'-dinitro-4-hydroxydiphenylamine, m. p. 208—210°; it also gives a piperonylidene, m. p. 151—153°, and a benzylidene derivative, m. p. 99—101°. Treatment of the last-

named compound with alcoholic potassium hydroxide and ethyl iodide yields 2 : 6-dichlorophenetidine, m. p. 105—107°, which forms an acetyl, m. p. 176—178°, a β -naphtholazo-, m. p. 171—173°, and a piperonylidene derivative, m. p. 133—135°, and condenses with 1-chloro-2 : 4-dinitrobenzene to give 3 : 5-dichloro-2' : 4'-dinitro-4-ethoxydiphenylamine, m. p. 160—162°.

T. H. POPE.

Condensation products of dextrose and *p*-phenetidine. II. M. AMADORI (Atti R. Accad. Lincei, 1929, [vi], 9, 68—73).—The compound, m. p. 118° (A., 1926, 60), has $[\alpha]_D^{20}$ —84° in fresh aqueous solution, this value gradually diminishing and the compound decomposing; in alcoholic solution $[\alpha]_D^{20}$ also falls from —88° to —91° to the constant value —35°. For the more stable compound m. p. 155° (now given as 115°) the value of $[\alpha]_D^{20}$ in methyl alcohol is initially —50° and falls slowly to —25°. Evidently α - and β -forms of these compounds exist and the presence of alkali in the solutions hastens the attainment of equilibrium. The conclusion is reached that the condensation of a primary aromatic amine with dextrose gives rise to (1) a glucosidic compound, resulting from the reaction of one of the aminic hydrogen atoms with the glucosidic hydroxyl of the dextrose, and (2) a basic compound, formed by the reaction of two aminic hydrogen atoms with the ketonic oxygen of the aldehyde group or of the lactonic linking of the dextrose.

T. H. POPE.

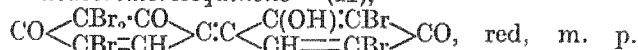
Replaceability of methoxy-group in 4 : 6-dinitro-*m*-tolyl methyl ether. J. G. KERKHOFF (Rec. trav. chim., 1929, 48, 251—253).—In support of de Capeller's (A., 1928, 631) claim that the dinitro-methoxytoluene isolated in the nitration of 5-methyl-2-*tert*-butylanisole (Barbier, A., 1928, 280) is 4 : 6-dinitro-*m*-tolyl methyl ether its interactions with the following reagents are described : boiling alcoholic ammonia, which gave 4 : 6-dinitro-*m*-toluidine, m. p. 195°; alcoholic methylamine under pressure, which furnished 4 : 6-dinitro-*N*-methyl-*m*-toluidine; boiling alcoholic hydrazine hydrate, giving 4 : 6-dinitro-*m*-tolylhydrazine.

R. J. W. LE FEVRE.

2-Substituted derivatives of *p*-cresol. M. COPISAROW (J.C.S., 1929, 251—253).—An improved preparation of 2-nitro-*p*-cresol, m. p. 76—77° (yield 79%), by nitration of *p*-tolyl carbonate is described (cf. Holleman and Hoefflake, A., 1917, i, 133); methylation with methyl sulphate and anhydrous sodium carbonate in toluene at 110° gives a 77% yield of 2-nitro-*p*-tolyl methyl ether (cf. Knecht, A., 1882, 968), also obtained directly from 2-nitro-*p*-tolyl carbonate (yield 60%); the ethyl ether may be prepared similarly. 2-Amino-*p*-cresol, m. p. 157—159°, is obtained in 79% yield by simultaneous reduction and hydrolysis of 2-nitro-*p*-tolyl carbonate with iron filings and acid, or preferably with sodium sulphide (cf. Knecht, A., 1882, 728; Wallach, A., 1883, 329; Maasen, A., 1884, 1145); 2-nitro-*p*-tolyl methyl ether on reduction with iron filings and acetic acid at 95—98° gives a 78—82% yield of 2-amino-*p*-tolyl methyl ether (cf. Knecht, *loc. cit.*). The preparation of *p*-tolyl chloroformate in 78—80% yield is also described.

C. W. SHOPPEE.

Oxidation of tribromoresorcinol. T. L. DAVIES and J. W. HILL (J. Amer. Chem. Soc., 1929, 51, 493—504).—Tribromoresorcinol (cf. Benedikt, A., 1883, 984), quantitatively prepared from resorcinol and bromine in chloroform, has been oxidised in benzene with aqueous chromic acid. In addition to bromine and carbon dioxide, a product (I) (33—37% yield) is obtained which contains about 60% of "rhodobromoresoquinone" (II),



215—220° (also +C₆H₆, +Et₂O, and +0.25 mol. CS₂). This is identified by reduction with sulphur dioxide in aqueous alcohol to tetrabromodiresorcinol (III), by bromination in glacial acetic acid to tribromoresoquinone (IV) (cf. Zincke and Schwabe, A., 1909, i, 241), and by iodometric determination of its oxidising power. Rhodobromoresoquinone is formed from IV and a mixture of bromine and benzene, reduction being brought about by hydrogen bromide. Its benzene additive product slowly decomposes at 120° into a colourless polymeride or isomeride of II, m. p. 228—229°, which cannot be brominated and has only half the oxidising power of II. The product I also contains a trace of IV and about 9% of colourless tetrabromoresoquinone, $\left| \begin{array}{c} \text{C} - \text{CH} = \text{CBr}_2 \\ \text{CO} \end{array} \right| > \text{CO}$,

m. p. 227—228° (decomp.), which decomposes in boiling glacial acetic acid into bromine and IV, and is quantitatively reduced to III by hydriodic acid. It is formed by brominating either II or IV. These results show that the oxidation of tribromoresorcinol probably yields first the monocyclic radical of di-

bromoresoquinone, $\left[\begin{array}{c} \text{C} - \text{CH} = \text{CBr} \\ \text{C}(\text{OH}) : \text{CBr} \end{array} \right]_2$, which is then brominated to the mixture I.

H. E. F. NOTTON.

Orientation in the benzene ring. Bromination of 2-aminoresorcinol dimethyl ether. A. A. LEVINE and H. LINFORD (J. Amer. Chem. Soc., 1929, 51, 524—527).—Attempts to brominate the free amine were unsuccessful. It is readily acetylated by acetic anhydride in glacial acetic acid at the ordinary temperature. The acetyl derivative gives in this solvent with 1 mol. of bromine 4-bromo-2-acetamidoresorcinol dimethyl ether (I), m. p. 161—162°, with 2 mols. at the ordinary temperature, dibromo-2-acetamidoresorcinol dimethyl ether, m. p. 213—214°, and at 100°, an isomeric dibromo-derivative, m. p. 187—188°. Hydrolysis of I with 2*N*-alcoholic potassium hydroxide gives 4-bromo-2-aminoresorcinol dimethyl ether, m. p. 67—68°, which is also formed by reducing 4-bromo-2-nitroresorcinol dimethyl ether (Kauffmann and Franck, A., 1907, i, 1092) with tin and hydrochloric acid.

H. E. F. NOTTON.

Chloro- and bromo-derivatives of 2 : 4-dihydroxydiphenylmethane and their germicidal action. E. KLARMANN and J. VON WOWERN (J. Amer. Chem. Soc., 1929, 51, 605—610).—4'-Chloro-2 : 4-dihydroxybenzophenone, m. p. 155°, from *p*-chlorobenzonitrile and resorcinol in presence of zinc chloride, is reduced by amalgamated zinc and hydrochloric acid to 4'-chloro-2 : 4-dihydroxydiphenylmethane, b. p. 200—225°/5 mm., m. p. 80.4°, which is also formed

from *p*-chlorobenzyl chloride and resorcinol in nitrobenzene in presence of aluminium chloride. 4'-*Bromo*-2:4-dihydroxybenzophenone, m. p. 169°, and 4'-*bromo*-2:4-dihydroxydiphenylmethane, m. p. 96°, are prepared similarly. 5-*Chloro*-, m. p. 122°, and 5-*bromo*-, m. p. 122.4°, derivatives are obtained by cautious addition of sulphuryl chloride and bromine (1 mol.), respectively, to 2:4-dihydroxydiphenylmethane in ether. 5-*Chloro*-, m. p. 136.7°, and 5-*bromo*-, m. p. 152.1°, 2:4-dihydroxydiphenylethanes are prepared similarly. The halogen derivatives are much more strongly bactericidal than the parent phenols, but the former undergo a proportionately greater reduction in efficiency in presence of gelatin and peptone. The 4'-halogenophenols are more active than the corresponding 5-derivatives. H. E. F. NOTTON.

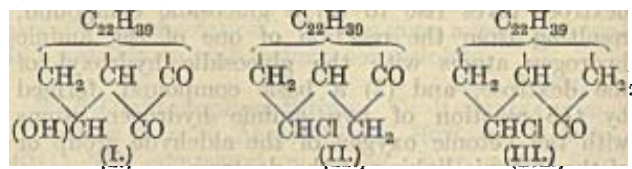
Molecular compounds from aromatic iodo-compounds. P. PFEIFFER, H. SCHMITZ, and T. INOUE (J. pr. Chem., 1929, [ii], **121**, 70—84).—Several iodo-derivatives of diphenyl and stilbene have been prepared and the possibility of compound formation with metallic salts, aromatic bases, and ketones has been investigated. By the usual methods the following are prepared from the corresponding amino-compounds: 4-iododiphenyl, m. p. 112° [iodochloride, m. p. 102° (decomp.); iodoso-compound, m. p. 225—230° (not pure)]; 4:4'-di-iodo-, m. p. 109—110°, 4:4'-dichloro-, m. p. 58—58.5°, and 4:4'-dibromo-, m. p. 71°, -3:3'-ditolyl (lit. gives m. p. 99—100°, 51°, and 58—59°, respectively); 4:4'-di-iodo-3:3'-dimethoxydiphenyl, m. p. 181.5—183° [iodochloride, m. p. 109—110° (decomp.)]; 4:4'-di-iodo-3:3'-dinitrodiphenyl, m. p. 246—247°; 4-iodostilbene, m. p. 152°; 4-iodo-2-nitrostilbene, m. p. 110°; 4-iodo-2-nitro-4'-methoxystilbene, m. p. 100—100.5°. By thermal analysis it is shown that no compounds are formed by these iodine derivatives with mercuric chloride or iodide, silver nitrate, piperonylideneacetophenone, dipiperonylideneacetone, sarcosine anhydride, α -naphthol, menthol, α -naphthylamine, or *s*-trinitrobenzene. Only in the case of dianisylideneacetone (2 mols.) and 4-iododiphenyl (1 mol.) is a compound formed. J. W. BAKER.

Action of aromatic aldehydes on phenols. O. HINSBERG (Ber., 1929, **62**, [B], 418—421).—Compounds provisionally regarded as derivatives of 9:10-diphenyl-9:10-dihydroanthracene are obtained when equivalent quantities of an aromatic aldehyde and phenol are heated with glacial acetic and concentrated hydrochloric acids under pressure. Thus benzaldehyde and phenol at 100° afford, after treatment of the product with acetic anhydride and a little zinc dust, 2:7(+2:6)-diacetoxy-9:10-diphenyl-9:10-dihydroanthracene, m. p. above 202°, hydrolysed to 2:7(+2:6)-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene, which darkens and softens at about 250°. Oxidation of the diacetoxydihydro-compound with potassium dichromate and glacial acetic acid yields 2:7(+2:6)-diacetoxy-9:10-diphenylanthracene, m. p. 215—235°, which is hydrolysed by alkali hydroxide to 2:7(+2:6)-dihydroxy-9:10-diphenylanthracene hydrate, $C_{26}H_{20}O_3$, derived from benzaurin. The hydrate crystallises with 1 mol. of water, which is removed at 120°, but the removal

of a second molecule of water, which should lead to dihydroxydiphenylanthracene, could not be effected. *p*-Cresol and *p*-nitrobenzaldehyde yield 4:5(+4:8)-dihydroxy-9:10-di-*p*-nitrophenyl-1:8(+1:5)-dimethyl-9:10-dihydroanthracene, m. p. above 270°.

H. WREN.

Oxidation of cholesterol with chromic acid. S. MINOVICI and M. VANGHELOVICI (Bull. Soc. Chim. Romania, 1928, **10**, 91—96).—The substance obtained by Mauthner and Suida (A., 1896, i, 425) by hydrolysis of the product of oxidation of cholesteryl acetate with chromic acid has now been obtained from cholesterol by oxidation with chromic acid in glacial acetic acid; it has m. p. 216—217° (decomp.), empirical formula $C_{27}H_{44}O_3$. The structure I is suggested. Cholesteryl chloride, similarly oxidised, yielded a neutral ketonic substance, $C_{27}H_{45}OCl$, m. p. 137° (*p*-nitrophenylhydrazone, m. p. 200°), isomeric with that obtained by Windaus (A., 1904, i, 1010) and that obtained by Mauthner (*ibid.*, 49). The *cis*- and *trans*-forms of II and III are possible structures for these isomerides.



C. W. SHOPPEE.

Cholesterol and its relations with the terpenes. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], **45**, 97—100).—The terpenic structure for cholesterol suggested by Steinle and Kahlenberg (A., 1926, 633) rests on inconclusive evidence, since certain unsaturated fatty acids give similar colour reactions with antimony pentachloride and the terpenes themselves do not give Liebermann's reaction. Cholesterol is converted by sulphuric and acetic acids into β -cholesterylene; terpenes yield an isomerisation or a hydration product with this reagent. Formic acid, which converts cholesterol into its formate, produces isomerisation with certain terpenes, and similarly with phthalic anhydride at 220°, which converts sesquiterpene alcohols into the hydrocarbons, cholesterol affords its phthalate, m. p. 157°. The sterols are accordingly regarded as constituting a distinct type of compound and not as belonging to the terpeno group. The formation of chrysene and homologous hydrocarbons by distilling cholesterol is attributed to the condensation of the indene rings from two molecules of cholesterol.

R. BRIGHTMAN.

Reactions of cholesterol. E. BAHL (Biochem. Z., 1929, **204**, 474).—Cholesterol gives a yellowish-brown coloration with a solution of benzidine in glacial acetic acid and an intensely red coloration with a faintly pink solution of rosaniline in chloroform. Both tests are parallel to those of Salkowski and Liebermann.

W. MCCARTNEY.

Preparation of styrene (with a note on the detection and identification of β -phenylethyl alcohol). S. SABETAY (Bull. Soc. chim., 1929, [iv], **46**, 69—75).— β -Phenylethyl alcohol when distilled with dry potassium hydroxide is converted quantitatively into styrene, b. p. 52—53°/28 mm., 143°/760

mm., 1.5440, d_{20}^{20} 0.9038. β -*p*-Tolylethyl alcohol is similarly converted into *p*-methylstyrene, b. p. 170—173° (dibromide, m. p. 45°). β -2-Naphthylethyl alcohol behaves similarly, but γ -phenylpropyl alcohol and phenylethylcarbinol are not dehydrated under these conditions. Phenylmethylcarbinol is partly decomposed but affords no styrene. The reaction is regarded as characteristic of the group $\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ and is attributed to the influence of the phenyl group on the mobility of the neighbouring hydrogen atom. The reaction can be applied to the detection or approximate determination of β -phenylethyl alcohol in mixtures, e.g., with rhodinol or geraniol, the styrene formed being converted into dibromide. R. BRIGHTMAN.

Comparison of the stability of isomerides according to their absorption spectra. Allyl and isoallyl derivatives of the benzene series. (MME.) RAMART-LUCAS and (MLE.) AMAGAT (Compt. rend., 1929, 188, 638—640).—The isoallyl derivatives of the benzene series have the ascending branch of their ultra-violet absorption curves nearer the visible than those of the allyl isomerides and therefore conform to the rules suggested by Ramart-Lucas (A., 1928, 1000), the latter being transformed into the former by heat. It is shown that whilst γ -phenyl-*n*-propyl alcohol gives allylbenzene on dehydration with thionyl chloride, it will also give the iso-compound when dehydrated at a sufficiently high temperature. The following are prepared by reduction of the corresponding amides: γ -anisyl-*n*-propyl alcohol, b. p. 160°/15 mm., m. p. 26°; and γ -piperonyl-*n*-propyl alcohol, b. p. 180°/13 mm. J. GRANT.

Ephedrine and structurally similar compounds. I. Synthesis of ephedrine. R. H. F. MANSKE and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 580—582).— α -Phenylpropane- α - β -dione, prepared from propiophenone and nitrogen peroxide, yields with anhydrous methylamine in light petroleum unstable β -methylimino- α -phenylpropan- α -one, which is hydrogenated (platinum) in alcohol to *dl*-ephedrine and (contrast other syntheses, A., 1920, i, 875; 1921, i, 45) only a little ψ -ephedrine. H. E. F. NOTTON.

Ultra-violet absorption of *p*-aminobenzoic esters in water solution. E. R. RIEGEL and K. W. BUCHWALD (J. Amer. Chem. Soc., 1929, 51, 484—492).—Ultra-violet absorption spectra (to 2100 Å.) are recorded for aqueous solutions of (a) *p*-aminobenzoic acid and the following *p*-aminobenzoates: methyl, ethyl, propyl, butyl, γ -di-*n*-butylamino-propyl and its sulphate (butyn), β -diethylamino-ethyl and its hydrochloride (procaïne), γ -dimethylamino- α - β -dimethylpropyl and its hydrochloride (tutocaine); also *p*-hydroxybenzoic acid; (b) *p*-dimethylaminobenzoic acid, aniline and its hydrochloride, benzoic acid, α -methyl- α -dimethylaminomethylpropyl benzoate hydrochloride (stovaine), α -bisdimethylaminomethylpropyl benzoate hydrochloride (alypine), cocaine sulphate, and benzene. The compounds in group (a) all show an intense absorption band which is of the same order of persistence as that previously found for substances of *p*-quinonoid structure (A., 1926, 734). It is therefore suggested that these exist in solution mainly

in the form $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{OR}$, and this is confirmed by the observation that compounds which cannot isomerise in this way such as those in group (b) exhibit only a weak selective absorption. Nitro- and nitroamino-guanidine in water show an intense band, but guanidine carbonate has no selective absorption in this region. H. E. F. NOTTON.

Sulphonphthaleins. W. C. HARDEN and N. L. DRAKE (J. Amer. Chem. Soc., 1929, 51, 562—566).—The following have been prepared by heating together a phenol and a tetrahalogeno-*o*-sulphobenzoic anhydride, alone, or in presence of stannic chloride at 120—140°: phenoltetrachlorosulphonphthalein (tetrabromo-derivative), phenoltetrabromosulphonphthalein (tetrabromo-derivative), *o*-cresoltetrachlorosulphonphthalein (dibromo-derivative), *o*-cresoltetrabromosulphonphthalein (dibromo-derivative), and *o*-cresoltetraiodosulphonphthalein (dibromo-derivative). The colour changes and useful p_H ranges of the products are tabulated. They are, in general, similar to those of the corresponding non-halogenated products. H. E. F. NOTTON.

Quinonoid tautomerism. Chlorination of *p*-nitrophenylacetonitrile. V. NEKRASSOV and A. V. SOKOLOV (Ber., 1929, 62, [B], 463—466).—*p*-Nitrophenylacetonitrile is converted by chlorine at 120° in bright daylight into dichloro-*p*-nitrophenylacetonitrile, $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{CCl}_2\cdot\text{CN}$, b. p. 149—149.5°/0.6 mm., d_{20}^{20} 1.4465, n_D^{20} 1.5710, hydrolysed by a boiling mixture of concentrated hydrochloric acid and ether to dichloro-*p*-nitrophenylacetic acid, m. p. 171—172° (slight decomp.). Oxidation of the nitrile by alkaline permanganate or hydrolysis of it by hydrobromic or sulphuric acid affords *p*-nitrobenzoic acid. Alcoholic solutions of the nitrile are coloured intensely permanganate-red by alkali and slowly become yellow when preserved. The colour disappears when the solutions are acidified but returns after addition of excess of alkali. Since a quinonoid or an imide structure cannot be attributed to the coloured salts, the constitution of the salt-like derivatives of the nitrophenylacetonitriles and analogous compounds cannot be regarded as established. H. WREN.

Nitritotricarboxylic acids. G. L. STADNIKOV and N. G. TITOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1501—1503).—The behaviour of α -phenyl- α' -dimethylnitritotriacetic acid (I) and the anhydride of α -phenyl- α' - α'' -tetramethylnitritotriacetic acid (II) in the presence of concentrated hydrochloric acid at 160° was investigated, to determine their stability. The acids were readily decomposed first to α -phenyl- α' -methyliminodiacetic (III) and α -phenyl- α' -dimethyliminodiacetic (IV), and then finally to aminophenylacetic acid. M. ZVEGINTZOV.

Synthesis of [2-]phenylindones from cinnamonnitriles. P. PFEIFFER, H. BEHR, H. KUBLER, and H. RUFING (J. pr. Chem., 1929, [ii], 121, 85—96).—The formation of 2-phenylindone derivatives by the action of sulphuric acid on phenylcinnamonnitrile (Pfeiffer and others, this vol., 184) has been extended to substituted derivatives of the general type $(p)\text{R}_1\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{C}_6\text{H}_4\cdot\text{R}_2(p)$. Only the *cis*-compound, the cyano-group of which is not hydrolysed by alcoholic hydrogen chloride, yields the indene

derivative and then only when $R_1=H$ or, with less ease, Cl , but not when $R_1=MeO$, NMe_2 , or NO_2 . Thus from the appropriate phenylcinnamionitrile are obtained 2-*p*-nitrophenylindone, m. p. 156—157° ($R_1=H$, $R_2=NO_2$); 6-chloro-2-*p*-nitrophenylindone, m. p. 195°, together with *p*-chloro- α -*p*-nitrophenylcinnamamide, m. p. 230° ($R_1=Cl$, $R_2=NO_2$); 2-*p*-carboxylamidophenylindone, m. p. 198°, from α -*p*-dicyanostilbene, m. p. 146—147° (obtained by condensation of *p*-cyanophenylacetonitrile with benzaldehyde), which is converted by methyl-alcoholic hydrogen chloride into methyl α -cyanostilbene-*p*-carboxylate, m. p. 146—147° (ethyl ester, m. p. 133—134°). On the other hand, α :4-dicyano-4'-methoxystilbene, m. p. 161—162° ($R_1=MeO$, $R_2=CN$), obtained by condensation of anisaldehyde with *p*-cyanophenylacetonitrile, yields no indone derivative, but is hydrolysed to methyl α -cyano-4'-methoxystilbene-4-carboxylate, m. p. 158°. Similarly, α :4-dicyano-4'-dimethylaminostilbene is converted by sulphuric acid into the corresponding diamide, m. p. 268°, which is hydrolysed by boiling 10% sodium hydroxide to α -carboxylamido-4'-dimethylaminostilbene-4-carboxylic acid, m. p. 264° (sodium and barium salts; methyl, m. p. 217°, and ethyl, m. p. 185°, esters). J. W. BAKER.

Mechanism of the reaction between organo-magnesium compounds and *N*-substituted cinnamanilides. N. MAXIM and N. IOANID (Bul. Soc. Chim. Romania, 1928, 10, 116—126; cf. A., 1928, 1004).—To distinguish between 1:2- and 1:4-addition of magnesium alkyl halides to *N*-substituted cinnamanilides, $CHPh:CH_2C(=O)NRPh$, decomposition of the organo-metallic complex has been effected with acetyl chloride; in the former case a ketone-anilide, yielding by hydrolysis a saturated ketonic acid, should result, whereas the product obtained is an unsaturated acetoxy-anilide, hydrolysed to a saturated acid, conforming to 1:4-addition. α -Phenylmethylamino- α -acetoxy- $\gamma\gamma$ -diphenyl- Δ^a -propylene, m. p. 154°, is obtained when the complex formed by magnesium phenyl bromide and *N*-methylcinnamanilide is treated with ethereal acetyl chloride; from the appropriate *N*-substituted cinnamanilides are obtained similarly: α -phenylethylamino- α -acetoxy- $\gamma\gamma$ -diphenyl- Δ^a -propylene, m. p. 138°, and α -diphenylamino- α -acetoxy- $\gamma\gamma$ -diphenyl- Δ^a -propylene, m. p. 148°. These acetoxy-compounds by hydrolysis with alcoholic potassium hydroxide yield respectively $\beta\beta$ -diphenylpropionmethylanilide, b. p. 261°/13 mm., $\beta\beta$ -diphenylpropionethylanilide, b. p. 278°/25 mm., and $\beta\beta$ -diphenylpropionic acid. The foregoing anilides are further hydrolysed by 40% hydrobromic acid to $\beta\beta$ -diphenylpropionic acid. C. W. SHOPPEE.

Hydrogenation of δ -lactones. C. MANNICH and A. BUTZ (Ber., 1929, 62, [B], 461—463; cf. this vol., 443).—Hydrogenation of the lactone of δ -hydroxy- $\beta\delta$ -diphenyl- Δ^a -pentenoic acid in acetone in presence of palladised charcoal proceeds without noticeable break until 2 mols. of hydrogen have been absorbed and yields $\beta\delta$ -diphenyl-*n*-valeric acid, m. p. 109—110°, also obtained in moderate yield by reduction of γ -benzoyl- β -phenylbutyric acid by amalgamated zinc and concentrated hydrochloric acid. If hydrogen-

ation is interrupted after 1 mol. of hydrogen has been absorbed, the product contains initial and fully hydrogenated substances together with the lactone of δ -hydroxy- $\beta\delta$ -diphenyl-*n*-valeric acid, m. p. 117°. Similarly, the lactone of δ -hydroxy- δ -phenyl- β -methylenedioxyphenyl- Δ^a -pentenoic acid affords δ -phenyl- β -methylenedioxyphenyl-*n*-valeric acid, m. p. 138—139° (derived also from γ -benzoyl- β -methylenedioxyphenylbutyric acid), and the lactone of δ -hydroxy- δ -phenyl- β -methylenedioxyphenyl-*n*-valeric acid, m. p. 132—133°. The reduction does not appear general, since the lactone of α -hydroxy- β -phenyl-*n*-valeric acid is not hydrogenated in the presence of palladium; the presence of a phenyl group in the δ -position appears to be the determining factor. H. WREN.

Constituents of kawa root. VIII. Kawaic acid. W. BORSCHKE and W. PEITZSCH (Ber., 1929, 62, [B], 368—373; cf. Borsche and Roth, A., 1921, i, 862; Murayama and others, A., 1922, i, 265).—Improved methods of treatment of kawa resin have yielded kawaic acid, m. p. 186° (decomp.), to which the composition $C_{14}H_{14}O_3$ instead of $C_{13}H_{12}O_3$ is now ascribed. The acid is distinguished from methystic acid by the absence of the methylenedioxy-group. Its stability towards alkali and ready conversion by acid into methyl alcohol and γ -cinnamylideneacetoacetic acid (or carbon dioxide and cinnamylideneacetone) show it to be β -methoxy- ζ -phenyl- $\Delta^{a\gamma\epsilon}$ -heptatrienoic acid, and this conception is confirmed by the partial demethylation of its methyl ester to methyl γ -cinnamylideneacetoacetate. Towards catalytic reduction, kawaic acid behaves similarly to methystic acid in that only two of its three ethylenic linkings are readily saturated. Tetrahydrokawaic acid (β -methoxy- ζ -phenyl- Δ^a -heptenoic acid), m. p. 109—110°, is smoothly decarboxylated when distilled under reduced pressure to β -methoxy- ζ -phenyl- Δ^a -hexene, b. p. 136—138°/16 mm. (converted by protracted boiling with alcoholic semicarbazide into the semicarbazone of ζ -phenylhexan- β -one, m. p. 141—142°), and decomposed by dilute acids into methyl alcohol, carbon dioxide, and ζ -phenylhexan- β -one. It is very slowly reduced to β -methoxy- ζ -phenylheptenoic acid. Synthesis of tetrahydrokawaic acid is effected by the action of a large excess of diazomethane on methyl β -keto- ζ -phenylheptate followed by hydrolysis of that portion of the product which is insoluble in alkali.

It appears probable that kawaic acid does not exist pre-formed in kawa resin, but as a doubly unsaturated lactone "kawain." H. WREN.

Catalytic hydrogenation of different types of unsaturated compounds. IV. Hydrogenation of conjugated systems: piperic acid. S. V. LEBEDEV and A. O. YAKUBCHIK (J.C.S., 1929, 220—225).—The catalytic hydrogenation of piperic acid as the potassium salt in aqueous solution with colloidal palladium (cf. Paal, A., 1912, i, 703) has been re-investigated, and found to conform to type II of the authors' classification (cf. A., 1928, 613). Hydrogenation proceeds similarly in alcoholic solution in the presence of platinum-black, and in both cases it is shown that dihydropiperic acids are formed prior to the tetrahydro-acid. Thus, using the former

method, the product of 50% hydrogenation contains 34.3% of unchanged piperic acid, 31.4% of dihydro- and 34.3% of tetrahydro-acid; with the latter method the corresponding figures are 26.3%, 47.4%, and 26.3%. The position of the "critical point," i.e., the point at which all piperic acid is exhausted, depends on the catalyst used and occurs at 75–76% of the hydrogen absorption in alcohol with platinum-black, and at 68–70% in water with palladium. The shapes of the hydrogenation curves, which are strikingly different beyond the critical point, and their interpretation are discussed.

C. W. SHOPPEE.

Molecular compounds of bile acids with fatty acids and alcohols. I. Deoxycholic and apocholic acids. H. RHEINOLDT [with E. FLUME and O. KÖNIG] (Z. physiol. Chem., 1929, 180, 180–186).—Complex molecular compounds have been prepared from the following substances and deoxycholic acid, the number of mols. of the latter per 1 mol. of the former being given in parentheses: palmitic acid (8), m. p. 184–185°; stearic acid (8), m. p. 186–187°; cetyl alcohol (8), m. p. 185–186°, and from the same substances and apocholic acid: palmitic acid (8), m. p. 184–185°; stearic acid (8), m. p. 185–186°; cetyl alcohol (8), m. p. 182.5°. H. BURTON.

Constituents of kawa root. VII. ψ -Methysticin. W. BORSCHÉ and W. PERTZSCH (Ber., 1929, 62, [B], 360–367; cf. A., 1927, 1192; Winzheimer, A., 1908, i, 805).— ψ -Methysticin is dihydromethysticin containing methysticin, since the volume of hydrogen used in its catalytic hydrogenation is only a fraction of that required to convert an equal weight of methysticin into homogeneous dihydromethysticin. This conception of the change is in accordance with the evidence of optical activity and with the observation that the methyl ester of " ψ -methystic acid," obtained by the action of sodium methoxide on ψ -methysticin, is separable by ether into methyl dihydromethystate, m. p. 50–51°, and methyl methystate, m. p. 162–163°. ψ -Methysticin can be prepared artificially by crystallising a mixture of methysticin and its dihydro-compound from methyl alcohol. The mixed crystals thus obtained cannot be separated smoothly into their components by repeated crystallisation and, since both compounds are found in kawa root, it is doubtful if homogeneous methysticin has ever been isolated.

Catalytic reduction of methysticin proceeds in three distinct phases with very differing rapidities. Dihydromethysticin, m. p. 117–118°, $[\alpha]_D^{25} +20.57^\circ$ in methyl alcohol, is the initial product. It is converted by sodium methoxide or *N*-potassium hydroxide into the optically inactive dihydromethystic acid (β -methoxy- ζ -methylenedioxyphenyl- $\Delta^{\alpha\gamma}$ -heptadienoic acid), m. p. 146–147° (decomp.) [methyl ester, m. p. 50–51°], transformed by boiling *N*-sulfuric acid into dihydromethysticone (methyl δ -methylenedioxyphenyl- Δ^{α} -butenyl ketone), b. p. 196–198°/14 mm. [2:4-dinitrophenylhydrazone, m. p. 147–148°; methysticone-2:4-dinitrophenylhydrazone has m. p. 236–237° (decomp.)]. The quantitative conversion of methysticin into its dihydro-derivative appears impossible, since tetrahydromethystic acid

is always produced even when only 1 mol. of hydrogen is used. The acid is more readily prepared by reduction of methystic acid. It is converted by distillation under diminished pressure into carbon dioxide and β -methoxy- ζ -methylenedioxyphenyl- Δ^{α} -hexene, b. p. 176–177°/14 mm., transformed by warm, dilute mineral acids into tetrahydromethysticone identified as the 2:4-dinitrophenylhydrazone, m. p. 129–130°. Catalytic reduction of the tetrahydro-acid to hexahydromethystic acid [β -methoxy- ζ -methylenedioxyphenylheptonic acid], m. p. 66–67°, is unexpectedly difficult. H. WREN.

Electrolytic reduction of the imides of cyclic acids. K. N. MENON and J. L. SIMONSEN (J.C.S., 1929, 302–305).—A preliminary account of work directed to the synthesis of cyclic 1-carboxy-2-acetic acids (cf. this vol., 52) by electrolytic reduction of cyclic dicarboxylamides in acid solution at 0–5° (cf. Tafel and Eckstein, A., 1902, i, 43). The imides were prepared by treatment of the anhydrides with dry ammonia at 180°. Caronimide, m. p. 120°, on reduction gave a 5% yield of 4:4-dimethyl-2-piperidone, liquid (benzoyl derivative, m. p. 114°; phosphomolybdate; phosphotungstate), with fission of the cyclopropane ring (cf. Iyer and Simonsen, A., 1926, 1042; Harihan, Menon, and Simonsen, A., 1928, 395). cycloButane-1:2-dicarboxylimide, m. p. 121°, yielded 15% of the γ -lactam of 2-aminomethylcyclobutane-1-carboxylic acid, m. p. 127–128° (nitroso-derivative, liquid; phosphomolybdate; phosphotungstate); cyclopentane-1:2-dicarboxylimide, m. p. 90°, gave a 25% yield of the γ -lactam of 2-aminomethylcyclopentane-1-carboxylic acid, m. p. 83° (p-nitrobenzoate, m. p. 123°; nitroso-derivative, liquid), which was unaffected by 10% baryta at 180°. Conversion into the nitroso-derivatives followed by treatment with warm 10% sodium hydroxide yielded the sodium salts of 2-hydroxymethylcyclobutane-1-carboxylic acid, and 2-hydroxymethylcyclopentane-1-carboxylic acid, respectively, isolated as the corresponding γ -lactones.

C. W. SHOPPEE.

Crystalline anhydrides of monosubstituted malonic acids. C. MANNICH and A. BUTZ (Ber., 1929, 62, [B], 456–460).— β -Benzoyl- α -phenylethylmalonic acid is converted by thionyl chloride in benzene at 70° into β -benzoyl- α -phenylethylmalonic anhydride, $\text{CH}_2\text{Bz}\cdot\text{CHPh}\cdot\text{CH}\begin{smallmatrix} \text{OO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix}\text{O}$, m. p. 153–154°, slowly converted by water or sodium carbonate, rapidly by sodium hydroxide, into the acid. With ethyl alcohol and ammonia respectively it affords ethyl hydrogen β -benzoyl- α -phenylethylmalonate, m. p. 122° (obtained also by semi-hydrolysis of the di-ester) and β -benzoyl- α -phenylethylmalonamic acid, m. p. 151° (decomp.) (ammonium salt). The anhydride decomposes at 175–205°/vacuum into carbon dioxide and the lactone of δ -hydroxy- $\beta\delta$ -diphenyl- Δ^{γ} -pentenoic acid, m. p. 88–89°, converted into methyl γ -benzoyl- β -phenylbutyrate, m. p. 94°, and γ -benzoyl- β -phenylbutyramide, m. p. 159°. Piperonylideneacetophenone and ethyl malonate afford ethyl β -benzoyl- α -methylenedioxyphenylethylmalonate, m. p. 94°, hydrolysed to β -benzoyl- α -methylenedioxyphenylethylmalonic acid, m. p. 159° (decomp.) (potassium hydrogen salt), which

is transformed by thionyl chloride into β -benzoyl- α -methylenedioxyphenylethylmalonic anhydride, m. p. 192° (decomp.). β -Benzoyl- α -methylenedioxyphenylethylmalonic acid, m. p. 145° (ammonium salt), and the lactone of α -hydroxy- δ -phenyl- β -methylenedioxyphenyl- Δ^7 -pentenoic acid, m. p. 94°, are described. The lactone is also prepared by boiling γ -benzoyl- β -methylenedioxyphenylbutyric acid, m. p. 154—155°, with acetic anhydride. γ -Benzoyl- β -methylenedioxyphenylbutyramide, m. p. 156°, is described. β -Acetyl- α -phenylethylmalonic acid yields the corresponding anhydride, m. p. 129°, from which ethyl hydrogen β -acetyl- α -phenylethylmalonate, m. p. 106°, and the lactone of δ -hydroxy- β -phenyl- Δ^7 -hexenoic acid, b. p. 167°/12 mm., are derived. H. WREN.

Chlorination of phthalic acid in alkaline solution. E. E. AYLING (J.C.S., 1929, 253—256).—Chlorination of phthalic acid in alkaline solution (cf. Auerbach, Chem.-Ztg., 1880, 4, 407; see also A., 1894, i, 289; 1913, i, 269; J.C.S., 1921, 119, 1788) proceeds most satisfactorily with 3 mols. excess of potassium hydroxide, yielding mainly 4-chlorophthalic acid together with some 4 : 5-dichlorophthalic acid. The mixed acids are readily separated by conversion into the methyl esters and fractional distillation; methyl 4-chlorophthalate, b. p. 186—187°/32 mm., m. p. 38° (cf. lit.), yields on hydrolysis 4-chlorophthalic acid, m. p. 151° (cf. von Braun, A., 1924, i, 48, m. p. 157°), converted by acetyl chloride into 4-chlorophthalic anhydride, m. p. 97°. A neutral phthalate solution reacts with chlorine but not with hypochlorite (cf. A., 1913, i, 269) and the reaction is regarded as direct chlorination of the phthalate, the excess of alkali yielding alkali chloride which assists isolation of the chlorinated products by salting out. With sodium hydroxide a much larger proportion of dichloro-acid is formed, which is attributed to the smaller solubility of potassium hydrogen 4-chlorophthalate than the sodium hydrogen salt, and is considered to support the above view of the reaction mechanism. C. W. SHOPPEE.

Naphthalic acid derivatives. K. DZIEWONSKI, O. GESCHWINDOWNA, and L. SCHIMMER (Bull. Acad. Polonaise, 1928, A, 507—522).—4-Bromonaphthalic anhydride, m. p. 221—222°, with methyl sulphate and aqueous sodium hydroxide furnishes methyl 4-bromonaphthalate, m. p. 102—103°; when treated with hydrazine sulphate in glacial acetic acid in the presence of sodium acetate at 100° it yields 4-bromonaphthalaminoimide, $C_{10}H_5Br \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot NH_2$, m. p. 217°; nitration with nitric acid (*d* 1.52) and sulphuric acid affords a dinitro-4-bromonaphthalic anhydride, m. p. 234—235°; fusion with potassium hydroxide at 225—230° yields, contrary to the literature, 3-hydroxynaphthalic anhydride, m. p. 279—280° (characterised as 4-benzeneazo-3-hydroxynaphthalic anhydride), the wandering of the hydroxyl group being explained by the initial addition of the elements of water in the 3-position, followed by substitution of the bromine in the 4-position by hydroxyl and subsequent elimination of water. Sulphonation of 4-bromonaphthalic anhydride with fuming sulphuric acid (25% SO_3) gives 4-bromo-3-

sulphonaphthalic anhydride [sodium salt; barium salt; aniline salt, m. p. 270°; sulphonyl chloride (I), m. p. 183—184°; 4-bromo-3-amidosulphonylnaphthalimide, m. p. 338°, by the action of concentrated aqueous ammonia on I at 100°]. 4-Chloronaphthalic anhydride, m. p. 216—217°, with fuming sulphuric acid (25% SO_3) gives 4-chloro-3-sulphonaphthalic anhydride (sodium salt; barium salt; aniline salt, m. p. 257°; sulphonyl chloride, m. p. 180—181°; 4-chloro-3-amidosulphonylnaphthalimide, m. p. 318°). 3 : 4-Disulphonaphthalic acid (barium salt) is prepared by the direct sulphonation of naphthalic acid with fuming sulphuric acid (*d* 1.9) or by the action of oleum (25% SO_3) on the 3-sulphonic acid. The anhydride forms a sodium aniline salt, m. p. above 360°, and a disulphonyl chloride, m. p. 192° (decomp.), giving 3 : 4-diamidosulphonylnaphthalimide, m. p. above 350°. The sodium salt of the disulphonaphthalic acid when fused with excess of potassium hydroxide at 180° furnished 3 : 4-dihydroxynaphthalic anhydride (II), m. p. 330°, identical with the product obtained at 240—260° from 4-bromo- and at 140—180° from 4-chloro-3-sulphonaphthalic acid by fusion with potassium hydroxide. The following derivatives of II are described: dimethyl ether, m. p. 280°; diacetyl derivative, m. p. 260°; dibenzoyl derivative, m. p. 235—236°; monophenylhydrazone, m. p. 252°; dinitro-derivative, m. p. 272° (decomp.), by the action of nitric acid (*d* 1.48) and glacial acetic acid at 40°; 3 : 4-dihydroxynaphthalphenylimide, m. p. 363°. A. I. VOGEL.

Diphenic acid series. III. H. W. UNDERWOOD, jun., and L. A. CLOUGH (J. Amer. Chem. Soc., 1929, 51, 583—587).—Methyl, methyl hydrogen, ethyl, and ethyl hydrogen diphenates do not react with acetic anhydride in glacial acetic acid at 145°. Diphenamic acid is converted by this mixture into diphenimide and a little 2-cyanodiphenyl-2'-carboxylic acid, m. p. 168°, and diphenamide into 2 : 2'-dicyanodiphenyl, m. p. 172°. 4 : 4'-Dibromodiphenic acid, unlike the 4 : 4'-dinitro-derivative, readily forms an anhydride. This indicates that anhydride formation is connected with the *op*-directing power of the substituents. In reply to Adkins' criticisms (A., 1924, i, 1198) it is shown that condensation of diphenic anhydride and resorcinol at 135° or 175° yields a mixture of products (cf. A., 1924, i, 176). The m. p. of resorcinoldiphenic is 178—179°, changing to 247—249° on keeping or heating.

H. E. F. NOTTON.

Derivatives of cyclobutanol. L. BLANCHARD (Compt. rend., 1929, 188, 503—504).—Condensation of α -dibromoisopropyl amyl ether with ethyl disodiummalonate yields ethyl 3-amyloxycyclobutane-1 : 1-dicarboxylate, b. p. 175°/12 mm., *d*¹² 1.011, *n*_D 1.44361, giving by hydrolysis 3-amyloxycyclobutane-1 : 1-dicarboxylic acid (copper salt). The acid loses 1 mol. of carbon dioxide at 155°, yielding 3-amyloxycyclobutane-1-carboxylic acid, b. p. 164—166°/10 mm., *d*¹² 1.003, *n*_D 1.45112 (silver salt).

B. W. ANDERSON.

Syringic acid and derivatives. M. T. BOGERT and B. B. COYNE (J. Amer. Chem. Soc., 1929, 51, 569—576).—Improved preparations of trimethyl-

gallic (3 : 4 : 5-trimethoxybenzoic) acid, syringic acid (4-hydroxy-3 : 5-dimethoxybenzoic acid; cf. A., 1919, i, 483), methyl syringate, and acetylsyringic acid (methyl ester) are described. The last is nitrated in acetic anhydride by fuming nitric acid at -5° to *nitroacetylsyringic acid*, m. p. 190° (decomp.) [methyl ester, m. p. 107.5° (corr.)], which is hydrolysed by boiling 5% hydrochloric acid to *nitrosyringic acid*, m. p. 218° , softening at 213° . This gives a *methyl ester*, m. p. 210° , but the preparation of the ester of m. p. 68.3° (A., 1916, i, 146) could not be repeated. Nitrosyringic acid is reduced by stannous chloride and hydrochloric acid at 45° to *aminosyringic acid*, m. p. 169° (decomp.) (*hydrochloride*, m. p. 185° ; *chlorostannate*), and by tin and boiling hydrochloric acid or by ferrous hydroxide to 3-amino-2 : 6-dimethoxyphenol hydrochloride, m. p. 198° (*benzoyl derivative*, m. p. 158.3°). Methyl aminosyringate, m. p. 126.5° (hydrochloride, m. p. 217° , darkening from 192°), gives on diazotisation and treatment with cuprous oxide methyl syringate. When kept with acetic anhydride and sodium acetate, aminosyringic acid yields the *diacetyl derivative*, m. p. 169° , of aminosyringic lactam, which is hydrolysed by hot water to *acetamidacetylsyringic acid*, m. p. 193° (methyl ester, m. p. 154° ; cf. *loc. cit.*). *Methylene-aminosyringic acid*, m. p. 195° (decomp.), from aminosyringic acid and formaldehyde in dilute hydrochloric acid, could not be converted into an indigotin derivative.

H. E. F. NOTTON.

6-Hydroxypiperonylic acid and allied compounds. M. T. BOGERT and F. R. ELDER (J. Amer. Chem. Soc., 1929, 51, 532—539).—The oxime of 6-nitropiperonal (*diethylurethane*, m. p. $207-208^{\circ}$) has been reduced to 6-aminopiperonaloxime, m. p. $182-183^{\circ}$ (cf. Haber, A., 1891, 704), which is converted by acetic anhydride and sodium acetate into 6-acetamidopiperonylonitrile and on further action into 6-diacetamidopiperonylonitrile, m. p. $146-147^{\circ}$. 6-Nitropiperonal has been converted into 6-aminopiperonal by the method of Riliet and Kreitmann (A., 1913, i, 1355) and also by direct reduction with ferrous sulphate and ammonia. 6-Acetamidopiperonal is oxidised by neutral permanganate to 6-acetamidopiperonylic acid, m. p. $124-125^{\circ}$. The diazonium salt from methyl 6-aminopiperonylate (cf. Oertly and Pictet, A., 1910, i, 485) (*acetyl derivative*, m. p. $183-184^{\circ}$) is converted by boiling aqueous copper sulphate into *methyl 6-hydroxypiperonylate*, m. p. $99-100^{\circ}$ (*acetyl derivative*, m. p. $97-98^{\circ}$), which is hydrolysed by 5% potassium hydroxide to 6-hydroxypiperonylic acid, m. p. $211-212^{\circ}$ (*acetyl derivative*, m. p. $155.5-156.5^{\circ}$, which is prepared and purified with difficulty).

H. E. F. NOTTON.

Indicators. XV. Phenolphthalein and some of its homologues. A. THIEL and L. JUNGFER (Z. anorg. Chem., 1929, 178, 49—72; cf. this vol., 41).—Determinations have been made of the absorption maxima in the visible region of the spectrum, the extinction in the ultra-violet, and of the p_H at which the colour change and subsequent bleaching with excess of alkali takes place for phenolphthalein and some of its homologues and derivatives. The asymmetric *o*- or *m*-substituted (with respect to the

central carbon atom of the side-chain) *p*-xylenolphthaleins are by far the most stable of these compounds towards alkalis. The mechanism of the bleaching action of excess of alkali on the phthaleins has been examined; the results indicate that the decolorisation is due to a splitting of the lactone ring and the entrance of a hydroxyl ion into the molecule to form a carbinolcarboxylic acid. An intermediate absorption of water into the molecule does not take place. A rise in the temperature of the solution displaces the equilibrium from the acid or from the alkaline colourless stage towards the intermediate coloured stage. The following new compounds have been prepared: *phenol-m-cresolphthalein* from *p*-hydroxybenzoyl-*o*-benzoic acid and *m*-cresol; *m-cresolphthalein*, m. p. 145° , from phthalyl chloride and *m*-cresol; and *p-xylenolphthalein*, m. p. 276° , from *p*-xylenol and phthalic anhydride. Condensation of *m*-cresol and phthalic anhydride with tin tetrachloride yields 2' : 2''-dimethylfluoran, m. p. $206-207^{\circ}$, in colourless crystals.

A. R. POWELL.

Synthesis of cyclobutane acids. I. Norpinic acid. C. A. KERR (J. Amer. Chem. Soc., 1929, 51, 614—619).—Attempts to prepare cyclobutane derivatives from methylene iodide and ethyl $\alpha\gamma$ -dibromo- $\alpha\beta\beta$ -trimethylglutarate or ethyl $\beta\beta$ -dimethylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate were unsuccessful. The sodio-derivative of $\alpha\gamma$ -dicyano- $\beta\beta$ -dimethylglutarimide (cf. Kon and Thorpe, J.C.S., 1919, 115, 686) is converted by methylene iodide in methyl alcohol into *dicyano-norpinimide* (1 : 3-dicyano-2 : 2-dimethylcyclobutane-1 : 3-dicarboxylimide), m. p. $305-306^{\circ}$ (*silver salt*). This is hydrolysed by acids with ring fission and by 2% sodium hydroxide to a mixture of *s-dicyano-norpinic acid* (1 : 3-dicyano-2 : 2-dimethylcyclobutane-1 : 3-dicarboxylic acid), m. p. $225-226^{\circ}$ (*methyl ester*, m. p. $139-140^{\circ}$), and *s-dicarbaminorpinic acid*, m. p. 190° . This is further hydrolysed by boiling water to *ammonium dihydrogen 1-carbamyl-2 : 2-dimethylcyclobutane-1 : 3 : 3-tricarboxylate* (free acid ?), and by aqueous sodium hydroxide to 2 : 2-dimethylcyclobutane-1 : 1 : 3 : 3-tetracarboxylic acid, m. p. 200° (*silver salt*; *methyl ester*, b. p. $100^{\circ}/25$ mm.), which is also obtained from the *s*-dicyano-derivative. It is decarboxylated at $200-205^{\circ}$ to *trans-norpinic acid* (cf. Perkin and Simonsen, J.C.S., 1909, 95, 1176).

H. E. F. NOTTON.

Synthesis of truxinic and truxillic acids. F. BACHÉ (J. pr. Chem., 1929, [ii], 120, 301—338; cf. A., 1928, 521).—Attempts have been made, generally without success, to synthesise truxinic and truxillic acids by direct methods. Thus, attempted condensation of stilbene dibromide and ethyl dipotassioethane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate yields stilbene; benzil and ethyl dibromosuccinate in presence of zinc afford hydrobenzoin; ethyl disodio- β -phenylpropane- $\alpha\alpha\beta\beta$ -tetracarboxylate and benzyldene chloride give ethyl benzylidenemalonate. When methyl benzylidenemalonate is reduced with aluminium amalgam in methyl alcohol about 20% of the two forms of methyl $\beta\gamma$ -diphenylbutane- $\alpha\alpha\delta\delta$ -tetracarboxylate, m. p. $163-164^{\circ}$ and $167-168^{\circ}$, respectively, are obtained (cf. *loc. cit.*). The previously described (*loc. cit.*) dimethyl dihydrogen 3 : 4-di-

phenylcyclobutane-1 : 1 : 2 : 2-tetracarboxylate, m. p. 203—205°, after elimination of carbon dioxide at 210° affords, in addition to methyl ζ -truxinate, a small amount of methyl δ -truxinate, m. p. 75—76°. Thus, two of the three theoretically possible truxinates are obtained from the *r*-diphenylbutanetetracarboxylate. The above methyl ester, m. p. 167—168°, is not convertible into a cyclobutane derivative, but on hydrolysis and elimination of carbon dioxide it yields the high-melting (*meso*) form of $\beta\gamma$ -diphenyladipic acid, thus demonstrating that the original ester is probably the *meso*-form, and that ring formation is not possible unless there is a swinging of the spatial configuration.

Addition of potassium to methyl benzylidenemalonate in toluene solution in an atmosphere of hydrogen, and decomposition of the resulting product with hydrochloric acid gives, in addition to oily products, some methyl $\beta\gamma$ -diphenylbutane- $\alpha\delta\delta$ -tetracarboxylate, m. p. 165—167°. The intermediate potassium derivative does not appear to be identical with that derived from the ester and potassium alkoxide. Condensation of benzil with ethyl cyanoacetate in presence of a small amount of piperidine or diethylamine gives *ethyl desylidenecyanoacetate* (I), $\text{CPhBz}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, m. p. 141° [methyl ester (II), m. p. 125°], also formed from benzil and ethyl bromocyanoacetate in presence of zinc and benzene. When a relatively large amount of base is used in the above condensation by-products are obtained, one of which is probably *ethyl $\alpha\alpha'$ -dicyano- β -benzoyl- β -phenylglutarate*, m. p. 172°. Hydrolysis of I and II with alcoholic potassium hydroxide affords *desylidenecyanoacetic acid* (III), m. p. 135°, whilst reduction with hydrogen in presence of alcohol and palladised barium sulphate affords *ethyl* (IV) and *methyl α -cyano- β -benzoyl- β -phenylpropionates*, m. p. 83° and 118°, respectively. Similar reduction of the sodium salt of III in aqueous solution gives *α -cyano- β -benzoyl- β -phenylpropionic acid*, m. p. 190° (decomp.). When bromodeoxybenzoin is condensed with ethyl sodio-cyanoacetate IV results. When IV is dissolved in piperidine or diethylamine a substance, m. p. 150°, having the same composition as the original ester, is obtained. The analogous compound from the corresponding methyl ester has m. p. 152°.

When ethyl disodioethane- $\alpha\alpha\beta\beta$ -tetracarboxylate is treated with benzoyl chloride in presence of toluene *ethyl $\alpha\beta$ -dibenzoylthane- $\alpha\alpha\beta\beta$ -tetracarboxylate*, m. p. 91°, results. Attempts to reduce this compound caused elimination of the benzoyl groups. Treatment of both forms of $\alpha\delta$ -dihydroxy- $\alpha\delta$ -diphenylbutane with phosphorus pentabromide gives a single $\alpha\delta$ -dibromo- $\alpha\delta$ -diphenylbutane, m. p. 139°. This is converted by treatment with potassium iodide in acetone into the corresponding di-iodo-derivative, m. p. 140°. When an acetone solution of the dibromoderivative is treated with zinc dust either in absence or presence of potassium iodide 1 : 2-diphenylcyclobutane (?) is formed.

H. BURTON.

Photochemical decomposition of benzaldehyde. A. DE HEMPTINNE.—See this vol., 409.

Colour and constitution. IV. Absorption spectra of nitrophenylhydrazones in alcohol and

in alcoholic potassium hydroxide. H. H. HODGSON and K. E. COOPER (J.C.S., 1929, 231—234).—The suggestion of Chattaway and Clemo (*ibid.*, 1923, 123, 3041), that the intense coloration developed by *p*-nitrophenylhydrazones in the presence of hydroxyl ions is due to conversion into a quinonoid ion, has been utilised to investigate the influence of a series of substituents R in the benzaldehyde nucleus on the colour of the ion. It is assumed that the greater the incipient ionisation of the molecule due to the substituent R the less will be the energy required to produce the quinonoid ion and the lower the frequency of the light absorbed by the ion. The wavelength of the head of the absorption band in alcoholic potassium hydroxide decreases through the sequence $\text{R}=\text{NMe}_3^+, \text{Cl}, \text{OMe}, \text{NMe}_2, \text{Me}, \text{O}^-$, which is also the serial order for the decreasing effect of these groups on ease of ionisation.

In absence of alkali the effect is in the order $\text{NMe}_2 > \text{OH} = \text{OMe} > \text{Cl} = \text{Me} > \text{NMe}_3^+$, the frequency absorbed increasing through the series. Minimum and maximum restraint of the electronic structure by the NMe_2 and NMe_3^+ groups, respectively, is thus accompanied by absorption of minimum and maximum frequency.

The following are described: *benzaldehyde-p-trimethylammonium iodide*, m. p. 152°; *benzaldehyde-p-trimethylammonium chloride* *p*-nitrophenylhydrazone, m. p. 196°; *p*-hydroxybenzaldehyde-*p*-nitrophenylhydrazone, m. p. 262°.

C. W. SHOPPER.

Carbohydrates and polysaccharides. XXII. Isomeric cinnamylideneglycerols. H. HIBBERT and M. S. WHELEN (J. Amer. Chem. Soc., 1929, 51, 620—625).—Cinnamaldehyde and glycerol yield in presence of a little sulphuric acid at 100° a mixture of $\alpha\gamma$ -cinnamylideneglycerol, m. p. 121° (cf. Peacock, J.C.S., 1915, 107, 816), and oily $\alpha\beta$ -cinnamylideneglycerol. These appear to be interconvertible on keeping and are identified by the very ready hydrolysis of their *methyl ethers*, m. p. 79—80°, and b. p. 164—165°, n_D^{20} 1.5455, respectively, by boiling dilute acid to β - and α -methyl glyceryl ethers.

H. E. F. NOTTON.

Hadromal, lignin, and coniferaldehyde; preparation and identification. Higher alkali condensates of acetaldehyde. H. PAULY and K. FEUERSTEIN (Ber., 1929, 62, [B], 297—311).—The main difficulty in the preparation of coniferaldehyde lies in the condensation of 3-methoxy-4-methoxymethoxybenzaldehyde with acetaldehyde (cf. Pauly and Wascher, A., 1923, i, 342); the necessary conditions are now described in greater detail. Pure coniferaldehyde forms sulphur-yellow crystals, b. p. 157°/2.5 mm., m. p. 82.5°, d_4^{20} 1.1562, n_D^{20} 1.63973, whereas vanillin crystallises in colourless, monoclinic crystals, b. p. 131°/2.7 mm., m. p. 82.5°, d_4^{20} 1.1772, n_D^{20} 1.56398, n_D^{25} 1.57294, n_D^{20} 1.59748. The differentiating behaviour of vanillin and coniferaldehyde towards a long series of reagents is described in detail. 3-Methoxy-4-methoxymethoxycinnamaldehyde is reduced in a fermenting mixture of sugar, ammonium phosphate, water, and yeast at 36° to 3-methoxy-4-methoxymethoxycinnamyl alcohol, b. p. 166—168°/2.5 mm. (*phenylurethane*, m. p. 86°),

whereas under similar conditions coniferaldehyde affords non-crystalline coniferyl alcohol (ammonium salt; *phenylurethane*, m. p. 108°). Coniferaldehyde is converted by a solution of phloroglucinol in 5*N*-hydrochloric acid into the dark carmine-red powder, $C_{22}H_{20}O_8$, m. p. not below 300°. With benzidine in boiling methyl alcohol, coniferaldehyde yields *di-4-hydroxy-3-methoxycinnamylidenbenzidine*, $[C_6H_4 \cdot N : CH : CH : CH \cdot C_6H_3(OMe) \cdot OH]_2$, m. p. 216° (*dihydrochloride*), whereas vanillin gives *di-4-hydroxy-3-methoxybenzylidenbenzidine*, m. p. 225.5° (*dihydrochloride*). A method for the detection of very small amounts of coniferaldehyde in the presence of much vanillin is based on the widely-differing solubilities of the respective benzidine derivatives in boiling benzene.

Repetition of the work of Hoffmeister (A., 1927, 1189) leads to the conclusion that hadromal does not contain even traces of coniferaldehyde, but consists mainly of vanillin mixed with wood gum, tannin (oak), pyrocatechol (pine), and minute amounts of other phenolic compounds. The m. p. after admixture with an equal quantity of vanillin is 82°, whilst with an equal amount of coniferaldehyde depressions of 20–24° are observed. The m. p. 86° recorded by Hoffmeister is higher than that of vanillin or coniferaldehyde. Further, the ability of hadromal to add 2 atoms of iodine is not shared by coniferaldehyde or its parent cinnamaldehyde. Hoffmeister's process for the synthesis of coniferaldehyde by the condensation of vanillin with acetaldehyde in the presence of sodium hydroxide gives unchanged vanillin to the extent of at least 97%. The isolation of coniferaldehyde as described would require condensation to have proceeded with at least 97% yield.

Repetition of the work of Klason (A., 1928, 277) shows that methoxymethylvanillin does not react quantitatively with acetaldehyde in dilute alkaline solution, but confirms the production of a substance with the properties and approximate composition of the supposed β -naphthylamine salt of coniferaldehydesulphonic acid. This, however, is not derived from intermediately-formed coniferaldehyde, but from two previously unknown substances formed by the autocondensation of acetaldehyde. Klason's compound cannot be derived from coniferaldehyde and aqueous sulphurous acid. Polymerisation of coniferaldehyde to Klason's "paraconiferaldehyde" does not appear to have taken place after preservation during 2 years, in the course of which vanillin is slowly produced.

The gradual addition of potassium hydroxide to an aqueous solution of acetaldehyde at 66–68° affords aldehyde resin, an *aldehyde*, $C_8H_{12}O_2$, b. p. 72–74°/14 mm., 176–178°/atmos. pressure, d_4^{20} 0.9767, 1.4967 (*semicarbazone*, m. p. 195°), and an *aldehyde*, $C_{10}H_{14}O_2$, b. p. 116–120°/12 mm., d_4^{20} 1.035, $n_{D, 20}^{20}$ 1.5447 (*semicarbazone*, m. p. 133°).

H. WREN.

Organic compounds of sulphur. XII. Formation of mercaptols by the action of aliphatic diazo-compounds on disulphides. A. SCHÖNBERG, O. SCHÜTZ, and J. PETER (Ber., 1929, 62, [B], 440–441; cf. this vol., 316).—Diphenyl disulphide is converted by diphenyldiazomethane in boiling

anhydrous benzene in an atmosphere of carbon dioxide and absence of light into diphenylthioldiphenylmethane, m. p. 138°, which decomposes at 230° with production of thiobenzophenone.

H. WREN.

Synthesis of methyl ketones from *p*-tert.-butyltoluene and *p*-cymene by the Friedel-Crafts reaction. A. LACOURT (Bull. Soc. chim. Belg., 1929, 38, 1–24).—The reaction between *p*-tert.-butyltoluene, b. p. 192–193°/760 mm., 1.49187, d_{20}^{20} 0.8614, and dry, finely-powdered aluminium chloride under reduced pressure has been studied at 20–35°. The following products were isolated: *isobutane*, b. p. –11°, *toluene*, *tert*.-butyltoluene, a liquid, $C_{15}H_{24}$, b. p. 245–249°/760 mm., d_{15}^{15} 0.9069, n_D^{15} 1.5164, probably 2:4-dibutyltoluene, a fraction b. p. 120–160°/6 mm., n_D^{15} 1.5460, not definitely identified, and a fraction b. p. 160–170°/4 mm., 1.5852, which contained a considerable proportion of 2:4:5-tributyltoluene, giving by oxidation with chromic and acetic acids terephthalic acid, with alkaline permanganate at 100° a toluenetetracarboxylic acid (?), m. p. about 290°, and with concentrated aqueous permanganate, pyromellitic acid. The reaction between *p*-cymene, b. p. 176.2–177.2°, 1.49083, d_{20}^{20} 0.8583, and powdered aluminium chloride was similarly studied; no gas was evolved during 10 days' contact at the ordinary temperature, and after decomposition of the reaction product with ice, benzene, toluene, xylene, *p*-cymene, and diisopropyltoluene were isolated. These experiments explain why a homogeneous product is not always obtained in the Friedel-Crafts reaction, and it is concluded that the most favourable conditions for the elimination of secondary products are low temperature and carrying out the reaction as rapidly as possible. Equimolecular mixtures of aluminium chloride, *tert*.-butyltoluene, and acetyl chloride under the above conditions give *isobutane*, b. p. –13.5° to –10°, *p*-acetyltoluene, b. p. 97–101°/10 mm., d_{20}^{20} 0.9943, d_4^{20} 1.0100, n_D^{20} 1.530 (oxime, m. p. 87.5–88°); acetyl-*p*-tert.-butyltoluene, b. p. 131–134°/10 mm. (*semicarbazone*, m. p. 189.8–190°; *oxime*, m. p. 121.8–122°), and products of high b. p. which were not identified with certainty. The reaction between an equimolecular mixture of aluminium chloride, *p*-cymene, and acetyl chloride under similar conditions gives *p*-acetyltoluene, b. p. 97°/12 mm., 1.0160, n_D^{15} 1.5350, unchanged *p*-cymene, an intermediate ketonic fraction, b. p. 126–132.5°/16 mm., n_D^{15} 1.5228, acetyl-*p*-cymene, b. p. 132.5–137.4°/16 mm., a fraction of b. p. 138–145°/16 mm., n_D^{15} 1.512, and a brown, viscous residue. The best yields of ketone, in which the by-products are reduced to a minimum, are obtained by adding an equimolecular mixture of the hydrocarbon and acetyl chloride to aluminium chloride in carbon disulphide at –10° to –15°. Pure acetyl-*p*-tert.-butyltoluene has b. p. 133.2–135°/12 mm., m. p. –1° to –3°, d_4^{20} 0.9757, d_{20}^{20} 0.9615, n_D^{20} 1.52071, whilst pure acetyl-*p*-cymene has b. p. 124.2–125.2°/12 mm., d_4^{20} 0.9864, d_{20}^{20} 0.9654, n_D^{20} 1.51849 (*semicarbazone*, m. p. 147°; *oxime*, m. p. 91–92.5°). Oxidation of the former with nitric acid (*d* 1.15) gave toluene-2:4-dicarboxylic acid, m. p. 332°, whilst oxidation of the latter indicated that the keto-group is *ortho* to methyl.

A. I. VOGEL.

Interpretation of rearrangements of pinacols and tertiary amino-alcohols from the electron theory of valency. M. MIGITA (Bull. Chem. Soc. Japan, 1928, 3, 308—316).—An electronic interpretation of the rearrangement of pinacols to ketones is offered. Since the change does not take place in neutral or alkaline solution it is assumed that the acid behaves both as a catalyst and a dehydrating agent. The order of "electro-negativity" of the groups which determines their wandering is taken as $\alpha\text{C}_{10}\text{H}_7 > p\text{-MeO}\cdot\text{C}_6\text{H}_4 > o,p\text{-MeC}_6\text{H}_4 > \text{Ph} > \text{Me} > \text{Et}, \text{Pr} > \text{CH}_2\text{Ph}$ (Kharasch and Marker, A., 1927, 165). A similar interpretation is given of the semipinacolinic deamination of tertiary amino-alcohols such as γ -amino- $\beta\gamma$ -diphenylisopropyl alcohol, and of the normal displacement of the amino-group in γ -amino- $\alpha\gamma$ -triphenylpropyl alcohol. The behaviour of γ -amino- $\alpha\gamma$ -diphenyl- β -benzylisopropyl alcohol towards nitrous acid is not in harmony with the electronic interpretation.

A. I. VOGEL.

Relative affinity capacities of various radicals in the transformation of trisubstituted ethylene oxides. (MLLE.) J. LEVY and A. TABART (Compt. rend., 1929, 188, 402—404; cf. A., 1926, 383, 818).—In addition to previous results the following transformations of ethylene oxides by heat are recorded; no experimental details are given. α -Phenyl- β -ethyl- Δ^a -butylene oxide gives α -phenyl- α -ethylbutaldehyde and α -phenyl- n -propyl ethyl ketone; α -phenyl- β -methyl- Δ^a -butylene oxide gives α -phenyl- α -methylbutaldehyde and α -phenyl- n -propyl methyl ketone (migration of an ethyl group); α -phenyl- β -methyl- Δ^a - n -amylene oxide gives α -phenyl- α -methylvaleraldehyde and α -phenylethyl n -propyl ketone (migration of a methyl group); α -phenyl- β -benzyl- Δ^a -propylene oxide, $\alpha\beta$ -diphenylethyl methyl ketone; α -phenyl- β -benzyl- Δ^a - n -butylene oxide, $\alpha\beta$ -diphenylethyl ethyl ketone; α -phenyl- β -benzyl- Δ^a - n -amylene oxide, $\alpha\beta$ -diphenylethyl n -propyl ketone. In the three last examples the migration of a benzyl group is involved.

G. A. C. GOUGH.

Additive properties of diacetylenic hydrocarbons. V. GRIGNARD and TCHÉOUFAKI (Compt. rend., 1929, 188, 527—530).—When an aqueous-alcoholic solution of Δ^a - $\alpha\delta$ -di-4- m -xylylbutadiene is agitated with oxygen, 4- m -xylyl 4- m -xylylmethylacetylenyl ketone, m. p. 125°, is formed, which yields an ozonide decomposing in carbon tetrachloride solution to give in turn 4- m -xylylacetic acid, m. p. 106°, and 4- m -xylylglyoxylic acid, m. p. 75° (+H₂O, m. p. 53—54°) (sodium hydrogen sulphite compound described). It is suggested that $\alpha\delta$ -addition precedes the formation of the above ketone. Agitation of Δ^a -decadiene with a 40% acetic acid solution of concentrated sulphuric acid yields *deca*- $\delta\zeta$ -dione, m. p. 147°. Tetradeca- Δ^a -diene yields similarly *tetradeca*- $\zeta\theta$ -dione, m. p. 237°, which affords the additive compound, C₁₆H₁₄Hg₂Cl₄.

G. A. C. GOUGH.

Is 2:3-diphenylindone resolvable into optically active antipodes? J. MEISENHEIMER and W. THEILACKER (Annalen, 1929, 469, 26—30).—The authors have been unable to repeat Schlenk, Bergmann, and Müller's resolution of 2:3-diphenylindone (A.,

1928, 1035). The small rotation observed by these authors is probably due to impurity. *N*-Diphenylindenyldenebornylamide has m. p. 126°, $[\alpha]_D^{25} + 232^\circ$ in chloroform (cf. *loc. cit.*).
H. BURTON.

***ms*-Alkylantracenes and "transannular tautomerism."** V. E. DE B. BARNETT and N. F. GOODWAY (Ber., 1929, 62, [B], 423—431; cf. A., 1927, 140; 1928, 52).—1:5-Dichloro-9-bromo-9-phenylanthrone is converted by methyl or ethyl alcohol in presence of calcium carbonate into 1:5-dichloro-9-methoxy-9-phenylantrone, m. p. 213°, or 1:5-dichloro-9-ethoxy-9-phenylantrone, m. p. 150°. With magnesium methyl iodide the methoxy-compound affords 1:5-dichloro-9-hydroxy-10-methoxy-10-phenyl-9:10-dihydroanthracene, m. p. 215°, converted by boiling methyl alcohol containing hydrochloric acid into a colourless substance, (C₂₂H₁₈O₂Cl₂)₂·MeOH, m. p. 191° (also +CH₃·CO·CH₃). 1:5-Dichloro-9-hydroxy-10-ethoxy-10-phenyl-9-methyl-9:10-dihydroanthracene, m. p. 205°, is described. Treatment of the methoxy-compound with methyl alcohol and hydrochloric acid at 100° or of the methoxy- or ethoxy-derivative with boiling ethyl alcohol and hydrochloric acid affords respectively 1:5-dichloro-10-phenyl-9-methoxymethylanthracene, C₆H₅Cl < $\begin{matrix} \text{C}(\text{CH}_3\text{OMe}) \\ \text{CPh} \end{matrix} > \text{C}_6\text{H}_5\text{Cl}$, m. p. 154°, and 1:5-dichloro-10-phenyl-9-ethoxymethylanthracene, m. p. 124°. The possibility of transannular migration of alkoxy-groups is thus established.

1:5-Dichloro-9-bromoanthrone is converted by benzyl alcohol in the presence of calcium carbonate into 1:5-dichloro-9-benzoyloxanthrone, m. p. 157°; 1:5-dichloro-9-benzoyloxymethylanthracene, m. p. 118°, is prepared similarly from 1:5-dichloro-9-bromomethylanthracene. Treatment of 1:5-dichloro-9-ethoxy- (or benzyloxy-)anthrone with ethereal magnesium benzyl chloride causes de-alkylation and the oils thus produced when dissolved in glacial acetic acid and treated with concentrated hydrochloric acid at the ordinary temperature yield 1:5:10-trichloro-9-hydroxy-9-benzyl-9:10-dihydroanthracene, m. p. 135° (decomp.), identified by conversion into 1:5-dichloro-9-hydroxy-10-piperidino-9-benzyl-9:10-dihydroanthracene (+1MeOH or 1CH₃·CO·CH₃), m. p. 169°, also prepared from 1:5-dichloro-9-piperidinoanthrone and magnesium benzyl chloride. (In a single instance, 1:5-dichloro-9-ethoxyanthrone was converted into a colourless substance, m. p. 144°, probably 1:5-dichloro-10-ethoxy-9-benzylidene-9:10-dihydroanthracene but differing from the product derived from ethyl alcohol, calcium carbonate, and dichlorobromobenzylanthracene.) Magnesium methyl iodide and 1:5-dichloro-9-benzoyloxanthrone yield 1:5-dichloroanthrone. The trichloro-compound (see above) is transformed by methyl alcohol in the presence of calcium carbonate into 1:5-dichloro-9-hydroxy-10-methoxy-9-benzyl-9:10-dihydroanthracene, m. p. 144°, and by aqueous acetone and calcium carbonate into 1:5-dichloro-9-benzyl-9:10-dihydroanthraquinol, m. p. 172°. 1:5-Dichloro-10-piperidino-9-benzylidene-9:10-dihydroanthracene, m. p. 194°, is described.

H. WREN.

Tautomerism of α -diketones. Two tautomeric forms of phenylbenzylglyoxal and phenyl-

anisylglyoxal. H. MOUREU (Compt. rend., 1929, 188, 504—506).—The form of phenylanisylglyoxal, m. p. 70° (*A*), when heated slowly above its m. p. recrystallises as its *isomeride*, m. p. 82° (*A*β). These keto-enolic *A* forms are transformed by distillation under pressures of about 1 mm. into a true ketonic *isomeride*, m. p. 23—24° (*B*), extracted from the resultant liquid by crystallisation at low temperature. The corresponding *A* forms of phenylbenzylglyoxal (cf. A., 1928, 180) are similarly transformed into a *B-isomeride*, m. p. 35—36°. The action of heat partly changes the *B* forms into the *A* forms. These transformations are markedly affected by alkaline catalysts (e.g., ordinary glass). B. W. ANDERSON.

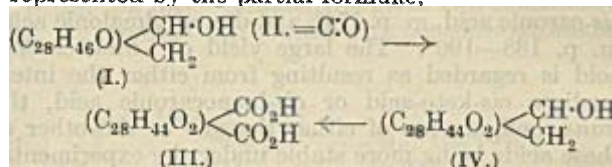
Structure of dihydroxybenzanthrone obtained from the condensation of alizarin with glycerol and sulphuric acid (G.P. 187,495). J. TURSKI and J. GRYNWASSER (Rocz. Chem., 1929, 9, 78—82).—2:3-Dihydroxyphenyl α -naphthyl ketone, m. p. 118° (diacetyl derivative, m. p. 135°), prepared by the action of α -naphthoyl chloride on pyrocatechol, yields when fused with aluminium chloride 5:6-dihydroxydihydro-1:9-benzanthrone, which on oxidation gives 5:6-dihydroxy-1:9-benzanthrone, m. p. 185° (diacetyl derivative, m. p. 109°). Phenyl 2:3-dihydroxy- α -naphthyl ketone, m. p. 179°, prepared by the Friedel-Crafts reaction from dihydroxynaphthalene and benzoyl chloride, is in a similar way to the above converted into 3:4-dihydroxy-1:9-benzanthrone, m. p. 285°. If Scholl's reaction is substituted for that of Friedel and Crafts in the above condensation, the product is 2:3-dibenzoyloxynaphthalene, m. p. 235°, which can be further condensed to Bz-2:3-dihydroxy-1:9-benzanthrone, m. p. 192° (dibenzoyl derivative, decomp. 320°). A comparison of these benzanthrones with the product obtained by the method described in G.P. 187,495 shows that the latter is 5:6-dihydroxy-1:9-benzanthrone. R. TRUSZKOWSKI.

Manufacture of anthraquinone derivatives [1-*o*-carboxyphenylanthraquinone]. I. G. FARBERIND. A.-G.—See B., 1929, 164.

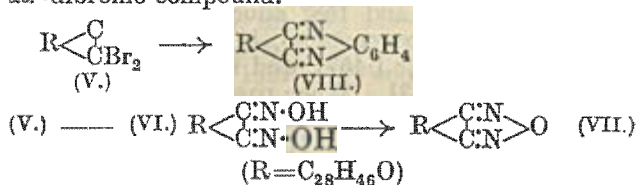
Manufacture of aminated sulphur-containing benzanthrone derivatives. I. G. FARBERIND. A.-G.—See B., 1929, 164.

Phytochemistry. V. *allobetulin*. O. DISCHENDORFER and O. POLAK (Monatsh., 1929, 51, 43—58; cf. A., 1927, 249).—Oxidation of *allobetulin* formate with chromic and acetic acids yields directly crystalline *oxyallobetulin formate*, m. p. 347—348° (decomp.), $[\alpha]_D^{25} +57.6^\circ$ in chloroform. Similarly, *allobetulin* acetate is oxidised either by chromic acid (cf. Schulze and Pieroh, A., 1922, i, 1045) or nitric acid (*d* 1.52) at -5° to *oxyallobetulin acetate*, $[\alpha]_D^{25} +63^\circ$ in chloroform. *Oxyallobetulin*, m. p. 360° (decomp.), $[\alpha]_D^{25} +47^\circ$ in pyridine, is obtained by hydrolysis of either ester and has the composition $C_{30}H_{48}O_3$ and not that assigned by Schulze and Pieroh (*loc. cit.*). Oxidation of *allobetulin* (I) with a mixture of nitric acid (*d* 1.52) and acetic acid at 0° yields the dibasic *oxyallobetulinic acid* (III), m. p. 283—284° (decomp.), $[\alpha]_D^{25} +57^\circ$ in pyridine (dimethyl ester, m. p. 230—231°, $[\alpha]_D^{25} +48.7^\circ$; diethyl ester, m. p. 191—193°, $[\alpha]_D^{25} +53^\circ$). The same acid is obtained by oxidation

of *allobetulin* (II) m. p. 239—241° (Schulze and Pieroh, *loc. cit.*, give 230—231°), with nitric acid (*d* 1.52) at -5° , or of *oxyallobetulin* (IV) with nitric (*d* 1.50) and acetic acids at -5° . These reactions are represented by the partial formulæ,



two hydrogen atoms in the C_{28} residue in I and II being replaced by oxygen. The acid III when heated with acetic anhydride yields an *anhydride*, m. p. 290—292° (decomp.), $[\alpha]_D^{25} +86^\circ$ in pyridine, and by distillation in an atmosphere of carbon dioxide above 300° yields a *ketone*, $C_{28}H_{44}O_2$, m. p. 340—342° (decomp.), $[\alpha]_D^{25} +153.5^\circ$ in pyridine [*oxime*, m. p. 304—306° (decomp.)]. The acid III is therefore most probably an azelaic acid and the ring which is opened in its formation a six-membered one (less probably a seven- or an eight-membered ring). Since this ketone is unchanged by treatment with nitric acid under normal oxidation conditions it is improbable that there is another methylene group next to the $-\text{CO}\cdot\text{CH}_2-$ grouping in *allobetulin*. Reduction of the latter by Clemmensen's method gives a *substance*, $C_{30}H_{50}O$, m. p. 232—233°, $[\alpha]_D^{25} +45^\circ$, in which the carbonyl group has been reduced to a methylene group. The action of less concentrated nitric acid on *allobetulin* (above) yields a *substance*, $C_{30}H_{44}O_7N_2$, m. p. 223—224° (decomp.), which is probably dinitro-oxyallobetulin. Dibromoallobetulin (V) (Dischendorfer and Grillmayer, A., 1927, 59) on prolonged heating with hydroxylamine yields a bromine-free *dioxime* (VI), m. p. 194—196° (decomp.), $[\alpha]_D^{25} +77.7^\circ$ in pyridine, which is oxidised by sodium nitrite in acetic acid to the *furoxan* (VII), m. p. 258—261° (decomp.), and condenses with *o*-phenylenediamine to yield a *phenazine* (VIII), m. p. 269—273° (decomp.). Hence (V) is an $\alpha\alpha'$ -dibromo-compound.



In agreement with this view, oxidation of dibromoallobetulin with nitric (*d* 1.52) and acetic acids at -5° yields, not a brominated oxyallobetulinic acid, but $\alpha\alpha'$ -dibromo-oxyallobetulin, $C_{30}H_{44}O_3Br_2$, m. p. 300—310° (decomp.). J. W. BAKER.

Indian turpentine from *Pinus longifolia*, Roxb.
V. Oxidation of *d*- Δ^3 -carene with Beckmann's chromic acid mixture. C. S. GIBSON and J. L. SIMONSEN (J.C.S., 1929, 305—311).—Treatment of *d*- Δ^3 -carene (1 part) with Beckmann's reagent (20 parts; cf. Henry and Paget, A., 1928, 295) afforded *l*-trans-caronic acid, m. p. 201—202°, $[\alpha]_{546}^{25} -12.3^\circ$ in alcohol (the optical purity could not be increased by crystallising the strychnine salt; compare Ruzicka and Staudinger, A., 1924, i, 510), and terpenylic acid, m. p. 57°, rising after dehydration over sulphuric acid

to 90° (ethyl ester, m. p. 37—38°), in relatively large yield, together with small quantities of *d*-homoterpenyl methyl ketone, m. p. 42—43°, [α]_D²⁰ +55.7° in water [*semicarbazone*, m. p. 195—196° (decomp.), [α]_D²⁰ +49.9° in alcohol], terebic acid, m. p. 173—174°, *cis*-caronic acid, m. p. 174°, and dimethylmalonic acid, m. p. 188—190°. The large yield of *l*-*trans*-caronic acid is regarded as resulting from either the intermediate *cis*-keto-acid or *cis*-homocaronic acid, the *trans*-configuration of either the one or the other of these acids being more stable under the experimental conditions; *d*- Δ^3 -carene has a *cis*-configuration. The isolation of *d*-homoterpenyl methyl ketone confirms the constitution of the hydrocarbon and eliminates the possibility of the ethylenic group occupying the Δ^2 -position. When *d*- Δ^3 -carene (10 parts), acetic acid (25 parts), and 50% sulphuric acid (1 part) are heated together at 60°, the main product is a *diterpene*, C₂₀H₃₂, b. p. 175°/10 mm., 0.9309, n_D^{20} 1.5168, [α]_D²⁰ +5.69°; a small quantity of a monocyclic terpene, b. p. 174—176°/755 mm., d_4^{20} 0.8500, n_D^{20} 1.4750, [α]_D²⁰ -6.5° (hydrochloride, b. p. about 115°/15 mm.), together with a trace of *l*-borneol, m. p. 204—205°, [α]_D²⁰ -26.9° (*p*-nitrobenzoyl derivative, m. p. 136—137°), the latter being probably due to the presence of a little pinene or camphene in the *d*- Δ^3 -carene, are also formed. A. I. VOGEL.

Irreversible catalysis of unsaturated cyclic hydrocarbons. VI. Contact transformations of nopinene, terpinene, and terpinolene. N. D. ZELINSKI and R. J. LEVINA (Ber., 1929, 62, [B], 339—343; cf. A., 1927, 670).—Nopinene, b. p. 163.5—165.5°/742 mm., n_D^{20} 1.4766, is hydrogenated in the presence of palladised charcoal at 170—175° to dihydronopinene, b. p. 167—167.5°/737 mm., d_4^{20} 0.8521, n_D^{20} 1.4628, the hydrocarbon thus yielding a single product in contrast with pinene. The latter compound in presence of nickel at 155—158° gives dihydro- α -pinene, b. p. 168.5°/748 mm., d_4^{20} 0.8392, 1.4541, whereas hydrogenation in presence of palladium at 195° and 158° affords dihydropinenes with the respective constants, b. p. 169—170°/768 mm., d_4^{20} 0.8453, 1.4577, and b. p. 169.5° (corr.), d_4^{20} 0.8351, n_D^{20} 1.4531. When passed over palladised asbestos at 190°, nopinene is converted into *p*-cymene and dihydropinene, b. p. 166—168°/752 mm., d_4^{21} 0.8447, d_4^{21} 0.8470, 1.4554; analogously, α -pinene gives cymene and dihydropinene, d_4^{21} 0.8467, n_D^{21} 1.4589. It is probable, therefore, that nopinene is initially isomerised to α -pinene. Terpinene, b. p. 178.5—180.5°/740 mm., 65.5—68°/14 mm., d_4^{20} 0.855, n_D^{21} 1.4783, is converted in presence of palladised asbestos at 190° into *p*-cymene and menthane, b. p. 168.5—169.5°/745 mm., 1.4452, whilst the same products are similarly derived from terpinolene, b. p. 75°/14 mm., d_4^{20} 0.8628, 1.4802, at 160—170°/40 mm. The differing positions of the two double linkings, within or outside the nucleus, in monocyclic terpene hydrocarbons appear without influence on the final products of their contact transformations.

Palladised charcoal may be used in place of palladised asbestos in contact transformations, but the former adsorbs an appreciable proportion of the molecules and protects them from contact with the

active surface of the catalyst, thus rendering repeated treatment necessary. H. WREN.

Individuality of humulene. A. C. CHAPMAN (J.C.S., 1929, 359—360; cf. A., 1928, 646).—A reply to Deussen (A., 1928, 1378). The author maintains that clove oil and also hop oil contain "humulene," a hydrocarbon which is not identical with caryophyllene, although the two hydrocarbons are closely related and may undergo intramolecular change in certain reactions, the one being transformed into the other.

A. I. VOGEL.

Sylvestrenes and carenes. J. L. KONDAKOV (Perfumerie Mod., 1927, 3—15).—A polemical discussion (mainly against W. H. Perkin and Wallach) of the generic relationships of these terpenes.

J. W. BAKER.

Syntheses and degradations in tetrahydrodiphenylene oxide series. F. EBEL (Helv. Chim. Acta, 1929, 12, 3—16).—Chlorination of cyclohexanol in presence of water and calcium carbonate affords 2-chlorocyclohexanone, b. p. 84—85°, which reacts with sodium phenoxide in light petroleum, yielding cyclohexanolone phenyl-lactolide, m. p. 64.5° (osazone, m. p. 152—153°) (cf. Kotz and others, A., 1913, i, 1201). When the reaction is carried out in phenol at 120°, 50% of the theoretical yield of 1:2:3:4-tetrahydrodiphenylene oxide (I) (cf. Honigschmid, A., 1901, i, 700) is obtained. Nitration of I by a 33% solution of concentrated nitric acid in acetic acid gives a *mono*-nitro-derivative, m. p. 120.5°. Hydrogenation of I with hydrogen and a platinum-palladium catalyst affords a hexahydrodiphenylene oxide, b. p. 137°/10 mm., identical with that described by von Braun (A., 1923, i, 103), whilst dehydrogenation with sulphur at 200—260° yields diphenylene oxide. When a solution of I in carbon tetrachloride containing small amounts of acetic acid and bromine is treated with ozone, δ -salicylvaleric acid is obtained, demonstrating that I is definitely the 1:2:3:4-tetrahydro-derivative. δ -Salicylvalerolactone peroxide has m. p. 191° (decomp.). δ -3:5-Dibromosalicylvaleric acid, m. p. 128.4°, is oxidised by hot nitric acid, yielding adipic acid, and by bromine water at 90° giving an acid, m. p. 88—89°, and a substance, m. p. 175—180°, both containing bromine.

2-Chlorocyclohexanone and sodium *o*-methoxyphenoxide react in toluene giving cyclohexanolone *o*-methoxyphenyl-lactolide, m. p. 67.5° [osazone (?), m. p. 159°], which when treated with concentrated sulphuric acid in the cold affords 8-methoxy-1:2:3:4-tetrahydrodiphenylene oxide, m. p. 39.5°. With sodium β -naphthoxide cyclohexanolone β -naphthyl-lactolide, m. p. 135°, is produced; this yields tetrahydrophenylenenaphthylene oxide, m. p. 60° (picrate, m. p. 145°). H. BURTON.

Furan compounds derived from sugars. II. Acetyl derivative of hydroxymethylfurfuraldehyde. J. KARASHIMA (Z. physiol. Chem., 1929, 180, 241—248).—Acetylation of ω -hydroxymethylfurfuraldehyde with acetic anhydride in presence of anhydrous sodium acetate gives the corresponding acetyl derivative (I) (Fenton and Gostling, J.C.S., 1901, 79, 807), which is oxidised by copper, silver, and mercuric oxides to hydroxymethylpyromucic acid,

and by alkaline potassium permanganate to muconic and oxalic acids. Condensation of I with acetic anhydride and sodium acetate at 160—170° gives *acetoxymethylideneacetic acid*, m. p. 134°, hydrolysed by barium hydroxide solution to *hydroxymethylideneacetic acid*, m. p. 139°. Administration of I to the dog, rabbit, or hen leads to the excretion in the urine of considerable amounts (49.7—73.3%) of hydroxymethylpyromucic acid (cf. A., 1927, 1107).

H. BURTON.

α[3]-Phenylcoumarins. G. BARGELLINI and (SIGNA.) L. MONTI (Atti R. Accad. Lincei, 1928, [vi], 8, 395—399; cf. A., 1927, 883).—3-*p*-Anisylcoumarin, prepared by the condensation of salicylaldehyde and sodium *p*-methoxyphenylacetate in presence of acetic anhydride, has m. p. 142—144°; 3-(3':4'-methylene-dioxyphenyl)coumarin, m. p. 170—172°, is obtained similarly from methylenedioxyphenylacetic acid. 7-Hydroxy-3-(3':4'-methylenedioxy)phenylcoumarin, m. p. 238—239°, obtained as *acetyl* derivative, m. p. 191—192°, from resorcydaldehyde and methylenedioxyphenylacetic acid, forms a *methyl ether*, m. p. 195—196°. 5:7-Dihydroxy-3-(3':4'-methylenedioxy)phenylcoumarin, decomp. from 260°, obtained as *diacetyl* derivative, m. p. 198—199°, from phloroglucinaldehyde and methylenedioxyphenylacetic acid, forms a *methyl ether*, m. p. about 170°.

T. H. POPE.

Grape pigments. II. Anthocyanins in Clinton grapes. R. J. ANDERSON and F. P. NABENHAUER.

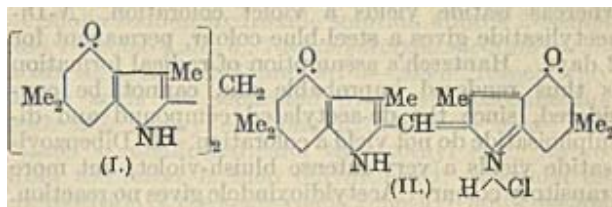
III. Anthocyanins in Seibel grapes. R. J. ANDERSON (N.Y. Agric. Exp. Sta., Tech. Bull. 146, July, 1928, 21 pp.).—See A., 1924, i, 1152, 1390.

Derivatives of 4:5:6:7-tetrahydroindole. I. C. D. NENITZESCU. II. Derivatives of 4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole. C. D. NENITZESCU and V. SCORTZEANU. III. Polynuclear derivatives of 4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole. C. D. NENITZESCU (Bul. Soc. Chim. Romania, 1928, 10, 131—133, 134—140, 141—148).—I. Ethyl sodioacetoacetate and 2-bromocyclohexanone condense in alcoholic solution to yield a product containing *ethyl cyclohexanonylacetoacetate*, which is converted into *ethyl 2-methyl-4:5:6:7-tetrahydroindole-3-carboxylate*, m. p. 132°, when treated with ammonium acetate in boiling glacial acetic acid.

II. Condensation of ethyl α-aminoacetoacetate and cyclohexane-1:3-dione furnishes *ethyl 4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole-2-carboxylate*, m. p. 171°, oxidised by warm nitric acid (*d* 1.40) to an alkali-soluble substance, C₁₃H₁₇O₈N₃, m. p. 193° (decomp.), and hydrolysed by aqueous-alcoholic potassium hydroxide to 4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole-2-carboxylic acid. The latter melts at 253°, giving carbon dioxide and 4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole, m. p. 162°. When the above indolecarboxylic ester is treated with bromine in glacial acetic acid or in chloroform, an orange-red compound, [C₁₄H₁₉O₈N₃Br_{2.5}], m. p. 132°, is obtained which loses bromine in a vacuum or in aqueous solution to regenerate the parent ester; in boiling glacial acetic acid, the compound gives hydrogen bromide and a compound, m. p. 202°

(decomp.), whilst in boiling alcoholic solution a second colourless compound, m. p. 208°, is obtained.

III. 4-Keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole and formaldehyde afford *bis*-(4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindyl)methane (I), m. p. 267°, whilst benzaldehyde gives two substances, m. p. 172° and 254°; it couples with benzenediazonium



chloride, giving 2-benzeneazo-4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole, m. p. 224° (decomp.). The substance I could not be converted into II by treatment with formic acid in the presence of hydrochloric or perchloric acid. 4-Keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole condensed with ethyl orthoformate yields *tri*-(4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindyl)methane, m. p. 284°, readily converted by dissolution in hydrochloric acid (*d* 1.19) into 2-(4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindyl)-2-(4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindolenyl)methene hydrochloride (II), m. p. 264°. To investigate the effect of the 4-keto-group on the ease of conversion of the pyrrole form into the pyrrolene form (occurring in II), 4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole was converted by hydrazine followed by sodium methoxide at 150—160° into 3:6:6-trimethyl-4:5:6:7-tetrahydroindole, m. p. 63° [*picrate*, m. p. 140° (decomp.)]; owing to the ease with which this substance oxidises, attempts to obtain a product by condensation with formic acid gave inconclusive results. In the Wolff-Kishner process described above, the *azine* of 4-keto-3:6:6-trimethyl-4:5:6:7-tetrahydroindole, m. p. above 300°, was also obtained. C. W. SHOPPEE.

Isatide or isatinpinacol. G. HELLER and H. LAUTH (Ber., 1929, 62, [B], 343—350).—Exact comparison of the properties of disulphoisatide (cf. Wahl and Féricéan, A., 1927, 470) and isatide discloses so many differences that the substances cannot possess similar structures and hence the constitution

$\left[\text{NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} \end{array} \text{C}(\text{OH}) \cdot \right]_2$ (cf. Kohn, A., 1912, i, 800; 1916, i, 607; Hantzsch, A., 1921, i, 598) cannot be ascribed to isatide. The constitution $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \text{NH} \end{array} \text{CO} + \text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OH}) \\ \text{NH} \end{array} \text{C} \cdot \text{OH}$ or $\text{NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} \end{array} \text{CO} \begin{array}{c} \text{OH} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \\ \text{OH} \cdot \text{C} \cdot \text{NH} \end{array}$ is suggested. During acetylation of isatide, a transformation into the pinacol form probably occurs and the compound is therefore regarded with some reserve as tetra-acetyl isatinpinacol.

Tetra-acetyl isatinpinacol (tetra-acetyl isatide) is converted by glacial acetic and hydrochloric acids at 50—60° or by phenylhydrazine (together with isatin-phenylhydrazone) into *diacetyl isatinpinacol*, m. p. about 317° after darkening at 280°. Complete de-acetylation of the *diacetyl* compound is effected by 85—90% sulphuric acid, acetic acid, and hydrochloric

acid or, preferably, acetic and phosphoric acids at 125°, but the product, decomp. about 265—270°, is not homogeneous, and, when re-acetylated, gives the tetra-acetyl compound in moderate yield. Isatide and 90% sulphuric acid appear also to yield isatin-pinacol. Dioxindole does not become coloured by pyridine-barium hydroxide in the absence of oxygen, whereas isatide yields a violet coloration. *N*-Di-acetylisatide gives a steel-blue colour, permanent for 2 days. Hantzsch's assumption of radical formation is thus rendered improbable and cannot be considered, since the de-acetylated compound and disulphoisatide do not yield a coloration. *N*-Dibenzoylisatide yields a very intense bluish-violet, but more transitory colour. Acetyldioxindole gives no reaction. Since *N*-phenyldioxindole and the corresponding isatide give a similar blue colour with alkali, it is probable that the action is due to the $-\text{NH}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})-$ group. Prolonged treatment of *N*-benzoylisatin or *N*-dibenzoylisatide with phenylhydrazine yields "iso-*N*-benzoylisatinosazone," $\text{C}_{27}\text{H}_{21}\text{ON}_5$, pale yellow crystals, m. p. 211—212°, converted by bromine in hot, glacial acetic acid into a substance, m. p. 266°. Similarly, *N*-acetylisatin and *N*-diacetylisatide afford "iso-*N*-acetylisatinosazone," m. p. about 130° (also + 10CMe_2); if the duration of the action is curtailed *N*-acetylisatin-3-phenylhydrazone can be isolated.

o-Benzoyldioxindole, m. p. 134°, is prepared by converting dioxindole by means of alcoholic potassium hydroxide into its potassium salt, which is treated with benzoyl chloride. *O*-Acetyldioxindole, m. p. 127°, is obtained similarly or from dioxindole and a slight excess of acetic anhydride in presence of a little concentrated sulphuric acid. The attachment of the acyl groups to the oxygen is established by the conversion of both substances into isatin-3-phenylhydrazone.

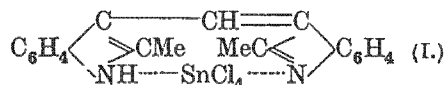
H. WREN.

***N*-Arylisatins and isomeric acridinemesocarboxylic acids.** J. MARTINET and A. DANSETTE (Bull. Soc. chim., 1929, [iv], 45, 101—109).—When *N*-phenyl- β -naphthylamine and ethyl mesoxalate are fused at 150°, or when the acetic acid solution of the mixture is boiled, there is formed ethyl 1-phenyl-4 : 5-benzodioxindole-3-carboxylate, m. p. 171° (? 181°) [ethyl 1-hydroxy-2-keto-3-phenyl-1 : 2-dihydro- β -naphthindole-1-carboxylate] (acetyl derivative, m. p. 177°) converted by potassium hydroxide in the absence of air into 1-hydroxy-2-keto-3-phenyl-1 : 2-dihydro- β -naphthindole, m. p. 95—102° (acetyl derivative, m. p. 150°), by 2% sodium or potassium hydroxide in 15 min. into 1-phenyl- β -naphthoisatin (1 : 2-diketo-3-phenyl-1 : 2-dihydro- β -naphthindole) (Stolle, A., 1923, i, 1125), m. p. 227° (phenylhydrazone, m. p. 195°), and by 10% potassium hydroxide into β -naphthacridine-12-carboxylic acid, m. p. above 300° (decomp.) (potassium, copper, barium, and lead salts), yielding naphthacridine, m. p. 131° (Ullmann and Baezner, A., 1902, i, 694), when distilled alone or with soda-lime. The isatin and naphthacridinecarboxylic acid are obtained in yields of 96—97%, 2-anilinonaphthalene-1-glyoxylic acid being probably an intermediate stage (cf. Friedlander and Kunz, A., 1922, i, 765; Stollé, loc. cit.), since potassium 2-anilinonaphthalene-1-glyoxylate (+ $3\text{H}_2\text{O}$) is obtained by the action of 30% potassium

hydroxide on 1-phenyl- β -naphthoisatin. Reduction with sodium hyposulphite in alcohol converts the isatin into the above hydroxy-compound, m. p. 95—102°, the acetyl derivative being obtained (yield 65—94%) by reduction in presence of acetic anhydride.

R. BRIGHTMAN.

Subsidiary valency forces of indole nitrogen. O. SCHMITZ-DUMONT and E. MOTZKUS (Ber., 1929, 62, [B], 466—473; cf. this vol., 328).—Indole differs from pyrrole in its behaviour towards stannic chloride, since it yields a normal additive compound, $(\text{C}_8\text{H}_7\text{N})_2\cdot\text{SnCl}_4$, m. p. 153° (decomp.) after softening at 133°, from which the indole may be almost quantitatively regenerated; the product is coloured blue by the presence of an impurity which can be removed by treatment with nitrobenzene. Indole does not yield a stable compound with stannic bromide, but with titanium tetrachloride and aluminium bromide gives the substances $(\text{C}_8\text{H}_7\text{N})_2\cdot\text{TiCl}_4$ and $\text{C}_8\text{H}_7\text{N}\cdot\text{AlBr}_3$, m. p. 140° after darkening at 130°. The dark violet colour of the titanium product is attributed to the particular valency of the metal in the compound; a reduction to the tervalent stage does not enter into the question. Polymerisation enhances the additive capacity of indole nitrogen, since tri-indole gives the compounds $(\text{C}_8\text{H}_7\text{N})_3\cdot\text{SnCl}_4$, m. p. 166—168°, $2(\text{C}_8\text{H}_7\text{N})_2\cdot\text{SnCl}_4$, m. p. about 150° after softening at 130°, $2(\text{C}_8\text{H}_7\text{N})_3\cdot\text{SnBr}_4$, m. p. 120—133° (decomp.), $2(\text{C}_8\text{H}_7\text{N})_3\cdot\text{TiCl}_4$, and $(\text{C}_8\text{H}_7\text{N})_3\cdot\text{AlBr}_3$. Introduction of the methyl group in position 1 depresses rather than enhances the additive power, since 1-methylindole does not give a normal product with stannic chloride, but with aluminium bromide affords the substance $\text{C}_8\text{H}_6\text{MeN}\cdot\text{AlBr}_3$, from which the base is regenerated unchanged. 2-Methylindole unexpectedly yields the compounds $\text{C}_8\text{H}_8\text{N}\cdot\text{SnCl}_4$, m. p. 149°, and $2\text{C}_8\text{H}_8\text{N}\cdot\text{HSnCl}_5$, m. p. 207°, from each of which the base is smoothly regenerated. Di-2-methylindylmethane with stannic chloride gives the compound I,



m. p. 201°, but could not be caused to react with stannic bromide. Di-2-methylindylmethane gives an additive product (1 : 1) with stannic chloride from which the initial material cannot be regenerated.

H. WREN.

Manufacture of 1 : 8-naphthoxyphenanthiophen. I. G. FARBENTIND.—See B., 1929, 200.

Derivatives of 5-aminoquinoline. R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 237—246).—5-Aminoquinoline and ethylcarbimide, when heated in ethereal solution at 100°, formed *N*-5-quinolyl-*N*'-ethylcarbamide, m. p. 219—220° (resolidification occurred at 220—260° with sublimation and remelting at 300°; these phenomena are ascribed to fission by heat: $\text{C}_9\text{H}_6\text{N}\cdot\text{NH}_2 + \text{Et}\cdot\text{NCO} \rightleftharpoons \text{C}_9\text{H}_6\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{Et} \rightleftharpoons \text{C}_9\text{H}_6\text{N}\cdot\text{NCO} + \text{NH}_2\text{Et}$; *s*-di-5-quinolylcarbamide and *s*-diethylcarbamide are then formed).

5-Aminoquinoline reacted with methyl and ethyl chloroformates in acetic acid-sodium acetate solution to give methyl quinoline-5-carbamate, m. p. 134°, and ethyl quinoline-5-carbamate, m. p. 137°. 5-Amino-

quinoline and potassium cyanate in dilute acetic acid solution formed 5-quinolylcarbamide, m. p. 280° after changing somewhat at 224°, together with a biuret derivative, $C_9H_6N \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH_2$, m. p. 305°.

Absolute nitric acid converted the above quinolyl-ethylcarbamide into N-nitro-N'-8-nitro-5-quinolyl-N-ethylcarbamide, m. p. 173° (decomp.), which, when heated with alcoholic ammonia or with water, gave 8-nitro-5-aminoquinoline, m. p. 280°, and ethyl-nitroamine. Nitration with absolute nitric acid and sulphuric acid and treatment of the product with aqueous ammonia led to 6 : 8-dinitro-5-aminoquinoline, m. p. 273—277° (decomp.).

Nitration of methyl quinoline-5-carbamate with absolute nitric acid gave small yields of methyl 8-nitroquinoline-5-carbamate, m. p. 180° (decomposition with sulphuric acid gave 8-nitro-5-aminoquinoline), accompanied by methyl 6 : 8-dinitroquinoline-5-carbamate, m. p. 195° (decomp.) (sulphuric acid decomposition led to 6 : 8-dinitro-5-aminoquinoline, m. p. 273°). Similar treatment of ethylquinoline-5-carbamate gave ethyl 8-nitroquinoline-5-carbamate, m. p. 156°, mixed-acid nitration giving ethyl 6 : 8-dinitroquinolyl-5-carbamate, m. p. 180—183° (decomp.).

R. J. W. LE FEVRE.

N-Aminoalkylation of amines. [Preparation of 8-(β -hydroxy-1'- γ -piperidylpropylamino)quinoline.]—I. G. FARBERIND.—See B., 1929, 164.

Carbazole. T. V. ARISTOV (J. Chem. Ind. Moscow, 1928, 5, 721).—In purification of carbazole with sulphuric acid, partial sulphonation appears to take place.

CHEMICAL ABSTRACTS.

Identification of alkylbarbituric acids. E. LYONS and A. W. DOX (J. Amer. Chem. Soc., 1929, 51, 288—291).—The following compounds have been prepared by heating barbituric acids with *p*-nitrobenzyl chloride or bromide in aqueous alcohol in presence of sodium carbonate: 1 : 3-Di-*p*-nitrobenzyl-5 : 5-diethyl-, m. p. 192°, -5-ethyl-5-isopropyl-, m. p. 160°, -5 : 5-diallyl-, m. p. 190°, -5-ethyl-5-butyl-, m. p. 146°, -5-ethyl-5-isomethyl-, m. p. 138°, -5-butyl-5-allyl-, m. p. 169°, -5-ethyl-5-amyl-, m. p. 131°; 5-phenyl-1 : 3-di-*p*-nitrobenzyl-5-ethyl-, m. p. 182°; 1-*p*-nitrobenzyl-5 : 5-diethyl-, m. p. 192°, -3-methyl-5 : 5-diethyl-, m. p. 104°, -3 : 5 : 5-triethyl-, m. p. 69°; 3-phenyl-1-*p*-nitrobenzyl-5 : 5-diethyl-, m. p. 133°; 3 : 5-di-*p*-nitrobenzyl-1-methyl-5-hexyl-, m. p. 139°; 1 : 3 : 5-tri-*p*-nitrobenzyl-5-isopropyl-, m. p. 187°, -5-butyl-, m. p. 180°; 1 : 3-diphenyl-5-*p*-nitrobenzyl-5-ethyl-, m. p. 218°; 1 : 3 : 5 : 5-tetra-*p*-nitrobenzyl- (not melting); and a poly-*p*-nitrobenzyl-barbituric acid, m. p. 264° (265°?).

The original contains several apparent misprints.

E. E. TURNER.

N-Alkyl- and -aryl-4 : 5 : 6 : 7-tetrahydroindazoles. K. VON AUWERS, J. CONRAD, A. ERNECKE, and B. OTTENS (Annalen, 1929, 469, 57—82).—A continuation of the indazole syntheses previously described (A., 1924, i, 325; 1925, i, 1181). Condensation of substituted ethyl cyclohexanone-2-oxalates with alkyl- and aryl-hydrazines affords a mixture of 1- and 2-alkyl- or -aryl-4 : 5 : 6 : 7-tetrahydroindazole-3-carboxylates. When hydrazine is used tetrahydroindazole-3-carboxylates result. Subsequent alkyl-

ation of these affords mixtures of the 1- and 2-derivatives. Elimination of carbon dioxide from the alkylated indazolecarboxylic acids gives the corresponding indazoles. Ethyl cyclohexanone-2-oxalate and methylhydrazine acetate react in presence of alcohol and dilute sodium hydroxide solution, giving a mixture of esters which after hydrolysis with alcoholic sodium hydroxide solution affords 2-methyl- and 1-methyl-4 : 5 : 6 : 7-tetrahydroindazole-3-carboxylic acids, m. p. 205—206° and 207.5—208.5°, respectively. These acids are separated by partial esterification with 3% methyl-alcoholic hydrochloric acid: the former is unaffected, and the methyl ester formed from the latter is then rehydrolysed. Thermal decomposition of the acids yields 2-methyl- and 1-methyl-4 : 5 : 6 : 7-tetrahydroindazole, b. p. 109—110°/11 mm. (picrate, m. p. 141—142°), respectively. Ethyl tetrahydroindazole-3-carboxylate, m. p. 106—107°, is ethylated by ethyl bromide and sodium ethoxide, affording after the above treatment 2-ethyl-, m. p. 148—149°, and 1-ethyl-tetrahydroindazole-3-carboxylic acids, m. p. 183—186° (methyl ester, m. p. 108—109°). The picrates of 2- and 1-ethyltetrahydroindazole, m. p. 103—104° and 150—151°, respectively, have been described previously (A., 1924, i, 328) as the 1- and 2-derivatives, respectively. 2-Benzyl-, m. p. 187—187.5°, and 1-benzyl-tetrahydroindazole-3-carboxylic acid, m. p. 157.5—158.5° (methyl ester, m. p. 69—70°), are obtained similarly. The corresponding indazole picrates have m. p. 132—133° and 128—129°, respectively. Ethyl 4-methylcyclohexanone-2-oxalate and hydrazine hydrate afford ethyl 5-methyl-4 : 5 : 6 : 7-tetrahydroindazole-3-carboxylate (I), b. p. 208—210°/14 mm., m. p. 110—111° (free acid, m. p. 274°), whilst condensation with methylhydrazine in presence of acetic acid gives after hydrolysis 2 : 5-dimethyl-tetrahydroindazole-3-carboxylic acid, m. p. 195—195.5°, as the chief product. If the condensation with methylhydrazine is effected in sulphuric acid at 0° 1 : 5-dimethyltetrahydroindazole-3-carboxylic acid, m. p. 185—186° (methyl ester, m. p. 114—115°), is the main product. Methylation of I with methyl iodide and alkali gives about equal quantities of the 1 : 5- and 2 : 5-derivatives. 1 : 5-Dimethyltetrahydroindazole (picrate, m. p. 155°) has b. p. 115—116°/12 mm. Ethylation of I gives *o*-methyl-2-ethyl-, m. p. 184—185°, and 5-methyl-1-ethyl-tetrahydroindazole-3-carboxylic acids, m. p. 147.5—149.5° (methyl ester, m. p. 44.5—45.5°). The m. p. of the corresponding indazole picrates (A., 1925, i, 1183) should be interchanged. Benzylation of I gives 40% of 2-benzyl-5-methyl-, m. p. 186—187°, and 60% of 1-benzyl-5-methyl-tetrahydroindazole-3-carboxylic acids, m. p. 142.5—143.5° (methyl ester, m. p. 98—99°), which when decarboxylated yield 2-benzyl-5-methyl- (picrates, m. p. 115—116° and 135—136°), and 1-benzyl-5-methyl-tetrahydroindazoles, b. p. 191—192°/12 mm. [picrate, m. p. 128—129° (cf. loc. cit.)]. Condensation of the above oxalate with phenylhydrazine gives 80% of ethyl 1-phenyl-5-methyl-4 : 5 : 6 : 7-tetrahydroindazole-3-carboxylate, m. p. 128—129° (methyl ester, m. p. 119—120°; free acid, m. p. 196.5—198.5°), together with 20% of 2-phenyl-5-methyl-4 : 5 : 6 : 7-tetrahydroindazole-3-carboxylic acid, m. p. 202—203°.

Ethyl 6-methylcyclohexanone-2-oxalate and hydr-

azine hydrate afford 43% of ethyl 7-methyl-4:5:6:7-tetrahydroindazole-3-carboxylate, b. p. 182°/11 mm., m. p. 87—88° (free acid, m. p. 212—214°), which with methyl iodide and sodium methoxide yields approximately equal amounts of 2:7-dimethyl-, m. p. 128—130°, and 1:7-dimethyl-tetrahydroindazole-3-carboxylic acids, m. p. 169.5—170.5° (methyl ester, b. p. 185—187°/11 mm.). 1:7-Dimethyltetrahydroindazole (picrate, m. p. 155.5°) has b. p. 111—112°/11 mm. Ethylation gives about equal amounts of 7-methyl-2-ethyl-, m. p. 43—49°, and 7-methyl-1-ethyl-tetrahydroindazole-3-carboxylic acids, m. p. (+H₂O) 94°, (anhydrous) 127.5—128.5° (methyl ester, b. p. 182—183°/10 mm., d_{4}^{20} 1.0899, 1.50485). 7-Methyl-1-ethyltetrahydroindazole (picrate, m. p. 136—137°) has b. p. 111—111.5°/10 mm. Benzylation gives 80% of 1-benzyl-7-methyltetrahydroindazole-3-carboxylic acid, m. p. (+H₂O) 119—121° (methyl ester, b. p. 242—246°/11 mm.), together with 20% of the 2-benzyl derivative, m. p. 154—154.5°. 1- and 2-Benzyl-7-methyltetrahydroindazoles, b. p. 188—191°/11 mm. and 189—190°/12 mm., respectively, are obtained in the usual way. Condensation of the above oxalate with phenylhydrazine in presence of hydrochloric or acetic acid yields 65% of 1-phenyl-7-methyltetrahydroindazole-3-carboxylic acid, m. p. 177—178° (methyl ester, b. p. 238—240°/12 mm.), and 35% of the 2-phenyl-acid, m. p. 180—181°.

Methylation of ethyl 4:6-dimethyl-4:5:6:7-tetrahydroindazole-3-carboxylate, b. p. 197°/12 mm. (methyl ester, b. p. 197°/12 mm., m. p. 90—91°; free acid, m. p. 269—270°), affords 83% of 1:4:6-trimethyl-tetrahydroindazole-3-carboxylic acid, m. p. 176—177° (methyl ester, m. p. 73—75°), together with 17% of the 2:4:6-trimethyl derivative, m. p. 179—180°. The picrates of 1:4:6- and 2:4:6-trimethyltetrahydroindazoles, m. p. 175—176.5° and 145—146°, respectively, have been previously described (*loc. cit.*) as the 2:4:6- and 1:4:6-derivatives. 4:6-Dimethyl-1-ethyltetrahydroindazole-3-carboxylic acid, m. p. 141—141.5° (methyl ester, b. p. 188—189°/11 mm., m. p. 64.5—65.5°), gives 4:6-dimethyl-1-ethyltetrahydroindazole, b. p. 126°/11 mm. [picrate, m. p. 137—138°, previously named 2-picrate (*loc. cit.*)], and 4:6-dimethyl-2-ethyltetrahydroindazole-3-carboxylic acid, m. p. 145—146.5°, yields the corresponding indazole [picrate, m. p. 117—118°, previously termed the 1-picrate (*loc. cit.*)]. 2-Benzyl-4:6-dimethyl-, m. p. 159.5—160.5°, and 1-benzyl-4:6-dimethyl-tetrahydroindazole-3-carboxylic acids, m. p. 137—138° (methyl ester, b. p. 242—243°/11 mm., m. p. 112—113°), are also described. 1-Phenyl-4:6-dimethyl-tetrahydroindazole [perchlorate, m. p. 183—184° (*cf. loc. cit.*)] is obtained from the corresponding 3-carboxylic acid, m. p. 192.5—193.5° (methyl ester, b. p. 240°/11 mm., m. p. 87—88°). 2-Phenyl-4:6-dimethyltetrahydroindazole-3-carboxylic acid has m. p. 223° (decomp.). Spectrochemical data for 14 substituted tetrahydroindazoles are given.

H. BURTON.

Synthesis and fission of quaternary tetrahydroindazolium salts. K. VON AUWERS, J. CONRAD, and A. ERNECKE (*Annalen*, 1929, 469, 82—92).—The following substituted 4:5:6:7-tetrahydroindazolium iodides have been prepared from the

requisite indazole and alkyl or aralkyl iodide at 100°: 1:2-dibenzyl-, m. p. 153°; 1-benzyl-2-ethyl-, m. p. 125—127°; 1:2:5-trimethyl-, m. p. 137.5° (bromide, an oil); 1:5-dimethyl-2-ethyl-, m. p. 84°; 2:5-dimethyl-1-ethyl-, m. p. 67—69°; 5-methyl-1:2-diethyl-, m. p. 115—117°; 2-benzyl-1:5-dimethyl-, m. p. 139—140°; 1-benzyl-2:5-dimethyl-, m. p. 175—176°; 2-benzyl-5-methyl-1-ethyl-, m. p. 167—168°; 1-benzyl-5-methyl-2-ethyl-, m. p. 142—144°; 1:2:7-trimethyl-, m. p. 121—123°; 7-methyl-1:2-diethyl-, an oil; 2-benzyl-1:7-dimethyl-, m. p. 175°; 1-benzyl-2:7-dimethyl-, m. p. 155°; 1:4:6-trimethyl-2-ethyl-, an oil; 2:4:6-trimethyl-1-ethyl-, m. p. 116—118°; 2-benzyl-1:4:6-trimethyl-, an oil, and 1-benzyl-2:4:6-trimethyl-, m. p. 119.5—120.5°. The compounds previously described as 1-benzyl-1-ethyl- and 2-benzyl-2-ethyl-tetrahydroindazolium iodides (A., 1924, i, 329) are the 1-benzyl-2-ethyl- and 2-benzyl-1-ethyl derivatives, respectively. The methiodide of 7-methyl-2-ethyltetrahydroindazole, m. p. 102—103° (*loc. cit.*), is the quaternary 2:7-dimethyl-1-ethyl salt. The methiodide, m. p. 175°, from 2-benzyl-7-methyltetrahydroindazole (*loc. cit.*) is also obtained from 1:7-dimethyltetrahydroindazole and benzyl iodide, and is, therefore, 2-benzyl-1:7-dimethyl-tetrahydroindazolium iodide. Fission of the above salts is accomplished by heating in a vacuum above the m. p. and converting the bases formed into the picrates. With the 1:2-dimethyl, 1:2-diethyl, and 1:2-dibenzyl derivatives approximately equal amounts of the 1- and 2-alkyltetrahydroindazoles are produced; occasionally an excess of the 2-derivative results. When dissimilar groups are attached to the 1- and 2-positions the one with the least affinity demand (*e.g.*, benzyl) is eliminated, in agreement with the results previously obtained (*cf. A.*, 1926, 847). In some of the decompositions a partial wandering of an alkyl group occurs. Thus, 1-benzyl-2:7-dimethyltetrahydroindazolium iodide affords in addition to 2:7-dimethyltetrahydroindazole a small amount of the 1:7-dimethyl derivative. 1:4:6-Trimethyl-2-ethyltetrahydroindazolium iodide gives 1:4:6-trimethyl-, 4:6-dimethyl-1-ethyl-, and 4:6-dimethyl-2-ethyl-tetrahydroindazoles in the ratio of 2:1:3. Similarly, 2:4:6-trimethyl-1-ethyltetrahydroindazolium iodide yields 1:4:6-trimethyl-, 4:6-dimethyl-1-ethyl-, and 2:4:6-trimethyl-tetrahydroindazoles in the proportion 3:3:1.

H. BURTON.

Acridine. III. Hydrogenation of acridine with sodium amalgam. K. LEHMSTEDT and H. HUNDERTMARK (*Ber.*, 1929, 62, [B], 414—418; *cf. A.*, 1927, 776; 1928, 1259).—Acridine is reduced by sodium and alcohol to a mixture of 9:10-dihydroacridine (acridan) and "insoluble hydroacridine." The former compound readily yields additive products, C₁₃H₁₁N, AgNO₃; C₁₃H₁₁N, HgCl₂; (C₁₃H₁₁N)₂, EtONa, m. p. 170°; with acridine hydrochloride in alcohol it affords the quinuhydrone-like compound, C₁₃H₁₁N, C₁₃H₉N, HCl, 1.5H₂O, immediately decomposed into its components by water or ether. Analyses of "insoluble hydroacridine" indicate the composition C₂₆H₂₂ON₂, the sodium amalgam thus appearing to operate as oxygen carrier. The compound is somewhat unstable and decomposes when

heated or continuously warmed with concentrated sulphuric acid into dihydroacridine, acridine, and water. The constitution $\begin{array}{c} \text{C}_{13}\text{H}_{10} > \text{NH} \\ \text{C}_{13}\text{H}_{10} > \text{NH} > \text{O} \end{array}$ is suggested. "Insoluble hydroacridine" loses water when dissolved in boiling pyridine and becomes transformed into the non-basic 9:9':10:10'-tetrahydro-10:10'-diacridyl, m. p. 220° when placed in a bath pre-heated to 205° or m. p. 208–210° (decomp.) after softening when more slowly heated. It decomposes when heated into acridine and dihydroacridine, but does not suffer fission when warmed with sulphuric acid, which causes production of a new base, not yet examined completely. H. WREN.

Porphyrins. XVIII. Porphyrin formation from β -hæmin. W. KÜSTER and W. VON DEGENFELD. **XIX. Porphyrin fission of substituted hæmins and constitution of hæmin.** W. KÜSTER and K. SCHLAYER (Z. physiol. Chem., 1929, 180, 259–269, 270–285).—XVIII. The crude hæmin from the blood of a horse inoculated with erysipelas culture has been examined. The chloroform-insoluble portion is soluble in 5% sodium hydroxide solution and is therefore not an ester. By the action of diazomethane only one methyl group is introduced into the double molecule, and treatment of a pyridine solution with alcoholic hydrochloric acid gives a monoethylhæmin, $(\text{C}_{36}\text{H}_{33}\text{O}_4\text{N}_4\text{ClFe})_2$. The chloroform-soluble part is a monoethylhæmin, partly methylated by diazomethane. Porphyrin fission of the crude hæmin by treatment with hydrogen bromide and acetic acid and finally water affords, in addition to unchanged hæmin, hæmatoporphyrin and an insoluble product, probably a β -bromo- α' -dihydroxymesoporphyrin, $\text{C}_{34}\text{H}_{37}\text{O}_6\text{N}_4\text{Br}$ (copper, zinc, and hydroxyiron salts), formed by initial addition of 2 mols. of hydrogen bromide to the acetylene residue and 1 mol. of hydrogen bromide to the vinyl group. This new porphyrin is methylated with diazomethane in chloroform suspension, yielding a dimethyl ester; it forms a dihydrochloride, completely hydrolysed by water at the ordinary temperature. The bromine is removed by successive treatment with hot 5% sodium hydroxide solution. When decomposed with hydrobromic and acetic acids and the residue, after removal of acid under reduced pressure, treated with methyl alcohol at 60° a small amount of bromodimethoxyporphyrin dimethyl ester, obtained.

XIX. Treatment of dichloro- α -dimethyl(chloro)-hæmin with a very large excess of boiling methyl alcohol gives a soluble chloromethoxydimethylhæmin (I), $\text{C}_{37}\text{H}_{37}\text{O}_5\text{N}_4\text{Cl}_2\text{Fe}$, together with 10% of an insoluble substance (II), $\text{C}_{36}\text{H}_{33}\text{O}_4\text{N}_4\text{Cl}_2\text{Fe}$, apparently formed by elimination of hydrogen chloride. Treatment of I with a mixture of hydrobromic and acetic acids and then with methyl alcohol affords chlorohæmatoporphyrin dimethyl ether (Küster and Fleischmann, A., 1928, 657) [complex zinc, copper, and iron chloride salts; dimethyl ester, m. p. 112° after sintering at 63° (complex iron chloride salt, m. p. 177° after sintering at 131°)], together with a bromine-containing product, which after the action of hydrobromic and acetic acids and methyl alcohol

gives chlorobromodimethoxymesoporphyrin together with the monomethoxy-ether and a "hæmin." When the residue from the hydrobromic-acetic acid treatment of I is treated with water or 1% hydrobromic acid a soluble chlorobromo-derivative (containing no methoxyl) and an insoluble chlorobromo-compound are obtained. Treatment of the latter with disodium hydrogen phosphate eliminates bromine, yielding a chlorohæmatoporphyrin, $\text{C}_{34}\text{H}_{35}\text{O}_6\text{N}_4\text{Cl}$ [dimethyl ester (complex zinc, copper, and iron chloride salts)]. When a pyridine solution of I is treated with dilute hydrochloric acid there appears to be formed (spectrum) a dichlorodimethylhæmin. Some change occurs in pyridine solution, since fission of the resulting product with hydrobromic and acetic acids gives a chlorobromodimethoxymesoporphyrin. Fission of II gave impure chlorobromodimethoxymesoporphyrin and the hydrobromide of a substance containing iron. Oxidation of chlorohæmatoporphyrin dimethyl ether with chromic anhydride and 30% sulphuric acid yields methyl(chloromethoxy)ethylmaleinimide, m. p. 65°. The formation of chlorohæmatoporphyrin dimethyl ether from I indicates that fission occurs thus: $\cdot\text{CH}(\text{OMe})\cdot\text{CH}\cdot\text{C}\cdot\text{CH}_2\text{Cl} \longrightarrow \cdot\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br} + \cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\text{Cl}$, with subsequent elimination of hydrogen bromide from the dibrominated residue and replacement of bromine by methoxyl, viz., $\cdot\text{CH}\cdot\text{CHBr} \longrightarrow \cdot\text{CH}\cdot\text{CH}\cdot\text{OMe}$. H. BURTON.

Protoporphyrin. A. HAMSÍK (Z. physiol. Chem., 1929, 180, 308–318).—When α -hydroxyhæmin (A., 1928, 1148) is treated with iron powder in presence of formic acid (cf. Fischer and Pützer, A., 1926, 854) protoporphyrin is formed together with by-products. Treatment with acetic, formic, or alcoholic hydrochloric acid and hydrazine hydrate, or hydrochloric acid and stannous chloride in acetone, gives varying amounts of protoporphyrin. Aqueous or acetic acid solutions of stannous chloride and hydrochloric acid are unsuitable. Similar experiments carried out with β - and ψ -hydroxyhæmins and α -chlorohæmin do not give such satisfactory results. Protoporphyrin is affected by treatment with dilute hydrochloric acid in acetone or hot acetic acid, the colour of the solution becoming reddish-brown. With reducing agents, except formic acid and hydrazine hydrate, there is also a colour change. The complex protoporphyrin tin salt previously described (A., 1926, 1265) is altered by dilute hydrochloric acid, giving a substance soluble in formic acid to a greenish-blue solution. H. BURTON.

Derivatives of 2:5-diphenyloxazole. S. MINOVICI, C. D. NENITZESCU, and B. ANGELESCU (Bul. Soc. Chim. Romania, 1928, 10, 149–159).—Synthesis of 2:5-diphenyloxazoles by condensation of aromatic aldehydecyanohydrins with aromatic aldehydes in the presence of dry hydrogen chloride (cf. Fischer, A., 1896, i, 262; Minovici, A., 1896, i, 703; Ingham, A., 1927, 459) has been extended to various substituted aldehydes and aldehydecyanohydrins. From benzaldehydecyanohydrin and *p*-nitrobenzaldehyde a considerable quantity of *p*-nitrobenzylidenemandelamide, m. p. 168°, is obtained, and with *p*-anisaldehydecyanohydrin and *p*-nitrobenzaldehyde the sole product is *p*-nitrobenzylidene-*p*-

methoxymandelamide, m. p. 168°. The basicity of these oxazoles is largely diminished by the presence of negative substituents in the two phenyl groups; thus the hydrochlorides of phenyloxazoles can be recrystallised from absolute alcohol, whilst those of nitrophenyloxazoles lose hydrogen chloride. The following substances have already been obtained by Lister and Robinson (J.C.S., 1912, 101, 1297) using a method other than that given above; the m. p. in parentheses are theirs. 5-Phenyl-2-*p*-tolylloxazole, m. p. 74° (77°) [hydrochloride, m. p. 160—161° (decomp.)]; 5-phenyl-2-*o*-chlorophenyloxazole, m. p. 83° (80—81°); 5-phenyl-2-*o*-nitrophenyloxazole, m. p. 123° (125°); 5-phenyl-2-*m*-nitrophenyloxazole, m. p. 154—155° (149°); 5-phenyl-2-*p*-nitrophenyloxazole, m. p. 208° (202—204°). The following are described: 2-phenyl-5-*p*-tolylloxazole, m. p. 81° [hydrochloride, m. p. 180° (decomp.)]; 2-*p*-anisyl-5-*p*-tolylloxazole, m. p. 88°; 5-phenyl-2-piperonyloxazole, m. p. 116—117° [hydrochloride, m. p. 193° (decomp.)]; 5-phenyl-2-*m*-chlorophenyloxazole, m. p. 107°; 5-*p*-anisyl-2-*p*-tolylloxazole, m. p. 90° [hydrochloride, m. p. 179° (decomp.)]; 5-*p*-anisyl-2-piperonyloxazole, m. p. 145°; 2-*o*-nitrophenyl-5-*p*-methoxyphenyloxazole, m. p. 116°; 2-*m*-nitrophenyl-5-*p*-methoxyphenyloxazole, m. p. 163°; 2-*o*-chlorophenyl-5-*p*-methoxyphenyloxazole, m. p. 108° (hydrochloride, m. p. 127°); 2-*m*-chlorophenyl-5-*p*-anisylloxazole, m. p. 123° [hydrochloride, m. p. 162° (decomp.)]; 2-phenyl-5-*p*-nitrophenyloxazole, m. p. 187° (cf. Minovici, *loc. cit.*), which is also obtained by nitration of 2 : 5-diphenyloxazole, and yields *p*-nitrobenzoic acid when oxidised. C. W. SHOPPEE.

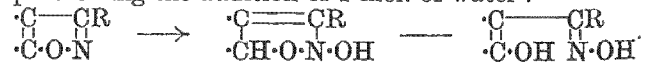
***o*-Benzidine rearrangement of 4-phenylhydrazino-5-phenyl-3-methylisooxazole.** G. WITTIG, H. KLEINER, and J. CONRAD (Annalen, 1929, 469, 1—16).—Reduction of 4-benzeneazo-5-phenyl-3-methylisooxazole (A., 1928, 779) either electrolytically or with aluminium powder and a small amount of sodium hydroxide solution in alcoholic solution affords 4-phenylhydrazino-5-phenyl-3-methylisooxazole, m. p. 136° (decomp.). When this is warmed with hydrochloric acid there is formed a mixture of 5-anilino-5-phenyl-3-methylisooxazol-4-one (I), m. p. 130° (decomp.), and 5-phenyl-5-*o*-aminophenyl-3-methylisooxazole-4-ketimine (II), m. p. 179—180° (decomp.; benzylidene derivative, m. p. 195.5—196°; acetyl derivative, m. p. 254°; chlorostannate, m. p. 127°). Thermal decomposition of I at 130° gives carbon monoxide and benzanilide, whilst acid or alkaline hydrolysis affords benzoic acid and aniline. The compound is unaffected by potassium permanganate or by hydroxylamine. Bromination of I in acetic acid solution yields benz-2 : 4-dibromoanilide, m. p. 139.5°, and magnesium phenyl bromide converts it into 4-hydroxy-5-anilino-4 : 5-diphenyl-3-methylisooxazoline, m. p. 173.5° (slight decomp.). Hydrolysis of this last compound with *N*-acetic acid in acetone gives an oxime, C₁₆H₁₅O₃N, m. p. 179—180° (decomp.), converted by further hydrolysis with 2*N*-sulphuric acid into benzil. Magnesium methyl iodide and I yield 4-hydroxy-5-anilino-5-phenyl-3 : 4-dimethylisooxazoline, m. p. 201° (slight decomp.), hydrolysed by 2*N*-sulphuric acid, forming aniline and γ -nitroso- β -benzoylbutan- β -ol, m. p. 145°. Bromination of II in

dry chloroform yields the hydrobromide, m. p. 172.5° (decomp.), of 5-phenyl-5-*p*-bromo-*o*-aminophenyl-3-methylisooxazole-4-ketimine, m. p. 175°, whilst hydrolysis with 30% potassium hydroxide solution gives 2-amino-3-hydroxy-3-phenylindole, m. p. 204° (decomp.), also formed by the action of an excess of magnesium methyl iodide on II. When this indole derivative is fused with alkali hydroxide *o*-aminobenzophenone and hydrogen cyanide are produced. Treatment of II with boiling dilute acetic acid affords 2 : 3-dihydroxy-3-phenylindole, m. p. 209—210° (*N*-acetyl derivative, m. p. 140—140.5°). H. BURTON.

Fission of the benzisooxazole ring. H. LINDEMANN and H. CISCHE (Annalen, 1929, 469, 44—57).—Methyl 6-nitrobenzisooxazole-3-carboxylate (Borsche, A., 1912, i, 652), when heated with slightly diluted sulphuric acid at 100°, gives 6-nitrobenzisooxazole-3-carboxylic acid (I), m. p. 189—190° with elimination of carbon dioxide. Alkaline hydrolysis affords an acid (II), C₈H₄O₆N₂·H₂O, m. p. 167—168° (cf. Borsche, *loc. cit.*), which when dried in a vacuum over phosphorus pentoxide loses water and gives I. Treatment of I with water affords II, indicating simple hydration. 4-Nitro-2-hydroxyphenylglyoximic acid (Borsche, *loc. cit.*) is probably II.

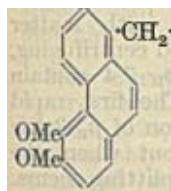
Treatment of an alcoholic solution of methyl 6-nitrobenzisooxazole-3-carboxylate with hydrazine hydrate affords the corresponding hydrazide, m. p. 170° (acetyl derivative, m. p. 213—214°), converted by nitrous acid into the corresponding azide, m. p. 135° (decomp.). Decomposition of this with acetic acid affords di-(6-nitrobenzisooxazole-3)-carbamide, m. p. 342°, whilst with acetic anhydride and a small amount of concentrated sulphuric acid 6-nitro-3-acetamido-, m. p. 230° (not sharp), and 6-nitro-3-di-acetamido-benzisooxazoles, m. p. 133°, are produced. When either of these acetyl derivatives is warmed with 2*N*-sodium hydroxide solution 3-4'-nitro-2'-hydroxyphenyl-5-methyl-1 : 2 : 4-oxdiazole, m. p. 124° (acetyl derivative, m. p. 162°), results, thus demonstrating fission of the isooxazole ring and subsequent reaction between the oximino- and acetamido-groupings. Hydrolysis of the acetyl derivatives with fairly concentrated sulphuric acid gives 6-nitro-3-aminobenzisooxazole, m. p. 234°, converted by treatment with nitrous acid into 6-nitro-3-hydroxybenzisooxazole, m. p. 85—88° (decomp.). Treatment of this last compound with acetic acid or the above amino-derivative with nitrous acid in presence of acetic acid gives 4-nitro-2-hydroxybenzacylhydroxamic acid, (NO₂)(OH)C₆H₃·C(N·OAc)·OH, m. p. 184° resolidifying with m. p. 241°, hydrolysed by 10% sodium hydroxide solution to the corresponding hydroxamic acid, m. p. 214°. When either of these acids is heated with methyl-alcoholic potassium hydroxide solution 6-nitrobenzoxazol-2-one, m. p. 241°, results.

Fission of the benzisooxazole ring is explained by postulating the addition of 1 mol. of water :



If the group R has no depressant action (e.g., OH, NHAc) on the conjugated system fission occurs, but when R depresses the conjugation (e.g., alkyl, NH₂) fission is inhibited. H. BURTON.

Opium alkaloids. X. Syntheses of *dl*-apomorphine dimethyl ether. E. SPATH and O. HROMATKA (Ber., 1929, 62, [B], 325—332).—2-Nitrohomoveratric acid is converted by phosphorus pentachloride into the non-crystalline chloride and thence by β -phenylethylamine in aqueous-alkaline solution according to the method of Kay and Pictet (J.C.S., 1913, 103, 947) into nitrohomoveratryl- β -phenylethylamide, m. p. 79° (lit. m. p. 98°); preferably, the acid is treated successively with thionyl chloride and an excess of β -phenylethylamine in benzene, whereby the amide, m. p. 79°, is obtained, although in a single instance the product had m. p. 118° after softening at 116°. Treatment of either amide with phosphoric oxide in boiling xylene or, preferably, toluene yields a mixture of 1:2'-nitro-3':4'-dimethoxybenzyl-3:4-dihydroisoquinoline, m. p. 129° (vac.), and a non-basic compound, $C_{21}H_{21}O_4N_2$, m. p. 124—126°, probably identical with that described by Kay and Pictet (*loc. cit.*). The dihydro-base is transformed through the *methiodide*, m. p. 203° (decomp.), into the *methochloride*. Reduction of the latter compound with tin and hydrochloric acid followed by treatment with nitrous acid and copper powder gives *dl*-apomorphine dimethyl ether. Since this product is not readily obtainable from natural sources, it is transformed by boiling benzoyl chloride into the benzoyl compound (I), $\text{CH}_2\text{CH}_2\text{NMeBz}$ m. p. 164.5—165°. The same treatment of *l*-apomorphine dimethyl ether yields this compound, since the nitrogen ring is ruptured at the position of the asymmetric



(I.)

carbon atom and an optically inactive compound is thus produced.

Complete methylation of *l*-apomorphine to non-crystalline *l*-apomorphine dimethyl ether is effected by prolonged treatment of a solution of the base in methyl alcohol with an excess of ethereal diazomethane; the *hydrogen d-tartrate*, m. p. 177—178° (vac., decomp.), is described.

Attempts to racemise *l*-apomorphine dimethyl ether by protracted heating of the base, by the action of alcoholic iodine and subsequent hydrogenation, or by oxidation with mercuric acetate were unsuccessful.

H. WREN.

Synthesis of *dl*-apomorphine dimethyl ether. H. AVENARIUS and R. PSCHORR [and, in part, H. HERZ] (Ber., 1929, 62, [B], 321—325; cf. Pschorr, A., 1906, i, 878; 1907, i, 635).—*vic*-2-Nitrovanillin methyl ether is condensed with hippuric acid in the presence of sodium acetate and acetic anhydride to 2-nitro- α -benzamido-3:4-dimethoxycinnamylactone (+1EtOH), m. p. 169°, converted by sodium hydroxide or 75% acetic acid into 2-nitro- α -benzamido-3:4-dimethoxycinnamic acid, decomp. 215° (ethyl ester, m. p. 149°). The lactone is transformed by aqueous-alcoholic hydrochloric acid at 100° into 2-nitro-3:4-dimethoxyphenylpyruvic acid, m. p. 172° (ethyl ester, m. p. 109°, and its *oxime*, m. p. 108°). The *oxime* of the acid, m. p. 156—157°, is converted at 150—160° into 2-nitro-3:4-dimethoxyphenylacetone, m. p. 66°.

β -Phenylethylamine is transformed by anhydrous formic acid at 150—180° into its *formyl* derivative, b. p. 210—214°/35 mm., which, when treated successively with potassium and methyl iodide, affords *N*-formyl-*N*-methyl- β -phenylethylamine. The latter compound is isomerised by thionyl chloride in boiling toluene to 1-hydroxy-2-methyl-1:2:3:4-tetrahydroisoquinoline, m. p. 110—111°. Condensation of molecular quantities of 2-nitro-3:4-dimethoxyphenylacetone with 1-hydroxy-2-methyltetrahydroisoquinoline in presence of sodium ethoxide followed by successive hydrolysis of the cyano-group and elimination of carbon dioxide by boiling hydrochloric acid and reduction by tin foil yields 1:2'-amino-3':4'-dimethoxybenzyl-2-methyl-1:2:3:4-tetrahydroisoquinoline (dihydrochloride, m. p. 198—199°). Treatment of the dihydrochloride with sodium nitrite and copper powder and of the product with methyl iodide affords the *methiodide* of apomorphine dimethyl ether, m. p. 195°, identical with the product derived from natural sources.

H. WREN.

Strychnos alkaloids. XLVIII. Fission of the oxime of brucinic acid by alkali. H. LEUCHS (Ber., 1929, 62, [B], 407—409).—The oxime of brucinic acid is converted by the prolonged action of *N*-alkali hydroxide mainly into a compound, $C_{21}H_{21}O_6N_3$, m. p. 295—300° (decomp.) after changing at 280°, which yields an *acetyl* derivative, $C_{23}H_{23}O_6N_3$, decomp. 240° after darkening at 225°. In addition, an *isomeride*, m. p. 250—258° (decomp.), is obtained, whilst about 50% of the acid is recovered unchanged.

H. WREN.

Action of magnesium phenyl bromide on phosphorus pentachloride. J. H. KOLITOWSKA (Rocz. Chem., 1928, 8, 568—575).—The products of the action of magnesium phenyl bromide on phosphorus pentachloride are diphenyl, triphenylphosphine, triphenyldihydroxyphosphine, *phosphorus tetraphenyl bromide*, $PBrPh_4 \cdot 2H_2O$, m. p. 286—288°, and a crystalline complex, $PhMgBr \cdot MgBr_2 \cdot MgCl_2 \cdot 4Et_2O$. The double compound formed between triphenylphosphine has the composition $(PPh_3)_2 \cdot HgCl_2$, and not $PPh_3 \cdot HgCl_2$, as stated by Michaelis and Soden (A., 1885, i, 1134).

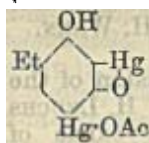
R. TRUSZKOWSKI.

Derivatives of mono- and di-aminohydroxyphenylarsinic acids. B. C. FISHER and G. W. RAIZISS (J. Amer. Chem. Soc., 1929, 51, 527—532).—3-Acetamido-4-hydroxyphenylarsinic acid gives *lithium* (+2H₂O), *calcium* (+2H₂O), *barium*, and *strontium* salts. 3-Nitro-4-hydroxyphenylarsinic acid is brominated in methyl alcohol in presence of iron to 5-bromo-3-nitro-4-hydroxyphenylarsinic acid, decomp. 280°, which is reduced by sodium hyposulphite to 5-bromo-3-amino-4-hydroxyphenylarsinic acid (*N*-acetyl derivative, decomp. 267—270°). 3:5-Diamino-4-hydroxyphenylarsinic acid (cf. A., 1921, i, 370) is readily acylated to 3:5-diformamido-, decomp. 200°; 3:5-diacetamido-, darkens at 235—240° (toxicity relatively low); 3:5-dipropionamido-, m. p. 197—198°; 3:5-dibutyramido-, m. p. 177°, and 3:5-dichloroacetamido-, m. p. 210—211° (decomp.), -4-hydroxyphenylarsinic acids (corresponding sodium salts).

H. E. F. NOTTON.

Derivatives of tri-*p*-tolylsilicane. A. R. STEELE and F. S. KIPPING (J.C.S., 1929, 357—358).—The fraction b. p. 250—300° isolated from the crude product of the interaction of silicon tetrachloride and magnesium *p*-tolyl bromide when kept for several weeks yields *tri-p*-tolylsilicyl chloride, m. p. 115—116°, slowly decomposed by cold water and converted by dilute ammonia in aqueous acetone into *tri-p*-tolylsilicol, m. p. 99—100°. When an alcoholic solution of the silicol containing a little aqueous sodium hydroxide is evaporated at 100° and the residue is then heated *tri-p*-tolylsilicyl oxide, m. p. 223—224°, is produced. A. I. VOGEL.

Mercuration of resorcinol and alkylresorcinols. R. B. SANDIN (J. Amer. Chem. Soc., 1929, 51, 479—483).—Ethylresorcinol (1 mol.) and mercuric acetate (2 mols.) in ethyl alcohol give quantitatively yellow *acetoxymercurianhydromercuriethylresorcinol* (? annexed formula), which darkens at 180°. This is



converted by dilute hydrochloric acid into 2:6-dichloromercuri-4-ethylresorcinol, decomp. 207—209°, and by carbon dioxide in alkaline solution into dark brown *hydroxymercurianhydromercuriethylresorcinol*. The phenol gives with 0.5 mol. of mercuric acetate in hot acetic acid 6(2)-*acetoxymercuriethylresorcinol*, m. p. 163—164° (decomp.), which is converted by aqueous sodium chloride into 6(2)-*chloromercuriethylresorcinol*, m. p. 145—146° (corr.). Hexylresorcinol (A., 1926, 838) affords similarly yellow *acetoxymercurianhydromercuriethylresorcinol* (darkens at 200°), 2:6-dichloromercuri-4-hexylresorcinol, m. p. 137—138°, and 6(2)-*acetoxymercuriethylresorcinol*, m. p. 177—178° (decomp.). Resorcinol (cf. Dimroth, A., 1902, i, 849; Leys, A., 1905, i, 433) yields with mercuric acetate (3 mols.) in alcohol yellow *diacetoxymercurianhydromercuriresorcinol* (darkens at 210°).

H. E. F. NOTTON.

Replacement of carboxyl by mercury in 3-substituted phthalic acids. I. F. C. WHITMORE and P. J. CULHANE (J. Amer. Chem. Soc., 1928, 51, 602—605).—The mercuration of 3-substituted phthalic acids has been examined in order to show that in the formation of the inner anhydride of *o*-hydroxymercuribenzoic acid from mercuric acetate and phthalic acid (Pesci, A., 1901, i, 576) the mercury displaces a carboxyl group and not an *o*-hydrogen atom. Prolonged refluxing of sodium 3-nitrophthalate with aqueous mercuric acetate gives the *anhydride* of 3-nitro-2-hydroxymercuribenzoic acid, which is not attacked by fuming nitric acid, but yields with boiling hydrochloric acid *m*-nitrobenzoic acid and with halogens the 2-halogeno-3-nitrobenzoic acid. 3-Bromo- and 3-chloro-phthalic acids also give gelatinous mercuration products which are hydrolysed by hydrochloric acid to 3-bromo- and 3-chloro-benzoic acids.

H. E. F. NOTTON.

Mol. wt. of haemocyanin of *Limulus Polyphemus*. T. SVEDBERG and F. F. HEYROTH (J. Amer. Chem. Soc., 1929, 51, 539—550).—The protein (I) has a partial specific vol. of 0.735 at 20° and a mol. wt. of 2.04×10^6 by the sedimentation velocity method in 0.98% solution in phosphate buffer at p_H 6.63. This is about one third of that of *Helix* haemocyanin (II)

at p_H 5.62 (cf. following abstract). At concentrations of 0.65—0.03% a progressive disintegration occurs with formation of increasing amounts of non-centrifugable matter. The change is largely, if not quantitatively, reversed when the protein is reprecipitated by dialysis. The decomposition is also shown by sedimentation equilibrium measurements and by the fact that the dilute solutions do not obey Beer's law. The absorption spectra of I and II near the isoelectric point are similar, but the spectrum of II is more intense throughout. In the visible region the curve for I approaches more nearly to that of the acid degradation product of II. The molecules of I, unlike those of II, deviate considerably from the spherical shape. H. E. F. NOTTON.

Hydrogen-ion activity and the stability of the haemocyanin of *Helix pomatia*. T. SVEDBERG and F. F. HEYROTH (J. Amer. Chem. Soc., 1929, 51, 550—561).—The mol. wt. by the sedimentation velocity method of *Helix* haemocyanin (cf. A., 1928, 783) in 0.089% solutions in dilute acetate and phosphate buffers is 5.0×10^6 between p_H 4.5 and p_H 7.4. As these limits are approached the molecules become hydrated and then break down into heterogeneous products. These are also the limits beyond which *Helix* serum increases rapidly in viscosity (cf. Stedman, A., 1927, 689). At p_H 3.9, particles of two different sizes are present together with matter which is precipitated only by high-speed centrifuging, whilst solutions more alkaline than p_H 7.4 contain in addition still smaller particles. The first rapid decomposition which occurs in a solution of p_H 3.4 is mainly reversed by neutralisation, but when the solution is kept a further irreversible splitting occurs.

H. E. F. NOTTON.

Correlation between total nitrogen of bases and arginine-nitrogen and between total nitrogen of bases and lysine-nitrogen of various proteins. R. K. LARMOUR (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 349—363).—A statistical examination of 214 results obtained by different authors of the total basic nitrogen and arginine-nitrogen values for different proteins gives a coefficient of correlation $+0.794 \pm 0.017$. The coefficient between total basic nitrogen and the deviation of arginine-nitrogen from the mean is $+0.211 \pm 0.044$. Considering 213 cases the coefficient of correlation between total basic nitrogen and lysine-nitrogen was found to be $+0.548 \pm 0.032$, and between total basic nitrogen and the deviation of lysine from the mean, $+0.03 \pm 0.046$. It is suggested that these results support Kossel's hypothesis that arginine is the nucleus of the protein molecule.

F. C. HAPFOLD.

Nitrogen distribution of gelatin. F. S. DAFT (Biochem. J., 1929, 23, 149—160).—Certain modifications of the method of analysis of proteins are advocated. Preliminary treatment of gelatin with acid or alkali has no effect on the percentage of non-amino-nitrogen and of basic nitrogen. S. S. ZILVA.

Fractionation of gelatin. M. KUNITZ and J. H. NORTROP (J. Gen. Physiol., 1929, 12, 379—390).—When gelatin is repeatedly washed with water at p_H 4.7 and 23° a residue which is insoluble in water even at 80°, and a soluble fraction result. The

insoluble fraction contains some soluble protein, does not swell in water, but swells in acid and in alkali. Alkaline gels of the insoluble fraction shrink more in acid than do similar gels of normal gelatin. As the two fractions cannot be converted back into gelatin it is assumed that they are bound together in the micellæ. Partial hydrolysis of gelatin at 90° yields a similar, although probably not identical, insoluble substance.

E. BOYLAND.

Absorption of ultra-violet light by some proteins. L. MARCHELEWSKI and J. WIERZUCHOWSKA (Bull. Acad. Polonaise, 1928, A, 471—478).—The absorption spectra of some proteins, in neutral aqueous solution unless otherwise stated, have been measured. Ovalbumin gives a band between 3109 and 2415 Å., serum-albumin a band at 2960 and 2411 Å., egg-globulin a band at 2975 and 2417 Å., serum-globulin a band at 3071 and 2434 Å., caseinogen in 0.02*N*-sodium hydroxide a band at 3176 and 2628 Å., vitellin in 0.04*N*-sodium hydroxide a band at 3441 and 2645 Å., whilst the nucleoprotein of the liver in 0.1*N*-sodium hydroxide gives a faint band at 3212 and 2295 Å. which is quite different from those given by the above proteins. It is concluded that albumins, globulins, caseinogen, and vitellin behave similarly towards ultra-violet light and that the absorption spectra can be used to distinguish albumins and globulins from phosphoproteins.

A. I. VOGEL.

New combination of sulphæmoglobin. A. D. VOLTA (Arch. Ital. Biol., 1926, 77, 6 pp.; Chem. Zentr., 1928, ii, 1467—1468).—Treatment of blood with freshly-prepared ammonium sulphide solution saturated with hydroxylamine hydrochloride or sulphate affords an olive-green coloration, due to "chlorohæmoglobin." Addition of pyridine changes the green colour to brick-red, and the hæmochromogen spectrum may then be observed. Spectrographic measurements are recorded.

A. A. ELDRIDGE.

Denaturation of proteins. VII. Denaturation versus coagulation. H. WU (Chinese J. Physiol., 1929, 3, 1—6).—After flocculation, denatured egg-albumin differs from coagulated egg-albumin in its solubility in acids, alkalis, or in concentrated carbamide solution. Denatured egg-albumin differs from the native protein in not being coagulated by alcohol or by shaking. Therefore, probably, denaturation is not a step in the coagulation of protein but the essential step in denaturation is hydrolytic fission, whilst in coagulation it is molecular condensation.

W. O. KERMACK.

Denaturation of proteins. IX. Liberation of non-protein substances on denaturation and coagulation of proteins. H. WU and T. T. CHEN (Chinese J. Physiol., 1929, 3, 75—79).—Highly purified egg-albumin was heated at 100° for 15 min. with various quantities of acid or alkali. The cooled and neutralised solutions were filtered from protein which had been coagulated or denatured and flocculated. Any conalbumin precipitated by further heating for 15 min. was removed by filtration. The filtrates were tested by the phenol reagent and sodium carbonate; at the isoelectric point there was no liberation of chromogenic substances on heating, but

on either side of this point there is some liberation, much more on the alkaline than on the acid side.

W. O. KERMACK.

Denaturation of proteins. V. Denaturation by acid. H. K. CUBIN (Biochem. J., 1929, 23, 25—30).—Determination of the velocity coefficients at different temperatures and for varying values of p_H of the denaturation shows that the critical increment for oxyhæmoglobin is 12,000 g.-cal. and for egg-albumin 36,000—48,000 g.-cal., i.e., lower values than those obtained by heat-denaturation. Formaldehyde diminishes the p_H range over which precipitation of denatured protein occurs.

S. S. ZILVA.

Protein denaturation. I. Denaturation by alcohol. M. SPIEGEL-ADOLF (Biochem. Z., 1929, 204, 1—13).—In contrast to serum-albumin, pseudo-globulin when precipitated by heat only partly regains its water-solubility on treatment with alkali. Even using high alcohol concentrations (88%) for long periods (6 weeks) only about 60—70% of serum-albumin remains insoluble; by treatment with alkali and electrodialysis it regains its water-solubility and typical properties. Under similar conditions egg-albumin remains practically insoluble; pseudo-globulin occupies an intermediate position. The presence of acid increases and of neutral salt diminishes the proportion of the alcohol precipitate of serum-albumin, which becomes soluble when treated with alkali.

J. H. BIRKINSHAW.

Capsule for incinerating [organic materials]. KÖNIG (Chem.-Ztg., 1929, 43, 130).—The ordinary small porcelain capsule is provided with an outside flange so as to permit the operator to grip it with the crucible tongs without danger of touching the contents of the capsule.

A. R. POWELL.

Device for carbon and hydrogen analysis of volatile, explosive, and easily carbonisable organic liquids. M. G. SEVAG (Ind. Eng. Chem. [Anal.], 1929, 1, 16—17).—The usual capillary bulb is replaced by a pyrex or silica tube packed with kieselguhr held in position by asbestos pads. The ends are closed by glass or rubber stoppers during weighing, and the liquid is dropped on the kieselguhr by removing one pad. No appreciable loss of even a volatile liquid occurs in handling and the combustion proceeds without either explosion or incomplete burning of the carbon content.

C. IRWIN.

Quantitative gas analysis. W. H. BENNETT.—See this vol., 420.

Micro-determination of iodine. J. F. REITH.—See this vol., 414.

Volumetric determination of dextrose. C. A. AMICK (Chemist-Analyst, 1928, 17, No. 4, 10—11).—The dextrose solution (10 c.c.) and 6*N*-sodium hydroxide solution are added to boiling 2*N*-copper sulphate solution (30 c.c.) and water (50 c.c.); carbonate must be absent. The mixture is heated on the water-bath for 15 min., then cooled to the ordinary temperature. Phosphomolybdate solution (50 c.c.; 100 g. of Na₂MoO₄ in 500 c.c. of water, 75 c.c. of 85% phosphoric acid, 275 c.c. of concentrated sulphuric acid, and water to 1750 c.c.) is added, and the tervalent

molybdenum is titrated with permanganate similarly standardised with dextrose.

CHEMICAL ABSTRACTS.

Determination of formaldehyde. F. LIPPICH (Z. anal. Chem., 1929, 76, 241—254).—The method is based on the principle that formaldehyde reacts with potassium cyanide to form the potassium compound of hydroxyacetonitrile which is stable in boiling 20% tartaric acid solution, whereas the excess of potassium cyanide is thereby decomposed. The reaction is carried out in a distillation flask provided with a side tube which passes down to the bottom and connected through a reflux condenser to an absorption flask containing 50 c.c. of 60% potassium hydroxide solution; a measured volume of 0.25*N*-potassium cyanide solution is placed in the distillation flask and the formaldehyde is added slowly with agitation. After 5 min. a 40% solution of tartaric acid is added in quantity sufficient to give a 20% solution of the acid in the flask. The liquid is boiled for 1—2 hrs., while a rapid current of air is passed through the apparatus to expel excess of hydrogen cyanide. The contents of the absorption flask are rinsed into a beaker, diluted to 200 c.c., treated with a little potassium iodide, and titrated with silver nitrate, about 0.5 c.c. of ammonia being added towards the end of the titration. Acetone causes the results to be slightly

high and acetaldehyde reacts quantitatively with cyanide in the same way as formaldehyde, so that the sum of both aldehydes may be obtained by this method. Formaldehyde may then be determined in a separate sample by Romijn's method (A., 1897, ii, 166).
A. R. POWELL.

Applications of the nitrile method. I. Fixation of hydrocyanic acid by protein, determination of formaldehyde in presence of pure proteins, and quantitative relationship between formaldehyde and protein. F. LIPPICH (Z. anal. Chem., 1929, 76, 255—260; cf. preceding abstract).—In the determination of formaldehyde by the nitrile method the presence of proteins in the solution causes only a very slight error due to irreversible combination of the cyanide with protein, but more serious errors are introduced by combination of the formaldehyde with the protein molecule, especially in the cases of gelatin and casein.
A. R. POWELL.

Micro-chemistry [detection] of theophylline. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 131—133).—The most suitable reactions are those with mercuric chloride, iodine, and bromine, which will detect 5 mg. at a concentration of 1 in 1000. Potassium antimony iodide will detect 1 mg. at the same concentration.
S. I. LEVY.

Biochemistry.

Seasonal influence on the respiratory combustion of the dog. F. MAIGNON and A. PAINVIN (Compt. rend., 1929, 188, 573—575).—The amount of oxygen used in respiration by a fasting dog shows maxima in the spring and the autumn; on a meat diet the effect is similar but less pronounced.

G. A. C. GOUGH.

Carbon dioxide capacity of human body. E. F. ADOLPH, F. D. NANCE, and M. S. SHILING (Amer. J. Physiol., 1929, 87, 532—541).—When the human body is saturated or desaturated to a new level of carbon dioxide tension, carbon dioxide is retained or given up by the body amounting to between 40 and 700 c.c. for each mm. change in alveolar carbon dioxide tension.
B. A. EAGLES.

Gas tension at skin surface of man. J. A. CAMPBELL (J. Physiol., 1929, 67, Proc. Physiol. Soc., viii—ix).—The carbon dioxide tension at the skin surface is about 40 mm. mercury, resembling that in the alveolar air. The skin is permeable outwards or inwards to carbon dioxide, but impermeable outwards to oxygen. It is slightly permeable inwards to oxygen at higher pressures.
B. A. EAGLES.

Hydrogen in tissues. J. A. CAMPBELL (J. Physiol., 1929, 67, Proc. Physiol. Soc., vi—vii).—Tensions of hydrogen, carbon dioxide, and oxygen in the gut and peritoneal cavity were determined. The gases in the gut differed in composition from gases in the peritoneal cavity, carbon dioxide and hydrogen being present at much greater tension in the gut, whilst oxygen was at much lower tension than in the peritoneal cavity.
B. A. EAGLES.

Carbon dioxide in venous blood. I. Effect of oxygenation and critical oxygen tension. M. C. G. ISRAELS and F. W. LAMB (J. Physiol., 1929, 67, 49—61).—Attention is directed to the effect of insufficient oxygenation of the lung blood in rebreathing experiments for determining the carbon dioxide content of the mixed venous blood. A method for carrying out rebreathing experiments without a rapid lowering of the oxygen tension in the rebreathing bag is described.
B. A. EAGLES.

Blood-cell metabolism. III. Effect of methylene-blue on oxygen consumption of eggs of sea urchin and starfish; mechanism of the action of methylene-blue. E. S. G. BARRON (J. Biol. Chem., 1929, 81, 445—457).—The oxygen consumption of the eggs of the sea urchin and starfish is increased by the presence of methylene-blue; the action of the dye is inhibited by narcotics (urethane derivatives), but is not affected by cyanides, which indicates that it is concerned with the anaerobic metabolism of the cells. In agreement with this, the effect of methylene-blue on the oxygen consumption of mammalian red blood-corpuscles is considerable and on avian blood-corpuscles negligible. The role of methylene-blue is that of a reversible hydrogen acceptor.
C. R. HARRINGTON.

Effect of removal of liver on alkali reserve and lactic acid content of blood. L. G. KILBORN, S. SOSKIN, and J. C. THOMAS (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 159—161).—There is a close relationship between the rise in the lactic acid content and the fall in carbon dioxide capacity of the blood. After

removal of the kidneys there was a small initial rise in lactic acid accompanied by a fall in the carbon dioxide capacity; these values then remained fairly constant. After evisceration or hepatectomy, the lactic acid content of the blood increased considerably with a corresponding decrease in the carbon dioxide capacity. It is suggested that the respiratory quotient is of doubtful value as an index of the type of metabolism proceeding in such preparations.

F. C. HAPFOLD.

Detection of specific blood. A. D. VOLTA (Arch. Ital. Biol., 1928, 79, 4 pp.; Chem. Zentr., 1928, ii, 1468).—The "chlorohæmoglobin" reaction is applied to the blood of various animal species.

A. A. ELDRIDGE.

Spectrographic study of the "chlorohæmoglobins" in the blood of various animals. A. D. VOLTA and E. VITERBI (Arch. Ital. Biol., 1928, 79, 4 pp.; Chem. Zentr., 1928, ii, 1468).

Diffusion of hæmoglobin. R. E. LIESEGANG and O. MASTBAUM (Biochem. Z., 1929, 205, 451—456).—Hæmoglobin diffuses into a gelatin gel much more readily than would be expected from the size of the molecule.

J. H. BIRKINSHAW.

Oxidase in the blood-leucocytes and the stability of the enzyme in various types of leucocytes. J. B. GOLDMAN (Zhur. exp. Biol. Med., 1928, 9, 552—558).—All myelocytes and monocytes give a positive oxidase reaction; basophiles are generally negative. The stability of the enzyme is greatest in eosinophiles, intermediate in neutrophils, and least in monocytes.

CHEMICAL ABSTRACTS.

Seasonal variation in calcium content of the blood-serum of the young white rat. A. T. CAMERON [with K. R. TURNER] (Trans. Roy. Soc. Canada, 1928, (iii), 22, V, 135—144).—A constant serum-calcium content is found throughout the year in the adult rat, irrespective of sex. The younger the rat the more susceptible it appears to be to influences which depress the serum-calcium content, and in animals of weight varying between 30 and 50 g. a normal figure was maintained only during the height of summer. This seasonal variation is possibly controlled by the effect of the solar ultra-violet radiation on the rats' food.

F. C. HAPFOLD.

Rotatory power of serum as a function of temperature. P. L. DU NOUY (Compt. rend., 1929, 188, 660—662).—The lævo-rotation of normal horse serum is constant between 0° and 50° at $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}}$ —49°. Slight variations are produced by heating for 10 min. at 50—55°, whilst above 55° there is a progressive increase which is rapid above 59° and increases with the duration of heating. The results are correlated with the changes in viscosity with temperature (A., 1926, 423), and with the probable changes in molecular structure of the protein constituents associated with the suppression of the "complementary power" of the serum.

J. GRANT.

Serum-albumin; crystallisation in the absence of ions. M. PIETTRE (Compt. rend., 1929, 188, 463—465).—After separation of serum-globulin (A., 1928, 912), the serum-albumin is purified by four

H H*

precipitations with acetone. It then gives a solution of about p_{H} 6.5 and contains no ionic impurities. When an aqueous solution is evaporated in a vacuum over sulphuric acid, a gummy mass is obtained which becomes crystalline (long prisms, softening with decomp. at 225—230°) when subjected to a series of sudden shocks. This preparation causes no immediate anaphylaxis in goats or dogs. G. A. C. GOUGH.

Decomposition of adrenaline by serum. M. CHIKANO and M. KOMINAMI (Biochem. Z., 1929, 205, 176—179).—The decomposition of adrenaline in serum is followed by the chemical (iodic acid method; cf. this vol., 474) and the biological methods. The decomposition curves proceed almost identically for the first 48 hrs. and then the rate becomes somewhat less as determined by the chemical than by the biological method. Adrenaline in phosphate buffer solution of the same p_{H} as blood is decomposed with almost the same velocity as in serum, but the velocity is considerably less in Ringer-Locke solution.

P. W. CLUTTERBUCK.

Choline content of blood at different points in the circulation. M. MAXIM and C. VASILIU (Bull. Soc. Chim. biol., 1929, 11, 70—73).—The choline contents of the blood of a normal dog in the abdominal aorta, the inferior vena cava, the portal vein, and the hepatic vein are 21, 25, 32.1, and 18.1 mg. per litre, respectively. It is suggested that the liver is concerned in these variations.

G. A. C. GOUGH.

Separation and determination of constituents of blood by means of selective adsorption. B. SJOLLEMA and A. EMMERIE (Biochem. Z., 1929, 204, 275—285).—Constituents of blood such as ergothioneine and glutathione can be separated and determined in the same blood filtrate by the use of two adsorbents which are free from sulphur, nitrogen, and phosphorus, the sulphur content of the filtrate before and after adsorption having been found. Similarly, from determinations of nitrogen, phosphorus, and reducing power the concentration of other constituents of blood can be deduced. The adsorbents are a sugar charcoal and aluminium hydroxide, prepared according to directions given.

W. MCCARTNEY.

Amide-nitrogen of blood. IV. S. BLISS (J. Biol. Chem., 1929, 81, 405—406).—Amide-nitrogen of blood (this vol., 339) is better expressed as mg. per 100 g. of blood-protein, rather than as mg. per 100 c.c.

C. R. HARRINGTON.

Ultrafiltration for removal of protein in the determination of amino- and residual nitrogen in blood. B. A. WILENSKI (Biochem. Z., 1929, 204, 433—438).—By means of a simple ultrafiltering apparatus which is easily prepared and cleaned, proteins can be removed at a satisfactory rate from biological fluids. Determinations of amino- and residual nitrogen in the ultrafiltrates show that this ultrafiltration method gives more constant and more satisfactory results than do precipitation methods.

W. MCCARTNEY.

Deproteinisation of blood for determination of total non-protein nitrogen and the index of polypeptidæmia. P. CRISTOL (Bull. Soc. Chim. biol., 1929, 11, 92—110).—Non-protein-nitrogen is

determined in the filtrate from deproteinisation with 20% trichloroacetic acid. The difference between this value and that of the filtrate after treatment with 0.6*N*-phosphotungstic acid is shown to be due probably to polypeptides. The consequent polypeptide-nitrogen is termed the "index of polypeptidæmia" and the value of this index in various pathological states is determined.

G. A. C. GOUGH.

Characterisation of the proteins of blood, muscles, and internal organs of rabbits and chickens by means of colour reactions. M. A. RAKUZIN and T. A. GENKE (*Zhur. exp. Biol. Med.*, 1928, 9, 225—229).

CHEMICAL ABSTRACTS.

Blood-sugar. O. FOLIN (*J. Biol. Chem.*, 1929, 81, 377—379).—The conclusions of Somogyi and Kramer (this vol., 207) are criticised.

C. R. HARRINGTON.

Ferricyanide method for determination of blood-sugar. O. FOLIN (*J. Biol. Chem.*, 1929, 81, 231—236).—Further technical details are given in connexion with the author's recent method for the determination of blood-sugar (*A.*, 1928, 786); it is important that toluene be not used as a preservative for the tungstic acid solution, especially if the latter be exposed to light; gum ghatti is recommended in place of gum arabic as a protective colloid for the ferric phosphate solution.

C. R. HARRINGTON.

Determination of reducing sugars in blood and urine. J. A. HAWKINS and D. D. VAN SLYKE (*J. Biol. Chem.*, 1929, 81, 459—467).—The rate of decolorisation of an alkaline solution of potassium ferricyanide on heating with a solution containing reducing sugars bears, within wide limits, a definite relationship to the concentration of the latter. On this fact is based a rapid method for the determination of reducing sugars in urine, or in protein-free blood filtrates, with an error of $\pm 5\%$.

C. R. HARRINGTON.

Blood-sugar regulation in mammals. II. Effect of fasting on alimentary hyperglycæmia. B. KISCH, A. SIMONS, and P. WEYL (*Biochem. Z.*, 1929, 205, 349—359; cf. this vol., 339).—The feeding of oats or dextrose to fasting rabbits produces only a slight hyperglycæmia which is perhaps more marked after 16 hrs. than 9 days' fast. Dextrose administered to the fasting dog produces marked reaction, hyperglycæmia followed by hypoglycæmia, which is strong after 1—3½ days' fast, weak after 16 hrs., and negligible after 7½—10½ days.

J. H. BIRKINSHAW.

Daily variations of blood-sugar values in man. L. M. KRASNJANSKIJ (*Biochem. Z.*, 1929, 205, 180—185).—Curves show the variations on a normal diet and during starvation.

P. W. CLUTTERBUCK.

Alimentary blood-sugar curves. IV. Sucrose in blood. V. Lævulose in blood. W. W. OPPEL (*Biochem. Z.*, 1929, 205, 31—46, 47—62).—IV. After enteral administration of sucrose (2—4 g./kg.) dextrose and lævulose, but not sucrose, could be detected in the blood. Injection of sucrose directly into the jejunum, however, causes sucrose to appear in the blood and the intestine is therefore permeable to it. After intravenous injection of

sucrose a regular curve is obtained showing its disappearance. Sucrose must remain therefore sufficiently long in the intestinal tract for the action of invertase to be completed.

V.—Lævulose, after enteral administration to rabbits, can be detected in the blood, its appearance in the peripheral circulation depending on the amount administered. With a dose of 2—3.5 g./kg., the first traces of lævulose are detected in the blood within 5 min. of administration; the maximal increase in blood-lævulose is 8—10 mg./100 c.c. of blood, and the sugar disappears in 2.5—3 hrs. After intravenous injection of 0.2—0.4 g. of lævulose, the sugar disappears from the blood in 30—60 min., part being retained by the liver and part appearing in the circulation.

P. W. CLUTTERBUCK.

Imitation of organic forms by means of albumin. L. A. HERRERA (*Atti R. Accad. Lincei*, 1928, [vi], 8, 637—639).—Further details are recorded (cf. this vol., 208).

Low cholesterol content of fatty substances of the chrysalides of Lepidoptera. A. COURTOIS (*Compt. rend.*, 1929, 188, 666—668).—The ratio unsaponifiable matter/total fatty acids for the fatty substances of the chrysalides of the Lepidoptera is of the same order as that for the invertebrates, but for those species of the former studied (*Attacus Pernyi*, *Sphinx Ligustri*, and *Saturnia Pyri*) the cholesterol content of the unsaponifiable matter is so small that the lipocytic coefficient (100 × cholesterol/fatty acids) is less than one tenth of the smallest value recorded for the animal series.

J. GRANT.

Isolation of methylhydantoin from extract of ox testes. J. P. COLLIP and R. SANDIN (*Trans. Roy. Soc. Canada*, 1928, [iii], 22, V, 185—186).—A crystalline substance isolated from an extract of ox testes has been shown to be β -methylhydantoin.

F. C. HAPFOLD.

Non-specific pressor substance. J. P. COLLIP (*Trans. Roy. Soc. Canada*, 1928, [iii], 22, V, 181—184; see also this vol., 208).—A highly potent pressor substance can be extracted from skeletal muscle, liver, kidney, spleen, ovary, testes, stomach, intestine, whole foetus, and several commercial preparations of both pepsin and pancreatin, by boiling the minced tissue with neutral or acidulated water. The active substance is freed from inorganic matter and much of the depressor substances by repeated extraction with acetone. Further methods of purification of the pressor substance and its stability to such treatment as exposure to acetic anhydride, heating with acid and alkali, etc. are described. Gynergen in doses of 0.5 mg. produces marked enhancement of the pressor action, with nicotine the action is slight, with atropine no effect is apparent, and with cocaine a marked, but transient antagonism is observed. The pressor extract obtained from the prostate glands of oxen is not antagonised by cocaine.

F. C. HAPFOLD.

Determination of adrenaline in human adrenals after death. M. PAGET and P. LOHEAC (*Compt. rend. Soc. Biol.*, 1928, 98, 1421—1423; *Chem. Zentr.*, 1928, ii, 1346).—The finely-divided material is ground with three times its weight of anhydrous sodium sulphate and 5—10 c.c. of "4/10

sulphuric acid; after 5 min. the mixture is diluted with water, frequently shaken during 15 min., and filtered. An aliquot part of the filtrate is treated with sodium acetate and a little mercuric chloride, when a red colour is produced (maximum in 45 min.) and compared with that produced by a solution of adrenaline.

A. A. ELDRIDGE.

Existence of adrenaline, free and otherwise, in human adrenals after death. LANGERON, M. PAGET, and P. LOHEAC (Compt. rend. Soc. Biol., 1928, 98, 1424—1426; Chem. Zentr., 1928, ii, 1346).—On incipient decomposition the adrenaline rapidly disappears (cf. preceding abstract).

A. A. ELDRIDGE.

Preparation of chondroitin-sulphuric acid. E. JORPES (Biochem. Z., 1929, 204, 354—360).—Tracheal cartilage from cattle after being treated with alcohol, dried in air, and ground was extracted for 8—10 hrs. at 0—3° with 2% sodium hydroxide solution. The extract was made faintly acid with acetic acid, filtered, and the filtrate treated with kaolin to remove protein. The filtrate then gave no biuret reaction and alcohol precipitated biuret-free calcium sodium salt of the acid. The yield of substance (4.5% S) was 50—80 g. from 1 kg. of cartilage. This substance was shaken with cold 10% sodium chloride solution for 12 hrs., 1.0—1.5% acetic acid was added, the liquid was filtered, and the filtrate treated with kaolin. After further filtration the product was precipitated with alcohol. A further quantity was obtained from the original powder by a slightly modified treatment. The method gives a purer product than previously used methods.

W. MCCARTNEY.

Tissue calcification. N. W. TAYLOR and C. SHEARD (J. Biol. Chem., 1929, 81, 479—493).—Determination of the refractive index of bone, dentine, and dental enamel indicates that the inorganic basis of these materials is of the apatite type; this conclusion is supported by X-ray diffraction photographs of various samples of normal and pathological bone powders.

C. R. HARRINGTON.

Characteristic colour reaction of thymus-nucleic acid. Z. DISCHE (Biochem. Z., 1929, 204, 431—432).—When a 0.25% solution of thymus-nucleic acid containing 0.5% of hydrochloric acid is heated at 100° for 5 min. with 0.1—0.2 c.c. of a 1% alcoholic solution of indole an intense orange colour develops and, on cooling, the liquid becomes turbid. If the turbid liquid is shaken with chloroform this remains colourless, but thick red flocks appear at the interface. If less than 0.5% of hydrochloric acid is present heating must be continued longer and the colour produced is reddish-brown. Sugars and aliphatic aldehydes give the test, although often only when present in high concentrations, and in the case of these substances the colours can be completely extracted with chloroform. It is concluded that the reaction is due to the carbohydrate component of the nucleic acid.

W. MCCARTNEY.

Pentosenucleic acids in the animal organism; pancreas-nucleic acids. E. JORPES (Veroffentl. Chem. Abt. Karol. Inst. Stockholm, 1928, 253—573; Chem. Zentr., 1928, ii, 1343).—Fresh pancreas con-

tains about 0.0437% of free phosphate-phosphorus and 0.1267% of lipin-phosphorus. Fresh (ox) pancreas contains 0.223% of nucleic acid-phosphorus, corresponding values being: liver 0.104, spleen 0.145, parotid 0.107, mucous membrane of fundus ventriculi 0.088%. When heated for 2.5 hrs. on the water-bath with 5% sulphuric acid, the phosphorus in purine-nucleotides is quantitatively removed, whilst only a portion is removed from pyrimidine-nucleotides. Half of the thymus-nucleic acid-phosphorus is removable by acid hydrolysis. The nucleic acid-phosphorus of the thymus amounting to 0.441%, the pentosenucleic acids, reckoned as pentosetetranucleotide, constitute 14.2% of the total nucleic acid-phosphorus. In the pancreas, with a pentose content of 0.445%, pentosenucleic acids form the major portion. About half of the pancreas-nucleic acid undergoes fission by acid hydrolysis; hence the pentosenucleic acids of the animal organism are considered to have a tetranucleotide character. No differences between carnivorous and herbivorous animals were observed. The nature of the pancreas-nucleic acids is discussed, and analytical methods are described.

A. A. ELDRIDGE.

Analysis of the liver of *Raja clavata*. O. FLOSSNER and F. KUTSCHER (Z. Biol., 1929, 88, 390—394).—The following substances have been isolated: adenine, choline, neosine, histidine, acanthine, lactic and *n*-valeric acids.

E. A. LUNT.

Alleged presence of carotin in pig's liver. L. S. PALMER (Amer. J. Physiol., 1929, 87, 553—557).—Pig's liver contains a minute quantity of unsaponifiable pigment soluble in light petroleum which resembles carotin in solubility and adsorption properties and gives some colour reactions, but not others, given by carotinoids. Its spectroscopic properties are both qualitatively and quantitatively unlike those of carotin and therefore the liver pigment cannot be carotin.

B. A. EAGLES.

Micro-determination of total creatinine in muscle. S. OCHOA and J. G. VALDECASAS (J. Biol. Chem., 1929, 81, 351—357).—Muscle is autoclaved for 25 min. at 125° with 0.2*N*-hydrochloric acid, the solution is treated with picric acid and filtered, and the filtrate made alkaline with sodium hydroxide; the resulting colour is compared with that obtained from a known amount of creatinine. The method is applicable to 5—100 mg. of muscle with an error of $\pm 2\%$.

C. R. HARRINGTON.

Hydrogen-ion concentration of isolated uterus. P. T. KERRIDGE and F. R. WINTON (J. Physiol., 1929, 67, 66—76).—The effect of the of a solution on the tone of a uterus cannot be attributed to the sign or magnitude of the difference of p_H between the muscle and the solution. The hydrogen-ion concentration of an isolated uterus is greater than that of the uterus *in situ*. This acid formation is largely irreversible and takes place during excision and before immersion in saline solutions.

B. A. EAGLES.

Body fluids of elasmobranchs. H. W. SMITH [with J. T. BAKER and H. SILVETTE] (J. Biol. Chem., 1929, 81, 407—419).—Figures are given for the con-

centrations of carbamide and of inorganic salts in the blood, cerebrospinal fluid, and pericardial and perivisceral fluids of various elasmobranchs. As found by previous workers, carbamide is present throughout in very large amount. Whilst the cerebrospinal fluid is practically an ultrafiltrate of the blood-plasma, differences between the composition of the latter and of the pericardial and peritoneal fluids indicate a probable excretory function of the pericardial and peritoneal membranes.

C. R. HARINGTON.

Nitrogenous constituents of the urine of the goosefish (*Lophius piscatorius*); presence of trimethylamine oxide. A. GROLLMAN (J. Biol. Chem., 1929, 81, 267—278).—The urine of the goosefish contains but little ammonia, carbamide, or uric acid; the nitrogen is present chiefly in the form of amino-acids, creatine, creatinine, and trimethylamine oxide. The urine of specimens kept in an aquarium contained less nitrogen and more salts (especially magnesium salts and chlorides) than that of specimens freshly caught.

C. R. HARINGTON.

Determination of hippuric acid in urine. A. VON BEZNAK (Biochem. Z., 1929, 205, 409—413).—The total ethereal extract of the urine is dissolved in 10 c.c. of water, 1 c.c. of sulphuric acid is added, and the mixture autoclaved for 3 hrs. at $2\frac{1}{2}$ kg./cm.² The amino-nitrogen of the hydrolysate determined by Van Slyke's method gives the hippuric acid originally present.

J. H. BIRKINSHAW.

Preparation of urea from urine. S. KANNEGIETER (Pharm. Weekblad, 1929, 66, 129—131).—The urine is shaken with 2—3% by weight of "norit," filtered, evaporated to one sixth of its original volume, cooled, and treated with nitric acid. Pure urea nitrate is obtained directly. The base is obtained by treatment with barium carbonate and extraction with alcohol.

S. I. LEVY.

Uric acid and its determination in blood and urine. FISCHER (Suddeut. Apoth.-Ztg., 1928, 68, 448—450; Chem. Zentr., 1928, ii, 1468).—A discussion, particularly of the degradation of nucleoproteins.

A. A. ELDRIDGE.

Does the oxidation quotient of dextrose-free urine change on keeping owing to decomposition? L. CHASKIN and G. NIGMANN (Biochem. Z., 1929, 205, 473—480).—Rabbit's or human urine kept for 24 hrs. at the ordinary temperature undergoes no change in oxidation quotient.

J. H. BIRKINSHAW.

Application of Grossfeld's method for the determination of fat to faeces. W. HEUPKE (Arch. Verdauungskrankh., 1927, 41, 329—335; Chem. Zentr., 1928, ii, 1469).—By weighing the residue from an aliquot part of the filtered solution of fat in solvent, sufficiently good accord with results obtained by Soxhlet's method can be obtained.

A. A. ELDRIDGE.

Lipin excretion. V. Partition of faecal lipins with reference to bacteria. W. M. SPERRY (J. Biol. Chem., 1929, 81, 299—319).—The faeces of dogs on a lipin-free diet were suspended in dilute hydrochloric acid, and separated by fractional centri-

fuging into bacteria, non-bacterial solids, and soluble substances. On the average, 40% of the total lipins were present in the bacteria, the greater part of the remainder being contained in the non-bacterial solids. Under these conditions, therefore, the lipins are associated entirely with the formed elements. Extraction and fractionation of the lipins revealed no significant difference between those of the bacteria and those of the non-bacterial residue; it is therefore possible that they represent a secretion into the intestine which is adsorbed on the formed elements of the faeces.

C. R. HARINGTON.

Blood regeneration in severe anaemia. XV. Liver fractions and potent factors. W. M. SPERRY, C. A. ELLEN, F. S. ROBSCHT-ROBBINS, and G. H. WHIPPLE (J. Biol. Chem., 1929, 81, 251—265).—The increased formation of haemoglobin in dogs suffering from simple anaemia (as the result of haemorrhage) which is obtained by administration of liver is observed also on administration of extracts of liver prepared by a variety of methods (e.g., extraction with alcoholic hydrochloric or aqueous sulphuric acid, enzymic digestion or autolysis of the liver, and extraction with alkali). The acid extracts are the most potent, containing more than 50% of the activity of the original liver; of the digests, the peptic hydrolysate is the most active. The activity of all fractions is in part due to salts, particularly those of iron; in general the therapeutic effect is complex. The purified extract, shown by Cohn and others (A., 1928, 790) to be effective in relieving human pernicious anaemia, represents 10—20% of the activity of the original liver with respect to the simple experimental anaemia in dogs.

C. R. HARINGTON.

Circulation during hyperaemia following anaemia. A. JARISCH and F. GAISBÖCK (Arch. exp. Path. Pharm., 1929, 139, 159—178).—From experiments determining the effect on the circulation and respiratory exchange of tying off the limbs and freeing them again it appears that in man the circulation through the extremities amounts to 28 c.c. per kg. per min. and that resting human skeletal muscle requires between 0.8 and 1.0 c.c. of oxygen per g. per hr.

W. O. KERMAK.

Cytolysis in cancer. III. N. WATERMAN, L. DE KROMME, and J. F. LEMMENS (Biochem. Z., 1929, 205, 1—20).—In cancer a spontaneous but small amount of lysis occurs which can be artificially increased. In the disintegration of pure cancer cells in suspensions, substances are formed which make fresh cells resistant to lysis and agglutination. A lytic substance may be extracted from all normal organs and from serum, the best yield being obtained from lymph glands, spleen, and thymus. It is combined with lipoprotein, is not identifiable with any simple known enzyme system, and is both activated and destroyed by exposure to X-radiation, the radiation effect being greater with the impure than with the purified preparation (cf. A., 1927, 1215; 1928, 86).

P. W. CLUTTERBUCK.

Is aerobic glycolysis specific for tumours? O. WARBURG (Biochem. Z., 1929, 204, 482—483).—Aerobic glycolysis is not specific for tumours. When

normal cells undergo aerobic glycolysis, they die, whereas cells of tumours undergoing glycolysis live and grow without limit while using the chemical energy of the glycolysis. The classification of body-tissues according to the magnitude of their respiration should be abandoned. The two kinds of disturbance to respiration which can be produced artificially in normal cells occur naturally in tumours.

W. McCARTNEY.

Carbohydrate exchange in tumours and normal tissue and its relation to the lactic acid economy of the body. C. FAHRIG (Z. Krebsforsch., 1927, 25, 146—228; Chem. Zentr., 1928, ii, 1357).—Noorden and Embden's postulated carbohydrate cycle is supported. In cancer a high lactic acid value is found only in pathological conditions of the liver. The content of glycogen, lower carbohydrates, and buffers in myoma, sarcoma, and carcinoma does not differ markedly from that in normal tissue.

A. A. ELDRIDGE.

Catalase of malignant tissue. M. R. LEWIS and H. COSSMAN (Amer. J. Physiol., 1929, 87, 584—593).—The infectious tumour of the chicken contains only a feeble catalase, in this respect being like the muscle. The tumour virus, however, is inactivated by hydrogen peroxide.

B. A. EAGLES.

Differentiation between normal and pathological sera; ease of oxidation of sera. R. DOURIS, C. MONDAIN, and M. PLESSIS (Compt. rend., 1929, 188, 587—588).—The reducing capacity of sera is determined empirically by oxidation by the method of Cordebard (A., 1928, 661) followed by back-titration with ferrous ammonium sulphate. The average values are found to increase in the order: cancerous, syphilitic, and normal serum.

G. A. C. GOUGH.

Metabolism of sulphur. XIV. Cystinuria. H. B. LEWIS and S. A. LOUGH (J. Biol. Chem., 1929, 81, 285—297).—The excretion of cystine by a cystinuric was independent of the amount of cystine in the diet; administration of a high protein-low cystine diet, however, led to increased excretion of cystine. Cystine, administered as such, was completely oxidised to the extent of 2—3 g. per day. The cystine excreted is therefore regarded as being principally of endogenous origin.

C. R. HARRINGTON.

Blood-sugar during the night and morning [in diabetics]. H. LANGE and J. SCHLOSS (Arch. exp. Path. Pharm., 1929, 139, 274—289).—The blood-sugar of diabetics has been followed at short intervals during the night and morning hours. A marked rise in the curve occurs in the early morning, beginning between 3 a.m. and 5 a.m. The theoretical and clinical significance of this observation is discussed.

W. O. KERMAK.

Significance of cholesterol in the formation of gall-stones. S. HANSEN (Acta chir. Scand., 1927, 67, 483—542; Chem. Zentr., 1928, ii, 1352).—A critical discussion.

A. A. ELDRIDGE.

[Cause of] the Millon reaction given by urine in mental disease. E. SCHEINER (Biochem. Z., 1929, 204, 361—370).—Normal urine contains small quantities of a substance, m. p. 40°, b. p. 70°, which

is present in much larger amounts in the urine of mentally diseased persons. The substance gives a strong reaction with Millon's reagent and is found in the "histidine" fraction of the urine. Its properties resemble those of the glyoxaline derivatives. It can be adsorbed on charcoal and quantitatively recovered with acetone.

W. McCARTNEY.

Composition of tissues in avitaminosis-A: phosphorus, lipid extract, and cholesterol. M. JAVILLIER, S. ROUSSEAU, and L. ÉMERIQUE (Compt. rend., 1929, 188, 580—582).—The course of avitaminosis-A in rats does not lead to any appreciable alteration in the nucleoprotein-phosphorus content of separate organs. In general the ratios cholesterol/lipid extract and cholesterol/fatty acids increase and the ratio cholesterol/lecithin decreases. The lipin content of the skin, liver, and the muscle falls; that of the spleen, kidney, lungs, and heart remains almost constant, and that of the brain and bone increases. With the exception of the skin, the cholesterol content of all the organs falls.

G. A. C. GOUGH.

Total proteins (serum-albumin and serum-globulin) of the serum of scorbutic guinea-pigs. Presence of albumin and hæmoglobin in urine in the final pathological state. A. MICHAUX (Compt. rend., 1929, 188, 582—584).—The albumin and globulin content of the serum of scorbutic guinea-pigs shows a slight temporary decrease at the beginning of the avitaminosis. After a certain period the urine decreases greatly in volume and shows the presence of small amounts of protein, including hæmoglobin.

G. A. C. GOUGH.

Tissue respiration. V. Utilisation of protein in tissue respiration. K. SINGER and O. POPPELMANN (Biochem. Z., 1929, 205, 63—70).—In a variety of animals, viz., mouse, cat, rabbit, dog, man, cow, and ox, the amounts of protein utilised as determined in the intact animal by the nitrogen excretion and in the respiration of surviving tissue by the formation of ammonia are compared. In each case the nitrogen excreted or formed varies within narrow limits and is independent of the kind and size of animal and of the intensity of the animal's metabolism. In the dog no definite difference could be established between the protein utilisation of living and surviving tissue, but in the larger animals the protein utilised in tissue respiration was much greater than in the intact animal.

P. W. CLUTTERBUCK.

Rôle of free oxygen in [egg] development. L. RAPKINE (Compt. rend., 1929, 188, 650—652).—The development of fertile sea-urchin eggs in air-free seawater at 20° is inhibited if methylene-blue is absent. Molecular oxygen can therefore act as an acceptor of hydrogen provided by donors. Since the r_H of the cellular medium remains constant, the principal rôle of oxygen is to ensure a definite cellular potential, and it may therefore substitute any other acceptor.

J. GRANT.

Water evaporated during work. J. A. CAMPBELL and T. C. ANGUS (J. Physiol., 1929, 67, Proc. Physiol. Soc., x—xi).—A study of the total water evaporated in subjects during work under various atmospheric conditions.

B. A. EAGLES.

Metabolism in athletes. O. FLOSSNER and F. KUTSCHER (*Z. Biol.*, 1928, 88, 382—389).—The urine from athletes has been examined and the following substances have been detected: hippuric acid, lactic acid, adenine, methylguanidine, γ -butyrobetaine, and choline. The lactic acid, adenine, and methylguanidine contents decrease after exercise, whilst the appearance of phenylalanine and γ -butyrobetaine is noted.
E. A. LUNT.

Metabolism of the retina of the frog and determination of Meyerhof quotients at different temperatures. F. KUBOWITZ (*Biochem. Z.*, 1929, 204, 475—478).—At temperatures above 35° the frog retina behaves similarly to the retina of warm-blooded animals. Within the range of temperatures which do not injure the cells the Meyerhof quotient (which is independent of the action of respiration on the fermentation) increases with rise of temperature.
W. MCCARTNEY.

Metabolism of the retina of the fish at different temperatures. M. NAKASHIMA (*Biochem. Z.*, 1929, 204, 479—481; cf. preceding abstract).—The fish retina behaves like that of the frog, but at 37° the respiration of the former is not small. It is concluded that, according to the species of animal, the same kind of injury to the retina produces aerobic glycolysis by arresting either respiration or the Pasteur reaction.
W. MCCARTNEY.

Utilisation of sulphur by animals. H. R. MARSTON and T. B. ROBERTSON (*Council Sci. Res., Australia*, 1928, Bull. 39, 5—51).—A review of the literature dealing with sulphur metabolism, compiled with the object of laying a foundation for research into the problem of the economic importance of sulphur in wool production.
B. A. EAGLES.

Phosphagen [in muscle]. W. DULIERE (*Compt. rend. Soc. Biol.*, 1928, 98, 1252—1254; *Chem. Zentr.*, 1928, ii, 1351).—Rigor is not associated with the presence of phosphagen; it may disappear while the phosphagen is intact. Phosphagen disappears in the course of rigor or exertion. Addition of dextrose to the Ringer solution does not affect the phosphagen content of the muscle.
A. A. ELDRIDGE.

Muscle-phosphorus. II. Acid hydrolysis of lactacidogen. H. A. DAVENPORT and J. SACKS (*J. Biol. Chem.*, 1929, 81, 469—477).—Fresh resting muscle was rapidly extracted with trichloroacetic acid solution and the extract hydrolysed with *N*-sulphuric acid at 100°; there resulted a rapid liberation of phosphoric acid during the first hour, followed by a prolonged and very much slower hydrolysis. The phosphoric acid rapidly liberated corresponds with that set free on incubation of the muscle extract, and represents a part of the lactacidogen (I); the portion hydrolysable with difficulty (designated lactacidogen II) corresponds with the ester examined by Lohmann (*A.*, 1928, 1054); the suggestion of Lohmann that the first acid-labile portion is pyrophosphate could not be confirmed. Brief stimulation of muscle resulted in a rise in lactacidogen II and in little or no change in lactacidogen I.
C. R. HARRINGTON.

Determination of digestibility of protein by Bergeim's method. W. D. GALLUP (*J. Biol. Chem.*, 1929, 81, 321—324).—Silica has been successfully substituted for the ferric oxide employed by Bergeim (*A.*, 1926, 1170).
C. R. HARRINGTON.

Oxidation of glutamic acid in the animal body. A. VON BEZNAK (*Biochem. Z.*, 1929, 205, 420—432).— β -Phenylglutamic acid given subcutaneously to dogs and rabbits increases the hippuric acid excretion. It is concluded that glutamic acid is oxidised in the animal body, not only at the α -carbon, but also at the β -carbon atom. γ -Phenylglutamic acid is lethal to dogs and rabbits in doses of 0.5 g./kg. body-weight.
J. H. BIRKINSHAW.

Relation of various organs to cholesterol, fat, and lecithins. S. V. NEDSVEDSKY and A. K. ALEXANDRY (*Pflüger's Archiv*, 1928, 219, 619—625; *Chem. Zentr.*, 1928, ii, 1459).—In fasting dogs the adrenals synthesise and deliver 8 mg. of cholesterol to 100 c.c. of perfusing blood. The other organs neither take up cholesterol from the blood nor give it up. During digestion all the organs except the kidneys accumulate cholesterol. The lecithin content of arterial blood (2.6 mg. per 100 c.c.) remains unchanged after feeding. Of venous blood that of the hepatic vein contains most lecithin (0.10—0.28).
A. A. ELDRIDGE.

Resorption. II. Significance of bile acids for fat resorption. F. VERZAR and A. KUTHY. **III. Acceleration of resorption by yeast extract.** E. VON KOKAS and G. GAL (*Biochem. Z.*, 1929, 205, 369—379, 380—387).—II. Palmitic, stearic, and oleic acids when finely emulsified in water give, in presence of sodium taurocholate and glycocholate, clear, diffusible, molecular-disperse solutions which are stable at acid reactions down to p_H 6.2. The function of the complex bile acids in fat resorption is therefore to render soluble the fatty acids at the slightly acid reaction of the intestine.

III. The effect of yeast extract (Harris powder) on the resorption of dextrose and peptone in the stomach and intestine of the rat was studied. The average resorption of dextrose was increased from 37.3% to 46.8% and of peptone from 31.5% to 57.6% in presence of the extract.
J. H. BIRKINSHAW.

Basal metabolism and specific dynamic action after extirpation of adrenals in rats. A. VON ARVAY (*Biochem. Z.*, 1929, 205, 441—448).—Extirpation of both adrenals of rats leads to a fall (max. —26%) in the basal metabolism to a minimum at the sixth day, followed by a rise to the normal value at about the twentieth day in the survivors. The specific dynamic action reaches its minimum (about half normal) at the third day and attains the normal value at the same time as the basal metabolism.
J. H. BIRKINSHAW.

Behaviour of blood-sugar in experimental adrenal insufficiency. H. LANGE and E. GROSSMANN (*Biochem. Z.*, 1929, 205, 306—317).—Fasting cats deprived of one adrenal show no diminution in blood-sugar. Removal of both adrenals reduces the blood-sugar to about one quarter of its original value. The convulsions ensuing can be cured by intravenous dextrose injections.
J. H. BIRKINSHAW.

Effect of electrolytes on sugar metabolism. I. ABELIN (Biochem. Z., 1929, 205, 457—466; cf. A., 1927, 276, 897).—The addition of phosphate, sodium hydrogen carbonate, or natural Carlsbad salt to a sucrose diet produces in rats a fall in the amount of glycogen deposited in the liver and in the respiratory quotient. A relationship is suggested between this phenomenon and the strong ketogenic action of sodium hydrogen carbonate and other alkaline salts.

J. H. BIRKINSHAW.

Physiology of surviving mammalian hearts. V. Sugar consumption of the surviving hearts of normal cats. G. AMBRUS (Biochem. Z., 1929, 204, 467—473).—The sugar consumption of the surviving hearts is greater than previously stated by other workers. The original view that the consumption is greatest in the earliest period of survival should, for various reasons, be modified and the second period should be regarded as that of greatest consumption. Small hearts consume relatively more sugar than large ones and results should be expressed in such a way as to allow for this and other facts.

W. MCCARTNEY.

Physiology of surviving mammalian hearts. VI. Sugar utilisation of the hearts of normal and thyroidectomised cats after administration of thyroxine. G. AMBRUS (Biochem. Z., 1929, 205, 194—213; cf. preceding abstract).—The sugar utilisation of surviving hearts of thyroidectomised cats is considerably smaller than that of the hearts of normal animals, the decrease being the greater the sooner the experiment is carried out after extirpation. The hearts of normal and of thyroidectomised cats to which thyroxine has previously been administered use more sugar than the hearts of corresponding animals not receiving such treatment.

P. W. CLUTTERBUCK.

Influence of food on regulation of blood-sugar. E. GEIGER and H. KROFF (Arch. exp. Path. Pharm., 1929, 139, 290—301).—The sugar tolerance of rabbits as shown by the blood-sugar curves obtained after giving dextrose by mouth is increased by feeding on oats or administration of alkali, but is decreased after feeding on green food or administration of acid. These results render doubtful the validity of the method of Staub (Z. klin. Med., 1922, 93, 123; 1926, 104, 587) for ascertaining the efficiency of the insulin apparatus in the human subject.

W. O. KERMACK.

Utilisation of pentoses in the animal organism. P. THOMAS, A. GRADINESCU, and (Mlle.) R. IMAS (Compt. rend., 1929, 188, 664—666).—The proportions of glycogen fixed in the liver and muscles of the male frog after ingestion of 4% solutions of certain pentoses have been determined by Pflüger's method. Assuming 1 mol. of pentose provides 1 mol. of lactic acid, which is subsequently transformed into glycogen, then the maximum possible yield of glycogen is 54%. Actually 51.24% of glycogen was formed from xylose and 54.90% from arabinose.

J. GRANT.

Hepatic glycogen formation from *d*- and *l*-lactic acid. C. F. CORI and G. T. CORI (J. Biol. Chem., 1929, 81, 389—403).—The glycogen content of the liver of 24-hr. fasting rats shows marked

increase after oral or subcutaneous administration of sodium *d*-lactate, a less pronounced effect after sodium *r*-lactate, and no change after sodium *l*-lactate; this confirms the recent suggestion (A., 1928, 1286) that adrenaline stimulates the transformation of muscle-glycogen into liver-glycogen through the stage of lactic acid.

C. R. HARRINGTON.

Muscle-glycogen in mammals. M. E. MCKAY (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 329—333).—The fall in glycogen content of the sartorius, gracilis, and gastrocnemius muscles of the rabbit and dog has been studied. With the intact muscle this fall is not rapid; it is greatest in the sartorius and least in the gastrocnemius. Decapitate and decerebrate cats and cats the spinal cord of which was severed between the seventh cervical and first dorsal vertebrae were stimulated for periods of 1—30 min. There was little evidence of the restoration of glycogen to the muscles following a period for recovery of 1 or 2 hrs.

F. C. HAPFOLD.

Removal of glycogen from living muscle. V. J. M. HERSHEY and M. D. ORR (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 151—157).—The effect of starvation, starvation and muscular exercise, severe exercise accompanied by cold, severe exercise and induced prolonged shivering on the liver- and muscle-glycogen of rats has been studied. None of these processes removed all the glycogen. There is a more thorough removal of glycogen when strychnine is injected due to the combined muscular convulsions and respiratory embarrassment; the removal is not, however, complete.

F. C. HAPFOLD.

Hæmopoietic action of bilirubin and other hæmoglobin derivatives. F. VERZÁR and A. ZIH (Biochem. Z., 1929, 205, 388—401).—Bilirubin and hemibilirubin, and also hæmoglobin and hæmatin (which give rise to bilirubin in the body), fed to rabbits have a hæmopoietic action, but biliverdin has a much weaker action. Lower degradation products of bilirubin, as the porphyrins and bilirubinic acid, are without action. Bilirubin in large doses has a hæmolytic action in common with hæmopoietic extracts of spleen and bone-marrow and with bile. Bilirubin is active even after removal of the spleen. It is suggested that the bilirubin and related products arising from the decomposition of the blood act as physiological stimulants for the formation of red blood-corpuscles.

J. H. BIRKINSHAW.

Hæmopoietic action of various organs. A. ZIH (Biochem. Z., 1929, 205, 402—408).—Bone-marrow, spleen, and lymph glands fed to rabbits have a variable hæmopoietic or hæmolytic action in contrast to lung and muscle, which are inactive. All hæmopoietically active organs belong to the reticulo-endothelial apparatus and breakdown products of hæmoglobin may be present in the extracts.

J. H. BIRKINSHAW.

Pharmacological synergism of stereoisomerides. D. I. MACHT (Proc. Nat. Acad. Sci., 1929, 15, 63—70).—Synergism is the term applied to the phenomenon exhibited by two or more drugs in which the pharmacodynamic effect of the mixture is not a simple summation of the effects of the com-

ponents. A study was made of the effects of a number of stereoisomerides on certain animals and plants. Timed observations showed in general that the toxic and pharmacological effects of the *d*-, *l*-, and racemic forms varied considerably, and that a *dl*-mixture exhibited a definite synergism.

N. M. BLIGH.

Physiological action of derivatives of salicylic acid. I. K. KASE. II. K. KASE and K. SEKI (Biochem. Z., 1929, 205, 21—26, 27—30).—I. The methyl esters and the amides of *o*- and *p*-hydroxybenzoic acids are more toxic than the corresponding free acids and their action resembles more closely that of the corresponding phenols.

II. The non-poisonous character of the hydroxybenzoic acids depends on the presence of a free carboxyl group.

P. W. CLUTTERBUCK.

Toxic effects of amines. A. R. JOHNSTON (J. Infect. Dis., 1928, 42, 473—484).—The toxic effects of pyridine, quinoline, fuchsin, *p*-phenylenediamine, and amines generally are described. No relationship exists between the number of amino-groups in the molecule and its toxicity. CHEMICAL ABSTRACTS.

Effects of derivatives of betaineamide and of choline ethers on the autonomic nervous system. R. HUNT and R. R. RENSLOW (J. Pharm. Exp. Ther., 1929, 35, 99—128).—The effect on the blood pressure of the anaesthetised or decerebrated cat of a large number of derivatives of betaine of the general formula $\text{NMe}_3\text{X}\cdot\text{CO}\cdot\text{NHR}$. (R = an aliphatic or aromatic radical and X = Cl or Br) as well as of several derivatives of choline and homocholine, has been studied. The muscarine-like action and the nicotine stimulating action are influenced by the substituents, the phenyl group in particular decreasing the muscarine action and increasing the nicotine stimulating action.

W. O. KERMACK.

Action of choline on gaseous metabolism. H. TANGEL (Arch. exp. Path. Pharm., 1929, 139, 220—225).—Subcutaneous injection of choline into fasting rats increases the metabolism, the maximum effect occurring 2—6 hrs. after administration.

W. O. KERMACK.

Guanidine structure and hypoglycæmia. F. BISCHOFF, M. SAHYUN, and M. L. LONG (J. Biol. Chem., 1929, 81, 325—349).—A number of guanidine derivatives have been studied with respect to their hypoglycæmic activity and their toxic effect on the liver and kidney, the latter being measured by changes in the carbamide- and amino-acid-nitrogen of the blood. In the aliphatic and alicyclic series, the toxicity towards the kidney appears to be characteristic of the guanidine group, whilst hepatic injury is produced by those derivatives which cause hypoglycæmia, and in a parallel degree. Aliphatic guanidine derivatives containing cyano-, carbonyl, carboxyl, or hydroxyl groups are devoid of toxicity and of hypoglycæmic activity; acylation reduces the toxicity of guanidine. Aromatic guanidine derivatives exercise a toxic effect distinct from that of the aliphatic compounds; some of them have also a hypoglycæmic action. The diguanidinopolymethyl enes (homologues of synthalin) show a higher degree of hypoglycæmic activity than other derivatives, the

activity increasing with the length of the carbon chain. Of the compounds studied so far, guanylpiperidine is unique in showing a definitely greater hypoglycæmic than toxic action, and in producing a rapid hypoglycæmia (preceding depletion of the glycogen stores) in which respect its action simulates that of insulin.

C. R. HARRINGTON.

Substances producing hypoglycæmia. I. Syntheses of guanidine derivatives. T. KUMAGAI, S. KAWAI, Y. SHIKINAMI, and T. HOSONO (Sci. Papers Inst. Phys. Chem. Tokyo, 1929, 9, 271—275).—Hexamethylenediguanidine, octamethylenediguanidine, and decamethylenediguanidine ("synthalin") are approximately equally effective in producing hypoglycæmia in rabbits. Octamethylene-diguanidine is slightly more active than the other two compounds. The following compounds are described, the guanidine derivatives being produced by the condensation of *S*-methyl-*p*-thiocarbamide with the appropriate amine; β -3-indolyethylguanidine hydroiodide, m. p. 141—142°; pentamethylene-diguanidine sulphate, decomp. 330°; hexamethylene-diguanidine hydrochloride, m. p. 179—180°; dibenzoyl-octamethylenediamine, m. p. 169.5°; octamethylene-diamine hydrochloride, m. p. 284° (decomp.); octamethylenediguanidine hydrochloride, m. p. 176.5°; decamethylenediamine hydrochloride, m. p. 309—310°, and decamethylenediguanidine hydrochloride, m. p. 193°.

W. O. KERMACK.

Distribution of quinine in the blood. O. S. GIBBS (Proc. Nova Scotian Inst. Sci., 1928, 17, 114—115).—Blood containing quinine was separated by centrifuging into a serum layer and a blood-cell layer. The quinine was found to be equally distributed between the two layers. When the blood is hæmolyzed before being centrifuged, the lower layer, containing the "ghosts" of cells, has 6—40% more quinine, owing probably to adsorption on the cells. A modification of Ramsden and Lipkin's method for the determination of quinine gave unsatisfactory results (cf. King and Acton, A., 1921, i, 474).

B. W. ANDERSON.

Action of vapours of ethyl and methyl alcohols, ether, and chloroform, and of illuminating gas on leucocytes. (SIGNA.) C. FORTI (Atti R. Accad. Lincei, 1928, [vi], 8, 700—705).—The amœboid activity of the leucocytes of toad's blood is paralysed in a few minutes by the vapour emitted by small quantities of ethyl or methyl alcohol, ether, or chloroform. Illuminating gas (40—50% of carbon monoxide) produces first increased, and later gradually diminishing movement of the leucocytes, complete arrest setting in only after 8 or 9 hrs. According to the duration of the action, these effects may be either permanent or transitory.

T. H. POPE.

Combined narcosis. I. Ether and chloroform. II. Nitrous oxide and ether. III. Acetylene and ether. L. LENDLE (Arch. exp. Path. Pharm., 1929, 139, 179—200, 201—210, 211—219).—I. When white mice are anaesthetised by mixtures of chloroform and ether the speed of narcotisation increases, whilst, relatively to the dose necessary for light narcosis, the narcotic range (cf. A., 1928, 920) decreases, as the proportion of ether in the mixture

is increased. The secondary toxic action of the anæsthetic also decreases with increase in the proportion of ether.

II. With mixtures of nitrous oxide and other the anæsthetic action is not additive, but with addition of nitrous oxide to the mixture the total anæsthetic effect tends to decrease. The narcotic ranges of the mixtures investigated were approximately the same as that of pure ether.

III. The relative narcotic range of mixtures of acetylene and ether is approximately independent of the proportion of the two anæsthetics. The anæsthetic effect of such mixtures is an additive function of the constituents. W. O. KERMACK.

Relative physiological properties of certain 5:5-dialkyl- and 1-aryl-5:5-dialkylbarbituric acids. A. M. HJORT and A. W. DOX (J. Pharm. Exp. Ther., 1929, 35, 155—164).—The anæsthetic action on mice has been studied. In the case of 5:5-diethylbarbituric acid the introduction of a 1-aryl group does not improve hypnotic properties, but in the cases of 5-ethyl-5-*n*-propyl-, 5-ethyl-5-*n*-butyl-, 5-ethyl-5-*isobutyl*-, and 5-ethyl-5-*isoamyl*-barbituric acids, the presence of a 1-aryl group decreases the toxicity of the compound and hence improves it as a hypnotic. Neither 1:3-diphenyl-5-ethylbarbituric acid nor the *p*-ethoxyphenylmonoureide of ethyl-*n*-butylmalonic acid has anæsthetic action. The following barbituric acids have been prepared: 1-*p*-tolyl-5:5-diethyl-, m. p. 152—153°; 1-*p*-anisyl-5:5-diethyl-, m. p. 126—127°; 1-*p*-ethoxyphenyl-5:5-diethyl-, m. p. 152—153°; 1-*p*-chlorophenyl-5:5-diethyl-, m. p. 135—136°; 1-*p*-bromophenyl-5:5-diethyl-, m. p. 186°; 1-phenyl-5-ethyl-5-propyl-, m. p. 152—153°; 1-phenyl-5-ethyl-5-*isobutyl*-, m. p. 149°; 1-phenyl-5-ethyl-5-*n*-butyl-, gummy; 1-phenyl-5-ethyl-5-*isoamyl*-, m. p. 130°; 1:3-diphenyl-5-ethyl-, m. p. 145°; also the *p*-ethoxyphenylmonoureide of ethyl-*n*-butylmalonic acid, m. p. 124—125°.

W. O. KERMACK.

"Noctal" and "pernocton." III. Behaviour in the organism. IV. Determination of the activity of similar barbituric acids. V. Influence of the structure of the alkyl group on the activity. F. BOEDECKER and H. LUDWIG (Arch. exp. Path. Pharm., 1929, 139, 353—356, 357—360, 361—372).—III. 5-*iso*Propyl-5-acetonylbarbituric acid and 5-*iso*propyl-5-carboxymethylbarbituric acid, into which "noctal" (5-*iso*propyl-5- β -bromoallylbarbituric acid) is presumably converted in the animal organism, are without toxic action. The corresponding *sec*-butyl compounds derived from "pernocton" (5-*sec*-butyl-5- β -bromoallylbarbituric acid) are likewise inactive.

IV. The following compounds are all strong hypnotics: 5-*iso*propyl-5- γ -bromoallyl-, 5-*iso*propyl-5- β -chloroallyl-, 5-*iso*propyl-5- β - γ -dibromoallyl-, 5-di-(β -bromoallyl)-, and 5:5-di(chloroallyl)-barbituric acids.

V. Of the following barbituric acids: 5- α -methylbutyl-5-allyl-, 5- α -methylbutyl- β -bromoallyl-, 5-*sec*-butyl-5-allyl-, 5-*sec*-butyl-5- β -chloroallyl-, 5- α -phenylpropyl-5-allyl-, 5-*iso*propyl-5- β -bromoallyl-, 5-*iso*propyl-5- β -chloroallyl-, 5- α -ethylpropyl-5- β -bromo-

allyl-, and 5-dimethylpropyl-5- β -bromoallyl-, those containing an asymmetric carbon atom are particularly potent hypnotics. The physiological and pharmacological actions of "pernocton" have been investigated.

W. O. KERMACK.

"Avertin." A. WELSCH (Arch. exp. Path. Pharm., 1929, 139, 302—312).—After administration of "avertin" the bromine of the compound is quantitatively excreted in the urine within 48 hrs. The urine gives Arnold's reaction (with sodium nitroprusside and alkali) much more markedly than does normal urine and it contains a substance which inhibits the reduction of Fehling's solution. From the urine after precipitation with lead acetate a barium salt was obtained which was apparently an impure mixture of the barium salts of cystine and of "avertin"-glycuronic acid from which this latter acid was isolated.

W. O. KERMACK.

Use of magnesium as an aid in anæsthesia. I. NEUWIRTH and G. B. WALLACE (J. Pharm. Exp. Ther., 1929, 35, 171—187).—Administration of magnesium sulphate or lactate to dogs by mouth or *per rectum* does not raise the magnesium content of the serum to the level at which analgesic action is produced, viz., 5 mg. per 100 c.c. This level is reached by the administration subcutaneously of 0.25 g. of magnesium sulphate per kg. body-weight. Profound anæsthesia occurs when the serum-magnesium is 20 mg. or more per 100 c.c. It is considered unlikely that magnesium salts are of use in colonic anæsthesia mixtures or in obstetrical analgesia when employed in the usual doses.

W. O. KERMACK.

Action of large amounts of iron. II. Action on blood, growth, fertility, and lactation. K. WALTNER (Biochem. Z., 1929, 205, 467—472; cf. *ibid.*, 1927, 188, 38).—Rats receiving an addition of 2% of reduced iron to a complete diet show no change in the blood, but with a rachitic diet anæmia develops. The iron also delays growth at the age susceptible to rickets. The lessened fertility and secretion of milk produced by the reduced iron are cured by vitamin-D.

J. H. BIRKINSHAW.

[Physiological] action of sulphur. L. PINCUSSEN and E. GORNITZKAJA (Z. klin. Med., 1928, 108, 369—377; Chem. Zentr., 1928, ii, 1347).—After application of sulphur the blood-sugar, -diastase, and -catalase are unchanged, but the tributyrin esterase is diminished.

A. A. ELDRIDGE.

Toxicology of bismuth. II. Distribution in the organism after injection of aqueous solutions of bismuth compounds. R. FABRE and M. PICON (J. Pharm. Chim., 1928, [viii], 9, 97—112; cf. A., 1928, 1280).—A study of the distribution of bismuth in the tissues after intravenous injections of aqueous solutions of bismuth cacodylate, "bismuth campho-carbonate," and ammoniacal bismuth citrate.

B. A. EAGLES.

Excretion of bismuth from the human organism. W. ENGELHARDT (Arch. Dermat. Syphilis, 1928, 156, 1—42; Chem. Zentr., 1928, ii, 1461).—Considerable quantities of bismuth are excreted in the fæces and urine during treatment of syphilis by bismuth preparations. Up to 50% is so excreted,

most rapid excretion taking place after intravenous injection. Oil suspensions are irregularly excreted.

A. A. ELDRIDGE.

Electrolytic determination of lead in urine. T. COOKSEY and S. G. WALTON (*Analyst*, 1929, 54, 97—99).—The urine is made acid with acetic acid and lead deposited electrolytically. The deposit is dissolved in nitric acid and converted into chloride, and lead is determined by comparing the turbidity resulting on addition of a solution of potassium metabisulphite against a standard. The lead content of normal urine varies between 0.02 and 0.05 mg./litre; mean, 0.04.

J. S. CARTER.

Resistance of the nematode, *Anguillula aceti*, Ehrenberg, to various protoplasmic poisons. J. BELEHRÁDEK and V. NEČÁSOVÁ (*Bull. Soc. Chim. biol.*, 1929, 11, 65—69; cf. A., 1928, 1279).—*Anguillula aceti* resists the action of 2.5% aluminium chloride and 2% barium chloride solutions for considerable periods. The times of survival to potassium cyanide, mercuric chloride, and cupric chloride are greater than those of *Cypris* and *Tubifex*. The resistance is probably connected with the constitution of the epidermal tissue.

G. A. C. GOUGH.

Strontium thioacetate as an antidote in poisoning by mercuric chloride. C. C. HASKELL and J. C. FORBES (*J. Pharm. Exp. Ther.*, 1929, 35, 147—153).—Dogs poisoned by mercuric chloride administered either orally or intravenously were apparently not benefited by the administration of strontium thioacetate.

W. O. KERMAK.

Effect of X-rays on the process of enzyme formation in the isolated pancreas. A. I. BOGAYEVSKI and B. GOLDSTEIN (*Zhur. exp. Biol. Med.*, 1928, 9, 328—334).—Stimulation of the gland cells by the action of X-rays on the perfused pancreas yields a fluid containing a greater concentration of amylase and lipase. An excessive dose diminishes the activity.

CHEMICAL ABSTRACTS.

Absolute absorption spectrum of the respiratory enzyme. Photochemical dissociation of iron pentacarbonyl. O. WARBURG and E. NEGELEIN (*Biochem. Z.*, 1929, 204, 495—499).—Certain results communicated in former papers (cf. A., 1928, 549, 851, 1390; this vol., 216) require to be multiplied by the factor 2.2. The photochemical dissociation of iron pentacarbonyl has been reinvestigated and it has been found that one molecule of carbon monoxide per quantum of light is split off.

W. MCCARTNEY.

Cytochrome and respiratory enzymes. D. KEILIN (*Proc. Roy. Soc.*, 1929, B, 104, 206—252).—Yeast cells contain a powerful indophenol-oxidase system which is easily revealed by the oxidation of *p*-phenylenediamine. The oxidase is thermolabile, being irreversibly destroyed by boiling or heating to 70°, is strongly inhibited by potassium cyanide and hydrogen sulphide but not by sodium pyrophosphate. This oxidase system is inhibited by the reducing systems of the cells and so is active only in presence of various narcotics such as urethane or after the cells have been warmed for 1½ hrs. at 52° or cooled to -2°. Dried yeast and zymine give only feeble reactions. The oxidase system is inhibited

by carbon monoxide, which appears to form an inactive compound with it. This compound is, however, readily destroyed by oxygen and by light. Quantitative measurements by means of a Barcroft manometer demonstrate that the amount of carbon monoxide combined with the yeast oxidase is proportional to the partial pressure of the carbon monoxide and that the oxidase molecule has much greater affinity for oxygen than for carbon monoxide. The oxidase activity of yeast-cells and the total respiratory activity are with a few exceptions similarly affected by reagents. An oxidase system with properties similar to but not identical with that found in yeast is present in a preparation of washed heart-muscle. The properties of polyphenol-oxidase from potato have also been investigated. This enzyme can be obtained as a clear solution unlike the former two, which it has not so far been possible to separate from cellular material. It is considered that the indophenol-oxidase plays an important rôle in cell metabolism. The properties of the components of living cells which are derivatives of hæmatin are described. Cytochrome is composed of three hæmatin compounds, a^1 , b^1 , and c^1 , and an unbound hæmatin compound similar to the protohæmatin of hæmoglobin, of which the components a^1 and c^1 are not, whilst the other two are autoxidisable. It appears that the factors, e.g., potassium cyanide, propionitrile, hydrogen sulphide, carbon monoxide, drying the cells, treating them with alcohol or acetone, which inhibit the activity of indophenol also inhibit the oxidation of cytochrome, whilst the factors, e.g., narcotics or warming to 52°, which have little effect on the activity of indophenol-oxidase do not inhibit the oxidation of cytochrome. It is concluded that cytochrome is oxidised by the indophenol-oxidase. Cytochrome in the living cell is reduced in presence of dehydroases by the hydrogen donors present, which are themselves oxidised. Cytochrome is thus considered to act as an oxygen carrier in the oxidation of the cell metabolites, being alternately oxidised through the action of the oxidase and reduced through the action of the dehydroase. Some other possible functions of intracellular hæmatin compounds are discussed as well as the nature of the oxidase.

W. O. KERMAK.

Dextrose-oxidase. II. D. MÜLLER (*Biochem. Z.*, 1929, 205, 111—143).—In the press juice and in the alcohol, alcohol-ether, and acetone precipitates of the press juice of *Aspergillus niger* an enzyme is present which can oxidise dextrose to gluconic acid, atmospheric oxygen being absorbed. The enzyme oxidises mannose and galactose less readily, but does not attack lævulose, xylose, arabinose, calcium gluconate, dihydroxyacetone, glycerol, and acetaldehyde. The oxidase does not act in an atmosphere of hydrogen. Its p_H optimum is 5.5—6.5 and its action increases from 0 to 30°, inactivation occurring at 73°. Its action is not assisted by phosphate or insulin. The activity of the oxidase rapidly decreases on keeping. The enzyme is also present in the press juice of *Penicillium glaucum*.

P. W. CLUTTERBUCK.

Action of ptyalin on starch. I. J. R. BROEZE (*Biochem. Z.*, 1929, 204, 286—302).—The decom-

position of starch by ptyalin has been followed by means of viscosity measurements. The velocity of enzymic hydrolysis was proportional to the concentration of the enzyme. The enzyme was not reduced in activity by its action on the starch. The temperature coefficient of the velocity of the reaction at 20–30° was 2. No regeneration of the heated enzyme could be observed. Evidence is given for supposing that the flocculation of the starch and the checking of the reaction which occur during the process are due, respectively, to the existence of sensitive spots on the starch particles and to the enveloping action of some of the particles, when swelling, on others.

W. McCARTNEY.

Action of fluorescent dyes in the dark on diastase. G. CLAUS (Biochem. Z., 1929, 204, 456–466).—Diastase from germinating roots grown from seeds treated with eosin is more active than that from normally grown roots. The dyes of the fluorescein series and phenosafranin added to starch-diastase solution accelerate the decomposition of the starch, the magnitude of acceleration varying according to the dye used and being greatest with phenosafranin and eosin and least with phloxin and erythrosin. The acceleration of decomposition occurs only at p_H values removed from the optimum for the action of diastase, but it exceeds considerably that produced at the most favourable p_H without addition of eosin. Diastases of different origins may, in consequence of the presence of impurities, produce different effects and malt diastase should always be employed. The action of diastase from saliva can also be stimulated by the dyes, although negative results were obtained with extract of *Aspergillus oryzae*.

W. McCARTNEY.

Determination of catalase in barley-malt. M. O. CHARMANDARIAN (Biochem. Z., 1929, 204, 389–396).—On continued extraction the catalase of malt from barley loses some of its power to decompose hydrogen peroxide, but the length of the period of extraction does not influence the reaction of the medium and hence factors which might affect the activity of the catalase are not introduced. Unextracted barley-malt always decomposes more hydrogen peroxide than do extracts and it is concluded that the variations which occur in the power of the catalase are chiefly due to the degree of its dispersion in the medium.

W. McCARTNEY.

Action of proteolytic enzymes on the benzoyl and phthalyl derivatives of polypeptides. I. Action of intestinal erepsin and of yeast protease on phthalylglycylglycine and phthalyl-diglycylglycine. II. Action of tissue proteases on benzoyl- and phthalyl-glycylglycine. III. Action of pancreatic proteases on benzoyl- and phthalyl-glycylglycine. S. UZINO (J. Biochem. Japan, 1928, 9, 453–463).—I. Yeast protease attacks both compounds, but intestinal erepsin hydrolyses only the latter.

II. Phthalylglycine and phthalylglycylglycine were not hydrolysed. Maceration juice hydrolyses glycylglycine and leucylglycine; pig-kidney maceration juice hydrolyses benzoylglycine, benzoylglycylglycine, and glycylglycine. Benzoyl- and phthalyl-glycyl-

glycine are not hydrolysed by beef muscle or pig-liver press juice, rabbit-muscle or -liver maceration juice, or rabbit-liver pulp.

III. The compounds are hydrolysed by pancreatin, pig-pancreas pulp, pancreas press-juice, and glycerol extracts of dry pancreas preparations, and by the trypsin fraction which hydrolyses edestin but not glycylglycine.

CHEMICAL ABSTRACTS.

Effect of alkaloids on an alcoholic extract of fibrin peptone (peptic digest). M. A. RAKUZIN and T. A. GENKE (Zhur. exp. Biol. Med., 1928, 9, 221–223).—Strychnine, brucine, quinine, codeine, morphine, or theobromine removes tyrosine from the extract. The action of the alkaloid is similar to that of enzymes, and it is suggested that alkaloids are crystalline toxins. Some alkaloids of high mol. wt. are considered to be colloidal.

CHEMICAL ABSTRACTS.

Stereochemical action of animal phosphatase. A. GUALDI (Biochem. Z., 1929, 205, 320–324).—Phosphatase from the liver and from the kidney of the rabbit, like mould phosphatase, first sets free *l*-borneol from salts of *dl*-borneolphosphoric acid.

J. H. BIRKINSHAW.

Sulphatase. X. P. WEINMANN (Biochem. Z., 1929, 205, 214–218).—The preparation of potassium 3-methylcyclohexylphenyl sulphate and its hydrolysis by takasulphatase are described, the hydrolysis being practically complete.

P. W. CLUTTERBUCK.

Significance of some auxo-substances in the urease reaction. M. KITAGAWA (J. Biochem. Japan, 1928, 9, 347–352).—Urease free from auxo-substance retains its activity provided that the inhibitor is completely removed from the system. Since the addition of an auxo-substance causes the formation of an undissociable compound with the inhibitor and liberates free active urease, the activity is determined by the relative amounts of auxo-substance and inhibitor in the system.

CHEMICAL ABSTRACTS.

Systematic study of some *Torulae*. F. C. HARRISON (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 187–225).

Plant phosphatides. VIII. Phosphatides of yeast. V. GRAFE (Biochem. Z., 1929, 205, 256–258).—Pure cultures of yeast are subject to autolysis at 28–30° for 36 hrs. and dialysed against distilled water. The dialysate contained considerable amounts of phosphatide but no protein.

P. W. CLUTTERBUCK.

Relation between the production of lactic acid and the growth of yeast. E. AUBEL (Compt. rend., 1929, 188, 578–580).—The hypothesis that the energy absorbed in the growth of yeast arises from the conversion of dextrose into lactic acid (A., 1926, 1277) is shown to be untenable, since the amount of the last-named product appears to possess no relation to the amount of growth.

G. A. C. GOUGH.

Sporulation of yeast. H. STANTIAL (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 257–261).—Experiments to determine the conditions of sporulation of yeast are discussed. Whether yeast will form spores or not depends on the presence or absence of some

constituent of wort, fruit juices, lettuce, etc. The juice of grape-fruit gave the best results.

A. J. MEE.

Persistence of acclimatisation to fluoride, after sporulation of yeast. H. STANTIAL (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 263—265).—Experiments are described which prove that yeast from "fluoride spores," i.e., yeast formed by the germination in fluoride-free wort of spores which had been formed in the absence of fluoride from acclimatised yeast, is much more tolerant of fluoride than is yeast formed in parallel experiments from unacclimatised yeast.

A. J. MEE.

Isolation and identification of bios I; its absorption by and recovery from yeast. E. V. EASTCOTT (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 267).—Pure bios I has been obtained from tea-dust and shown to be identical with inactive inositol. The amount of inositol taken up by yeast is 1.2×10^{13} g. per cell.

A. J. MEE.

Chemical derivatives of bios II. E. M. SPARKING (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 271).—Bios II may be purified by conversion into some derivative which can itself be more easily purified, and then treating this with alkali. Acylation seems the most promising method. The product of this treatment is without effect on the rate of reproduction of yeast until "activated" by sodium hydroxide.

A. J. MEE.

Giant yeast cells. M. HOLT (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 269—270).—Yeast left to bud in a solution of sugar and salts to which certain amino-acids have been added gives rise to abnormally large cells. The substances capable of promoting this growth are aspartic acid, glutamic acid, glycine, and alanine. This reaction may be peculiar to certain races of yeast.

A. J. MEE.

Extraction and purification of co-zyzyme from yeast. K. MYRBACK (Svensk Kem. Tidskr., 1929, 41, 3—8; cf. A., 1924, i, 918; 1927, 993; 1928, 1284).—Brewer's yeast is washed in running water until the effluent is almost colourless, filtered, and pressed. The powdered material is stirred with 4 vols. of water at 80° for 10 min., and the solution filtered hot, whereby an average extraction of 60% of the total co-zyzyme is obtained. For further purification the extract is evaporated in a vacuum and dialysed, the co-zyzyme passing through the collodion membrane. After removal of inactive impurities from the dialysate by precipitation with neutral lead acetate, the co-zyzyme can be precipitated by the addition of lead acetate and sodium hydroxide to the filtrate, but as an excess of either reagent prevents complete precipitation it is difficult to obtain a good yield. A better method is to precipitate the excess of lead with hydrogen sulphide, and remove the latter from the filtrate by a current of air. An excess of mercuric acetate is added, the precipitate separated by centrifuging after keeping for 2 hrs., suspended in water, and treated with hydrogen sulphide. The filtrate after removal of hydrogen sulphide contains 90% of the co-zyzyme originally present. The purity of the product can

be determined by the method of Euler and Myrback (A., 1924, i, 918). Attempts to separate co-zyzyme, in view of the marked pentose reactions it exhibits, by precipitation with a mixture of copper sulphate and calcium hydroxide were not successful.

H. F. HARWOOD.

Regulated enzymic dismutation by the keto-aldehyde mutase of *B. subtilis*. A. GUALDI (Biochem. Z., 1929, 205, 318—319).—Dismutation of phenylglyoxal hydrate by *B. subtilis* gives a preponderance (84%) of *d*-mandelic acid. J. H. BIRKINSHAW.

Question of the identity of mutase and keto-aldehyde mutase. C. NEUBERG and M. KOBEL (Z. physikal. Chem., 1928, 139, 631—646).—A kinetic study of the dismutation of acetaldehyde and methylglyoxal by the action of various bacteria. Experiments with freshly-prepared suspensions of bacteria were carried out at 37° with solutions 0.01*M*, 0.02*M*, 0.04*M* for methylglyoxal and 0.02*M*, 0.04*M*, 0.08*M* for acetaldehyde. The course of the reaction was followed by determining the amount of unchanged substance by titration, using the hydroxylamine sulphate method for acetaldehyde and the iodometric method for methylglyoxal. Two series of experiments were carried out; to the first only the bacterial suspension was added but to the second calcium carbonate was also added in order to maintain a constant p_H throughout the reaction. With *B. Pasteurianum* and *B. ascendens* transformation of both substances follows the same course; it is also the same with these two bacteria whether the solution is acid or neutral. On the other hand with *B. Delbrücki* the dismutation of methylglyoxal proceeds much more quickly than that of acetaldehyde, whether in neutral or acid solution. The same difference is found with *B. lactis aerogenes*, but not to such a marked extent. Using yeast the change of both substances proceeds at nearly the same rate in dilute solution, but in more concentrated solutions methylglyoxal is transformed more quickly than acetaldehyde.

R. N. KERR.

Characterisation of the group of *Aspergillus niger*. II. Importance of acid substrates for the characterisation and growth of the mould. K. BEENHAUER (Biochem. Z., 1929, 205, 240—244).—*A. niger* is very sensitive to acids and only small amounts are formed unless some means for its neutralisation, e.g., calcium carbonate, is present. The mould is differently resistant to different acids. Successive sowing of spores on acid substrates increases the acid-forming power. P. W. CLUTTERBUCK.

Formation of citric and oxalic acids by *Aspergillus niger*. S. KOSTYTSHEV and V. TSCHESNOKOV (Planta, Arch. wiss. Bot., 1927, 4, 181—200; Chem. Zentr., 1928, ii, 1452).—Formation of citric acid is favoured by acidity, and of oxalic acid by alkalinity, of the medium. In young cultures citric acid is not formed so long as nitrogen is utilised from the nutrient solution. Citric acid is considered to be necessary for the synthesis of amino-acids.

A. A. ELDRIDGE.

Fermentative hydrolysis of asparagine by the mycelium of *Aspergillus niger*. D. BACH (Bull. Soc. Chim. biol., 1929, 11, 119—145).—A more

detailed account of work already published (this vol., 108).

Formation of diastase by *Aspergillus oryzae*. G. L. FUNKE (Rec. trav. bot., 1927, 24, 583—630; Chem. Zentr., 1928, ii, 1444).—On buffered solutions (0.5% of potassium monohydrogen phosphate) *A. oryzae* forms large quantities of diastase; the chemical composition of the nutrient solution is without influence. On unbuffered solutions the mould grows less readily, forms more acid and scarcely any diastase; aerobic respiration takes place. The acid is apparently oxalic, which may inactivate the enzyme by chemical union.

A. A. ELDRIDGE.

Chemical constituents of the spores of *Aspergillus oryzae*. M. SUMI (Biochem. Z., 1929, 204, 412—413).—The sterol isolated from the spores (cf. A., 1928, 927) is now found to be ergosterol.

W. MCCARTNEY.

***Penicillium glaucum*. Production of methyl ketones from triglycerides or fatty acids in the metabolism of the mould.** II. O. ACKLIN (Biochem. Z., 1929, 204, 253—274).—The normal fatty acids (except butyric and valeric acids) are decomposed by *P. glaucum* in such a way that corresponding methyl ketones are formed. β -Hydroxy-acids are not formed as intermediate stages in the process and evidence is given for supposing that keto-acids are first produced. These, if stable, are converted directly or indirectly into methyl ketones (or even, finally, into secondary alcohols by reduction); if unstable, they are converted first into β -hydroxy-acids, then into carbon dioxide and water. Quantitative experiments on the decomposition by *P. glaucum* of hexoic acid (or of trihexoin) show that the course of the process depends greatly on the concentration of the acid (or glyceride) and of the nutrient medium as well as on the p_H of the system, the production of methyl propyl ketone being most favoured by low concentrations of the acid (or glyceride), high concentration of the medium, and p_H on the alkaline side. Hæmin has no catalytic effect on the formation of the ketone. In general, it is concluded that both qualitatively and quantitatively the course of the decomposition of normal fatty acids to methyl ketones by *P. glaucum* depends on the lengths of the carbon chains of the acids concerned.

W. MCCARTNEY.

Dissimilation of salts of fatty acids and carbohydrates by thermophilic bacteria. C. COOLHAAS (Zentr. Bakt. Par., 1928, II, 75, 161—170; Chem. Zentr., 1928, ii, 1342—1343).—A mixture of ammonium chloride (1 g.), potassium monohydrogen phosphate (1 g.), magnesium sulphate (0.5 g.), and calcium acetate (10 g. per litre), inoculated with mud and kept at 63°, exhibited fermentation in 5—14 days, yielding 50—60 c.c. of a mixture (2:1 vols.) of methane and carbon dioxide per hr. The reaction was: $\text{CaC}_4\text{H}_6\text{O}_4 + \text{H}_2\text{O} = 2\text{CH}_4 + \text{CO}_2 + \text{CaCO}_3$. With calcium formate, $2\text{CaC}_2\text{H}_3\text{O}_4 = \text{CH}_4 + \text{CO}_2 + 2\text{CaCO}_3$, 94.4% of the theoretical quantity of methane being obtained, together with small amounts of hydrogen. Calcium isobutyrate, oxalate, lactate, and gluconate were readily, propionate more slowly, and butyrate very slowly, fermented. When sucrose, in an

inorganic nutrient medium, was inoculated with canal mud, the gas produced consisted of carbon dioxide and hydrogen. Inoculation with acetate-fermenting bacteria, however, produced the fermentation $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} = 6\text{CO}_2 + 6\text{CH}_4$, the process gradually reverting to the hydrogen fermentation. Cellulose, inoculated with faeces, at 60° gives varying proportions of methane and hydrogen. Cabbage waste yields thus more methane at 60° than at 26°.

A. A. ELDRIDGE.

***Bacterium gluconicum*, occurring in "Kom-bucha" (Japanese or Indian tea fungus).** S. HERMANN (Biochem. Z., 1929, 205, 297—305; cf. A., 1928, 330).—*B. gluconicum* is a Gram-negative non-sporing organism with ovoid cells 0.8/0.6 μ . Its physiological behaviour on various sugars is given; in its reactions it closely resembles *B. xylinum*. On dextrose it gives a transitory Selivanov reaction for keto-groups.

J. H. BIRKINSHAW.

Cellulose as source of energy for nitrogen-fixing micro-organisms. P. TUORILA (Zentr. Bakt. Par., 1928, II, 75, 178—182; Chem. Zentr., 1928, ii, 1340).—With a mixture of cellulose (5 g.), calcium carbonate (0.2 g.), potassium monohydrogen phosphate (150 c.c. of 0.075% solution), garden soil (0.5 g.), and varying quantities of ammonium chloride kept for 30 days at 31°, the micro-organisms assimilated considerable quantities (up to 18 mg.) of atmospheric nitrogen only when the concentration of ammonium chloride was small or zero. The chief source of energy was the degradation products of cellulose. In a culture containing cellulose and mannitol the latter was the sole source of energy for a pure culture of *Azotobacter*. Mixed cultures of soil bacteria and *Azotobacter* with cellulose as principal nutrient fix much nitrogen; apparently certain bacteria decompose the cellulose and others, e.g., *Azotobacter*, utilise the products. A. A. ELDRIDGE.

Fixation of atmospheric nitrogen by *Azotobacter*. O. MEYERHOF and D. BURK (Z. physikal. Chem., 1928, 139, 117—142).—The growth and respiration of *A. chroococcum* under varying experimental conditions have been studied in liquid cultures for short periods of time at 28°. A deficiency of calcium or phosphate in the culture medium is accompanied by decreased respiration. The optimum p_H of the solution lies at 6.8—7.6. Respiration in the presence of dextrose, levulose, galactose, and mannitol is ten to fifteen times as great as in solutions free from carbohydrate, is almost independent of concentration between 0.1 and 5%, but is reduced considerably at a concentration of 10%. It is retarded by even small amounts of ammonium sulphate, narcotics, and potassium cyanide. The effect of potassium cyanide is less marked in pure oxygen than in air. Respiration measured with respect to unit dry weight falls rapidly with an increase in age of the culture, whilst the rate of growth decreases after the first 24 hrs., which is attributed to aggregation of the bacteria. Under average conditions the increase in number of bacteria, the increase in dry weight, and that of nitrogen fixed run parallel. Maximum respiration occurs at 15—20% of oxygen and outside these limits falls rapidly. In

pure oxygen it is one third to one half that in air, but on the other hand is independent, for short periods of time, of the presence of nitrogen; in mixtures of oxygen and hydrogen it equals that in oxygen-nitrogen mixtures. In the absence of ammonium salts, the increase in respiration, taken as a measure of growth, is dependent on the nitrogen content. In oxygen-hydrogen mixtures this increase is nil during the first 6 hrs., with 5% of nitrogen it becomes noticeable, and with 20% is approximately as large as in air. The oxygen concentration has an important effect on the nitrogen fixation and on the ratio nitrogen fixed/oxygen used. Maximum fixation and growth occur with 4–5% of oxygen, but the ratio increases continuously with decreasing pressure of oxygen. The assimilation of ammonia in a nitrogen-free atmosphere also increases with decreasing oxygen pressure, but the ratio nitrogen assimilated/oxygen used is practically unaltered. L. S. THEOBALD.

Diphtheria toxin. A. LOCKE and E. R. MAIN (J. Infect. Dis., 1928, 43, 41–59).—Toxin is not accumulated in cultures in the absence of a definite growth momentum, of a concomitant growth inhibition, and of buffers, *e.g.*, proteoses. Toxin preparations were of lipoprotein character and contained no carbohydrate. Antigenicity, antitoxin-binding power, and toxicity of bacterial toxins may be manifestations of their combining avidity.

CHEMICAL ABSTRACTS.

Action of hæmotoxins on oxygenated and reduced blood. I. *Bacillus Welchii* toxin. G. B. REED, J. H. ORR, and W. A. CAMPBELL (J. Infect. Dis., 1927, 41, 434–438).—Atmospheric oxidation of *B. Welchii* toxin causes considerable loss of hæmotoxic action. A higher concentration of the toxin is required for hæmolysis of oxygenated red cell suspensions than for that of reduced red cell emulsions.

CHEMICAL ABSTRACTS.

Determination of indole in bacterial cultures. H. B. PIERCE and R. B. KILBORN (J. Biol. Chem., 1929, 81, 381–387).—Indole can be successfully determined in bacterial cultures by a slight modification of the method employed by Bergeim (A., 1918, ii, 23) for faeces. Added indole can be recovered from water and from bacterial cultures in peptone-water to the extent of 95% and 91%, respectively.

C. R. HARRINGTON.

Pneumin. A respiratory autacid from the adrenal cortex. S. VINCENT and J. H. THOMPSON (J. Physiol., 1929, 67, Proc. Physiol. Soc., iii–iv).—Extirpation of both adrenals or ligation of the total blood supply to them causes rapid death in decerebrate cats due to cessation of respiration. It is concluded that a substance, for which the name *pneumin* is proposed, essential for the normal movements of respiration, is secreted by the adrenal cortex and passes into the veins by way of the lymphatics.

B. A. EAGLES.

Attempt to concentrate the active principle of the adrenal cortex. A. T. CAMERON and F. D. WHITE (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 145–149).—An active fraction, capable of accelerating growth, is obtained when the fresh whole adrenal gland of the ox is extracted with 0.1N-hydrochloric

acid, concentrated to dryness, and extracted with 95% alcohol. The fraction precipitated by 80% alcohol and not by 60% and that precipitated by 90% but not by 80% show a definite increase in growth-promoting value; this increase, it is suggested, is due to a removal of adrenaline, which has an antagonising action. Concentration of the active factor has been effected by extracting with methyl alcohol. The antagonising action of adrenaline is removed by simple oxidation. F. C. HAPPOLD.

Action of adrenaline on the creatine-phosphoric acid content of muscles. O. FEINSCHMIDT and D. FERDMANN (Biochem. Z., 1929, 205, 325–328).—Injection of adrenaline into the breast-muscle of the pigeon causes an increase in inorganic phosphorus which is not accounted for by the increased creatine-phosphoric acid hydrolysis. There is also an increase in the phosphorus compounds which yield phosphoric acid after hydrolysis for 2 hrs. with 2% sodium hydrogen carbonate solution and a decrease in the residual phosphoric acid. The higher lactic acid content is not directly related to the augmented creatine-phosphoric acid hydrolysis.

J. H. BIRKINSHAW.

Influence of adrenaline in gluconeogenesis. E. WERTHEIMER (Arch. exp. Path. Pharm., 1929, 139, 378–380).—Polemical against Geiger and Schmidt (cf. A., 1928, 1160).

W. O. KERMACK.

Influence of amino-acids and their derivatives on adrenaline hyperglycæmia. M. CHIKANO (Biochem. Z., 1929, 205, 154–165).—Tyrosine has no effect on the blood-sugar level, but increases 3–4 hrs. after subcutaneous injection into rabbits the hyperglycæmia caused by adrenaline. Tryptophan causes a slight hyperglycæmia and increases adrenaline hyperglycæmia. Dihydroxyphenylalanine causes considerable hyperglycæmia. Leucine and histidine inhibit hyperglycæmia by adrenaline. Phenylalanine, glutamic acid, and glycine have no action on the blood-sugar level. *p*-Hydroxyphenylpyruvic acid increases adrenaline hyperglycæmia, but *p*-hydroxyphenyl-lactic acid does not. Pyrocatechol causes considerable hyperglycæmia but protocatechuic and anthranilic acids have no effect.

P. W. CLUTTERBUCK.

Antagonism between adrenaline and ergotamine. U. VON EULER (Arch. exp. Path. Pharm., 1929, 139, 373–377).—In exceedingly small concentrations (1 in 10^{12}) ergotamine tartrate and ergotoxin phosphate increase cell oxidation as measured by the methylene-blue technique. The rise in cell oxidation caused by adrenaline (1 in 10^{12}) is prevented by ergotamine in similar concentration.

W. O. KERMACK.

Micro-determination of adrenaline, and its application in the investigation of intermediate metabolism. M. CHIKANO (Biochem. Z., 1929, 205, 166–175).—Adrenaline can readily be determined in aqueous solutions by adding iodic acid and determining the excess of the acid by titration with thiosulphate in acid solution after addition of potassium iodide. With normal rabbit's serum, blank determinations gave a value for the substances present which react with iodic acid, and when known

amounts of adrenaline were then added to serum the difference in value corresponded very closely with the amount added. With fresh defibrinated rabbits' blood, however, and with suspensions of washed corpuscles, the blank value was about five times as large as for serum and the percentage of adrenaline found by analysis was only 56–32% of that added, the value decreasing with decreasing amount of adrenaline added. The substances reacting with iodic acid are therefore present chiefly in the corpuscles and include the so-called adrenaline-like substances, urea and uric acid, and some end and intermediate products of protein metabolism.

P. W. CLUTTERBUCK.

Hormone of heart motion. X. Experiments with warm-blooded animals. L. HABERLANDT (Pflüger's Archiv, 1928, 220, 203–211; Chem. Zentr., 1928, ii, 1345).

Influence on the heart of a substance present in heart muscle and other tissues. A. N. DRURY and A. SZENT-GYÖRGYI (J. Physiol., 1929, 67, Proc. Physiol. Soc., xiv–xv).—A crystalline substance, m. p. 190–200° (decomp.), which when injected intravenously in the frog, dog, rabbit, or cat produces a transient sinus bradycardia and in the guinea-pig a transient high-grade heart block, has been isolated from heart muscle. It is probably a derivative of nucleic acid. Elementary analyses and calculation of the residue as metaphosphoric acid gives the formula $C_{16}H_{21}O_{12}N_8.HPO_3$.

B. A. EAGLES.

Effect of insulin on distribution of non-protein-nitrogen of blood. S. E. KERR and V. H. KRIKORIAN (J. Biol. Chem., 1929, 81, 421–424).—Administration of insulin to dogs causes a preliminary fall in the carbamide and increase in the amino-acids of the blood, these changes being reversed as the hypoglycæmia increases (cf. Luck and others, A., 1928, 676, 1058).

C. R. HARRINGTON.

Glycogenic function of skeletal muscle in dehepatatised dog and rôle of insulin. J. MARKOWITZ, F. C. MANN, and J. L. BOLLMAN (Amer. J. Physiol., 1929, 87, 566–583).—In a dehepatatised dog, administration of dextrose (1 g. per kg. body-weight per hr.) for several hours leads to a definite rise in muscle-glycogen. This rise in the glycogen content of muscle cannot be demonstrated in dehepatatised and depancreatized dogs. Administration of large doses of insulin to such dogs may produce a rise in muscle-glycogen. Unless relatively enormous doses of insulin are injected into dehepatatised dogs which have received several administrations of dextrose, no hypoglycæmic effect can be demonstrated. It is suggested that the liver possibly plays a major part in the action of insulin in the intact animal.

B. A. EAGLES.

Behaviour of insulin on irradiation with X-, radium, and ultra-violet rays. D. DEN HOED, S. E. DE JONGH, and A. E. J. PEEK (Biochem. Z., 1929, 205, 144–153).—In the absence of air insulin is stable to X-, radium, and ultra-violet irradiation, but in presence of air, whereas X-rays have no effect, radium, and still more so ultra-violet, irradiation destroys it gradually.

P. W. CLUTTERBUCK.

Oestrus-producing hormone in bile. M. A. GSELL-BUSSE (Arch. exp. Path. Pharm., 1929, 139, 328–340).—Certain commercial samples of purified bile salts contain the oestrus-producing hormone, but this is probably present as an adsorbed impurity. Ether extracts of the bile of various animals including man contain the hormone, the activity being particularly great in the extracts of human bile, especially that of females. Extracts of the bile of patients suffering from various diseases have reduced activity or none at all. No hormone could be extracted from 0.5 kg. of fresh liver. Meconium is particularly rich in the hormone.

W. O. KERMACK.

Effect of parathyroid hormone on the structure of bone. C. G. LAMBIE, W. O. KERMACK, and W. F. HARVEY (Nature, 1929, 123, 348).—Administration of parathyroid hormone to rats appears to cause a change in the form in which calcium exists in the bones.

A. A. ELDRIDGE.

Action of secretin on gaseous metabolism. H. TANGI and F. THAN (Arch. exp. Path. Pharm., 1929, 139, 226–230).—Subcutaneous injection of secretin into fasting rats decreases the rate of consumption of oxygen and thus raises the respiratory quotient.

W. O. KERMACK.

Effect of minimal doses of thyroxine on gaseous metabolism in invertebrates. B. ROMERIS and J. WUST (Naturwiss., 1929, 17, 104–105).—In contrast with its action on vertebrates, thyroxine appears to be without influence on the morphology of invertebrates. The respiration of butterfly pupæ (*Papilio podalirius*) has now been studied, definite concentrations of thyroxine in solutions isotonic with the lymph being injected. Relatively concentrated solutions caused a 30–50% increase in oxygen consumption. With much more dilute solutions the gas consumption remained at first unchanged, but after the fourth or fifth day following the injection a sudden increase occurred to as much as 30–40 times the normal value. The high rate was maintained for 1–2 days and then rapidly fell to even below the normal value in 1–2 days. Further dilution merely delayed the appearance of the sudden increase without affecting the order or magnitude of the change. The effect was obtained with 2×10^{-11} g. of thyroxine on pupæ weighing 0.8 g. In spite of the great change in gaseous metabolism no shortening of the period of metamorphosis was noticed. Apparently, therefore, the primary action of thyroxine is on the respiration process, whilst the normal morphological effect is connected with secondary factors absent in this case.

R. A. MORTON.

Effect of thyroxine on the metabolism of surviving tissue. K. J. ANSELMINO, O. EICHLER, and H. SCHLOSSMANN (Biochem. Z., 1929, 205, 481–488).—The respiration of sections of the surviving liver, spleen, and kidney of rats is unaffected by previous subcutaneous injection of thyroxine into the animals. The anaerobic glycolysis of these organs is increased only in the case of the kidney. The thyroid hormone affects principally the anaerobic phase of metabolism.

J. H. BIRKINSHAW.

Incretion and avitaminosis. X. Action of thyroxine and pituitary extract on basal metabo-

ism and specific dynamic action after thyroid extirpation and in avitaminosis. A. VON ARVAY (Biochem. Z., 1929, 205, 433—440).—There is strong similarity in the decrease in basal metabolism, specific dynamic action, and action of thyroxine in thyroidectomised rats and in rats deprived of vitamin-A and -B. Thyroxine restores the basal metabolism and specific dynamic action to normal in both cases, pituitary extract is without effect. Extirpation of the hypertrophied adrenals in avitaminosis leads to death of the animal. J. H. BIRKINSHAW.

Action of vitamins and surface activity. I. Vitamin-free substances which have surface activity in avitaminosis in guinea-pigs. N. E. SCHEPILJEVSKAJA (Biochem. Z., 1929, 204, 371—388).—Phenolphthalein, alcohol, magnesium sulphate, and (except in solutions of the order of 0.015%) sodium oleate have no prophylactic or therapeutic effect in experimental scurvy in guinea-pigs. Consequently the views of Hahn (cf. A., 1925, ii, 664) concerning the vitamin-like action of substances having high surface activity are not confirmed as far as substances not used as food are concerned. W. MCCARTNEY.

Experimental hypervitaminosis in rats caused by large doses of irradiated ergosterol. J. A. COLLAZO, P. RUBINO, and B. VARELA (Biochem. Z., 1929, 204, 347—353).—A daily dose of 5 mg. of the vitamin-D preparation "vigantol" per animal produces hypervitaminosis and eventually death in rats, and hence excess as well as lack of vitamin may have pathological results. W. MCCARTNEY.

Oxidative capacity and peroxidic-oxygen content of cod-liver oil: influence of ultra-violet light. P. DELORE (Bull. Soc. Chim. biol., 1929, 11, 74—91).—Olive, linseed, and especially cod-liver oil gain weight owing to absorption of oxygen on exposure to air in the absence of light. Possibly some volatile substances are lost in the process. Preliminary irradiation of the oils by ultra-violet light enhances the rate of autoxidation up to a limit beyond which it is decreased. In these experiments and in comparison with other oils, cod-liver oil behaves as if it had been already irradiated. The autoxidation is accompanied by a decrease in the iodine value and increases in the viscosity and refractive index. The peroxidic-oxygen content of the oils, determined by the liberation of iodine from potassium iodide acidified with acetic acid, shows a relation to the time of irradiation similar to that of the increase in weight. G. A. C. GOUGH.

Experimental blacktongue and the blacktongue preventive in yeast. J. GOLDBERGER, G. A. WHEELER, R. D. LILLIE, and L. M. ROGERS (U.S. Public Health Service, 1928, Reprint No. 1216, 1—38).—Experiments indicate that blacktongue in dogs is due to a dietary deficiency capable of correction by a preventive present in yeast. This preventive, which can be distinguished from the antineuritic factor, shows considerable heat-resistance, and is probably identical with the anti-pellagra vitamin. E. A. LUNT.

Velocity of absorption of ions by plants. M. VON WRANGELL (Z. physikal. Chem., 1928, 139, 351—364).—The velocity of absorption of the phosphate

and ammonium ions by plants, especially maize, has been measured colorimetrically in nutrient solutions of various concentrations and composition. From very dilute solutions (0.1 mg./litre), the absorption of the phosphate ion is slow, but that of ammonia is much quicker and is complete in 0.5—2 hrs. The optimum concentrations for absorption lie between 0.001 and 0.01 g./litre. During short time-intervals, the absorption is independent of the usual growth factors such as light, and the nutrient ions potassium, nitrate, etc., but the absorption of phosphate is increased by the presence of calcium. Temperature has a significant influence on salt absorption, which appears to be primarily a physico-chemical and not a physiological process. The velocity is not governed apparently by the diffusion of the ions or by Henry's or the Fechner-Weber law and is best interpreted as an adsorption process. L. S. THEOBALD.

The p_H of the cell sap of flowers. B. H. BUXTON and F. V. DARBISHIRE (J. Roy. Hort. Soc., 1929, 54, 203—213).—Colorimetric determinations have been made of the variation with time of the p_H of aqueous solutions of dried petals from various flowers. E. A. LUNT.

Origin of chlorophyll and its relation to blood pigments. K. NOACK (Naturwiss., 1929, 17, 104).—The magnesium of protochlorophyll can be removed by means of acid and re-introduced through the Grignard reaction. The magnesium-free compound is a red dye practically identical with phylloerythrin (bipurpurin) as regards absorption spectrum. Phylloerythrin, obtained from the bile of herbivorous animals, has been converted into a green pigment as a result of the introduction of magnesium and the material possesses almost the same absorption maxima as protochlorophyll. One or more carboxyl groups can be set free in phylloerythrin, lactone or lactam groups being probably present initially. By reduction in acid solution phaeophytins (the magnesium-free derivatives of chlorophyll *a* and *b*) are readily converted into magnesium-free protochlorophyll derivatives, without hydrolysis of the ester groups in the phaeophytin. Hydrolysis of the reduction products yields substances which can be identified spectroscopically with phylloerythrin derivatives. The acids undergo photo-oxidation to form green substances. Thus a simple reduction forms a bridge between blood and leaf pigments. Further, it would appear that in the animal, phylloerythrin is a reduction product of chlorophyll, and that in the plant the last step in the synthesis of chlorophyll is a photo-oxidation. An explanation is also provided for the role of iron in the formation of chlorophyll, since minimal quantities of the metal are known to catalyse the photo-oxidation of fluorescent colouring matters. R. A. MORTON.

Determination of small quantities of starch in vegetable tissue. E. J. B. BISH (Biochem. J., 1929, 23, 31—34).—The dried powdered tissue is extracted with absolute alcohol to remove sugars, chlorophyll, and some proteins. It is then hydrolysed with takadiastase and the remaining proteins, tannins, and mucilages are removed by either lead acetate or mercury salts. The copper-reducing power of the hydrolysed starch is compared with the

reducing power of known quantities of a carefully purified starch preparation. S. S. ZILVA.

Physiology of the organic acids in green plants. III. *Rheum hybridum hort.* W. RUHLAND and K. WETZEL (Planta, Arch. wiss. Bot., 1927, E, 3, 765—769; Chem. Zentr., 1928, ii, 1222—1223).—Of the nitrogen in resting rhizomes, two thirds is soluble. Considerable synthesis of protein takes place in the stalks of young leaves, amino-acids being supplied from the rhizome. Old stems contain much ammonia-nitrogen. In deficiency of carbohydrate or of light there is increase of ammonia formation. The rhizome contains about 0.90% of oxalic acid and 0.73% of succinic and malic acids, the latter diminishing with development of the aerial organs. Young stems contain little oxalic acid. In growing stems vigorous deamination produces ammonia, which is removed by acid formation; succinic and malic acids appear first, and diminish in quantity as oxalic acid is produced.

A. A. ELDRIDGE.

l-Asparagine in the fresh flowers of *Ulex europæus*. M. BRIDEL (Bull. Soc. Chim. biol., 1928, 10, 1378—1379).—*l*-Asparagine (7.7 g. from 25 kg. of fresh flowers) is obtained from the mother-liquor from the preparation of ulexoside (A., 1926, 1183).

G. A. C. GOUGH.

Alkaloids of *Corydalis ambigua* (Yen-Hu-So). II. *Corydalis*. F. G. CHOU and T. Q. CHOU (Chinese J. Physiol., 1929, 3, 69—74).—In addition to the five alkaloids (*corydalis A*, or *corydaline*, *corydalis B*, *C*, *D*, and *E*) previously isolated from the tubers of *C. ambigua* (A., 1928, 927) there have now been isolated three more alkaloids, *corydalis F*, $C_{26}H_{23}O_4N$, m. p. 237° [α]_D²⁵ —250° in chloroform (*hydrobromide*, m. p. 222°; *hydrochloride*, m. p. 234°), *corydalis G*, m. p. 237°, [α]_D²⁵ +300° in chloroform, possibly identical with *corypalmine* isolated by Spath, Mosettig, and Trothandl (cf. A., 1923, i, 593) from *C. tuberosa*, and *corydalis H*, obtained as *bromide*, m. p. 235°, optically inactive. *Corydalis F* and *G* are phenolic. *Corydalis H* when treated with barium hydroxide and extracted with chloroform yields a *base*, m. p. 153° (*hydrobromide*, m. p. 228°). Two *sulphates* of *corydalis B* are described, one acid, m. p. 238°, and one neutral, m. p. 220°.

W. O. KERMAK.

Alkaloids of *Bocconia frutescens*, L. E. R. MILLER (J. Amer. Pharm. Assoc., 1929, 18, 12—14).—The leaves of *B. frutescens*, L., contain at least four alkaloids, γ -homochelidonine, m. p. 168—169°, protopine, m. p. 206—207°, a third, probably β -homochelidonine, m. p. 159—160°, and probably *chelyerythrine*. The bark of the large plants is rich in alkaloids and on account of the large leaves and their high alkaloidal content the plant is probably the best known source of protopine. E. H. SHARPLES.

Jute seeds (*Corchorus capsularis*). II. Composition of corchorus oil. N. K. SEN (J. Indian Chem. Soc., 1928, 5, 759—767).—Extraction of jute seeds with light petroleum gives 14.73% of an oil which after purification with alkali has the following constants: d_{20}^{25} 0.923, n_D^{20} 1.4615, solidifying pt. —20°, iodine value 102.6, saponification value 184.6, acid value 1.5, acetyl value 27.3, Reichert-Meissl value

0.16. The oil contains a small amount of unsaponifiable matter, probably a mixture of sterols, small quantities of palmitic, stearic, and "crude arachidic" acids, triolein (39.18%), and trilinolein (44.63%). The refined oil is suitable as a food and burns satisfactorily.

H. BURTON.

Rind of California oranges. M. B. MATLACK (J. Amer. Pharm. Assoc., 1929, 18, 24—31).—The following substances have been identified in the fat from the rind of sweet oranges: oleic, linoleic, linolenic, stearic, and palmitic acids, sitosterol, a sterol, m. p. 150° (acetyl derivative, m. p. 113.5—114°), probably identical with paraphytosterol, a phytosterolin, m. p. 280° (benzoyl derivative, m. p. 198°; acetyl derivative, m. p. 164—164.5°), which is probably sitosterol-*d*-glucoside, ceryl alcohol, and small amounts of resin and carotinoid colouring matter. E. H. SHARPLES.

Mineral constituents of cranberries. F. W. MORSE (J. Biol. Chem., 1929, 81, 77—79; cf. A., 1928, 1407).—Figures are given for the constituents of the ash of cranberries grown on Cape Cod.

C. R. HARRINGTON.

Action of thorium-X on the content of active principles in certain medicinal plants. AVERSENQ, JALOUSTRÉ, and MAURIN (Compt. rend., 1929, 188, 345—347).—The alkaloid contents of the root and the stems of the pomegranate and the leaves and the seeds of *Datura stramonium* increase when the plant is treated with aqueous suspensions of thorium-X. Similar increases in the fat contents of the seeds of the castor-oil plant and the total anthraquinone derivatives of the stem of French rhubarb are observed. The treatment leads to a decrease in the allylthiocarbimide content of seeds of black mustard.

G. A. C. GOUGH.

Conversion of starch granules into calcium oxalate crystals in plant cells by ultra-violet light. G. NADSON and E. ROCHLINE (Compt. rend. Soc. Biol., 1928, 99, 131—133; Chem. Zentr., 1928, ii, 1108).—Ultra-violet light stimulates oxidation processes in the cell; thus oxalic acid is produced from starch, sugar being an intermediate stage.

A. A. ELDRIDGE.

Characterisation of the anthocyanins and anthocyanidins by means of their colour reactions in alkaline solutions. A. ROBERTSON and R. ROBINSON (Biochem. J., 1929, 23, 35—40).—The examination of the colour reactions of apigeninidin chloride, pelargonidin chloride, cyanidin chloride, 5-*o*-benzoylcyanidin chloride, peonidin chloride, malvidin chloride, cyanin chloride, and malvin chloride in a range of buffer solutions has shown that this method is by far the most trustworthy for purposes of comparison and characterisation. Various properties such as ψ -base formation and colour base precipitation, ease of oxidation are incidentally revealed in this examination. Fear and Nierenstein's observation (A., 1928, 646) that cyanidin chloride from cyanin behaves differently from synthetic 3:5:7:3':4'-pentahydroxyflavylium chloride is not confirmed.

S. S. ZILVA.

Action of certain substances on the zoospores of *Pseudoperonospora humuli* (Miy et Takah), Wils. W. GOODWIN, E. S. SALMON, and W. M. WARE

(J. Agric. Sci., 1929, 19, 185—200).—Zoospores of *Pseudoperonospora humuli* and *Phytophthora infestans* are extremely susceptible to the action of dilute solutions of soap or saponin. In solutions containing 0.1% of soft soap disintegration occurs within 60 sec. Glycerol, iodine, bromine, and aluminum-lime mixtures also killed the spores rapidly. A. G. POLLARD.

Sodium nitrate and development of chlorosis in rice. W. H. METZGER and G. JANSSEN (J. Agric. Res., 1928, 37, 589—602).—Rice plants become chlorotic when they suffer from a lack of available nitrogen, particularly ammonia, in the early stages of growth. B. A. EAGLES.

Biochemistry of dry-rot in wood. G. C. BARTON-WRIGHT and J. G. BOSWELL (Biochem. J., 1929, 23, 110—114).—A comparison of analytical data of sound spruce and spruce decayed by the action of the fungus *Merulius lacrymans*. There is a removal in the latter of galactan, mannan, and cellulose fractions. The hemicelluloses and lignin are not affected by the fungus. S. S. ZILVA.

Behaviour of lignins in the natural disintegration of plants. F. FISCHER and R. LIESKE (Biochem. Z., 1928, 203, 351—362).—In the natural disintegration of plants (decayed pinewood, ferns, etc.) the hydrolysable constituents are first decomposed and the lignin substances concentrated. The microscopic structure of the wood is not destroyed during the decomposition of the cellulose. During natural disintegration the p_n does not diminish as far as in experiments with pure cultures of moulds, the acid formed initially being removed naturally either by washing or by the action of micro-organisms. Bacteria sensitive to acid can therefore take part in the disintegration. P. W. CLUTTERBUCK.

Double staining of mitochondria and bacteria in plant tissues. J. DUFRENOY (Stain Tech., 1929, 4, 13—15).—A favourable report on the use of Milovidov's technique (Compt. rend. Soc. Biol., 1928, 98, 555). H. W. DUDLEY.

Jena filter plates of porous glass in biological analysis. E. CATTELAÏN (J. Pharm. Chim., 1928, [viii], 8, 549—550, and Bull. Soc. Chim. biol., 1928, 10, 1385—1386).—Jena porous glass filter crucibles can replace Gooch crucibles in biological analysis. E. H. SHARPLES.

General apparatus for micro-analysis. I. Ashing in a sealed system. E. TSCHOPP (Biochem. Z., 1928, 203, 267—277).—An apparatus is described in which organic substances may be ashed in a closed space and without using large amounts of sulphuric acid and the inorganic content determined. P. W. CLUTTERBUCK.

Modification of the Northrop-Kunitz micro-cathaphoresis cell. H. A. ABRAMSON (J. Gen. Physiol., 1929, 12, 469—472).—The original cell (*ibid.*, 1925, 7, 729) is made more compact; agar reversible electrodes and the lowest possible EMF are used. E. BOYLAND.

Application of the method of Hagedorn and Jensen to the determination of larger quantities of reducing sugars. C. S. HANES (Biochem. J.,

1929, 23, 99—106).—The method has been extended to permit the determination of about ten times the amount of reducing sugar. Standardisation data are given for dextrose and maltose. The amounts of dissolved oxygen in sugar solutions do not affect the reducing values found by this method. S. S. ZILVA.

Microscopical differentiation of neutral and hydrolysed fat. W. HEUPKE (Arch. Verdauungs-krankh., 1927, 40, 357—364; Chem. Zentr., 1928, ii, 1018).—The material, e.g., faeces, is treated while hot with cupric nitrate and mixed on the slide with alcoholic dimethylaminoazobenzene; green copper soaps are formed, the neutral fat being coloured yellow. A. A. ELDRIDGE.

Salicylates. XVII. Phosphoric acid distillation method of determining salicylic and salicyluric acids. C. C. JOHNSON (J. Pharm. Exp. Ther., 1928, 34, 437—444).—The Thoburn-Hanzlik method of phosphoric acid distillation (A., 1916, ii, 58) gave 88% of salicylic acid from salicyluric acid, whilst the Holmes method (A., 1926, 90) gave a much lower recovery. The results of determinations in urine after administration of salicylic acid indicate that some salicylic acid is decomposed in the body. E. BOYLAND.

Determination of tryptophan by means of p -dimethylaminobenzaldehyde. W. J. BOYD (Biochem. J., 1929, 23, 78—82).—Errors can arise in the determination of tryptophan in proteins by May and Rose's method (A., 1923, i, 160) through unequal illumination of the reacting mixture and through the presence of reducing substances such as hydrogen sulphide or aldehydes. In carrying out the test 3 drops of 0.5% sodium nitrite solution should be added to the reaction mixture after 24 hrs.' incubation at 36° and 3 days at the ordinary temperature and again after a further 3 days, the colorimetric comparison being made next day or later. By this modification higher values are obtained for cod-muscle protein and edestin. S. S. ZILVA.

Occurrence of iodine and fluorine in the organism. I. A. MAYRHOFER and A. WASITZKY (Biochem. Z., 1929, 204, 62—77).—A review is given of the principal methods for the determination of iodine and fluorine in organic matter. The method recommended consists in ashing the substance with sodium hydroxide. The residue is then ground up with 90% alcohol which dissolves the sodium iodide. The iodine in the alcohol may be determined volumetrically after oxidation to iodate and liberation of iodine by addition of potassium iodide and acidification. The iodine-free residue is dissolved in acetic acid and the fluorine precipitated with lanthanum acetate. Hydrogen fluoride set free by sulphuric acid is allowed to etch glass and determined by the loss of weight of the glass thus treated. J. H. BIRKINSHAW.

Determination of organic arsinic acids. E. URBSCHAT (Biochem. Z., 1928, 203, 223—225).—A method is described for the nephelometric determination of 2-hydroxypyridine-5-arsinic acid and used for its determination in the urine of animals to which it had been administered. P. W. CLUTTERBUCK.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MAY, 1929.

General, Physical, and Inorganic Chemistry.

Monochromatic light filters. II Use of Goldberg's spectrodensograph. E. ELYEGARD, W. STAUBE, and F. WEIGERT (*Z. physikal. Chem.*, 1929, **B**, 2, 149—160; cf. Weigert and Staube, *A.*, 1928, 40).—The principle of autocollimation is applied to the method of producing a strong beam of monochromatic light described previously. The purity of the light was tested by means of Goldberg's "spectrodensograph," the spectral intensity curve of the light source being determined. The method of using the instrument for this purpose is described.

A. J. MEE.

Para- and ortho-hydrogen. K. F. BONHOEFFER and P. HARTECK (*Naturwiss.*, 1929, **17**, 182).—According to Heisenberg's theory, two modifications of molecular hydrogen should occur. Dennison concludes that ordinary hydrogen contains para- and ortho-hydrogen in the ratio 1 : 3. Heat conductivity measurements at low pressures show that the transformation is incomplete at the end of a year, but at high pressures (350 atm.) in metal vessels at the temperature of liquid air practically the theoretical quantity of parahydrogen can be obtained in a week. At the ordinary temperature parahydrogen is a gas which is fairly stable for a week in glass vessels. At 100 atm. it slowly reverts to ordinary hydrogen in metal vessels, but in the presence of platinised asbestos the change occurs at once. Adsorption on charcoal at the temperature of liquid air gives practically pure parahydrogen. After one day, liquid hydrogen contains about 10% of the equilibrium quantity of parahydrogen. Freshly-solidified hydrogen contains parahydrogen in the proportion 1 : 3. R. A. MORTON.

Perturbations in the band spectrum of helium. G. H. DIEKE (*Nature*, 1929, **123**, 446—447).—Kronig's theory of perturbations in band spectra (*A.*, 1928, 1067) is illustrated by the band spectrum of helium.

A. A. ELDRIDGE.

Stark effect of helium $2P-6D$ line by quantum mechanics. Y. FUJIOKA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1929, **10**, 99—106).—The theoretical displacements and intensities due to the Stark effect on the $2P-6D$ line have been calculated. The effect has been examined experimentally and found to be in fair agreement with the predictions.

W. E. DOWNEY.

Simple relations between the most intense radiations and the highest chemical elements in the luminous atmosphere of the sun. H. DESLANDRES (*Compt. rend.*, 1929, **188**, 669—673).—Further examples are provided of the rule proposed

by the author (this vol., 223), 21 elements, of which 10 have atomic numbers higher than 20, now being included. Apparent exceptions may be explained, *e.g.*, by the effect on the observed line spectra of hydrogen or helium in the chromosphere. Differences between the intensities of the lines of the same elements in the chromosphere and those obtained in the laboratory are also discussed. J. GRANT.

Absorption measurements in the caesium principal series. Widening due to vapour pressure. F. WAIBEL (*Z. Physik*, 1929, **53**, 459—482).—The intensities of the 5th to 14th members of the principal series of caesium and the widening due to vapour pressures of 10—32 mm. were determined. There is an appreciable asymmetry in the absorption edges for the lower members of the series. This disappears gradually with the higher members. The widening of the lines is approximately proportional to the square root of the vapour density. The half-value widening increases with the higher members of the series, ultimately becoming constant. The half-value widening of the stronger components is considerably larger than that of the weaker. The ratio of intensities of the components was determined for the 5th and 6th doublets. The total absorption and the number of resonators per atom were determined for the 5th to 14th members of the series, inclusive. The apparatus is described and a table of vapour pressures of caesium from 6.65 mm. at 355.5° to 760 mm. at 670° is given. A. J. MEE.

Series in the As VI spectrum. P. PATTABHIRAMIAH and A. S. RAO (*Z. Physik*, 1929, **53**, 587—591).—The As VI spectrum has been investigated in the usual way. It is found that the singlet and triplet *P*, *D*, and *S* terms of the d^3p order are strongly combined with the a^3D and a^1D terms of the d^3s order, in agreement with Hund's theory. A. J. MEE.

Effect of resistance on spark spectra. O. OCCHIALINI (*Atti R. Accad. Lincei*, [vi], 8, 579—584).—A continuation of the author's work to perfect a method of quantitative spectroscopic analysis (this vol., 374). Using apparatus described previously, the effect of variable resistance, in the discharge circuit, on the spark spectrum of lead is demonstrated.

G. E. WENTWORTH.

Arc spectrum of samarium. Measurements at normal pressure between 3100 and 2750 X. S. PINA DE RUBIES (*Compt. rend.*, 1929, **188**, 780—781).—The lines and their intensities are tabulated together with those ascribed to impurities.

J. GRANT.

Measurement of the relative intensities of two emission lines (1S—3P and 2S—3P) from sodium atoms, arising from the same initial state, as regards the ratio of the corresponding transition probabilities. C. WEISS (Ann. Physik, 1929, [v], 1, 565—612).—The intensity of an emission line arising from the spontaneous transition of an atom from a state k to a state i is given by $J_{\nu_{ki}} = N_k a_{ki} h \nu_{ki}$, N_k being the number of atoms in the state k , h Planck's constant, and ν_{ki} the frequency of the line, whilst a_{ki} is the transition probability. Bohr has shown that the transition from 3P to 2S (for sodium atom) should occur much more frequently than that from 3P to 1S. Detailed experiments on the intensities of the lines 3302.6 and 22070 Å. have shown that the ratio $a_{2S-3P}/a_{1S-3P} = 25$ with a maximum error of 50% and a mean error of $\pm 15\%$. An exact determination of a_{2S-3P} was not possible, but it is certainly smaller than a_{2S-1P} . R. A. MORTON.

Singlets and triplets in the spectra of two-electron systems. W. V. HOUSTON (Physical Rev., 1929, [ii], 33, 297—304).—Theoretical. The Darwin-Pauli treatment of the electron is applied to the Schrödinger equation for a two-electron system, with the restriction that one electron must be in an s -orbit. The results show that the division into singlets and triplets is justified only as a limiting case. Expressions are derived which give the position of the levels, the Zeeman effect, and the intensities of the lines when the division into singlet and triplet cannot strictly be made, and also give the observed facts of several spectra. N. M. BLIGH.

Stark effect for the diffuse lines of silver and lithium. R. H. SNYDER (Physical Rev., 1929, [ii], 33, 354—360).—The Stark effects on the 5^2P_1 — 6^2D and 5^2P_1 — 6^2D groups of silver lines were studied experimentally by the Lo Surdo method. In the former group the violet s -component was split into two branches, the stronger outer one being designated the $2D_3$ branch and the weak inner one the F branch. The red s -component had only one, the $2D_2$ branch. Both the violet and red p -components showed only one branch, the $2D_3$ violet and $2D_2$ red branch. In the second group the violet s -component was also split into a strong inner F branch and a weak outer G branch. The single red s -component was designated the $2D_2$ branch. Both the violet and red had only a single branch, the violet F and the red $2D_2$ branch (cf. Fujioka and Nakamura, A., 1928, 2). The lithium line 4602.51 Å. was resolved into three s - and three p -components in an electric field, with the violet side having a stronger outer and a weaker inner component for the p -vibration, and a weaker outer and a stronger inner component for the s -vibration. The line 4132.93 Å. was resolved into three s - and three p -components. N. M. BLIGH.

Tables of theoretical Zeeman effects. C. C. KEISS and W. F. MEGGERS (Bur. Stand. J. Res., 1928, 1, 641—684).—The splitting of spectrum lines into components, when the source is in a magnetic field, furnishes theoretically an absolute identification of the terms involved in the production of the lines. The Zeeman effects of various term combinations have been computed on the basis of Lande's work,

and are presented in tables giving results for terms from S to I in the doublet, quadruplet, sextet, and octet systems, in the triplet, quintuplet, and septet systems, and in the doublet-quadruplet, quadruplet-sextet, sextet-octet, singlet-triplet, triplet-quintuplet, and quintuplet-septet intersystems.

C. J. SMITHELLS.

Excitation of sodium by ionised mercury vapour. H. W. WEBB and S. C. WANG (Physical Rev., 1929, [ii], 33, 329—340).—The method used allowed a comparison of the spectrum produced by excited mercury atoms with that due to the ions. The former showed marked resonance and the latter also showed excitation corresponding with the excitation energy of the metastable mercury atom. Theoretical explanations are proposed. Data from photomicrometric measurements on typical spectrograms and from the behaviour of mercury and sodium lines with varying amounts of sodium vapour present are fully tabulated. The spectrum excited by ionised mercury resembled the chemiluminescence spectrum resulting from mixing sodium and mercuric chloride vapours. The spark line of mercury 3984 Å., not previously found in the luminous mercury stream, was found when sodium was present. N. M. BLIGH.

Persistence of $\lambda 2537$ in mercury at low pressures. H. W. WEBB and (MISS) H. A. MESSENGER (Physical Rev., 1929, [ii], 33, 319—328).—The persistence of this line excited by electron impact was measured for vapour pressures corresponding with the temperature range 78° to -19° (cf. Zemansky, A., 1927, 491), using an alternating-potential method (cf. A., 1927, 85). Between 78° and 17° the persistence varied inversely as the first power of the pressure, and was much too small to be explained as depending on the life of the metastable atoms; it approached a limiting value of the order of 10^{-7} sec. as the pressure was lowered. The life of 1849 Å. was found to be less than 3×10^{-9} sec. A radiation process probably associated with the 7.1 break in the critical potential curves had a life of $1/470,000$ sec., which is suggested as the life of an infra-red transition to the 6.7 volt level, followed by the radiation of 1849 Å. A process associated with an excitation potential between 5 and 6 volts had a life of about $1/120,000$ sec. N. M. BLIGH.

Transition of excited 2^3P_1 mercury atoms to the metastable state 2^3P_0 . H. KLUMB and P. PRINGSHEIM (Z. Physik, 1929, 52, 610—626).—Data are given for the absorption of the line 4047 Å. in mercury vapour as a function of the partial pressure of added gas and the effects produced by helium-neon mixture, argon, nitrogen, carbon monoxide and dioxide, and water vapour have been examined. The results are discussed in relation to the authors' theory and to that of Foote (A., 1927, 999). All the above gases facilitate the transition $2^3P_1 \rightarrow 2^3P_0$; nitrogen, however, has an abnormally great influence.

R. W. LUNT.

Excitation of mercury vapour by the resonance line. (LORD) RAYLEIGH (Nature, 1929, 123, 488, 569).—Experiments show that with a blast of mercury vapour the source of re-emitted radiation of wave-length 2537 Å. can be observed separated in

space from the source of the continuous bands which are of molecular origin. It appears that the interval between excitation and emission may be considerably greater than 10^{-7} sec. As the temperature of the mercury vapour is progressively raised, and a rapid stream of vapour is generated, the secondary source, originally symmetrical on either side of the primary beam, elongates on, and is finally wholly on, the down-stream side. A. A. ELDRIDGE.

Energies of dissociation of cadmium and zinc molecules from an interpretation of their band spectra. J. G. WINANS (Phil. Mag., 1929, [vii], 7, 555—565).—New observations have been made on the absorption spectrum in cadmium vapour. At low pressure the cadmium resonance line at 2288 Å. appears as a narrow absorption line which broadens symmetrically to the limits 2207—2800 Å. with increasing pressure. At pressures above 130 mm. a set of broad and diffuse flutings over the range 2650—2780 Å. develop on this band. The bands at 2212 and 2114 Å. appear at a pressure of 7 mm., the former broadening slightly towards longer wavelengths and the latter increasing symmetrically with increasing pressure. The electrodeless discharge in cadmium vapour exhibits a continuous spectrum with maxima at 2288, 2980, 3000, and 4400 Å. The band at 2212 Å. does not appear. The absorption band 2207—2800 Å. is attributed to the absorption of light by the collision of two atoms to produce a stable excited molecule. The energy of dissociation of the cadmium molecule calculated from the main absorption band is 0.200 volt. Similar measurements on the absorption spectrum of zinc vapour lead to the value of 0.246 volt for the energy of dissociation of the zinc molecule. The dissociation energies of cadmium, zinc, and mercury molecules are shown to be proportional to their atomic heats of fusion. The flutings observed in the main absorption band of cadmium are attributed to the absorption of light by colliding atoms to form an excited molecule and the subsequent emission of this light when the excited molecule returns to the normal state. The fluctuations of intensity arising from this are shown by the flutings in the spectrum. A. E. MITCHELL.

Flutings in the absorption spectrum of a mixture of mercury and cadmium vapours. J. G. WINANS (Phil. Mag., 1929, [vii], 7, 565—566; cf. preceding abstract).—The absorption spectrum of a mixture of cadmium and mercury vapour behaves similarly to that of pure cadmium vapour under changes in pressure. A new set of flutings extending from 2488.6 to 2406.8 Å. appears. These are not present in the spectrum of pure cadmium or pure mercury vapour and are attributed to HgCd molecules. A. E. MITCHELL.

Resonance as a result of collisions and its bearing on fluorescence and chemiluminescence. H. BEUTLER and B. JOSEPHY (Z. Physik, 1929, 53, 747—765; cf. A., 1928, 459).—Irradiation of a sodium-mercury vapour mixture by the mercury line 2537 Å. causes resonance of the sodium atoms by collisions with mercury atoms excited to the transition $2^3P_1-1^1S_0$. The resonance of the sodium atoms results in the transition 1^2S-7^2S . Admixture of

nitrogen causes a rearrangement of 2^3P_1 state of the mercury atoms to the 2^3P_0 state, with a consequent change in the resonance transition of the sodium atoms to 1^2S-5^2S , in agreement with the $2^3P_0-1^1S_0$ transition of the mercury atoms. Similar resonance effects are observed in the chemiluminescence of dilute gas reactions. W. E. DOWNEY.

Second spark spectrum of potassium, K III. T. L. DE BRUIN (Z. Physik, 1929, 53, 658—664).—Making use of the chlorine arc spectrum, Cl I, and the first argon spark spectrum, A II, and with the aid of the law of irregular and regular doublets, the principal terms in the second spark spectrum of potassium, K III, are identified. A doublet and quadruplet system are found. A. J. MEE.

Spectrum of ionised rubidium. R. MAJUMDER (Naturwiss., 1929, 12, 198—199).—By comparison of the spectra of the group Ge^+ to Sr^+ the lines in the spectrum of Rb^+ have been classified.

R. N. KERR.

Spark producer as atomiser of salt solutions for flame spectra and the photography of their spark spectra. W. HIRSCHL (Chem.-Ztg., 1929, 53, 218—219).—See A., 1928, 449.

Anomalous terms in the spectrum of doubly-ionised lead. S. SMITH (Nature, 1929, 123, 566).—In an analysis of the spectrum of doubly-ionised lead, Pb III, combinations involving the anomalous terms arising from the state of the doubly-ionised atom of lead when both the two remaining valency electrons occupy $6p$ orbits were found; these are: 995.75, 1165.05 Å. 4004.16, 3925.23 Å. ($6^1D_2-6^3F_{3/2}$), 1439.42, 3832.83 Å. ($6^1P_1-6^1D_2$ and respectively). In the first spark spectrum of thallium, Tl II, the lines $6^3P_{1/2}-6^1D_2$ and $6^1P_1-6^1D_2$ have been found. A. A. ELDRIDGE.

Recombination spectra of ions and electrons in caesium and helium. F. L. MOHLER and C. BOECKNER (Bur. Stand. J. Res., 1919, 2, 489—500).—Spectrophotometer measurements of intensity distribution were made in connexion with probe wire measurements of electrical conditions. Intensity depends on the ion concentration independent of discharge current and voltage. Measurements of intensity distribution in the $2P$ band of caesium and electron velocity distribution were made under a variety of discharge conditions. Photographs and approximate intensity measurements on continuous bands of helium show a strong band beyond 2^3P and fainter bands beyond 2^3S , 2^1P , and 2^1S . The caesium afterglow is characterised by a more rapid decrease in intensity of the continuous bands with decreasing wave-length. W. E. DOWNEY.

Corona discharge in neon. F. M. PENNING (Phil. Mag., 1929, [vii], 7, 632—633).—Experiments similar to those of Huxley (A., 1928, 567) are described in which it was found that with pure neon the starting potential for the negative discharge (wire cathode and cylinder anode) was less than that for the positive discharge. This result is in opposition to those of Huxley. Small quantities of argon give a reproduction of Huxley's results. It is concluded that Huxley's results offer no evidence against the theory that

electrons can be set free from the cathode by the action of positive ions. A. E. MITCHELL.

High-frequency discharges in helium and neon. R. L. HAGMAN (Phil. Mag., 1929, [vii], 7, 586—596).—In cylindrical discharge tubes of constant diameter and with a constant oscillation frequency, at each distance between the electrodes there is a certain pressure at which the starting potential is a minimum. The potential at this minimum increases with the distance between the electrodes. With tubes of different diameters it was found that the starting potential decreases with increasing diameter. Over the wave-length range of 40—640 metres the starting potentials increase with the wave-length for pressures up to 6 mm., above which the potential is approximately constant for all wave-lengths. With each gas there is a certain pressure at which the potential required to maintain the discharge is a minimum. With increasing pressure the maintenance potential increases almost directly proportionally to the increase of pressure. The maintenance potentials vary considerably with the wave-lengths, indicating that the potential comprises two parts, (1) the potential fall in the main column of the gas which is under uniform electric force which is independent of the wave-length, and (2) the potential drop at the electrodes which is independent of the length of the discharge and roughly proportional to the wave-length. All the discharge phenomena in helium and neon are highly sensitive to impurities in the gases. A. E. MITCHELL.

High-frequency discharges in gases. J. S. TOWNSEND and W. NETHERCOT (Phil. Mag., 1929, [vii], 7, 600—616).—Methods for the determination of the relationship between the current and the *E.M.F.* in high-frequency discharges are described. Experiments have been made with high-frequency and continuous-current discharges in nitrogen. The results are in agreement with the theory of Townsend (Compt. rend., 1928, 186, 55). A. E. MITCHELL.

High-frequency discharge in gases. B. C. MUKHERJEE and A. K. CHATTERJI (Nature, 1929, 123, 605).—The striations obtained with internal and external electrodes differ, the former, except at low pressures, having a comb-like appearance. As the pressure is lowered, the thickness of the striæ increases; the glow extends beyond the electrodes, and striations are also observed in this region. The same glow discharge can be obtained with only one external electrode. A. A. ELDRIDGE.

Direct transition from the independent to the dependent conduction of electricity in strongly ionised gases at high pressures. R. THALLER (Physikal. Z., 1929, 30, 59—61).—The normal current-voltage characteristic curve of a gas ionised by means of X-rays, β - and α -rays, or ultra-violet light shows (a) an increase of current proportional to the voltage, (b) at higher voltage the current increases more slowly and reaches a saturation value maintained until the saturation voltage has been exceeded several times over, when (c) a very sudden increase in current makes its appearance. An arrangement is described whereby the transition from the stage where Ohm's law is obeyed (a) to the third stage (c) occurs without

the appearance of the saturation stage (b) (cf. this vol., 114). R. A. MORTON.

Thermionic emission of copper tubes filled with salts. T. PECSALSKI and J. CHICHOCKI (Compt. rend., 1929, 188, 699—701).—The positive thermionic current obtained from a copper tube filled with nickel, chromium, or calcium chloride and heated electrically at a pressure of 10^{-6} mm. increases with time more rapidly than the negative emission and exists even when the tube is at zero potential. The phenomena are most marked with nickel salts.

J. GRANT.

Photo-electric effect with change of state of the cathode. A. GOETZ (Z. Physik, 1929, 53, 494—525).—In order to examine the change in the photo-electric effect caused by change of state of the cathode, and to see whether the change is analogous to that in the thermionic emission, the photo-electric effect with molten tin and two of its allotropes has been investigated. The metal tin alone possesses the properties required of an element for this work. An apparatus is described by means of which both the thermal progress of the phase change and the electric effect can be observed simultaneously. The photo-electric emission was measured by a Hoffmann electrometer of extreme sensitiveness. The temperature range used was 50—550°, and the wave-length range 2300—2900 Å. Within these ranges the photo-electric emission is independent of the temperature for the three phases examined, provided there is no change in the phase. The three phases have different wave-length limits, the emission energy increasing with decreasing energy content of the metal. A change in phase alters the intensity of the emission. The wave-length limits are: for liquid tin 2925 ± 10 , for hexagonal (γ) tin 2820 ± 10 , for tetragonal (β) tin 2740 ± 10 Å. The transition point from γ - to β -tin determined by this method is $200 \pm 2^\circ$, but the velocity of transition is very small. The emission for short wave-lengths follows an exponential law, involving two constants, from one of which the capacity of the surface for optical absorption and the photo-electric quantum equivalent can be found. It is probable that the quantum equivalent changes with the phase, the modification with the denser packing (i.e., β -tin) having a larger equivalent than that with the less dense packing (i.e., γ -tin). There is a parallelism between thermionic and photo-electric phenomena for the three phases.

A. J. MEE.

Photo-electric emission and thermionic emission. E. H. HALL (Proc. Nat. Acad. Sci., 1929, 15, 126—127).—It is shown that it does not follow from the experiments of Du Bridge on platinum (cf. A., 1928, 340) and of Warner on tungsten (cf. A., 1927, 391) that the amount of work required to overcome resisting forces is the same for an electron taken from the free state within to the free state outside the metal as for an electron taken by photo-electric action out of the metal. The values of the constants in the thermionic emission formula are discussed.

N. M. BLIGH.

Temperature dependence of electron emission under high fields. W. V. HOUSTON (Physical Rev., 1929, [ii], 33, 361—363).—Theoretical. N. M. BLIGH.

Photo-electric effect and the continuous X-spectrum. E. SEVIN (*Compt. rend.*, 1929, 188, 911—912; cf. Decombe, *ibid.*, 1927, 185, 1265).—The photo-electric law and the maximum frequency of the continuous X-spectrum resulting from the law of Duane and Hunt are deduced from the author's theory of light (*ibid.*, 1929, 188, 290). J. GRANT.

Photo-electric effect of ultra-violet rays on gases. R. DANTINNE and P. LENAERTS (*Arch. Sci. Phys. Nat.*, 1929, [v], 11, 5—14).—The photo-electric action of ultra-violet rays on gases depends on the nature of the gas, the frequency of the light, and probably to a considerable degree on the pressure. It is a volume effect in contradistinction to the photo-electric effect on solids, which is a surface effect. The characteristics of the photo-electric effect with solids lead to the view that it is the adsorbed gas and not the solid which furnishes the photo-electrons. This view implies a parallelism between the relative intensities of the effects with different gases and the relative intensities of the effects brought about by the same radiation on a metallic surface surrounded by the same gases. A special apparatus has been constructed for measuring the photo-electric effect caused by the light from an aluminium spark on oxygen, air, carbon dioxide, and sulphur dioxide. The relative values of the ionisations produced in the different gases agree well with the data for the photo-electric effect at a metallic surface in the same gases. The active element (for the frequencies used) appears to be oxygen. R. A. MORTON.

Form and structure of sparks. V. Long sparks in different gases. T. TERADA, U. NAKAYA, and R. YAMAMOTO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1929, 10, 43—68).—The sparking potential in sulphur dioxide at normal pressure is three times that in air. Long sparks in acetylene and in carbon dioxide have an afterglow of 10^{-4} sec. duration. W. E. DOWNEY.

Average "forward" momentum of photo-electrons. E. J. WILLIAMS (*Nature*, 1929, 123, 565—566).

Astrophysical estimate of the ionisation potential of vanadium. A. V. DOUGLAS (*Nature*, 1929, 123, 606—607; cf. A., 1928, 632).—From periodic intensity changes the value of the ionisation potential of vanadium is estimated to be 6.74 volts, in agreement with Russell's value from spectroscopic data of 6.76 (*Astrophys. J.*, 1927).

A. A. ELDRIDGE.

Polarisation of electron waves. E. RUPP (*Z. Physik*, 1929, 53, 548—552; cf. Davisson and Germer, *this vol.*, 7).—A beam of electrons was twice reflected from the surface of a copper crystal. The number of electrons reflected showed no selective reflexion maxima depending on the rotation of the two reflectors about the axis of the beam. A homogeneous external magnetic field has no effect on the reflexion. A selective maximum was obtained for electrons of velocity 150 volts when reflected from the {111} face of copper, which might be attributed to polarisation, but the angle of the beam with the reflector for this was small (12°) and there are many experimental

difficulties involved in finding out whether it is a case of real polarisation. A. J. MEE.

Effects of an homologous series of amines on the mobilities of ions in hydrogen gas. L. B. LOEB and K. DYK (*Proc. Nat. Acad. Sci.*, 1929, 15, 146—156; cf. A., 1928, 932, 809, 609).—Following a study of the effect of ammonia (cf. A., 1927, 181), that of the amines was investigated, as the size of the molecule could be varied without markedly changing the electro-chemical properties of the gas. The reciprocal mobility for positive and negative ions is plotted against the percentage of amine present, and compared with Blanc's law. For pure methylamine, the mobilities in the amine were somewhat less than in ammonia; for methylamine and hydrogen mixtures the negative ion showed a marked departure from Blanc's law for small percentages of amine; for mixtures of propylamine and hydrogen the smallest trace of amine reduced the mobility; for methylamine-hydrogen-ammonia mixtures the mobilities were decreased slightly more by the ammonia in accordance with Blanc's law. Theoretical explanations are given. N. M. BLIGH.

Ionisation of gases by positive ions. R. M. SUTTON (*Physical Rev.*, 1929, [ii], 33, 364—372).—Using a simple tube, positive potassium ions were driven by controllable accelerating potentials up to 750 volts into neon and argon. Curves are given showing the variation of ionisation with pressure over a range of 0.05—1 mm., and the number of new ions formed per positive ion per cm. path reduced to 1 mm. pressure. The efficiency of the effect is less than for electron bombardment, and had not reached a maximum at 750 volts. The pressure range showing ionisation effect is higher than expected from kinetic theory, and indicates the presence of long mean free paths for the positive ions (cf. Kennard, A., 1928, 453; Durbin, *ibid.*, 103). N. M. BLIGH.

Nature of the ions in air. H. A. ERIKSON (*Physical Rev.*, 1929, [ii], 33, 403—411; cf. A., 1927, 1002; *this vol.*, 114).—The transference of an electron from an H_2O molecule to the final positive air ion is further studied and results are given showing the production and ageing of the initial positive ion in dried air and nitrogen. When the final positive air ion of mobility 1.36 is passed into moist air the final ions disappear and a swifter 1.87 ion appears; these in turn change back into a 1.36 ion. This is interpreted as due to a neutral H_2O molecule giving up an electron to the final 1.36 two-molecule positive ion, thus giving a one-molecule positive ion having a higher mobility. This H_2O^+ ion ages by attaching itself to another molecule forming a slower 1.36 ion. The initial and final positive ions are considered to be one and two molecules large, respectively. N. M. BLIGH.

Formation of monatomic hydrogen by collisions with slowly moving electrons. K. E. DORSCH and H. KALLMANN (*Z. Physik*, 1929, 53, 80—91).—Experiments are described in which electrons of energy from 7 to 16 volts are allowed to collide with hydrogen molecules; the blackening of lead chloride in the hydrogen stream was used as an index of the formation of monatomic hydrogen. In

accordance with theory and the earlier experiments of Hughes and Skellett (A., 1927, 811), appreciable dissociation takes place only above the first resonance potential, 10.8 volts, and increases greatly when the potential is 16 volts corresponding with ionisation. Evidence has been obtained that with 7-volt electrons a small formation of monatomic hydrogen occurs, probably due to absorption of the electron energy as nuclear vibrational energy, since the dissociation energy corresponds with 4.3 volts. Under such conditions not more than 1 in 4×10^5 collisions results in dissociation. Experiments are also described which establish that monatomic hydrogen is also formed by a secondary process in which hydrogen ions react.

R. W. LUNT.

Electron- and ion-streams in gases at low pressures. G. SPIWAK (Z. Physik, 1929, 53, 805—839).—Mathematical.

W. E. DOWNEY.

Electronic charge e . J. H. J. POOLE (Nature, 1929, 123, 530).—The possibility that a new value of π should be used in obtaining the value of $hc/2\pi e^2$ is suggested (cf. Birge, this vol., 368; Backlin, *ibid.*, 369).

A. A. ELDRIDGE.

Electromagnetic field of an electron. The electron as a gravitational phenomenon. D. MEKSYN (Phil. Mag., 1929, [vii], 7, 425—433).—Mathematical. An electron is assumed to represent the same entity as a neutral mass in which the matter or energy is spread throughout the space instead of being located in a small region. The electron is thus a gravitational field of potential m/r . It is shown that there are no stresses in such a field.

A. E. MITCHELL.

Phenomena of projected electrons. T. J. I. BROMWICH (Phil. Mag., 1929, [vii], 7, 470—476).—A definite statement of the deductions from the author's previous treatment (*ibid.*, 1928, [vii], 5, 636) of the Einstein theory of relativity is given.

A. E. MITCHELL.

Thermodynamical properties of the electron and atomic theory. R. D. KLEEMAN (Phil. Mag., 1929, [vii], 7, 493—504; cf. this vol., 379).—The equation of state of electron gas is shown to be $pv = RT\xi$, where ξ is less than unity and decreases as v increases. This result combined with kinetic deductions is used to show that the velocity of an electron in an electron gas gradually decreases between two consecutive collisions and increases during a collision, whilst the internal energy of an electron under the same conditions increases between consecutive collisions and decreases during collisions. Since these changes can be achieved only by changes in the electric fields of the colliding electrons, it is concluded that decreases in internal energy must result in radiation into space. These results are employed in the discussion of the formation of atoms.

A. E. MITCHELL.

Vapour-pressure separation of isotopes by fractional distillation. I. Distillation experiments with carbon tetrachloride. H. G. GRIMM (Z. physikal. Chem., 1929, B, 2, 181—199).—In the hope of separating two different carbon tetrachlorides containing the two isotopes of chlorine, the pure liquid was subjected to extensive fractional distillation.

The densities of the fractions were found, and were shown not to differ within the experimental error of 2×10^{-5} . Using this estimated error it is possible to calculate the upper limit for the density difference between the compounds containing neighbouring isotopes. Using an empirical formula due to F. D. Brown, it is shown that the difference in b. p. between the two forms of carbon tetrachloride differing in mol. wt. by two units cannot exceed 10^{-3}° , and the vapour pressures cannot differ by more than 0.03 mm. Calculations using this value point to the existence of energy at 0° Abs.

A. J. MEE.

Vapour-pressure separation of isotopes by fractional distillation. II. Experiments in the fractionation of chlorine on the large scale. H. G. GRIMM and L. BRAUN (Z. physikal. Chem., 1929, B, 2, 200—206).—When 60,000 kg. of chlorine were fractionally distilled, the fractions converted into ammonium chloride, and the densities of the saturated solutions of the salt determined, the results were the same for all the fractions within the experimental error. Any possible at. wt. difference of the fractions must be smaller than 0.002% of the at. wt. of chlorine.

A. J. MEE.

Constitution of oxygen. F. W. ASTON (Nature, 1929, 123, 488—489).—There is no evidence that oxygen is other than a simple element (cf. Giaque and Johnston, this vol., 369). Faint lines which might be ascribed to the existence of O^{18} are capable of other interpretations.

A. A. ELDRIDGE.

Separation of isotopes. J. N. BRONSTED and G. HEVESY (Phil. Mag., 1929, [vii], 7, 631—632).—Exception is taken to the view expressed by Harkins and Mortimer (A., 1928, 1301) that the mercury used by Bronsted and Hevesy in their work on the separation of the isotopes of mercury was impure. An outline of the methods used to establish the purity of their material is given.

A. E. MITCHELL.

Quantum theory of radioactive disintegration. G. GAMOW (Z. Physik, 1929, 53, 601—604).—Mathematical. Earlier work on the solution of the wave equations (cf. this vol., 7) is further discussed in connexion with the views of Laue.

A. J. MEE.

Adsorption of radium emanation. A. BECKER and K. H. STEHBERGER (Ann. Physik, 1929, [v], 1, 529—555).—The adsorption of emanation by carbon and silica gel has been investigated by a static method. Adsorption on solids, like absorption by liquids, is characterised by the appearance of stationary equilibrium states determined solely by the concentration ratio of emanation in the solid or liquid and in the surroundings, this ratio depending on the temperature. The law governing adsorption of ordinary gases is thus confirmed at partial pressures of a very low order. The equilibrium distribution of emanation is independent of the nature and pressure of the accompanying gas, of the amount of adsorbing solid, of the volume of the container, and of the partial pressure of emanation; it depends solely on the adsorbing material and the temperature. The adsorption coefficient has been measured over the temperature range -80° to 100° , and the validity of the thermodynamic equation for the reaction isochore is demon-

strated. The specimen of carbon exhibited a high absolute value for the adsorption coefficient which varied greatly with temperature. The silica gel was less effective, since the adsorption coefficient at the temperature of solid carbon dioxide was equal only to that of carbon at the ordinary temperature. The reason for the difference between the two substances is not clear.

The dynamic method of investigating the adsorption of emanation in a gas stream is attended by special difficulties, but quantitative data can be obtained if due precautions are taken.

R. A. MORTON.

Straggling of α -particles from polonium in passing through gases. H. EYRING (Physical Rev., 1929, [ii], 33, 386—388; cf. A., 1928, 4).—The straggling coefficients in the gases ethylene, air, nitrous oxide, carbon dioxide, methyl iodide, ethyl bromide, and ethyl iodide have been determined from the ends of the Bragg ionisation curve. The average values are found to be greater than those calculated theoretically, except in the case of methyl iodide.

N. M. BLIGH.

Volatilisation of polonium. P. BONÉT-MAURY (Ann. Physique, 1929, [x], 11, 253—341).—The concept of temperature of vaporisation as applied to the radio-elements is examined critically and abandoned. A method is described of investigating the distribution in space of the active atoms vaporised, and Lambert's law of cosines is verified. A detailed study is made by an improved experimental method of the vaporisation of polonium deposited electrochemically or by condensation on platinum or nickel. Curves are given showing the quantity of polonium vaporised as a function of time at a number of different temperatures. The quantity vaporised is independent of the time, and is a simple function of the temperature. A reverse phenomenon is indicated, and is presumed to be a thermal diffusion tending to cause polonium to penetrate into the surface on which it is deposited. The removal of a polonium atom from platinum requires more energy than its removal from nickel. Results from condensed polonium are less regular than from samples deposited electrochemically.

N. M. BLIGH.

Counting of scintillations produced by α -particles. I. II. **Determination of the efficiency of transformation of the kinetic energy of α -particles into radiant energy.** III. **Practical applications.** J. CHARITON and C. A. LEA (Proc. Roy. Soc., 1929, A, 122, 304—319, 320—334, 335—352).—I. A systematic investigation has been made of the factors involved in the scintillation method of counting α -particles and of its limitations. An apparatus is described for producing regular point flashes of light of known spectral constitution, the conditions under which scintillations are observed being imitated as closely as possible.

II. A determination of the luminous efficiency of the process of scintillation formation necessitates the measurement of the candle-power of a zinc sulphide screen when bombarded by a known number of α -particles of known energy. To obtain the spectral distribution, spectrograms were taken of various zinc sulphides when bombarded by α -particles, using an

α -ray tube filled with radon which could be covered with different preparations of zinc sulphide. The numbers and energies of the α -particles producing the radiation could not be determined with precision, owing to irregularities of the glass walls of the tube. The brightness of the α -ray tube was therefore compared with that of a plane screen of the same zinc sulphide bombarded by a known number of α -particles of known energy. Since the spectral distributions of the light were the same in both cases, the intensities could be compared by comparing the blackening produced in a photographic plate illuminated directly by light from the two sources. The values obtained for the radiant and luminous efficiencies of various zinc sulphides when bombarded by α -particles are surprisingly high—viz., about 25 and 12%, respectively—whilst the value obtained by Marsden for the radiant efficiency was 1.5%. The high values, however, are in agreement with those calculated from data for radioactive luminous paints.

III. An investigation of the influence of the numerical aperture of the microscope employed on the results of counting showed that, when scintillations produced by α -particles of 2.7 cm. range are observed with a microscope of magnification 50 and of variable numerical aperture, the scintillations become invisible when the numerical aperture is reduced below 0.08. For this value of the numerical aperture the energy entering the eye from a single scintillation evaluated as green light ($\lambda=0.505 \mu$) is 290 quanta. Scintillations observed with the eye placed at varying distances from the screen become invisible when the eye receives less than 30 quanta per scintillation. The velocity of the slowest α -particles capable of producing a scintillation observable in a microscope of magnification 50 and numerical aperture 0.45 was found to be 2.7×10^8 cm./sec. The energy entering the eye from such a scintillation, using the value previously obtained for the efficiency of the zinc sulphide employed, is 300 quanta of green light ($\lambda=0.505 \mu$).

The experimental results obtained in the three parts of the paper are interpreted and discussed. It is considered that the explanation of the fact that a smaller fraction of the light from a scintillation produces a visual sensation when the eye is unaided than when a microscope is used lies in the optical properties of zinc sulphide crystals. If the "size" of a scintillation is the same as that of a crystal of zinc sulphide, then the dimensions of the retinal image will be greatly increased when a microscope is used. The mechanism of the scintillation process is discussed, with special reference to the high values obtained for the radiant efficiencies.

L. L. BIRCUMSHAW.

γ -Radiation of radioactive elements. E. CHALFIN (Z. Physik, 1929, 53, 130—133).—Polemical.

Quantum mechanics and radioactivity. II. J. KUDAR (Z. Physik, 1929, 53, 134—137).

Course of the α -change. D. ENSKOG (Z. Physik, 1929, 53, 639—645).—The assumption that through a quantum switch there is a decrease in the number of magnetons from the two which the α -particle is supposed to possess in the normal state, to one, is further examined. The calculations show

that the quantum switch for fast rays occurs with an increase in energy, and for the slower rays with a decrease. The calculated velocity range for rays of the former type agrees with observed values.

A. J. MEE.

Ionisation method for the examination of corpuscular rays and its application to the detection of atomic particles. A. WEGERICH (Z. Physik, 1929, 53, 729—746).—The construction of an ionisation cell filled with helium-neon mixture is described. The cell is used to examine corpuscular rays, in particular the atomic particles resulting from the bombardment of certain elements with α -particles. In the direction 130 — 150° with respect to the direction of the α -particles, H-particles were emitted from carbon, aluminium, iron, copper, and zinc.

W. E. DOWNEY.

Range of fluctuations of α -rays. P. PREISLER (Z. Physik, 1929, 53, 857—886).—The fluctuations in range of α -particles from thorium-C' in air, mica, and bismuth have been measured.

W. E. DOWNEY.

Internal absorption of γ -rays. J. A. GRAY and A. J. O'LEARY (Nature, 1929, 123, 568).—A previous estimate (A., 1925, ii, 84) of the internal absorption of the γ -rays of radium-D and the fraction of the atoms emitting γ -rays is revised. Of 43 atoms disintegrating, 24 emit γ -rays, and of these 24 γ -rays, 19 suffer internal absorption. Less than one atom of radium-E in 25,000 atoms emits a β -ray of energy 2×10^6 volts.

A. A. ELDRIDGE.

Successive α -transformations. G. GAMOW (Nature, 1929, 123, 606).—The paradox that, although the probability of emission increases enormously with the energy, the slowest α -particles are the first to be emitted, is explained if it is assumed that all the α -particles are originally in the same quantum state.

A. A. ELDRIDGE.

Duration of elementary light emission. J. STARK (Ann. Physik, 1929, [v], 1, 323—340).—The oscillation period is defined as the time occupied in the transition between a higher and a lower equilibrium position of an atomic electron with respect to the atomic ion. For the line H_γ , Traubenberger and Gebauer (A., 1927, 1002) obtained an experimental value of 10^{-9} sec. The author's views (cf. this vol., 223) now indicate a theoretical value of 10^{-13} sec. The experimental work on the luminescence of canal rays has therefore been repeated under improved conditions. It is shown that the effect of an electric field on the lines H_α , H_β , and H_γ arising from particles moving at about 7×10^7 cm. sec.⁻¹ is restricted to the first 0.1 mm., from which result it is concluded that the emission process for the three lines, and therefore the time occupied in the transitions between equilibrium positions, must be less than 10^{-10} sec. A suggestion is made that the discrepancy between this result and the work of Traubenberger and Gebauer (which can be confirmed if glass tubes are used instead of fused quartz tubes) arises from an electric field between the cathode and the wall of the tube. The earlier observations on the time factor in light emission from canal rays are reconsidered and it is concluded that the moving atoms are charac-

terised by outer electrons distributed over a series of energy levels.

R. A. MORTON.

Structure of the solar chromosphere. L. D'AZAMBUJA (Compt. rend., 1929, 188, 773—775).—The granular structure of the monochromatic solar spectrographs has been examined by simultaneous photography of the two couples of lines Ca 4227—Fe 4384 and Ca 4227—Fe 4202, but no appreciable difference in the form and distribution of the grains was detected, and the difference between the heights of the two iron rays (1200 and 700 km., respectively) is apparently too small to affect them. A similar granulation was observed for the H_α ray, which occurs at a higher level.

J. GRANT.

Energy transference in nuclear collisions. W. KUHN (Z. Physik, 1928, 52, 151—157).—In the collision between an α -particle and an atomic nucleus only a fraction of the energy is transferred to the latter. The energy required for the disruption of the nucleus is considered a measure of the nuclear stability. The astrophysical significance of this is discussed with reference to the elements occurring under the conditions which exist in the fixed stars.

G. E. WENTWORTH.

Efficiency of quenching collisions and the radius of the excited mercury atom. E. GAVIOLA (Physical Rev., 1929, [ii], 33, 309—318).—The assumption of Foote (cf. A., 1927, 999) that every collision of a foreign gas molecule with an excited mercury atom is efficient in quenching the resonance radiation is discussed critically. A new calculation of the efficiency of collisions leads to the value unity for carbon monoxide, hydrogen, and perhaps oxygen, and less than unity for water vapour, nitrogen, argon, and helium. The radius of the excited mercury atom is calculated using an improved value for the amount of resonance radiation re-absorbed in the resonance vessel and found to be 2.91×10^{-8} cm., or 1.62 times as large as for the normal atom, for the case of hydrogen, and 5.5×10^{-8} cm. or three times the normal for the case of carbon monoxide. Actually carbon monoxide has a greater quenching efficiency than hydrogen.

N. M. BLIGH.

Evaporation of thorium from tungsten. (MISS) M. R. ANDREWS (Physical Rev., 1929, [ii], 33, 454—458).—The rate of evaporation from pure and from carbonised tungsten, of thorium deposited by evaporation either from thoriated filaments or from metallic thorium was measured between 2000° and 2500° Abs. Evaporation from both surfaces was found to vary directly with the fraction covered, and was more rapid from pure than from carbonised tungsten, the respective heats of evaporation being calculated as 177,000 and 202,000 g.-cal./g.-atom.

N. M. BLIGH.

Polarisation of the Compton scattering according to the Dirac theory. Y. NISHINA (Z. Physik, 1929, 52, 869—877).—Mathematical.

R. W. LUNT.

Nuclear levels and artificial disintegration. R. W. GURNEY (Nature, 1929, 123, 565).—Attention is directed to the possibility of resonance phenomena if the solutions of the Schrödinger equation which for certain ranges of energy give ψ -functions the amplitude

of which inside the nucleus is large compared with that outside, are taken into account.

A. A. ELDRIDGE.

Boundary of the solar chromosphere. W. H. MCCREA (*Nature*, 1929, 123, 527—528).

Quantum mechanics of energy transfers between atoms. H. KALLMANN and F. LONDON (*Z. physikal. Chem.*, 1929, B, 2, 207—243).—The transfer of excitation energy between atoms can be interpreted as a resonance phenomenon. The amounts of energy that an atom can take up or lose are not optically "sharp," but distributed over a range. A resonance curve could be drawn to express the probability of transfer of each given energy. This is analogous to the shortened life period of an oscillator (and consequent broadening of a zone of anomalous dispersion) when the radiation forcing it is intense. The sharpness of resonance between an atomic "resonator" and a light wave will depend on the strength of the atomic field; the stronger the field the broader is the resonance. Quantum mechanics is applied to such a resonance, and the modification of stationary states when two atoms approach adiabatically is calculated. Consideration is given to the elementary processes involved and to the kinetics in the case of an excited gas. The effective cross-section for collisions in which energy transfer takes place depends on the sharpness of resonance. The limiting case of sharp resonance is considered separately, and the effect of velocity of the gas atoms discussed. The effective cross-section for a transfer corresponding with a "permitted transition" is very great. These ideas are applied to some special cases of collisions of the second kind: (1) the production of the ultra-violet bands observed by Lyman in hydrogen mixed with argon, (2) the calculation of intensities of the sodium lines produced in a mixture of sodium atoms with mercury atoms excited to the 2^3P_0 and 2^3P_1 states, (3) resonance by the switch $2^3P_1 \rightarrow 2^3P_0$ in mercury itself, and (4) the quenching of fluorescence of sodium vapour by nitrogen and hydrogen. Further application is made in the case where a transfer of excitation energy occurs in one atom only, and to the various ways in which the degree of polarisation of resonance radiation can be influenced. The simple formulæ will explain the excitation of the two *D* lines by the radiation of one, and the results of iodine vapour resonance experiments. The possibilities of energy transfer in chemical reactions, particularly catalytic reactions and the dissociation of hydrogen molecules by excited mercury atoms, are discussed. The broadening of spectral lines by collisions is examined in the light of the supposed transfer mechanism.

A. J. MEE.

Quantum laws and the uncertainty principle of Heisenberg. G. N. LEWIS and J. E. MAYER (*Proc. Nat. Acad. Sci.*, 1929, 15, 127—139).—Mathematical.

Doubling of X-ray and optical terms through electronic rotation, and the intensity of the caesium lines. G. GENTILE and E. MAJORANA (*Atti R. Accad. Lincei*, 1928, [vi], 8, 229—233).—Theoretical. It is shown that the potential of Fermi not only allows of the satisfactory *a priori* determin-

ation of the energy levels of the heavy atoms, but also gives derived values of great accuracy, considering the statistical nature of this theory of the atom, for the doubling of the X-ray and optical terms.

F. G. TRYHORN.

Theory of electron emission of metals. L. NORDHEIM (*Physikal. Z.*, 1929, 30, 177—196).—A review.

Transmutation of the lighter elements in stars. R. D'E. ATKINSON and F. G. HOUTERMANS (*Nature*, 1929, 123, 567—568).

Beryllium and helium. (LORD) RAYLEIGH (*Nature*, 1929, 123, 607).—Since beryl contains helium but no appreciable quantities of radioactive substances (A., 1908, ii, 649), the isotope Be^8 may have existed and have broken up as suggested by Atkinson and Houtermans (preceding).

A. A. ELDRIDGE.

Distribution of electrons in atoms. L. M. ALEXANDER (*Phil. Mag.*, 1929, [vii], 7, 517—522).—It is assumed that the electronic relationships between sublevels of a group are similar to the relationships postulated by Bohr for the principal groups. The suggestion of Stoner (A., 1925, ii, 85) that the number of electrons in an atom associated with each sublevel is equal to double the inner quantum number, is discarded. A classification of the electron distribution in the *K*, *L*, *M*, *N*, *O*, and *P* levels of thirty atoms with atomic numbers from 1 to 85 is given.

A. E. MITCHELL.

New regularities in the series of the elementary ionic radii. A. M. BERKENHEIM (*Z. physikal. Chem.*, 1929, 144, 35—40; cf. A., 1928, 1191).—The ionic radii of the elements in any horizontal row of the periodic table can be arranged as an arithmetical series with a constant difference which is different for each series. Taking the radius of the positive carbon ion as unity, the radii of the positive and negative ions can be arranged in regular series of simple numbers; e.g., the ions C^{++++} , B^{+++} , Be^{++} , Li^{+} have radii represented by the numbers 1, 2, 3, 4; the ions C^{++++} , Si^{++++} , Ti^{++++} , Zr^{++++} , Ce^{++++} have the radii 1, $2\frac{1}{2}$, 4, $5\frac{1}{2}$, $6\frac{1}{2}$, and the neon atom with the negative ions F^{-} and O^{--} form the series 10, $9\frac{1}{2}$, 8 $\frac{1}{2}$. The absolute values of the ionic radii calculated by this method agree well with the values of Goldschmidt.

O. J. WALKER.

Optical experiments with perylene and its derivatives. II. Visible absorption spectra of some di-derivatives. A. DADIEU (*Z. physikal. Chem.*, 1929, B, 2, 253—261; cf. A., 1928, 1071).—The absorption spectra of the following di-derivatives have been investigated: 3:9-dipropionyl-, 3:9-di-butyl-, 3:9-di-*o*-toluoyl-, 3:9-dianisoyl-, 3:10-dinitro-, and 3:10-diamino-perylene, perylene-3:10- and -1:12-quinone. The influence of the substituents is to displace, widen, and alter the intensity of the bands. The results are discussed on the basis of the electronic theory.

A. J. MEE.

Absorption spectra of pyrrole and its derivatives. IV. Ethyl and methyl esters of 1-anilino-2-phenyl-5-methylpyrrole-4-carboxylic acid. V. Certain pyrrolecarboxylic acids and their ethyl esters. VI. Ethyl 2:5-dimethyl-

pyrrole-3:4-dicarboxylate and 2:4-dimethylpyrrole-3:5-dicarboxylate. VII. Ethyl 1-phenyl-2:5-dimethylpyrrole-3:4-dicarboxylate and 1-anilino-2-phenyl-5-methylpyrrole-carboxylate. VIII. Ethyl 2:5:2':5'-bispyrrole-3:4:3':4'-tetracarboxylate. G. KORSCHUN and (MME.) C. ROLL (Bull. Soc. chim., 1928, [iv], 43, 1075—1085).—IV. The absorption spectra of these two esters are nearly identical, each consisting of a single band, the intensity of which is a little stronger for the ethyl than for the methyl ester. The *methyl* ester was prepared from methyl phenacyl-acetoacetate (from methyl acetoacetate and phenacyl bromide) and phenylhydrazine, the *monohydrazide*, m. p. 113° (indef.), being obtained as an intermediate.

V. The absorption spectra of the following have been examined: 1:2:5-trimethylpyrrole-3:4-dicarboxylic acid and its monoethyl ester, mono- and diethyl esters of 1-phenyl-2:5-dimethylpyrrole-3:4-dicarboxylic acid, 1-anilino-2-phenyl-5-methylpyrrole-4-carboxylic acid, the diethyl and 3-monoethyl esters of 2:4-dimethylpyrrole-3:5-dicarboxylic acid, 1-carbamido-2:5-dimethylpyrrole-3-carboxylic acid and its ethyl ester. The general conclusion is reached that the effect of the replacement of a carbethoxyl by a carboxyl group depends on intramolecular compound formation. If the latter does not occur, the nature of the curve is unaltered. Where complex formation is probable between the nuclear pyrrole nitrogen atom and the carboxyl group, a displacement of the curve towards the red and an increase in the intensity of the absorption occur. On the other hand, if the complex is formed between the nitrogen atom of a substituent in position 1 and the carboxyl group, displacement towards the ultra-violet and a decrease in the intensity are produced. When the saturation of a substituent in position 1 is increased, in addition to the displacement to the ultra-violet previously noted (A., 1925, ii, 258), a decrease in intensity occurs.

VI. The curves for these two ethyl esters are nearly coincident, the intensity of the asymmetric ester being a little stronger than that of the symmetrical one.

VII. Replacement of a methyl group in position 1 by a phenyl group has very little effect on the absorption curve, but when a methyl group attached to a nuclear carbon atom is replaced by phenyl displacement towards the red occurs.

VIII. A displacement towards the ultra-violet is noticed when the absorption spectrum of this ester is compared with that of the ester of 2:5-dimethylpyrrole-3:4-dicarboxylic acid. Two feeble absorption bands can be distinguished in the curve for the bispyrrole derivative. R. N. KERR.

Absorption spectrum of fluorspar. S. VAN DER LINGEN (Z. Physik, 1929, 53, 581—586).—The absorption spectra of various specimens of fluorspar were investigated by means of a Hilger infra-red spectrometer. The different specimens gave different spectra, but some general features are to be noted. In order to discover whether the presence of any gas was the cause of the colour of some fluorspars, some broken mineral was placed in a dried evacuated tube. The emission spectrum of the gas in the tube was found to

give only a trace of the strong ultra-violet hydrogen band and the carbon monoxide lines. A. J. MEE.

Polarised fluorescence. (FRL.) E. HAKENBECK (Ann. Physik, 1929, [v], 1, 457—496).—The absorptive properties and the polarised fluorescence of sodium fluorescein (uranine) in glycerol or aqueous glycerol have been studied. A formula has been deduced and confirmed experimentally for the degree of polarisation as a function of the direction of vibration of the incident light. Values for the molecular radius, correct as regards order of magnitude, have been obtained from the degree of polarisation as a function of the viscosity of the solvent, using Perrin's formula. The hitherto accepted mechanism of the fluorescence does not suffice for the explanation of the observations. The mean constants for the quasi-elastic forces have been determined approximately from refractive indices. Beer's law is not obeyed.

R. A. MORTON.

Ultra-violet absorption spectra of *o*-, *m*-, and *p*-cresol. J. SAVARD (Compt. rend., 1929, 188, 782—783).—The energy of electronic activation of the cresols decreases in the order, *o*-, *m*-, *p*-, the *o*- and *m*-compounds having two states of activation and the *p*- only one. The results are compared with those for the dihalogen compounds of benzene, to which they are similar, and with those for benzene, toluene, and phenol. It is shown that the molecular deformability calculated from the frequencies in the active and normal states is increased by the introduction of a methyl group into the benzene nucleus, and that when two substituents are present the deformability is least for the *p*-compound.

J. GRANT.

Transformation spectrum of the ruby. E. L. NICHOLS and H. L. HOWES (Proc. Nat. Acad. Sci., 1929, 15, 139—146).—The spectrum of an incandescent ruby heated in a hydrogen flame was found to have superimposed upon the general radiation 21 narrow emission bands termed transformation bands, and visible for a temperature range, 600—775°, which corresponds with profound changes in the absorption of light by the ruby. The wave numbers of the bands and also of the absorption and fluorescence bands are tabulated and shown to occur in sets having a constant frequency interval of 36.7. The phenomena are analogous to those observed in the incandescence of solids containing various rare earths as activators.

N. M. BLIGH.

Molecular spectrum of ammonia. I. Two types of infra-red vibration bands. G. A. STINCHCOMB and E. F. BARKER (Physical Rev., 1929, [ii], 33, 305—308).—The infra-red spectrum of ammonia (cf. Robertson and Fox, A., 1928, 1073) was studied, and the absorption bands at 3.0 and 1.9 μ were examined, using ruled gratings, and their fine structures shown to be of different character. The 3 μ band is associated with a vibration of the electric moment parallel to the symmetry axis of the molecule, yielding one zero branch and a simple rotation series. The vibration giving rise to the 1.9 μ band is normal to the symmetry axis. The band probably corresponds with one of the four fundamental frequencies.

N. M. BLIGH.

Zeeman effect in the Ångström carbon monoxide bands. II. F. H. CRAWFORD (Physical Rev., 1929, [ii], 33, 341—353).—A continuation, with improved experimental methods, of previous work (cf. A., 1927, 1119). Observations of the Zeeman effect were extended from the bands at 5610, 5198, and 4835 to include 4511 and 4394 Å. For fields from 18,000 to 36,000 gauss the widths of the Zeeman patterns were proportional to the field strengths. The weighted average of the pattern widths for M (the ordinal number of the line in a branch) = 1 is 97.7% $\Delta\nu_n$, and $M=2$, 66.3% $\Delta\nu_n$, where $\Delta\nu_n$ is the normal Lorentz triplet half width. The new quantum mechanics predicts 100% $\Delta\nu_n$ and 66.7% $\Delta\nu_n$ for these widths, respectively, as against 88.9% and 64% on the old quantum theory. Thirteen out of eighteen patterns predicted for the first two lines of the P , Q , and R branches were resolved and measured in agreement with theory. Intensity asymmetries were found to behave qualitatively, but not quantitatively, in accordance with Kronig's treatment (cf. A., 1928, 340). Three, and possibly four, new bands of the Ångström group were observed. N. M. BLIGH.

Enlargement and displacement of spectral lines by molecular diffusion. J. CABANNES and P. SALVAIRE (Compt. rend., 1929, 188, 907—908; cf. A., 1928, 812).—The displacements obtained by the lateral diffusion of the mercury line 4358 Å. with alcohols, acetic acid, cyclohexane, benzene, and phosphorus tribromide and studied by means of a Perot-Fabry interferometer, are of the order of 0.05 Å. in the direction of the red, and are accompanied by an enlargement of the radiation due to fluctuations in density of less than 0.1 Å. These phenomena, which are comparable with the Compton effect, are not to be confused with the Raman effect (*loc. cit.*).

J. GRANT.

Study of the absorption of a sample of blue rock salt. P. LEROUX (Compt. rend., 1929, 188, 904—907).—The absorption coefficient (K) at 18° of a cleavage plane about 0.1 cm. thick of blue salt from Stassfurt increases with the wave-length of the source (3655—5790 Å.), but is decreased for each wave-length after heating at 220—250° and cooling to 18°. The absorption minimum is displaced towards the higher wave-lengths, and the salt appears colourless. A colourless sample showed effects of the same order except that above 4358 Å. K was less both before and after heating than for the blue salt. J. GRANT.

Influence of boric acid on the phosphorescence of zinc sulphides prepared by the explosion method. F. PREVET (Compt. rend., 1929, 188, 903—904).—Boric acid decreases the violence of the explosive reaction of zinc and sulphur, but to a smaller extent than other substances (this vol., 524), and the resulting sulphide increases in hardness and stability with the amount used. Between 5 and 20% of boric acid produces an increased intensity of phosphorescence, the actual optimum depending on the size of the grains, whilst the permanence of the phosphorescence is slightly higher than that of the best commercial products. J. GRANT.

Use of crystalline quartz for spectrographic work. J. W. ELLIS (J. Opt. Soc. Amer., 1929, 18,

82—88).—In the study of the infra-red absorption of a solution of benzophenone in chloroform, using a cell having quartz end-plates, spurious effects in the absorption record were observed. These were found to be due to a polarisation phenomenon in the quartz plate and to a slight departure from parallelism between the optic axis and surfaces of the plate. The errors due to these causes and practical methods for their elimination are discussed. N. M. BLIGH.

Structure and activation of the molecules of aliphatic aldehydes. II. Formaldehyde, acet-aldehyde, propaldehyde, and chloral. S. A. SCHOU (J. Chim. phys., 1929, 26, 1—43; cf. this vol., 236).—From its moments of inertia the formaldehyde molecule is concluded to be Y-shaped, the distances C—O, C—H, and H—H having the values 1.09×10^{-8} , 1.3×10^{-8} , and 1.3×10^{-8} cm., respectively. The normal molecule probably possesses 4 valency electrons and is in the state $3p^3P_{0,1,2}$; it has the fundamental frequencies 1572.3 and 441 cm.⁻¹, the former of which corresponds with the vibration of the carbon and oxygen atoms and the latter with the vibration of the hydrogen atoms. On activation, the molecule passes into the state $4s^3P_{0,1,2}$ and the vibration frequencies fall to 1231.3 and 398 cm.⁻¹, showing that the distances between the atoms have increased. The limit for the predissociation of the molecule is at 2670 Å. at the ordinary temperature, but at higher temperatures is shifted towards the red. In the absorption spectrum of acetaldehyde vapour 60 bands have been detected, the fundamental frequency for the normal molecule being 825 and for the activated molecule 517 cm.⁻¹ From the fine structure the moment of inertia is 2.43×10^{-40} , from which it is concluded that the atoms C:C:O lie in a straight line. The vapour of propaldehyde shows discontinuous absorption. Chloral, on the other hand, shows two regions of continuous absorption. A new triple absorption band at 2060 Å. has been found in the absorption spectrum of carbon monoxide.

R. CUTHILL.

Band spectra of carbon monoxide in the electrodeless discharge. G. HERZBERG (Z. Physik, 1929, 52, 815—845).—Following a description of the various forms and colours which characterise the electrodeless discharge in carbon monoxide, the spectroscopic data are discussed in detail, and it is shown that the distribution of intensity in the various band systems is very similar to that observed in the case of nitrogen. The data are thought to indicate that the dissociation of CO⁺ takes place thus: CO⁺ = C⁺ + O. A similar mechanism appears to hold for the dissociation of CN. R. W. LUNT.

Life period of excited molecules in aqueous fluorescing solutions. S. I. VAVILOV (Z. Physik, 1929, 53, 665—674).—The extinction of fluorescence by the addition of foreign substances is examined. The theory of extinction due to collisions of the second kind is applied to the observations of Jette and West (this vol., 8) on the extinction of fluorescence in various solutions by addition of potassium iodide. The effect of temperature on the extinction phenomena is investigated. Results agree with the theory. The mean value for the life period is in agreement with the

direct value obtained by Gaviola (A., 1927, 712). The life period is independent of the exciting wavelength. The polarisation of fluorescence also gives a method of determining the life period. The depolarisation of fluorescence with decreasing exciting wavelength is discussed. A. J. MEE.

Intensity measurements of molecular rays in gases. F. KNAUER and O. STERN (Z. Physik, 1929, 53, 766—778).—The stream of molecules passes through an opening into an otherwise closed vessel, setting up a pressure therein which is measured by means of a hot-wire manometer. W. E. DOWNEY.

Reflexion of molecular rays. F. KNAUER and O. STERN (Z. Physik, 1929, 53, 779—791).—Molecular streams from hydrogen and helium are reflected from highly-polished surfaces on which they fall at grazing incidence. The power of reflexion is in accordance with the de Broglie wave theory. W. E. DOWNEY.

New phenomenon of diffusion: Raman effect. A. CARRELLI (Atti R. Accad. Lincei, 1929, [vi], 9, 165—169).—Mathematical. The Raman effect is discussed on the basis of the dispersion formula derived from the Schrödinger wave theory. The ratio of the intensities of the two radiations of frequency $\nu + \nu_R$ and $\nu - \nu_R$ is calculated, and is shown to be of the right order of magnitude. The degree of depolarisation of the Raman light is calculated and compared with that of the Tyndall light. The intensity of the Raman light is directly proportional to the fourth power of the frequency emitted, but depends also on certain factors, which are characteristic for each line in the dispersion formula of the substance considered. O. J. WALKER.

Difference between the absorption and the Raman spectrum. G. H. DIEKE (Nature, 1929, 123, 564).—The fact that some Raman lines do not correspond with infra-red absorption frequencies supports the validity of Kramers' theory of dispersion (cf. Langer, this vol., 379). A. A. ELDRIDGE.

Raman effect in some organic liquids. S. VENKATESWARAN (Phil. Mag., 1929, [vii], 7, 597—600).—The Raman spectra of acetic, butyric, and propionic acids have been determined and the results employed in the calculation of the characteristic infra-red frequencies of the acids. The values so obtained for acetic and butyric acids agree closely with those obtained by Coblenz and Weniger. In addition to the Raman lines, the spectrum of light scattering in the three acids shows a continuous spectrum the intensity of which is approximately the same in acetic and propionic acids, but is greater in butyric acid. This greater intensity is attributed to the greater viscosity of butyric acid. A. E. MITCHELL.

Raman effect and fluorescence. P. DAS (Nature, 1929, 123, 607).—A relation is revealed by probability considerations. A. A. ELDRIDGE.

Line absorption spectra in solids at low temperatures in the visible and ultra-violet regions of the spectrum. S. FREED and F. H. SPEDDING (Nature, 1929, 123, 525—526).—The absorption spectra of gadolinium, samarium, and erbium chloride hexahydrates from the ordinary temperature to that of liquid hydrogen have been studied. At the ordinary

temperature the entire spectrum (about 60 lines) of gadolinium was in the ultra-violet extending to about 2350 Å.; on lowering the temperature new faint lines appeared in the visible portion and most of the original lines shifted slightly towards the red. Many of the closely-spaced lines appear to have originated by the splitting up of a "normal" energy level because of the influence of the electrostatic fields of the neighbours of the gadolinium ions, principally water molecules. With samarium, the spectrum consisted of diffuse lines and bands chiefly between 3000 and 5000 Å.; on lowering the temperature the lines sharpened and the bands became narrower, some lines disappeared and others appeared. The samarium ion in the solid state is a mixture of electronic isomerides. With erbium, the spectrum at the ordinary temperature consisted of very diffuse bands, the bands being resolved into lines at low temperatures. The structure of the groups of lines suggested the multiplets of gaseous atoms under the influence of external fields. Few lines were found below 3000 Å. A. A. ELDRIDGE.

Origin of the ultra-violet beryllium hydride band spectrum. E. BENGTSOON (Nature, 1929, 123, 529).—The two band systems of the beryllium arc in hydrogen are emitted by two different molecules. The ionised BeH^+ molecule is the only possible origin of the ultra-violet bands. A. A. ELDRIDGE.

Spectral absorption of monoazo-dyes. I. Effect of position isomerism on the spectral absorption of methyl derivatives of benzene-azophenol. W. R. BRODE (Bur. Stand. J. Res., 1929, 2, 501—540; cf. A., 1926, 884).—Solutions of azobenzene, benzeneazophenol, and the mono- and di-methyl derivatives of benzeneazophenol in alcohol, aqueous hydrochloric acid, and aqueous sodium hydroxide were examined. The differences found in the spectral absorption of alcohol solutions or of hydrochloric acid solutions of the position isomerides studied were small. Marked differences were found in the absorption of 3% aqueous sodium hydroxide solutions. W. E. DOWNEY.

Magnetic susceptibilities of several organic gases. F. BITTER (Physical Rev., 1929, [ii], 33, 389—397).—Using an improved method in which the investigated gas was diluted with hydrogen and the concentration determined for which the volume susceptibility of the mixture was equal to that of nitrogen, the following results given in molecular susceptibility $\times 10^6$ were obtained: methane —12.2; ethane —27.3; propane —40.5, butane —57.4, isobutane —56.3, ethylene —12.0, acetylene —12.5, using as standards hydrogen —3.94 and nitrogen —11.8. It is shown that the results cannot be reconciled with the assumption that the susceptibilities of the constituent atoms are additive. It is suggested that the susceptibilities of the substances are determined by the binding electrons. N. M. BLIGH.

Electrical dipole moment of pentaerythritol by the method of molecular rays. J. ESTERMANN (Z. physikal. Chem., 1929, B, 2, 287—288).—By measurement of the deviation of a molecular ray in a non-homogeneous electric field, the free molecules of

pentaerythritol have been shown to possess a dipole moment estimated at about 2×10^{-18} c.g.s. unit (cf. A., 1928, 1309).

R. CUTHILL.

Magnetic moment of lithium. J. B. TAYLOR (Z. Physik, 1929, 52, 846—852).—The magnetic moment of lithium has been determined by the molecular streaming method; the value found is of the order of one third of a Bohr magneton.

R. W. LUNT.

Electric polarisation in insulators. E. BRODY (Z. Physik, 1929, 52, 884—889).—A mathematical analysis shows that the application of an accelerating field to an insulator containing ions of widely differing mobilities will produce an electric moment in the material. The possibility of experimentally investigating the matter is discussed.

R. W. LUNT.

Chemical phenomena connected with the contraction of hydrogen in discharge tubes. R. DELAPLACE (Compt. rend., 1929, 188, 708—710).—The observed contraction in volume of hydrogen and the appearance of carbon monoxide and methane (A., 1928, 933) are not due to gases contained in the aluminium electrodes or to the state of the walls of the discharge tube, but may be explained partly by the oxidation of adsorbed mercury vapour which is subsequently reduced by the hydrogen, and by the fact that Pyrex glass emits small quantities of hydrogen, oxides of carbon, and methane after bombardment by cathode rays. Oxygen would thus be available from dissociation of the carbon dioxide.

J. GRANT.

Magnetic rotatory power in an anisotropic medium. R. DE MALLEMANN (Compt. rend., 1929, 188, 863—865).—The molecular theory of magnetic rotation in a homogeneous medium is analogous to that of the natural rotation (this vol., 495). The normal magnetic rotatory power is therefore defined by the projection of the rotation vector on the normal to the wave, and its anisotropy is a result of the refringence anisotropy of the electrons, atoms, or molecules. The ratios of the three principal rotations are a function of the intramolecular birefringence.

J. GRANT.

Super-dispersion. T. TAKEUCHI (Z. Physik, 1929, 53, 148—150).

Microscopic images. C. LAKEMAN and J. T. GROOSMULLER (Z. Physik, 1929, 53, 628—638).—An arrangement of apparatus is described by means of which it is possible to project on a screen images of microscopic objects. A parallel beam of light is diffracted by the object, and the spectra of the various orders are later recombined. The working of the apparatus with different kinds of illumination and structures of different sizes is shown.

A. J. MEE.

Molecular refraction and number of molecules in unit volume. W. HERTZ (Z. anorg. Chem., 1929, 179, 211—214).—The product of the molecular refraction and the number of molecules per unit volume at the b. p. has an approximately constant value, viz., $1.2-2 \times 10^{23}$, for all substances except a few elements of very low b. p. The value holds more closely for groups of analogously constituted substances.

H. F. GILLBE.

Modification of Baeyer's strain theory. E. E. AYLING (Chem. News, 1929, 138, 164—165).—Short's expression for the tertiary carbon atom (cf. A., 1926, 1028) is shown to be identical with one of the equations derived by Ingold, whilst the expression for the secondary carbon atom yields results identical with those obtained from Ingold's expression. The differences between the results of Short and Ingold arise from the use of different atomic volumes. The use of Le Bas' atomic volumes in place of Traube's in calculating valency angles is suggested, and Ingold's expressions are preferred, since in this way uniformity can be preserved with the case of a carbon atom included in a polymethylene ring.

R. A. MORTON.

Quantum mechanical theory of the natural optical activity of liquids and gases. L. ROSENFELD (Z. Physik, 1928, 52, 161—174).—Mathematical.

G. E. WENTWORTH.

Boric acids. L. F. GILBERT and (Miss) M. LEVI (J.C.S., 1929, 527—535).—From vapour-pressure measurements evidence is brought forward to show that eight boric acids exist, $n\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$, where $n = 1-8$. The heat of hydration of boric oxide to ortho-boric acid is approx. 54,363 g.-cal.

F. J. WILKINS.

Surface energy and the orientation of molecules in surfaces as revealed by surface energy relations. W. D. HARKINS [with B. GINSBERG, R. W. WAMPLER, T. F. YOUNG, J. W. MORGAN, and N. BEEMAN] (Z. physikal. Chem., 1928, 139, 647—691).—A summary. The principle that the molecules in a surface are always oriented so that the change from one phase to the next is as continuous as possible is treated from the thermodynamical aspect. Application of the second law leads to the general entropy principle that in a one-component system the average molecular kinetic energy which is converted into molecular potential energy, when molecules move from one region to another, depends merely on the change of state. From consideration of the evidence for the orientation of molecules in the surface of a pure liquid, with respect to molecular symmetry and evaporation, it is stated, given complete orientation, that the value of e/j (e —mean total surface energy per molecule, j —energy of thermal emission) should be a criterion of symmetry of the molecule, and hence of the orientation. Evidence is also adduced for orientation from the energy of adhesion as related to the energy of cohesion. Films, the spreading of liquids and the spreading coefficient, the surface film on an aqueous solution of an organic substance, the thickness of water films on salt solutions, and the stabilisation of emulsions by unimolecular soap films are also discussed.

G. E. WENTWORTH.

Chemical combination as an electrostatic phenomenon. IV. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 182—184).—The measurements of the distances between the oppositely-charged ions in the alkali halide salts are arranged to show that these distances are additive properties of the ions, as would be expected if atoms and ions could be regarded as hard balls. Differences in volatility of similar compounds of elements of increasing at. wt. in a family of the periodic table are ascribed to the degree to which the central atom (e.g., boron or

aluminium in the fluorides) is enveloped by the surrounding atoms, which is regarded as determined by the relative sizes of the atoms. Other properties are considered similarly.

S. I. LEVY.

Electron exchange and the formation of molecules. W. HEITLER (Nachr. Ges. Wiss. Gottingen, 1927, 368—374; Chem. Zentr., 1928, ii, 1523).—A preliminary discussion of the statistics whereby the stationary state of an electronic system arises.

A. A. ELDRIDGE.

Constitution of boron hydrides. E. WIBERG (Helv. Chim. Acta, 1929, 12, 225—227).—The fact that pentaborane can take up four molecules of ammonia is difficult to explain by means of Ephraim's structure for the boron hydrides (cf. this vol., 123), but is readily accounted for by means of the author's more unsymmetrical formula (A., 1928, 936).

O. J. WALKER.

Capillary-tube method for the simultaneous determination of surface tension and density. A. FERGUSON and J. A. HAKES (Proc. Physical Soc., 1929, 41, 214—223).—An apparatus is described for measuring the surface tension of liquids by forcing the meniscus down to the end of a capillary immersed in the liquid. By varying the depth of immersion the density of the liquid can also be measured. It is shown how the results should be calculated from the shape of the meniscus.

J. L. BUCHAN.

Surface tension. A. W. PORTER (Phil. Mag., 1929, [vii], 7, 624—630).—The validity of the assumptions of Rayleigh (Proc. Roy. Soc., 1915, A, 92, 184) in his treatment of the rise of liquids in a capillary tube has been established from an analysis of the curvature of the vertex of the liquid. The weights of liquid drops from tubes of various diameters have been examined and it is concluded that the viscosity of the liquid has little influence on the weight. The problem of vanishing of surface tension close to the critical point has been examined and it is shown that if it be recognised that the molecules cannot approach nearer to one another than their diameter it is not necessary to accept Laplace's deduction that vanishing of the surface tension can take place only when the densities of the two phases are the same. This result is offered in confirmation of the observations of Callendar (A., 1928, 1179) on the vanishing of the surface tension of water at a temperature 6° below the critical.

A. E. MITCHELL.

"Resistance" limits, peaks in conductivity curves, and X-ray interferences in metallic mixed crystals. G. TAMMANN (Ann. Physik, 1929, [v], 1, 309—317, 321—322).—The existence of sharp "resistance" limits to the action of reagents on metallic mixed crystals is re-affirmed. Good agreement obtains between the results of X-ray spectroscopy and chemical reactivity in mixed-crystal series as well as in systems showing compound formation. "Resistance" limits and peaks in the conductivity curves are not related phenomena, the latter possessing neither precise physical significance nor certain value as a test for compound formation. The criticism of the author's theory (A., 1919, ii, 398, 406) by Le Blanc, Richter, and Schiebold (A., 1928, 1082) based

on the copper-gold mixed crystals is refuted and the data are stated to show no essential discrepancy with either the work of Tammann or the interpretation,

R. A. MORTON.

"Resistance" limits, peaks in conductivity curves, and X-ray interferences in metallic mixed crystals. M. LE BLANC, K. RICHTER, and E. SCHIEBOLD (Ann. Physik, 1929, [v], 1, 318—320).—A reply to Tammann (cf. preceding abstract).

R. A. MORTON.

Fine structure of the K-edge. V. DOLEJSEK and K. PESTRECOV (Z. Physik, 1929, 53, 566—573).—The limit of the K-series for the free elements in the first halves of the short periods of the periodic system has been investigated, thus completing earlier values. The frequency values for all such elements are in agreement with the equation $\nu/R = a + bN + cN^2 + dN^3 + eN^4$. The difference between the observed and calculated values of ν/R , when plotted against the atomic number, N , shows periodic fluctuations.

A. J. MEE.

Character of interference lines in X-ray diagrams of highly crystalline material. II. H. MOLLER and A. REIS (Z. physikal. Chem., 1929, B, 2, 317—339; cf. this vol., 246).—The relation of the effective width of the focus of the primary radiation and the variation of intensity across it to the character of the lines obtained in the Debye-Scherrer method of X-ray investigation, using non-parallel radiation, has been examined theoretically. The various arrangements to secure sharpness and accuracy are described.

R. CUTHILL.

Origin of soft X-rays with the lighter elements. B. B. RAY and R. C. MAZUMDAR (Z. Physik, 1929, 53, 646—657).—On the assumption that an atom loses two electrons from the same or different energy levels, it is possible that besides the ordinary types of radiation a new one occurs, which is caused by the simultaneous switch of both electrons. The frequency of the radiation emitted is equal to the sum of the frequencies of the single switches. Both electrons can thus combine to give monochromatic radiation. This assumption of simultaneous switch can be applied to a large number of unexplained experimental determinations of critical potentials. The existence of critical potentials for the excitation of X-rays in the range 40—200 volts for the elements iron, cobalt, nickel, and copper is thus explained. It is shown that the critical potentials of manganese and chromium can be treated in the same way.

A. J. MEE.

Polarisation from the Compton effect. P. LUKERSKY (Z. Physik, 1929, 53, 792—804).—Examination of the distribution of the directions of the scattered secondary rays shows that the emission is polarised.

W. E. DOWNEY.

Fine structure of absorption edges in metals. B. B. RAY and P. C. MAHANTI (Nature, 1929, 123, 528—529).—The non-appearance of fine structure edges when metallic plates or crystals (powder) are used as absorption screens can be explained on the hypothesis of the existence of free electrons in metals.

A. A. ELDRIDGE.

Diffraction of X-rays by a two-dimensional crystal lattice. W. LINNICK (Nature, 1929, 123,

604–605).—When mica is cleft into thin layers by heating and cooling, and a thin beam of X-rays is passed through the plate, a system of spectra corresponding with a series of two-dimensional lattices is obtained. The spectra obtained accord with the assumption that the molecules are distributed at the summits of equilateral triangles of side 5.2 Å. More diffuse photographs are obtainable with gypsum and Iceland spar.

A. A. ELDRIDGE.

Photographic measurement of the relative intensities of the La_1 , α_1 , α_2 lines of silver. H. C. WEBSTER (Proc. Physical Soc. 1929, 41, 181–191).—The crystal was rocked so that the reflexion angles of the three lines La_1 , α_2 , α_3 were covered by its sweep. The exposure was taken on a standard film which was developed under specified conditions and the lines were measured on a Moll type micro-photometer. The interpretation of the curves so obtained is discussed, and it is shown that D , the density of the part of the film under consideration, is a function of Nt , where N is the number of quanta absorbed per second by the emulsion and t is the time of exposure. The relative intensities of the lines are $La_1 : La_2 : La_3 :: 100 : 12 : 4.6$ to 7.3, it being found that the intensity of La_3 varies with the tube voltage. The ratio $La_1 : L\beta_1$ has also been determined and found to be 100 : 40.

J. L. BUCHAN.

Spark satellites of the $L\alpha$ lines of silver. H. C. WEBSTER (Proc. Physical Soc., 1929, 41, 192–193; cf. preceding abstract).—Spark satellites have been observed on the hard side of La_1 . Their wavelengths were found to be $a_2' = 4134.7$ X, a_1' (or a_3)—4130.5 X, $a_2'' = 4125.6$ X, and a_1'' (or a_4)—4119.0 X, whilst the decreasing order of intensities of the lines is a_1' , a_1'' , a_2'' , a_2' .

J. L. BUCHAN.

Precision measurements of X-ray reflexions from crystal powders. Lattice constants of zinc carbonate, manganese carbonate, and cadmium oxide. J. BRENTANO and J. ADAMSON (Phil. Mag., 1929, [vii], 7, 507–517).—Exact determinations of the spacing and of the rhombohedral angle of zinc carbonate and of manganese carbonate have been derived from X-ray measurements on the crystal powders mixed with cadmium oxide as a reference substance. The rhombohedral angle of zinc carbonate is found to be $103^\circ 27'$, in agreement with the usually accepted value of $103^\circ 28'$ of Rose (Pogg. Ann., 1852, 85, 132). The value of the d_{100} spacing is 5.493 ± 0.005 Å., as compared with 5.44 Å. obtained by Levi and Ferrari (A., 1924, ii, 760). These values lead to $a = 5.928 \pm 0.005$ Å., and $v = 1.877 \pm 0.015 \times 10^{-22}$ cm.³, whence $d = 4.406$ as compared with $d = 4.51$ obtained by Levi and Ferrari. For manganese carbonate $\alpha = 102^\circ 50'$, in agreement with $\alpha = 102^\circ 50.3'$ obtained from goniometric measurements, $d_{100} = 5.666 \pm 0.005$ Å., $a = 6.064 \pm 0.005$ Å., and $v = 2.039 \pm 0.015 \times 10^{-22}$ cm.³, whence $d = 3.747$. These values are used in conjunction with the analogous measurements of Brentano and Dawson (A., 1927, 297) on magnesium carbonate to verify calculated lattice constants of the isomorphous carbonate series. When the values are combined with a fixed parameter for the CO_3 group the results are in good approximation to the observed, but are not quite in agreement.

It is thus concluded that terms characteristic of the various elements must be included.

A. E. MITCHELL.

Distribution of charge in the chlorine ion in rock salt. G. W. BRINDLEY and R. G. WOOD (Phil. Mag., 1929, [vii], 7, 616–623).—It is pointed out that the experimental and theoretical values of the X-ray scattering factor for the chlorine ion differ by an amount greater than that which can be attributed to experimental error, for values of $(\sin \theta)/\lambda$ of the order 0.4–0.5. It is assumed that this difference is due to a change in the radial distribution of the charge on the ion. The difference between the charge distribution in a free chlorine ion, as determined by Hartree and others (A., 1928, 462), and in a chlorine ion in a rock-salt lattice has been calculated from a Fourier analysis of the difference between the experimental and theoretical scattering factors and the result have been employed to determine the charge distribution in a chlorine ion in rock salt.

A. E. MITCHELL.

Crystal structure of trimethylethylammonium chlorostannate. R. W. G. WYCKOFF and R. B. COREY (Amer. J. Sci., 1929, [v], 17, 239–244).—Trimethylethylammonium chlorostannate, $(NMe_3Et)_2SnCl_6$, has a cubic structure, the length of a unit cube being 13.17 Å. Its density is 1.487. The size, shape, and distribution of the chlorostannate groups are the same as in analogous compounds. The resulting structure resembles that of calcium fluoride.

C. W. GIBBY.

Crystalline structure, lattice constants, and density of rhenium. V. M. GOLDSCHMIDT (Z. physikal. Chem., 1929, B, 2, 244–252).—See this vol., 382.

A. J. MEE.

[X-Ray] structure of crystalline uraninite from Katanga (Belgian Congo). A. HADDING and R. VAN AUBEL (Compt. rend., 1929, 188, 716–717). Katanga uraninite, which is the primary mineral from which the cryptocrystalline pitchblende of the district is derived, has been shown by Debye's method to have the structure of a face-centred cube of side 4.67 Å. The spectral data are tabulated.

J. GRANT.

Translation lattice of cellulose hydrate. K. WEISSENBERG (Naturwiss., 1929, 17, 181).—By means of an improved focussing method sharp X-ray interferences can be obtained with cellulose, cellulose hydrate, and natural silk. The structure hitherto ascribed to the hydrate is probably erroneous. The following dimensions are given: $a = 14.66$, $b = 8.89$, $c = 10.35$ (all $\pm 2\%$), $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 85^\circ \pm 5^\circ$. The cell contains eight $C_6H_{10}O_5$ groups (d 1.60), whereas the earlier view was in favour of four such groups, d 1.46. Natural cellulose appears to have a structure very similar to that suggested for the hydrate.

R. A. MORTON.

Domain of the atom of bismuth in its crystal. H. PERLITZ (Scientists Soc. Tartu, 1928, 35, 113–120).—Theoretical. In crystalline bismuth every atom has six neighbours in two triplets. The decrease of volume at fusion suggests that the domains of atoms cannot intersect. From the distribution of the shared electrons it is inferred that the electrons of the outer completed shell, consisting of two sub-shells, occur in pairs, and that diameters of the inner and

outer sub-shells are equal to the shorter and longer inter-atomic distances and form the boundaries of Bi^+ and Bi^{--} , respectively. A distribution of electrons of the outer shell in vertices of two regular tetrahedra is indicated. The observed and calculated rise of conductivity at fusion are in good agreement, assuming that the non-shared electrons in the crystal carry the electric current, and that the shared electrons are liberated on melting. N. M. BLYTH.

Structure of artificial ultramarines. IV. Ultramarines of thallium, and the analogous derivatives of the bivalent metals calcium, strontium, barium, zinc, manganese, and lead. F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 156—166; cf. A., 1928, 463).—Thallium, calcium, strontium, barium, zinc, manganese, and lead were substituted for sodium in Guimet's blue, $\text{Na}_6\text{Al}_3\text{Si}_6\text{O}_{13}\text{S}_3$. The substitution of the sodium (or silver in silver ultramarine) by the bivalent metals took place easily and completely. The method used was to heat the silver ultramarine with five times the theoretical quantity of the iodide of the substituting metal and a little water in sealed tubes for 50 hrs. at 160° . In the case of calcium, strontium, and barium, pure olive-green calcium-, strontium-, and barium-silver ultramarines of the formula $\text{R}^{\text{II}}\text{Ag}_4\text{Al}_6\text{Si}_6\text{O}_{28}\text{S}_3$ were formed. By melting with the iodides of the metals colourless ultramarines were produced. X-Ray powder spectrograms of all the ultramarines showed the original characteristics of the ultramarines. Although the original character of the ultramarine spectrogram is preserved, the relative intensities of the images are different from those of ordinary ultramarines. Various other ultramarines were prepared and their structure was investigated. A lead-sodium compound, rich in silicon, was prepared by heating Guimet's blue in sealed tubes at 160° for 50 hrs. with five times the theoretical quantity of lead nitrate, and data of its spectrogram are given. By heating silver ultramarine with lead chloride a lead-silver ultramarine was obtained, dark grey in colour. Attempts were made to prepare mercurous and mercuric ultramarines from Guimet's blue by methods similar to the above. The compounds formed, however, were not true ultramarines and the powder spectrogram did not correspond with cubic symmetry. A. J. MEE.

Structure of artificial ultramarines. V. Absorption phenomena with ultramarine, and the structure of nosean, hauyne, and the ultramarines. F. M. JAEGER and F. A. VAN MELLE (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 167—181; cf. preceding abstract).—The progress of the reaction between silver ultramarine and alkali halides used in the preparation of ultramarines is studied. It was found that the substitution took place more rapidly during the early part of the reaction and the more concentrated the reactants. The occurrence of adsorption phenomena is indicated. The structure of nosean and the ultramarines is deduced. The reason why all the ultramarines give inconstant results on analysis appears to be due to a mixture of isomorphous substances. This also explains the identity of the X-ray spectrograms. A. J. MEE.

X-Ray study of the system palladium-hydrogen. J. D. HANAWALT (Physical Rev., 1929, [ii], 33, 444—453).—An X-ray study of the lattice parameter of palladium as influenced by hydrogen occluded by electrolysis, from the gas phase, and by sputtering in hydrogen showed, in the first two cases, a unique value $a_0 = 4.017$ stable up to 80° , and associated with the concentration Pd_2H . The effect of the hydrogen on the L_{111} absorption limit of palladium is to cause a shift of the main edge and the occurrence of a secondary absorption towards shorter wave-lengths, suggesting the combination PdH . Impurities in the palladium showed a marked effect on the occlusion of hydrogen. N. M. BLYTH.

Electronic analysis; structure of oxides of magnesium, zinc, and cadmium. Louis de Broglie's law. M. PONTE (Compt. rend., 1929, 188, 909—910).—It is shown that electronic analysis by the author's method (this vol., 367), using electron speeds equivalent to 16670—10870 volts, may be applied to the oxides mentioned with the same degree of accuracy as Bragg's method. The structure of zinc oxide is obtained from de Broglie's law with an accuracy of 1%. J. GRANT.

Changes in the crystalline form of sodium nitrate in accordance with the composition of the solution from which it separates. P. P. ORLOV (Bull. Acad. Sci. U.R.S.S., 1928, 529—548).—Sodium nitrate crystallised from water in presence of acid amides, e.g., formamide, or hydroxy-acids, e.g., lactic acid, α -hydroxyisobutyric acid, glycollic acid, glyceric acid, or if crystallised from concentrated solutions of chromic nitrate changes its usual rhombohedral form. A. FREIMAN.

X-Ray investigation of the structure of hardened carbon steels. G. KURDJUMOW and E. KAMINSKY (Z. Physik, 1929, 53, 696—707).—The effect of carbon content on the value of the ratio of the axes and the parameter in the tetragonal lattice in carbon steels is investigated. The tetragonal lattice was found, by careful polishing, to exist throughout the steel, and not only on the surface as has been previously stated. The ratio of the axes increases linearly with the carbon content; the parameter c increases with the carbon content, whilst the parameter a decreases somewhat. Austenite was found in all the types of steel dealt with; its quantity increased with increasing carbon content. The asymmetry of the tetragonal structure is one of the causes of the indefiniteness of the lines in the diagram. Tempering at 100° changes the tetragonal structure to cubic. A. J. MEE.

X-Ray structure and magnetic properties of single crystals of Heusler alloy. H. H. POTTER (Proc. Physical Soc., 1929, 41, 135—142).—Using the single-crystal rotation method, Heusler alloy has been found to crystallise as a body-centred cube with lattice constant 2.95 \AA . The aluminium atoms are distributed so as to lie on a face-centred cube of lattice constant 5.9 \AA . Directional magnetic properties are found to be identical with those of nickel, which has a face-centred cubic structure. It is suggested that this may be interpreted as indicating that the manganese atoms (the positions of which cannot

be determined by X-ray analysis) also lie in a face-centred cubic lattice.

W. E. DOWNEY.

Structural relationships of rhodonite to other silicates. B. GOSSNER and K. BRÜCKL (Zentr. Min. Geol., 1928, A, 316—322; Chem. Zentr., 1928, ii, 1756).—The constants of the triclinic unit cell of rhodonite are a 7.77, b 12.45, c 6.74 Å., α 85° 10', β 94° 4', γ 111° 29', whence the axial ratios are $a:b:c=0.624:1:0.541$. The units of the cell are very similar to those of babingtonite and anorthite, whilst the angles are interchanged. The unit cell contains 2 mols. of $\text{MnSiO}_3 \cdot \text{Mn}_3\text{CaSi}_4\text{O}_{12}$.

A. A. ELDRIDGE.

Spiral markings on carborundum crystals. W. HUGHES (Nature, 1929, 123, 603—604).—When a film of molten sulphur on clean glass cools, centres of crystallisation appear, and rings grow outwards in succession from these points. When the logarithm of the number of rings counted from a centre is plotted against the logarithm of the distance of the rings, a straight line is obtained. The formation of the rings is ascribed to the evolution of latent heat on crystallisation diminishing the surface tension of the surrounding sulphur, which is then drawn outwards to form a circular ridge, this quickly crystallising and continuing the effect. The rings observed on carborundum crystals by Menzies and Sloat (this vol., 381) also give straight lines when the above data are plotted, and may have a similar origin. No particular significance is ascribed to the spiral nature of the markings.

A. A. ELDRIDGE.

Crystal structure of *n*-butyl-, amyl-, hexyl-, and heptyl-ammonium halides. S. B. HENDRICKS (Z. Krist., 1928, 68, 189—203; Chem. Zentr., 1928, ii, 1858).—The structures of the above compounds are similar to that of methylammonium iodide. The space-group is $4D-2$, $4d-3$, $4Di-7$, $4c-1$, $4e-1$, or $4C-1$. Measurements of the dimensions of the unit cell are recorded.

A. A. ELDRIDGE.

Artificial preparation of diamonds. L. SESTA (Phil. Mag., 1929, [vii], 7, 488—493).—In reply to a statement that no one has yet succeeded in producing diamonds in the laboratory and that all who have made this claim have been deceived by mistaking crystals of spinel for diamonds, reference is made to the work of La Rosa (A., 1909, ii, 311, 399) and of the author (Trans. Faraday Soc., 1910, 5). Experimental evidence is produced to show that the author has produced diamonds and that from the nature of the method employed there was no chance of the formation of spinel, as was possible in the original method of Moissan.

A. E. MITCHELL.

Theory of ferromagnetic crystals. G. S. MAHAJANI (Phil. Trans., 1929, A, 228, 63—114).—Mathematical. An atomistic theory of ferromagnetism is developed for two types of crystal—iron and pyrrhotite. The results of Webster (A., 1925, ii, 369) are accounted for qualitatively and quantitatively.

C. W. GIBBY.

Method for measuring Joule magneto-strictive effect in a cold-drawn wire. J. H. HANDLEY (J. Sci. Instr., 1929, 6, 84—88).

K K

Effect of tension and a longitudinal magnetic field on the thermo-electromotive forces in permalloy. A. W. SMITH and J. DILLINGER (Physical Rev., 1929, [ii], 33, 398—402).—The specimens consisted of wires containing 78, 81, and 84% of nickel, the remainder being iron. The effect of tension on the change of thermo-electromotive force produced by a longitudinal magnetic field was, for the three specimens, respectively, to decrease the maximum value, relatively no effect, and a decrease for low, but an increase for higher magnetic fields. In each case there is relatively no effect for tensions beyond about 10 kg./mm.² In all cases the magnetic field produces a decrease in the thermo-electromotive force.

N. M. BLIGH.

Electrical conductivity of carborundum. H. J. SEEMANN (Physikal. Z., 1929, 30, 143—144).—Measurement of the electrical conductivity for six samples of carborundum at 17° and —80° shows that the ratio at these temperatures varies between 4 and 6. No relationship emerges from the presence of impurities. The nature of the conductivity of carborundum is discussed. The specific conductivity is of the order obtained with solid electrolytes, but it is considered that carborundum should be regarded as a half-conductor in the sense of Königsberger's theory.

R. A. MORTON.

Magnetic behaviour of organic crystals. C. V. RAMAN [with S. BHAGAVANTAM] (Nature, 1929, 123, 605).—The diamagnetic anisotropy of naphthalene is very pronounced (cf. Bragg, Nature, Suppl., May 7, 1927), the susceptibilities along the three magnetic axes of the crystal having the approximate ratio 16:7:4. The axes of maximum diamagnetic susceptibility and of minimum optical dielectric constant are approximately coincident. The observation explains why aromatic liquids exhibit a strong positive magnetic birefringence. In crystals of aliphatic compounds the anisotropy is less pronounced and the relation between the magnetic and optical characters is more varied; in iodoform the axes are parallel, whilst in carbamide they are crossed.

A. A. ELDRIDGE.

Apparent Mie effect and atmospheric optics. G. I. POKROWSKI (Z. Physik, 1929, 53, 67—71).

Theory of optical activity in a homogeneous medium. R. DE MALLEMANN (Compt. rend., 1929, 188, 705—707).—A mathematical interpretation of the role of the "rotation vector" involved in the author's general molecular theory of optical activity (this vol., 13). It is concluded that both the variation of rotatory power and its change of sign are perfectly continuous.

J. GRANT.

Reflecting power of beryllium, chromium, and several other metals. W. W. COBLENTZ and R. STAIR (Bur. Stand. J. Res., 1929, 2, 343—354).—Curves are given for the ultra-violet reflecting power of beryllium, chromium, cobalt, nickel, silver, speculum, stellite, and stainless steel. For chromium and beryllium the observations extend into the infra-red. Unlike most metals, beryllium has a high reflectivity at 250 m μ in the ultra-violet, followed by a lower reflectivity with a minimum at 400 m μ in

the visible spectrum. Chromium has a higher reflectivity than nickel in the ultra-violet, and is conspicuous for its high maximum (70%) at 425 m μ , followed by a flat minimum extending from 600 to beyond 2000 m μ in the infra-red.

C. J. SMITHELLS.

Elastic constants of uniaxial aluminium and gold. E. GOENS (*Naturwiss.*, 1929, 17, 180).—The elasticity and torsion moduli, E and G , of uniaxial aluminium and gold have been determined at the ordinary temperature in relation to the crystal orientation. For aluminium, $E_{(111)}:E_{(100)}=1.18$ as against 2.7 for gold, whilst $G_{(111)}:G_{(100)}=1/1.13$ for aluminium and 1/2.2 for gold. The cubic compressibility of uniaxial aluminium is practically the same as that of the polycrystalline material. The results show gold to be markedly anisotropic in its elastic properties.

R. A. MORTON.

Flowing of metallic crystals under torsion. R. KARNOP and G. SACHS (*Z. Physik*, 1929, 53, 605—618).—Experiments were carried out with an aluminium-copper alloy (95% Al, 5% Cu). The force required to produce permanent set varies with the orientation of the crystal in the ratio 2.2:1 (cubic:octahedral). Assuming that there is a flowing surface layer the theoretical value 1.85:1 is obtained. An attempt is made to explain the effect of orientation on the basis of different slipping ratios for the different forms. The elastic limit of the crystals varies in the ratio 1.73:1. The effect of orientation on the elastic constants of the alloy is determined.

A. J. MEE.

Metastability of the elements as a result of enantiotropy or monotropy. XIII. The differential gas dilatometer of C. J. Smith and its accuracy. E. COHEN and H. L. BREDEE (*Z. physikal. Chem.*, 1929, 140, 199—222).—The accuracy of Smith's dilatometer (*A.*, 1927, 954) has been tested by determination of the density and coefficient of expansion of mercury. The error for the former is 0.02% and for the latter 0.05%. The transition temperature and volume change in the transition of α - to β -silver iodide have also been determined. The values found are in good agreement with those obtained by other methods (this vol., 22). This dilatometer is therefore considered to be specially suitable for the quantitative study of volume alteration in polymorphous changes.

R. N. KERR.

Change of volumes and electric resistances of antimony and arsenic at fusion. H. PERLITZ (*Scientists Soc. Tartu*, 1928, 35, 121—125).—Theoretical. Antimony having been proved to expand during solidification, the diameter of the spherical domain of its atom is calculated as 3.09, and from two crystal lattice data as 3.04 and 3.06 Å. The corresponding value for arsenic from its crystal lattice is 2.75 Å. From this value it is deduced that liquid arsenic should expand during solidification by 5.1%, and it is estimated that the electrical resistance at the m. p. of liquid arsenic is about 0.4 of that of the solid phase.

N. M. BLYTH.

Electrical resistances of some metals below the b. p. of oxygen. W. TRYS (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, 32, 115—123).—The

resistances of cadmium, crystalline copper, gold, indium, lead, platinum, thallium, tin, zinc, and a single crystal of tin were measured at temperatures from 1.40° (or the superconducting temperature) to 90° Abs. Tables of the resistances are given.

A. J. MEE.

Resistance-hysteresis phenomena of tin, lead, indium, and thallium at the temperature of liquid helium. W. J. DE HAAS and J. VOOGD (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, 32, 206—213).—To ascertain whether the hysteresis phenomena in the change of resistance appearing with the magnetic disturbance of the superconductivity of tin and mercury hold for other superconductors, indium, thallium, and lead were examined. The magnetic transition curve for tin corresponds completely with that for mercury. For the indium used the resistance disappeared with one jump, the curves not being rounded as in other cases. This may be due to the fact that the wire used consisted of a single crystal. It is shown that hysteresis phenomena appear in all superconducting metals, but best only when there are large crystals and the metal is in a homogeneous magnetic field.

A. J. MEE.

New superconductors. E. VAN AUBEL, W. J. DE HAAS, and J. VOOGD (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, 32, 218—225).—The resistances of compounds of two metals are investigated. The compounds used were Cu_3Sb , Ag_3Sb , Ag_3Sn , Cu_3Sn , Bi_5Ti_3 , Sb_2Sn , and Sb_2Sn_3 . The resistances were determined over the range 0° to -259°. A table showing the specific resistances at 0° is given. The resistances of Cu_3Sb , and Ag_3Sb depend little on temperature, and the resistance of all the compounds decreased less than that of their components. All the resistance curves show a point of inflexion, a phenomenon which is known to occur in some simple conductors. At the temperature of liquid helium it was found that Bi_5Ti_3 , Sb_2Sn , and Sb_2Sn_3 behave as superconductors. The rod of Bi_5Ti_3 actually became superconducting above the b. p. of helium, although its components themselves have much lower transition points. Cu_3Sn remained a non-superconductor even at the lowest temperatures used.

A. J. MEE.

Superconductivity of gallium. W. J. DE HAAS and J. VOOGD (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, 32, 214—217).—At the lowest temperatures used (1.1° Abs.) gallium did not become superconducting, but from the appearance of the temperature-resistance curves it may be presumed that at a temperature slightly lower than this it would become so. This phenomenon may be due to the presence of a trace of indium. Certain abnormal phenomena were noted. The fall of the resistance is abnormal. The resistance-temperature graph is very curved at low temperatures, the transition stage (should the metal become superconducting) extending over several degrees. With ordinary superconductors the transition stage occupies only a few hundredths of a degree. The resistances are very sensitive to current.

A. J. MEE.

Electron theory of metals. H. M. BARLOW (*Phil. Mag.*, 1929, [vii], 7, 459—470).—Experiments

designed to examine the assembly of free electrons in the interior of a conductor are described. The results show that these behave as a perfectly incompressible fluid and offer no confirmation of Sommerfeld's theory (*Z. Physik*, 1928, 57, 1, 43) of the persistence of an electron gas interpenetrating the atoms of a metal.

A. E. MITCHELL.

Simple method for determining C_p/C_v . E. RUCHARDT (*Physikal. Z.*, 1929, 30, 58—59).—Glass tubing is now available in which the circular cross-section is so accurate that a commercial steel ball used for precision work slides along the tube, maintaining the air-tight condition. If such a tube is inserted in a rubber stopper closing a 5- or 6-litre vessel, the ball undergoes vertical oscillations with a period of the order of 1 sec. The measurement of the period makes possible an instructive lecture experiment for the determination of C_p/C_v for the gas in the large vessel. The adiabatic elasticity of a gas is clearly demonstrated. The method has been applied to carbon dioxide and air.

R. A. MORTON.

Triple point of water as a fixed point on the temperature scale. H. MOSER (*Ann. Physik*, 1928, [v], 1, 341—360).—A thermostat is described which allows the temperature of the triple point of water to be established in a volume of about 10 c.c. and maintained for long periods. The precautions necessary for the greatest constancy in temperature are described, special attention being directed to the purity of the water. Refined experimental methods permit the measurement of very small temperature differences, and it is shown that the fluctuations in the thermostat over a period of several hours need not exceed $\pm 0.5 \times 10^{-4}$ degree. The lowering of the m. p. when air-free water is in contact with ice as a result of an increase in pressure from 0 to 1 atm. is $0.00748^\circ + 0.00005$, in agreement with the Clausius-Clapeyron equation. The temperature of the triple point, having regard to the depression of the normal m. p. of ice caused by water saturated with air, is therefore $+0.0098^\circ$. In consequence of the great constancy attainable at the triple point of water, it is suggested that for temperature measurements involving the highest accuracy the normal m. p. of ice should be replaced by the triple point as a fixed point on the temperature scale. The zero point should be re-defined as a temperature differing from the triple point by a numerical quantity (about 0.01°).

R. A. MORTON.

Limiting value of latent heat of vaporisation. J. E. VERSCHAFFELT (*Z. physikal. Chem.*, 1929, 140, 64).—Polemical against Kolosovski (cf. *ibid.*, 1928, 136, 314).

H. F. GILLBE.

Detection of the transformation of antisymmetrical to symmetrical hydrogen molecules. A. EUCKEN (*Naturwiss.*, 1929, 17, 182).—According to the wave-mechanics there are two forms of hydrogen characterised by symmetrical and antisymmetrical functions. At sufficiently low temperatures a gradual change in the relative proportions should occur and be detectable by means of specific heat determinations. The heat capacity of hydrogen in steel vessels at 50 atm. and at 106 — 149° Abs. has been

measured initially, after 6 days and after $12\frac{1}{2}$ days. The results are in agreement with the assumption that the molecular fraction (γ) of the hydrogen present as the antisymmetrical form changes from 0.750 to 0.689 and then to 0.636. If the limiting value of γ is about 1 at the temperature of liquid air, the change in γ with time should follow the equation $\log(4\gamma-2) = -kt$. This relation is in accord with experience.

R. A. MORTON.

Constitution of aromatic substances and their chemical and physical properties. VI. Crystalline symmetry. I. PASTAK (*J. Chim. phys.*, 1929, 26, 65—68; cf. A., 1925, ii, 759; 1926, 340).—The symmetry of the crystalline forms of aromatic organic substances can be related to the symmetry of the molecules as deduced from melting points and solubilities. For disubstituted benzene derivatives in which the substituents are either the same or belong to the same group, the sequence in which the symmetry varies is $m > o > p$. If the substituents belong to different groups the sequence is $o > m > p$. For diphenyl derivatives the crystalline symmetry of the *oo'*-isomeride is greater than that of the *pp'* and for the substituted naphthalenes that of the α - is greater than that of the β -isomeride.

R. N. KERR.

Fusion curve of helium. I. F. SIMON, M. RUHEMANN, and W. A. M. EDWARDS (*Z. physikal. Chem.*, 1929, B, 2, 340—344).—The fusion curve of helium has been followed from 12° to 20° Abs., corresponding with a range of pressure of 800—1800 kg./cm.². If p is the pressure and T the temperature, the results may be expressed by the equation $\log_{10} p = 1.5537 \log_{10} T + 1.233$ (cf. this vol., 386). Measurements of the latent heat of fusion indicate that there is no critical point crystalline-fluid near this temperature region.

R. CUTHILL.

Corrections to be applied to the platinum scale of temperature. F. E. HOARE (*J. Sci. Instr.*, 1929, 6, 99—102; cf. this vol., 385).—Using the equation $t - pt - d(t-100)t$, where t , pt , are respectively the temperatures on the centigrade and platinum scales, and $d = 1.50 \times 10^{-4}$, the corrections to be applied to the platinum scale between 0° and 1000° to convert into gas scale temperature have been tabulated.

F. G. TRYHORN.

Majorana thermal effect. A. L. T. MOESVELD (*Z. physikal. Chem.*, 1929, A, 140, 423—428).—A discussion of the temperature difference which was found by Majorana (*Atti R. Accad. Lincei*, 1926, [vi], 4, 419) to exist between two pieces of the same metal placed in a constant-temperature bath, when one of the pieces had previously been heated. It is considered improbable that this phenomenon is due to the heat developed by a gradual gas adsorption, and it is suggested that the temperature difference is due to the heat evolved during the slow attainment of equilibrium between metastable states in the piece of metal which has been previously heated. Evidence for this view is obtained from the work of Cohen on the metastability of elements and compounds.

O. J. WALKER.

B. p. in homologous series. B. NEKRASOV (*Z. physikal. Chem.*, 1929, 140, 342—354).—

The b. p. of a series of homologous compounds are considered as a function of two variables, viz., the mass and the volume of the molecules, and the empirical relationship $T\sqrt{MR}/(M-MR)-k$ is derived, which represents the b. p. (T) of such a series in terms of a constant k which is characteristic for each series and involves only the mol. wt., M , and the specific refractivity, R . According to the Clausius-Mosotti theory R is proportional to the actual volume of the molecules in unit mass of the substance. In the simplest case of the saturated hydrocarbons the introduction in the above equation of MR , the molecular refractivity as calculated from optical data in the usual way, gives a constant value of k . With polar compounds, however, for each polar group a certain empirical correction must be applied to MR in order to give a constant value for k , and the possible physical meaning of this correction is discussed.

O. J. WALKER.

Effect of intensive drying on certain physical properties of benzene. H. V. A. BRISCOE, J. B. PEEL, and P. L. ROBINSON (J.C.S., 1929, 368—377).—No material change was observed in the density and surface tension of benzene during drying for 16 months with phosphoric oxide. F. J. WILKINS.

Critical state. II. Limiting curve of ethyl ether. E. SCHROER (Z. physikal. Chem., 1929, 140, 241—253; cf. A., 1927, 1029).—The temperature-density curve of ethyl ether in the critical region has been determined by means of a new apparatus permitting observations for wide volume limits. Within the limits $d=0.23$ to $d=0.29$, change from the two-phase to the one-phase system is independent of the mean density. The following values are found: critical temperature= $193.4^\circ \pm 0.15^\circ$, critical pressure= $36.15 \text{ kg./cm.}^2 \pm 0.05$, critical density= $0.265 \text{ g./cm.}^3 \pm 0.004$. The influence of stirring and of adiabatic dilatation and compression on the critical opalescence has been studied; the effect is attributed to an emulsion of the two phases formed before the actual temperature of miscibility is reached. The nature of the temperature-density curve is explained by means of the critical isotherm. R. N. KERR.

Critical state. III. Behaviour of ethyl ether under isothermal compression in the critical and hypercritical region. E. SCHROER (Z. physikal. Chem., 1929, 140, 379—390; cf. preceding abstract).—Using the apparatus described in the previous paper, the isotherms of ethyl ether have been determined from 185° to 250° and 30 to 75 kg./cm.², and the following values of the critical temperature, pressure, and volume obtained: $t_c=194.6^\circ \pm 0.3^\circ$, $p_c=36.7 \pm 0.2 \text{ kg./cm.}^2$, $v_c=3.77 \pm 0.02 \text{ cm.}^3$. From the diagram of state the coefficient of compressibility (β) of ether is calculated. For each temperature β rises to a sharp maximum at a definite pressure. The maximum becomes flatter with rise of temperature, but is still observable at 250° , and its position alters only slightly with the temperature. An examination of the variation of β with volume shows that it can be represented qualitatively by van der Waals' equation.

O. J. WALKER.

Maxwell-Clausius and Clapeyron relations. V. KARPEN (Compt. rend., 1929, 188, 778—779).—

A generalisation of the author's previous deductions (this vol., 138) in which the Maxwell-Clausius relation is shown to be obtainable for any fluid, independently of Carnot's principle, by replacing the condition imposed by the latter by the condition of equilibrium between the liquid and the saturated vapour above it.

J. GRANT.

Equation of state for ethylene. L. J. GILLESPIE (J. Physical Chem., 1929, 33, 354—360).—Beattie and Bridgeman's equation of state (A., 1927, 819) has been applied to gaseous ethylene. The constants of the equation found from the data of Amagat are $A_0=6.152$, $a=0.04964$, $B_0=0.12156$, $b=0.03597$, and $c=22.68 \times 10^4$, when $T=273.13+t^\circ$ and $R=0.08206$. Amagat's data are well represented up to a density of 7 mol./litre, and fairly so up to 8, slightly above the critical density, the average deviations being 0.36 and 0.45%, respectively. The calculated normal density, 1.2599, supports the value of Batuecas (1.2604) as against that of Stahrfoos (1.2610).

L. S. THEOBALD.

F. p. of organic compounds. XI. Compounds with 5 and 6 carbon atoms. I. SIMON (Bull. Soc. chim. Belg., 1929, 38, 47—70).—Precise measurements of the f. p., b. p., densities at 0° , 15° , and 30° , viscosities at 15° and 30° , and refractive indices for the red, yellow, and violet helium lines, and the D , H_α , H_β , and H_γ lines have been made for a number of derivatives of *n*-amyl alcohol and *n*-hexoic acid. By interaction of potassium sulphide and the alkyl iodide in alcoholic solution, *n*-amyl sulphide, m. p. -51.3° , b. p. $230.1 \pm 0.05^\circ/760 \text{ mm.}$, has been prepared. The f. p. of ethyl hexoate is -67.5° . Using the new data to supplement existing figures, the relationships existing between the f. p. of the various members in homologous series have been examined.

R. CUTHILL.

Density, internal friction, dielectric constant, and solvent and ionising powers of hydrogen cyanide. K. FREDENHAGEN and J. DAHMLOS (Z. anorg. Chem., 1929, 179, 77—88).—The dielectric constant of hydrogen cyanide of specific conductivity $0.60 \times 10^{-6} \text{ ohm}^{-1}$ has been determined from -13.4° to $+22.1^\circ$. Considerable divergence from Bredig's figures is observed, especially at the lowest temperatures; the temperature coefficient decreases as the temperature rises. The viscosity from -7.5° to $+20.2^\circ$ has been determined, and is about 20% of that of water. Density measurements from -13° to 0° are in good agreement with those of other observers. A number of Kahlenberg and Schlundt's measurements of the solubilities and conductivities of inorganic salts in hydrogen cyanide have been confirmed, and the conclusion of these authors, that hydrogen cyanide, despite its abnormally high dielectric constant, has only a moderate solvent and ionising power, is supported.

H. F. GILLBE.

Metastability of elements and compounds as a result of enantiotropy or monotropy. XIV. Investigation of potassium nitrate by means of the differential gas dilatometer. E. COHEN and H. L. BREDEE (Z. physikal. Chem., 1929, 140, 391—405).—By means of the Smith differential gas dilatometer (cf. Cohen and Bredee, this vol., 496) the

densities and expansion coefficients of the rhombic (α) and rhombohedral (β) forms of potassium nitrate have been determined with greater accuracy at temperatures below and above the transition point, which was found to be $127.0^\circ \pm 1^\circ$. The volume change in the transition from the α to the β form is very small. A third, γ , form of potassium nitrate has been found which is monotropic and has a higher density than the other two forms.

O. J. WALKER.

Physico-chemical investigation of dioxan. W. HERZ and E. LORENTZ (Z. physikal. Chem., 1929, 140, 406—422).—A large number of physico-chemical data have been determined for pure dioxan and for mixtures with water and with methyl and ethyl alcohols between 20° and 90° , viz., densities (d_{20}^{20} 1.0330); the mixtures with water have higher, those with alcohol lower densities than correspond with the addition law; viscosities (ϕ_{20} —0.01255); surface tension (γ_{20} —35.42 dynes/cm.²); specific heat, c_p —0.420 at 23° . The heat of evaporation, L —86.2 g.-cal./g., gives a Trouton's constant of 20.3. Ebullioscopic, cryoscopic, and vapour-pressure data are also given. The critical temperature and pressure are calculated to be 583° and 44 atm., respectively. Dioxan has the normal mol. wt. (found 89.1) in benzene. The heat of combustion is 6602 g.-cal./g. Refractive index measurements have been made for pure dioxan and for aqueous solutions. The molecular refractivity of dioxan is 21.6. The solubilities of the following substances in various dioxan-water mixtures at 25° have been determined: sodium, potassium, and ammonium chlorides; potassium bromide, chromate, and dichromate; oxalic, malonic, succinic, benzoic, and salicylic acids.

O. J. WALKER.

Constants of elasticity with respect to the periodic system of the elements. M. KAHANOVIEZ (Atti R. Accad. Lincei, 1929, [vi], 8, 584—590).—Young's modulus and the moduli of rigidity and bulk have been comprehensively studied with regard to the periodic position of the elements. Unlike other physical properties of the elements, elasticity is shown to be a progressive function of the atomic number. In the transition elements, however, as given by the electronic theory, the moduli of bulk and shear show a periodicity. G. E. WENTWORTH.

Elastic constants of fused quartz. Change of Young's modulus with temperature. H. D. H. DRANE (Proc. Roy. Soc., 1929, A, 122, 274—282).—Measurements have been made of the deflexion at a fixed temperature (15°) of a small loaded cantilever of fused quartz and of the changes in deflexion as the temperature of the specimen varied over the range -183° to 700° . Similar results were observed with three specimens of quartz of different geological origin, the general behaviour being a continuous increase in Young's modulus with rise of temperature. The large changes and irregularities reported by Lees (Proc. Physical Soc., 1923, 36, 405) were not confirmed, but indications were observed of some irregularity of behaviour between -183° and the ordinary temperature. Re-tests of the various specimens showed that heating caused an apparent increase in

the viscosity, and semi-permanent changes were also found in the value of the modulus after cooling to the ordinary temperature. It is suggested that a close relation exists between the observed irregularities in mechanical behaviour and the optical anomalies found by Rayleigh in examining specimens of vitreous silica (Proc. Roy. Soc., 1921, A, 98, 284).

L. L. BIRCUMSHAW.

Compressibility of crystals and the exponent of the force of repulsion between atoms. N. RASCHEVSKY (Nature, 1929, 123, 448—449).—It is considered possible that practically the whole change of volume of a crystal (consisting of a large number of small, perfect crystals with a system of submicroscopic cracks between them) is due to the decrease in size of the cracks. If this is the case, the exponents of the forces of repulsion between the ions are considerably greater than Born's value of 9.

A. A. ELDRIDGE.

Determination of forces of attraction from chemical equilibria. R. LORENZ (Z. physikal. Chem., 1928, 139, 1—11).—The new mass action law (A., 1926, 126) as developed for condensed systems is further discussed and its significance in determining the forces of attraction between atoms or molecules is pointed out. It is shown that the only unknowns in the expressions connecting α and α' with the van der Waals constants a and b are the constants $a_{1,2}$ and $a_{3,4}$, which represent, respectively, the attractions of the molecules (or atoms) of the first component for the second, and of the third for the fourth; α and α' , and $a_{1,2}$ and $a_{3,4}$ are not arbitrary, empirical constants, and in general $a_{1,2} > (a_1 \cdot a_2)^{1/2}$. Values of $a_{1,2}$ (metal phase) and of $a_{3,4}$ (salt phase) have been calculated for equilibria of the type $A + BCl_2 \rightleftharpoons B + ACl_2$, and are tabulated for the following pairs of metals: cadmium and lead (600°), tin and cadmium (600°), tin and lead (chloride and bromide, at 400° , 500° , and 600°), zinc and cadmium (600°), copper and silver (900°), and lead and silver (900°). The values of $a_{1,2}$ and $(a_1 \cdot a_2)^{1/2}$, and of $a_{3,4}$, and $(a_3 \cdot a_4)^{1/2}$, respectively, are of the same order of magnitude throughout the series, and for a given equilibrium are approximately equal. The physical significance of these facts is that in a liquid mixture two dissimilar molecules are drawn together by a force approximately equal to that obtaining between two similar molecules. The values of $a_{1,2} - (a_1 \cdot a_2)^{1/2}$ and of $a_{3,4} - (a_3 \cdot a_4)^{1/2}$ are measures of the chemical attraction which for a mixture of two different substances makes itself felt over and above the mutual attraction of the molecules.

L. S. THEOBALD.

Viscosity constants and surface layers. J. TAUSZ and F. VON KOROSY (Z. physikal. Chem., 1929, 140, A, 263—272).—The experiments of Traube and Whang have been repeated (this vol., 129). It is shown that the change in rate of flow of water in a capillary tube produced by coating the tube with amyl alcohol or oleic acid is due entirely to a change in the hydrostatic pressure which forces the water through the tube. This change of pressure is caused by the smaller capillary rise of water in the equilibrium position in these cases because of lowering of surface tension. Contrary to the results of Traube and

Whang, the rate of flow is increased by coating the capillary with a film of paraffin; this is due to the smaller capillary rise of water on a paraffin surface than on glass. Traube's viscosimeter had been used to determine the absolute viscosity of water; the value found is 5% too high. Care must be taken in using this viscosimeter for different liquids that the equilibrium position of the liquid in the capillary is always the same.

R. N. KERR.

Influence of surface tension on viscosity measurements. S. ERK (Z. physikal. Chem., 1929, 140, 309—315).—The results of Traube and Whang are criticised on grounds similar to those used by Tausz and Korosy (preceding abstract). An equation is deduced from the Hagen-Poiseuille law which connects the viscosity and the height of the capillary rise at equilibrium. The capillary rise in the different tubes has been measured and the times of flow are calculated from this equation. Good agreement is obtained with those found by Traube and Whang.

R. N. KERR.

Thermal conductivity of gas mixtures. T. L. IBBS and A. A. HIRST (Proc. Roy. Soc., 1929, A, 123, 134—142).—By comparing Wachsmuth's values for the thermal conductivity of helium-argon mixtures (Physikal. Z., 1908, 7, 235) with the catharometer calibration curve for the same pair of gases (Ibbs, A., 1925, ii, 376), a curve is constructed showing the relation between catharometer deflexion and thermal conductivity at 0° over a wide range of values. By interpolation, the conductivity which corresponds with the galvanometer deflexion for any gas or mixture can then be determined. Data are given for the relation between conductivity and composition for the mixtures hydrogen and carbon dioxide, hydrogen and argon, hydrogen and nitrogen, hydrogen and carbon monoxide, and hydrogen and nitrous oxide. The results for hydrogen-carbon dioxide mixtures are in good agreement with those of Weber (Ann. Physik, 1917, [iv], 54, 481). The accuracy and advantages of the method are discussed.

L. L. BIRCUMSHAW.

Viscosity formula for binary mixtures taking into account the association of the constituents. II. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1929, 4, 25—31; cf. this vol., 387).—A study of the field constant k in the formula previously proposed indicates that its value is characteristic of a given liquid, and, further, that for homologous liquids the value of k is proportional to the product $D\sigma$, where D is the dielectric constant and σ the molecular diameter. Thus, for methyl, ethyl, and n -propyl alcohols the values of $D\sigma \times 10^8/k$ are respectively 264, 260, 266, and for methyl and ethyl acetates, 15.6 and 15.7. Extended to the case of binary gaseous mixtures the formula becomes $\eta = \eta_1/[1 + kz_m/(1 - z_m)] + \eta_2/[1 + (1 - z_m)/kz_m]$.

In the application of the author's formula to binary liquid mixtures in which molecular compounds are formed the deviation of the measured viscosity (η) from that calculated from the formula (η_0) is termed the solvation viscosity, $\delta = \eta - \eta_0$. The magnitude of δ is determined by the extent of the reaction between the two constituents. It is assumed that if

reaction occurs between v_1 and v_2 molecules of the two components to form a molecular compound, then the solvation viscosity $\delta = c(1 - z_m)^{v_1} \cdot z_m^{v_2}$, where z_m is the concentration of the second component. This assumption has been tested by reference to the mixtures water-methyl alcohol, water-ethyl alcohol, and water-acetic acid. Evidence is found for the existence of the molecular compounds $\text{AcOH} \cdot \text{H}_2\text{O}$, $\text{MeOH} \cdot 2\text{H}_2\text{O}$, $\text{EtOH} \cdot 3\text{H}_2\text{O}$ (in solutions up to 40 mol.-% of EtOH), $\text{EtOH} \cdot 2\text{H}_2\text{O}$ (in solutions containing more than 40 mol.-% of EtOH).

F. G. TRYBORN.

Mixed crystals, solutions, and fusions of the system $(\text{K} \cdot \text{NH}_4)(\text{Cl} \cdot \text{NO}_3)$. E. JÄNECKE (Z. angew. Chem., 1929, 42, 318).—Corrigenda to an earlier paper (cf. A., 1928, 1095).

Logarithmic mixture law. J. DEJMEK (Physikal. Z., 1928, 29, 907—908).—The relation between the simple and the logarithmic mixture laws is discussed. The latter is applicable to the calculation of electrical and thermal conductivity for alloys of the cadmium-bismuth, aluminium-bismuth, and silver-lead types, and also to the calculation of the viscosity of liquid mixtures.

R. A. MORTON.

Crystal form in the production of solid solutions. IV. Analysis of the anhydrous systems $\text{MgCl}_2\text{--FeCl}_2$ and $\text{CdCl}_2\text{--FeCl}_2$. A. FERRARI and M. CARUGATI (Atti R. Accad. Lincei, 1928, [vi], 8, 306—309; cf. this vol., 388).—The similarity of the crystal lattices of the anhydrous chlorides of magnesium, cobalt, and nickel and bivalent iron and manganese suggests complete miscibility in the solid state. F.-p. determinations demonstrate the formation of a complete series of solid solutions for the two systems examined.

G. E. WENTWORTH.

Structure of some ternary alloys of copper, zinc, and aluminium. A. J. BRADLEY and C. H. GREGORY (Mem. Manchester Phil. Soc., 1927—1928, 72, 91—100).—An attempt is made to elucidate the problem of so-called intermetallic compounds. The resemblance between the structures of analogous phases in the systems Cu-Zn, Cu-Al suggested that ideal solid solutions of a ternary alloy could be produced from binary alloys of similar structure. This has been proved.

G. E. WENTWORTH.

Some physical constants of pure, carbon-free chromium-iron and vanadium-iron alloys. K. RUF (Z. Elektrochem., 1928, 34, 813—818).—For the two kinds of alloy, curves showing the influence of temperature and composition on the specific resistance, on the thermoelectric force against platinum, and on the thermal expansion are reproduced. The specific resistance at 20° of electrolytic chromium, remelted in a vacuum, was found to be 0.284 ohm mm.²/m. For electrolytic iron with less than 0.02% C, d^{20} is 7.876. The density curves are linear for alloys with up to 18% V and for those with up to 50% Cr, and extrapolation of the chromium curve gives d^{20} 7.014 for the pure metal as compared with d^{20} 7.011 found for the electrolytic chromium remelted in a vacuum. The thermal expansion curves are convex to the composition axis, and the temperature-thermal expansion curves show that

addition of vanadium causes a disappearance of the change of state observed in pure iron at 850—900°. Alloys containing up to 12% Cr show discontinuities (less marked than in the case of iron) in these curves at temperatures above that of the corresponding discontinuity in electrolytic iron. This effect decreases with an increase in chromium content and disappears with alloys containing 13% Cr or more.

L. S. THEOBALD.

Limits of reactivity of the magnesium-cadmium alloys, and their potential-concentration curves. C. KROGER (Z. anorg. Chem., 1929, 179, 27—48).—The reactivity of the magnesium in the alloys has been determined as a function of the composition by measuring the quantity of hydrogen evolved when the alloy is treated with methyl alcohol; the "reactivity coefficient" α is the fraction of the total magnesium dissolved, and for cadmium concentrations up to about 0.25M is approximately unity; with increase of cadmium content α decreases very rapidly to zero. Tempering the alloys decreases α between 0.375 and 0.5M, whilst even at a cadmium concentration of 0.25M α is very small. Treatment of the alloys with ethereal ethyl iodide solutions leads to analogous results. The protective action of the cadmium atoms is explained by consideration of the relative positions of the atoms of the two metals in the mixed crystal lattice. The variation with time of the *E.M.F.* of the cell $\text{Cd}|\text{N-MgSO}_4||\text{Cd}_2\text{Mg}_{1-x}$ has been determined for a number of values of x . For alloys of lower cadmium concentration than 0.5M the *E.M.F.* falls for several hours, remains constant for a lengthy period, and finally falls again, whereas for alloys richer in cadmium the *E.M.F.* at first rises rapidly to a maximum and then decreases somewhat to a steady value. The significance of these results for the fine structure of the alloy is discussed.

H. F. GILLBE.

Aluminium and the formation of mixed crystals with silicon. L. ANASTASIADIS (Z. anorg. Chem., 1929, 179, 145—154).—At the eutectic temperature the specific resistance curve shows that the terminal point of the mixed crystals series lies at 1.48% Si. Aluminium seems to undergo no transition, for its resistance is not influenced by prolonged cooling or by suddenly cooling from 630°. Aluminium containing 0.31% Si exhibits an increase of resistance after chilling, and even with 0.18% Si a small effect is to be observed. It follows that mixed crystals are formed between these concentrations at the ordinary temperature. The value 36.8×10^{-4} is recorded for the electrical conductivity of (99.94%) aluminium.

H. F. GILLBE.

Deviations from Dalton's partial pressure law and their chemical significance. M. TRAUTZ and M. GURSCHING (Z. anorg. Chem., 1929, 179, 1—26).—Accurate measurements have been made of the changes of pressure which occur when equal volumes of pairs of gases are mixed at constant pressure. Primary deviations from the simple laws in the case of pure gases and binary mixtures are attributed to the formation of associated molecules which in the case of mixtures may contain two similar or two different molecules. For such systems equations

of state corresponding with that of van der Waals have been derived, wherein the constant a is replaced by a dimerisation constant. The Berthelot equation $a_{1,2} = \sqrt{a_1 a_2}$ assumes the form $a_{1,2} = \frac{1}{2} \sqrt{K' a_1 a_2}$, where K' is the equilibrium constant of the process $A_2 + B_2 = 2AB$, A and B being the component gases. On the basis of this theory and of the measurements which have been made, the gaseous compounds Me_2O , CO_2 , Me_2O , SO_2 , and Me_2O , MeCl have been detected. The thermal changes with dimethyl ether indicate the formation of the known compound between methyl ether and hydrogen chloride. The association of ethylene and hydrogen is not the same as the hydrogenation of ethylene to ethane. The degree of association may be calculated simply from equilibrium considerations if the pressure change on mixing exceeds about 2% of the initial pressure: with smaller pressure changes the newly-derived equations are more readily applicable, since account is therein taken of association in the component gases. The significance of the duration of collision between gas molecules which is involved in the theory of binary association is considered in reference to the internal friction of gases. H. F. GILLBE.

Diffusion coefficients of gases in water, and their temperature relationships. G. TAMMANN and V. JESSEN (Z. anorg. Chem., 1929, 179, 125—144).—The diffusion coefficients K and their variations with temperature have been measured for carbon dioxide, acetylene, hydrogen, nitrogen, and oxygen diffusing through agar-agar solutions. Excepting for oxygen the value of K increases linearly with rise of temperature. The anomalous behaviour of oxygen is due to absorption of the gas by the agar-agar solutions.

H. F. GILLBE.

Dissolution of silver in water. H. KŘEPELKA and F. TOUL (J. Czechoslov. Chem. Comm., 1929, 1, 155—164).—By accurate nephelometric determinations and measurements of the *P.D.* of the electrode $\text{Ag}|\text{pure conductivity water}$, it was found that the solubility of pure silver in pure water in the dark, out of contact with air, at 18—20° is 0.037 mg./litre. The silver passes into solution as the ion, dissolution being due to surface oxide, to oxygen absorbed on the surface, or to oxygen dissolved in the water. When the surface of the silver has been previously reduced in pure dry hydrogen at 400°, the metal does not dissolve in pure water carefully freed from dissolved gases. Solubility measurements made in glass vessels are, on the average, 0.003 mg. higher than those obtained in silver vessels, this difference being due, probably, to the effect of alkali dissolved from the glass.

J. W. BAKER.

Solubility of iodine in solutions of halides. J. S. CARTER and C. R. HOSKINS (J.C.S., 1929, 580—585).—The solubility of iodine in solutions of halides has been measured at 25°. Owing to the reaction between iodine and fluorides in aqueous solution, the solubility in the case of fluoride solution could not be determined. Over the very large range of concentrations investigated it is shown that the solubility of iodine can be simply expressed in terms of two opposing factors, (a) the salting-out effect and (b) the tendency to form perhalides. With iodides the

former is negligible, but with bromides and chlorides it is of considerable importance. F. J. WILKINS.

Diffusion in hydrotropic solutions. H. FREUNDLICH and D. KRUGER (Biochem. Z., 1929, 205, 186—193).—The diffusion of benzoic acid in pure water and in solutions of hydrotropic salts (sodium benzenesulphonate and *p*-toluenesulphonate) is measured by Oehlm's method. The diffusion coefficient in hydrotropic solutions is as great as or greater than in pure water but is not constant. The diffusion coefficient of brucine both in aqueous solution and in solutions of sodium benzenesulphonate is not constant, but is rather smaller in hydrotropic solutions than in pure water.

P. W. CLUTTERBUCK.

Distribution of acetone through a rubber membrane. D. S. MORTON (J. Physical Chem., 1929, 33, 384—397).—The distribution of acetone between methyl alcohol and water separated by a rubber membrane at the ordinary temperature over a composition range of 0—70%, can be represented by the equation $G_1/G_2 = 2.24(G_1/G_3)^{1.09}$, where G_1 , G_2 , and G_3 are the mol fractions of acetone, alcohol, and water, respectively. The results have been checked by a deduction of the distribution curve from measurements of the vapour pressures of the three pairs of binary mixtures; these were made by means of an interferometer at 20°. Equations representing the partial pressure of acetone for acetone-methyl alcohol solutions and for acetone-water solutions are given. The results indicate that distribution of a solute between two phases is primarily a function of mass concentrations. L. S. THEOBALD.

Adsorption isothermals for a plane platinum surface. W. G. PALMER (Proc. Roy. Soc., 1929, A, 122, 487—497; cf. A., 1927, 722).—Petrol of b. p. 40—60° was purified by shaking with saturated alkaline permanganate and dried over sodium wire. A fraction of the product, b. p. 40—44°, gave a film only with difficulty and showed a cohering voltage of <0.2. The adsorption on a plane platinum surface of benzene, ethyl alcohol, and acetic acid has been studied by the coherer method (*loc. cit.*), using the above hydrocarbon as diluent. The results confirmed Langmuir's formula $a = a_{\infty}[pc/(1+pc)]$, where p is a constant representing the average life of a molecule of adsorptive in the film. The similarity in the values of p for the three adsorptives indicates that the lives of the adsorbed molecules on the surface are almost equal. The variation in the apparent area available for the adsorption of different substances is discussed in relation to the mechanism of adsorption and catalytic action.

L. L. BIRCUMSHAW.

Formation of sulphur films on a mercury surface. A. FRUMKIN (Kolloid-Z., 1929, 47, 229—231).—When drops of a solution of sulphur in a volatile solvent (ethyl ether, benzene, light petroleum) are dropped on to a surface of clean mercury, the first drops spread out very rapidly and subsequent drops more slowly until finally a stage is reached where addition of another drop does not cause further spreading. It is shown that at this stage the mercury is covered with a unimolecular layer of sulphur and

that the area of the surface occupied by each sulphur atom is of the order of magnitude of the cross-section of a mercury atom. The linking between the mercury and sulphur atoms would therefore seem to be of the same type as in a chemical compound of these elements. A similar effect cannot be obtained with solutions of iodine, but the effect is produced by drops of solutions of iodoform. E. S. HEDGES.

Formation of thin films of organic colloids on mercury surfaces. R. L. KEENAN (J. Physical Chem., 1929, 33, 371—380; cf. A., 1928, 702).—A technique for obtaining thin films of organic colloids on mercury is described. Cellulose esters and isoelectric gelatin form rigid films of an irregular shape. Data for cellulose acetates of varying viscosities and in different solvents are given, and with cellulose nitrates the limiting film thickness, which is independent of dilution, varies inversely as the viscosity. Films of rubber are elastic. The limiting thickness increases with increasing complexity of the atom groups; thus rubber, cellulose, and gelatin have the values 1.5, 2.5—5.0, and 7.0 Å., respectively. The results indicate that the films consist of long chains or ribbon-like molecules which lie flat on the mercury surface or have an open-work, net-like structure. L. S. THEOBALD.

Reversal of Traube's rule in adsorption of homologous compounds by sugar charcoal. T. SABALITSCHKA (Pharm. Ztg., 1929, 74, 382—384).—Whilst the degree of adsorption of organic acids from aqueous solutions by blood charcoal, bone charcoal, and vegetable charcoal increases with the mol. wt. of the solute, the reverse is found to be the case with sugar charcoal. This reversal is observed with both monobasic and dibasic acids.

S. I. LEVY.

Hydrolytic adsorption by humic acid. A. GANGULI (Phil. Mag., 1929, [vii], 7, 317—322).—The adsorption of electrolytes by humic acid causes a liberation of free acid in direct proportion to the concentration of the electrolyte. The change in hydrogen-ion concentration is due to the adsorption of the cations to form a complex electrolyte. There is a marked effect of valency and for a common anion cations give the regular order $Al > Ba > K > Na$, whilst for anions $Cl < SO_4$. The results are in agreement with those of Michaelis and Rona (Biochem. Z., 1914, 94, 240) and offer a confirmation of Mukherjee's theory of the acidity of soils (A., 1923, i, 79).

A. E. MITCHELL.

Adsorption. (FRL.) M. T. ISSELSTEIN (Physikal. Z., 1928, 29, 873—878).—The adsorption of carbon disulphide, pentane, and chloroform on powdered glass has been studied. The area of glass was measured by the methods of Schmidt and Durau (A., 1924, ii, 238) and of Schelte (A., 1925, ii, 286). Adsorbed layers up to 35 molecules in thickness have been observed, the thickness decreasing, however, with decreasing pressure. When the temperature is well above the condensation point there is little tendency towards the formation of even a unimolecular adsorbed layer, but as the conditions for condensation are approached the adsorption increases.

R. A. MORTON.

Adsorption of carbon dioxide and ammonia by silica gel. A. MAGNUS and R. KIEFFER (*Z. anorg. Chem.*, 1929, 179, 215—232).—The adsorption of carbon dioxide by silica gel has been determined at temperatures between -21.2° and 100° and at pressures between 0.1 and 760 mm. The heat of adsorption, calculated from the isotherms, is an approximately linear function of the temperature, whilst the repulsion constant of Magnus' equation of state has at the higher pressures a constant value at each temperature. Variation of the water content of the gel has but little influence on the isotherms. Experiments have been made with titanium and zinc oxides, calcium and barium fluorides, barium sulphate, and nickel bromide with the object of finding other adsorbents which would behave in the same manner as silica gel, but in each case the drying and degassing processes appear to render the adsorbent chemically active towards the gas. The influence of water on the adsorption of ammonia by silica gel has been determined. The heat of adsorption has been determined from the isotherms for a nearly water-free gel as a function of the pressure, and by extrapolation to zero pressure the value of Q is found to be about 12,000 kg.-cal., which agrees with the value obtained by calorimetric measurements using an almost water-free gel. H. F. GILLBE.

Absorption of dextrose by protein precipitates. J. H. CASCAO DE ANCIAES and C. TRINCAO (*Compt. rend. Soc. Biol.*, 1928, 98, 1003—1004, 1586—1588; *Chem. Zentr.*, 1928, ii, 1700).—Absorption of dissolved dextrose by albumin is prevented by addition of sodium chloride. A. A. ELDRIDGE.

Optical study of adsorbed films. J. H. FRAZER (*Physical Rev.*, 1929, [ii], 33, 97—104).—Rayleigh and Drude's method for the study of surface transition layers has been applied in the investigation of adsorption on glass. Only water and methyl alcohol show definite adsorption, and two successive unimolecular layers are indicated. The method is applicable to the study of surface conditions at the interface between any two phases. N. M. Blich.

Invisible oxide films on metals. F. H. CONSTABLE (*Nature*, 1929, 123, 569).—If reduced copper is acted on by a mixture of hydrogen sulphide (1 vol.) and air (5 vols.), two complete colour sequences are produced in a few minutes; if, however, the copper surface is left exposed to air for some hours, and then subjected to the action of hydrogen sulphide and air, the interference colours are developed very slowly. The results support Evans' conclusion that a thin film of oxide is formed when copper is exposed to air at the ordinary temperature.

A. A. ELDRIDGE.

Elliptical polarisation produced by reflexion at the surface of solutions of fatty acids in water. C. BOUHET (*Compt. rend.*, 1929, 188, 59—61).—Earlier experiments (*ibid.*, 1927, 185, 200) have been extended to the measurement at 15 — 21° of the ellipticities (K) of solutions in water of fatty acids of the series acetic to myristic acid. The curves connecting K (as ordinates) with the concentration of acid show minimum values of the former which decrease as the carbon content of the acid increases,

and in the case of the higher acids these correspond with saturated solutions. It is inferred that although a layer of acid molecules may be adsorbed on the surface of the solution, its orientation in the case of solutions showing minimum ellipticities differs completely from that for the pure acid. J. GRANT.

Interfacial tension between mineral oils and aqueous solutions. Influence of time and p_H . H. WEISS and E. VELLINGER (*Compt. rend.*, 1929, 188, 901—903).—The interfacial tension between a mineral oil and a solution of an electrolyte increases or decreases with the time to an extent which depends on the p_H value of the latter, and the value obtained by extrapolation to zero time is the most trustworthy. The interfacial tension- p_H curves are of two characteristic types, one almost parallel with the p_H -axis but having slight maxima at p_H 6 and 11, and the other showing a rapid fall in interfacial tension above p_H 7. Smaller variations are due to the nature of the buffer substances used. J. GRANT.

Creeping of crystals. II. H. ERLENMEYER (*Helv. Chim. Acta*, 1929, 12, 264—269; cf. A., 1928, 12).—Further observations are recorded. The addition of 1% of glycerol almost entirely prevents creeping in a saturated solution of potassium chloride. Sucrose and thymol have a similar effect. This is not due to a decrease in evaporation. Experiments are also described relating to the factors which influence the height to which crystals will creep up a glass rod placed in a saturated solution of a salt.

O. J. WALKER.

Synthetic kidneys. W. D. BANCROFT and R. L. NUGENT (5th Coll. Symp. Mon., 1928, 149—158).—The kidney glomerulus is not a simple ultra-filter, since changes occur in the concentration of solutes, due to some form of dialysis or electrical endosmosis. If manganese sulphate is added to aqueous acetone on one side of a rubber membrane, the acetone content of a similar mixture on the other side is considerably increased. The concentration effects in *Valonia* and in the kidney are discussed.

CHEMICAL ABSTRACTS.

Artificial membranes electively permeable to anions. R. MOND and F. HOFFMANN (*Pflüger's Archiv*, 1928, 220, 194—202; *Chem. Zentr.*, 1928, ii, 1659).—The membranes were obtained by deposition of rhodamine-B in the pores of collodion membranes. *E.M.F.* determinations with 0.1*N*-sodium chloride on one side and 0.1*N*-sodium thiocyanate, nitrate, iodide, bromide (chloride), acetate, sulphate, and with potassium chloride and nitrate, showed that only the anions are electromotively active in the above order. The *P.D.* between potassium nitrate solutions (1:10) diminish with the absolute concentrations; the more dilute solution is negative towards the more concentrated. A. A. ELDRIDGE.

Electrolyte equilibria at elective ion-permeable membranes and its biological significance. H. NETTER (*Pflüger's Archiv*, 1928, 220, 107—123; *Chem. Zentr.*, 1928, ii, 1576).—From thermodynamic and statistical considerations it is inferred that all permeating ions on both sides of an elective cation- or anion-impermeable membrane must become distributed in equal ratio. Experiments with anion-

impermeable collodion membranes illustrate the effect, the biological significance of which is considered.

A. A. ELDRIDGE.

Refraction constants and solution volumes of some organic compounds in aqueous solution. E. BERNER (Z. physikal. Chem., 1929, **141**, 91—124).—The refractive indices and densities of dilute aqueous solutions of ethyl alcohol, *n*- and *sec*-propyl and butyl alcohols, acetone, methyl ethyl ketone, and the methyl esters of the isomeric tartaric acids have been measured at 20°. The molecular refractivities of the solutes agree well with the values for the pure substances, and are therefore additive. The molecular solution volumes, however, are dependent on the structure and configuration of the compounds.

The hydration of the anhydrides of succinic, methylsuccinic, and glutaric acids has been followed by dilatometric and interferometric measurements, and the molecular refractivities and solution volumes of the anhydrides and of the corresponding free acids have been calculated. The oxygen ring in glutaric anhydride has a larger refractivity and a smaller solution volume than in succinic and methylsuccinic anhydrides.

O. J. WALKER.

Effect of ionisation on optical rotation. IV. Amino-acids and peptides. P. A. LEVENE, L. W. BASS, A. ROTHEN, and R. E. STEIGER (J. Biol. Chem., 1929, **81**, 687—695).—Figures are given for the optical rotations of *l*-valine, *l*-leucine, glycyl-*d*-valine, glycyl-*l*-valine, and glycyl-*d*-isovaline in presence of varying amounts of acid or base. The results confirm the previous conclusion (A., 1927, 625) that such measurements afford a satisfactory means of determining the dissociation constants.

C. R. HARRINGTON.

Ebullioscopic researches on mixtures of salt solutions. G. PRONIEWSKI (Rocz. Chem., 1929, **9**, 115—130).—The b. p. of mixtures of equimolecular solutions of the chlorides of ammonium, sodium, potassium, magnesium, calcium, barium, zinc, cadmium, and mercury have been measured. Deviations from the theoretical value are given by all pairs consisting of one alkali or alkaline-earth chloride and of zinc, cadmium, and mercuric chlorides; in the case of cadmium and zinc, the b.-p. deviation curves exhibit a maximum at 60% of alkali or alkaline-earth salt solution, and the position of this maximum is little affected if solutions other than equimolecular are used. Maximum deviations of b. p. appear at about 50% of 3*M*-alkali salts on progressive dilution. On similarly diluting solutions of cadmium, zinc, and mercuric chlorides both negative and positive deviations are obtained, according to the salt in question and its initial concentration. It follows from the above results that the b.-p. deviation maxima obtained at about equimolecular proportions of pairs of salts do not necessarily indicate the formation of double salt, as was assumed by Bourion and Rouyer (A., 1927, 415). No combinations of the nitrates of sodium, magnesium, and zinc give mixtures with anomalous b. p., whilst in the case of sulphates the b. p. is raised only for the pair sodium sulphate-zinc sulphate.

R. TRUSZKOWSKI.

Measurements of albedo in artificial layers of fog. E. REGENER (Z. physikal. Chem., 1928, **139**, 416—244).—An investigation has been made to determine the maximum value to which the diffuse reflecting power of a layer of fog can be raised by increasing the concentration of the particles. The fog was illuminated by parallel rays from the sun at a height of 28—44° and the light reflected perpendicularly to the surface was measured by means of a photometer. Comparison was made with a gypsum plate with an albedo approximately equal to that of an absolutely white body. Fogs of sulphur trioxide, paraffin oil, and ammonium chloride were investigated. In order to obtain fogs with a sharp, flat surface it was found necessary to use carbon dioxide instead of air for their production.

R. N. KERR.

Dispersoidal synthesis of gold by means of alkaline formaldehyde solutions. I. P. P. VON WEIMARN (Bull. Chem. Soc. Japan, 1929, **4**, 35—47).—In accordance with the author's theory of dispersoidal synthesis it has been found possible to prepare reproducible gold sols of red or orange colour by reducing gold chloride solutions with formaldehyde rendered alkaline by the addition of potassium hydroxide or carbonate. Under suitable conditions these stable sols may be obtained without rigorous purification of the water or reagents employed. The effect of increasing purity of the reactants is to yield sols which may be concentrated to a greater degree without the development of a blue colour on cooling.

F. G. TRYHORN.

Colloidal solutions of practically insoluble gold compounds and their transformation to gold sols. P. P. VON WEIMARN (Kolloid-Z., 1929, **47**, 231—235).—Colloidal solutions of gold iodide may be prepared by adding a very dilute solution of chloroauric acid to a boiling dilute aqueous solution of iodine, or by mixing dilute solutions of chloroauric acid and potassium iodide in presence of potassium hydroxide. Using potassium thiocyanate in place of potassium iodide, sols of gold thiocyanate are produced. The properties of these sols depend on the concentration of the reagents, temperature, etc.; they change spontaneously to gold sols, thus casting doubt on the usual simple explanation of the production of gold sols.

E. S. HEDGES.

Production of colloidal solutions of lead or lead salts. M. C. REINHARD, K. W. BUCHWALD, and K. P. TUCKER (J. Cancer Res., 1928, **2**, 160—165).—Lead acetate in gelatin and 10% sodium orthophosphate are used; the influence of *p_H* and of protective colloids, and the microscopical characters of the products, were studied. CHEMICAL ABSTRACTS.

Colloidal potassium ferrocyanide solutions. A. KUTZLNIGG (Kolloid-Z., 1929, **47**, 221—222).—Colloidal solutions of potassium ferrocyanide are obtained when the solid salt is shaken with water to which has been added ethyl, methyl, or propyl alcohol, or acetone. The best condition is to shake 0.1 g. of the salt with 100 c.c. of ethyl alcohol and 50 c.c. of water. The sols are much deeper in colour than a true solution of the same concentration, they sometimes show a yellow, blue, or red opalescence, and exhibit the Tyndall phenomenon. Addition of more

alcohol causes the precipitation of a white amorphous mass or gel of potassium ferrocyanide. The more concentrated sols are sensitive to light.

E. S. HEDGES.

Colloidal behaviour of antimony pentoxide. S. GHOSH and N. R. DEAR (J. Indian Chem. Soc., 1929, 6, 17—25).—By dialysing a mixture of potassium antimonate and dilute nitric acid a negatively charged sol of antimony pentoxide has been obtained, which behaves normally towards dilution and mixtures of electrolytes, and follows the Schulze-Hardy law. The viscosity, electrical conductivity, acidity, and stability towards electrolytes change slightly on ageing or on boiling. A coagulum of antimonous acid can be reprecipitated very easily by washing when the sol has been precipitated by univalent ions, but with difficulty when coagulated by multivalent ions. It is a reversible colloid, and the hydrate $\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, obtained by drying the sol at the ordinary temperature, passes into the colloidal state on the addition of water. About 0.5% of the colloid is in the dissolved condition.

O. J. WALKER.

Colloid types. E. G. BINGHAM (5th Coll. Symp. Mon., 1928, 219—228).—From the point of view of plastic flow, colloids are differentiated as polar, emulsions, and non-polar. Measurement of the "solubility" of polar colloids is discussed.

CHEMICAL ABSTRACTS.

Tactosols. H. ZOCHER and K. JACOBSON (Kolloidchem. Beih., 1929, 28, 167—206).—The term "tactosols" is given to sols containing non-spherical particles which have the property of spontaneously arranging themselves in parallel order. This property has been studied with sols of vanadium pentoxide, benzopurpurin, ferric oxide, tungsten trioxide, and chrysophenin. Vanadium pentoxide separates on ageing into a concentrated anisotropic phase—the tactosol—which later precipitates out, and a dilute isotropic phase, which is termed the atactosol. This process has been followed microscopically. Addition of arsenic acid retards the process greatly, whilst addition of other electrolytes does not affect the ageing, but produces different forms of tactoids in the sense of a closer crowding of the particles. When an electrical *P.D.* is applied, the particles arrange themselves with their long axes parallel to the direction of the current, but if an alternating current is applied the orientation of the particles is perpendicular to the current. In a magnetic field, the particles are arranged parallel to the lines of force. Tactoids are readily produced by cooling a 2% boiling sol of benzopurpurin-4B, and with difficulty from 1.5 or 1% sols. Benzopurpurin-6B exhibits the effect better, even in a 1% sol. Addition of electrolytes has an effect similar to that observed in the case of vanadium pentoxide. In a magnetic field, the particles become arranged with their long axes perpendicular to the lines of force. Measurements have been made of the concentration and conductivity of the atactosol remaining after the separation of the tactosol from tactosols of aged ferric oxide sols. Tactosols of tungsten trioxide have disc-like particles bearing a negative charge, and evidence is given that the particles consist of a

number of parallel platelets having a constant "period" or distance apart. A method is given for preparing tactosols the particles of which have different periods. Measurements of conductivity show that the period is smaller the higher is the electrolyte content of the sol. It is also possible to diminish the periodicity of the layering by direct addition of hydrochloric acid, sodium hydroxide, sodium tungstate, or sodium chloride. The gelatinous precipitate from heated chrysophenin solutions of various concentrations and electrolyte content has been studied microscopically. At certain concentrations the tactoids attain macroscopic dimensions. Unshaken solutions of this concentration show negative streaming-double refraction, whilst shaken solutions are positive. The tactoids of chrysophenin consist of long, lamellar, negative anisotropic crystals.

E. S. HEDGES.

Dispersity of dissolved cellulose. H. ZEISE (Kolloid-Z., 1929, 47, 248—251).—A criticism of papers by Hess and others (B., 1924, 88) and by Baur (A., 1925, ii, 662) on the state of cellulose dissolved in cuprammonium hydroxide solution.

E. S. HEDGES.

Number of nuclei formed during crystallisation of gels. P. A. THIESSEN and E. TRIEBEL (Z. anorg. Chem., 1929, 179, 267—276).—The relation between the degree and period of supercooling and the number of centres of crystallisation in dilute sodium oleate gels is analogous to that observed in single-component systems. The number of such centres varies linearly with the concentration.

H. F. GILLBE.

Characterisation of colloidal solutions by the degree of polarisation of Tyndall light. R. O. HERZOG and B. LANGE (Ber., 1929, 62, [B], 491—495).—Parallel rays from an arc lamp pass through a slit into the solution under investigation. At right angles to the incident ray the emergent beam passes through a doubly-refracting Wollaston prism and monochromator. The intensities of the two components are determined by a half-shadow apparatus with Nicol prism. The depolarisation is calculated from the formula $\Delta = \tan^2 \alpha$. Spherical particles, small in comparison with the wave-length of light, cause complete polarisation of the Tyndall light ($\Delta = 0$). Increase in α is observed with increasing size of particles. Observations are recorded for cellulose trinitrate in methyl acetate and acetone, glycogen and inulin in water, cellulose acetate in methyl acetate and acetone, "total caoutchouc" and polystyrene in benzene, gelatin in water and cresol. Congo-red and vanadium pentoxide in water.

H. WREN.

Optical properties of turbid solutions containing non-metallic particles and the Pulfrich step-photometer. (FRL.) U. MILTHALER (Ann. Physik. 1929, [v], 1, 229—259).—The application of the Pulfrich photometer to the measurement of absorption, Tyndall effect, and depolarisation in turbid media has been investigated. Beer's law is shown to hold for gamboge solutions provided the initial solution is not too concentrated. The optical properties of mastic solutions have also been studied.

R. A. MORTON.

Double refraction of bentonite. R. BRADFIELD and H. ZOCHER (*Kolloid-Z.*, 1929, 47, 223).—The streaming-double refraction of natural bentonite is negative, but is positive after electro-dialysis. It is possible that the change of sign through electro-dialysis is due to an alteration in the constitution of the anisotropic colloidal particles, which lose their bases. The constitution of the particles is analogous to that of zeolite crystals, both allowing of exchange of bases.

E. S. HEDGES.

Streaming-double refraction and thixotropy of bentonite suspensions. A. VON BUZAGH (*Kolloid-Z.*, 1929, 47, 223—229).—Bentonite, from which coarsely disperse particles have been removed, is peptised by water in two fractions. The more readily peptisable part contains considerably less alkali and alkaline earths than the other fraction and is positively doubly refracting, whilst the more difficultly peptisable part exhibits negative streaming-double refraction. The negative doubly refractive bentonite can be made positive doubly refracting by electro-dialysis. This can be intensified by adding potassium hydroxide, but addition of calcium hydroxide produces weak negative streaming-double refraction. The original bentonite gives with certain proportions of water thixotropic pastes, the time of setting of which decreases greatly with increasing content of bentonite. Electro-dialysed bentonite does not behave in this way, but gives thixotropic pastes when dilute alkali solutions are employed instead of water. The time course of the peptisation of natural bentonite with water and of electro-dialysed bentonite and of kaolin with alkali has been followed. In each case the curve passes through a maximum.

E. S. HEDGES.

Effect of electrolytes on emulsions. H. V. TARTAR, C. W. DUNCAN, T. F. SHEA, and W. K. FERRIER (*J. Physical Chem.*, 1929, 33, 435—446).—The effect of acids, bases, and sodium chloride on the stability of benzene-water emulsions stabilised by sodium oleate has been investigated. These emulsions are destroyed by hydrochloric, acetic, and oxalic acids when approximately sufficient acid is present to decompose the soap. A high concentration of oleic acid inverts the benzene-in-water emulsion, but sodium hydroxide does not increase its stability. Emulsions of benzene, toluene, or xylene in water, with sodium oleate as stabiliser and containing small amounts of sodium hydroxide, are inverted by sodium chloride. With benzene-in-water emulsions, there exists a well-defined zone of instability between concentrations 0.25 and 0.45*N* with respect to sodium chloride, and the point of inversion varies slightly with the concentration of sodium hydroxide in the system. With the toluene and xylene emulsions, the inversion point lies at 0.35—0.40*N*-sodium chloride and is independent of the concentration of hydroxide. Similar emulsions in which potassium stearate replaces sodium oleate are more easily prepared, are more stable, and are not inverted by the addition of potassium chloride. Nitrobenzene readily gives stable emulsions which are of the oil-in-water type at all concentrations of sodium chloride with sodium oleate as stabilising agent; with potass-

ium stearate, the emulsions are even more stable. Dimethylaniline is emulsified readily with both soaps, giving the oil-in-water type; *o*-toluidine also gives stable emulsions of the same type, but these are not formed in the presence of small amounts of sodium and potassium hydroxide, and chlorides. Discussion of the results is reserved for a future communication.

L. S. THEOBALD.

Coagulation of blood and milk by electrolytes and the similarity between the clotting of blood and the formation of jellies. N. R. DHAR and S. PRAKASH (*J. Physical Chem.*, 1929, 33, 459—466).—Blood and milk belong to that class of colloids which absorb ions bearing the same charge as the sols. On dilution they are less readily coagulated by sodium citrate, tartrate, and acetate, potassium fluoride and oxalate, ammonium nitrate, and hydrochloric acid. The addition of saponin and gelatin (less than 1%) renders blood and milk less stable towards salts. Saponin only has a sensitising effect in the case of hydrochloric acid. The action of gelatin is attributed to the presence of hydrogen ions. In the presence of small amounts of the above salts and of potassium hydroxide, blood and milk are stabilised with respect to the coagulating action of ammonium nitrate and copper sulphate; this is attributed to the adsorption of negative ions from the salt solutions. The clotting of blood is analogous to the formation of gels of vanadium pentoxide and silicic acid.

L. S. THEOBALD.

Kinetics of coagulation of colloids of the second order. K. JABŁCZYŃSKI and H. JASZCZOŁTÓWNA (*Rocz. Chem.*, 1929, 9, 111—114).—The expressions derived previously (Jabłczynski and Soroczynski, *A.*, 1928, 360) for the kinetics of coagulation of ferric hydroxide sols are shown to hold also for suspensions of silver bromide and chloride, in the presence or absence of protective colloids.

R. TRUSZKOWSKI.

Change of precipitating concentrations of electrolytes with the purity and temperature of some hydroxide sols. N. R. DHAR and V. GORE (*J. Indian Chem. Soc.*, 1929, 6, 31—43).—Sols of ferric, chromium, and zirconium hydroxides of different degrees of purity have been prepared, and it is shown that the ratio of the precipitating concentrations of uni-, bi-, and ter-valent ions decreases considerably as the purity of the sol is increased. The viscosity of a sol increases with its purity even when its concentration is constant. The ratios of the precipitating concentrations of uni- and bi-valent ions measured with stannic, zirconium, and ceric hydroxide sols are smaller at 60° than at 30°. The precipitating concentrations of uni-, bi-, and ter-valent ions are very seldom in the ratio 1 : x : x^2 , as demanded by Whetham's rule, and tend towards the ratio 1 : $\frac{1}{2}$: $\frac{1}{3}$ in the case of sols which are not hydrolysed. The ratios of the precipitating concentrations are always smaller in the cases of those sols which can be obtained readily in the pure state without peptisation by means of large quantities of electrolytes, and also smaller in the case of sols which have been exposed to light. The difference in the coagulating powers of different ions towards the same sol prepared by different investigators is mainly due to

the difference in the peptising agents retained by the sol. The difference in the precipitating concentrations is more marked with univalent ions than with multivalent ions.

O. J. WALKER.

Coagulation of strongly solvated sols by organic substances and salts. III. B. JIRGENSONS (*Kolloid-Z.*, 1929, 47, 236—243).—Experiments on the coagulation of sols of casein, hæmoglobin, and albumin by high concentrations of salts in presence of varying amounts of capillary-active organic substances (ethyl alcohol, acetone, isopropyl alcohol) have given the following results. The organic substance has a sensitising effect when present in concentrations between 30 and 40 vol.-%, but a stabilising effect at concentrations of 40—60 vol.-%; coagulation is observed at still higher concentrations of the organic substance. In some cases, the curves connecting the coagulation number with the concentration of the organic substance exhibit a maximum or a minimum. For substances having a very small dielectric constant the coagulation minimum lies nearer to the ordinate than for substances of higher dielectric constant. The stabilisation is always in direct relation to the concentration of salt and in inverse ratio to the concentration of colloid. In the coagulation of casein and hæmoglobin sols in presence of capillary-inactive organic substances, the results are not of so general a nature. Ethylene glycol has a sensitising effect on the coagulation of both casein and hæmoglobin, but stabilises at high concentrations of the organic substance or of the salt. At relatively small concentrations, dextrose has a weak stabilising effect and carbamide is strongly stabilising. The results are discussed from the point of view of the dipole theory.

E. S. HEDGES.

Periodic precipitation. F. E. LLOYD and V. MORAVEK (*Plant Physiol.*, 1928, 3, 101—130).—Photographic records were obtained of precipitation resulting from the action (in tubes, or between glass slides and cover glasses) of ammonium sulphide or hydroxide on sodium cobaltinitrite or cobalt nitrate in gelatin. The surface of the enclosing vessel gives rise to a ring and disc structure. In tubes of a certain diameter the precipitate is attached to the walls as a ring, no disc being observed. This critical diameter is related to the rate of movement of the ions concerned. Bradford's view, that the precipitate furnishes surfaces towards which the surrounding solute moves, is supported.

CHEMICAL ABSTRACTS.

Sensitisation of sols of mastic, gum dammar, and Odén sulphur in presence of gelatin and some carbohydrates. L. S. BHATTIA, S. GHOSH, and N. R. DEAR (*J. Indian Chem. Soc.*, 1929, 6, 129—142; cf. *A.*, 1927, 414).—Gelatin sensitises dialysed and undialysed sols of mastic, gum dammar, and sulphur towards potassium chloride; with larger amounts of gelatin the sols are stabilised. These sols are acidic, and when increasing amounts of gelatin are added the p_H increases to a maximum and then decreases. The amount of gelatin which produces maximum sensitisation is that which corresponds with the maximum p_H value. Sols exposed to sunlight are more readily sensitised by gelatin than sols which are kept in diffused daylight.

It is suggested that the sensitisation observed with proteins and some negatively charged sols is due to neutralisation of the charge of the colloid particles by positively charged proteins which have been formed by the adsorption of hydrogen ions. Carbohydrates in small amounts sensitise mastic and gum dammar sols and increase their p_H values, and in larger amounts stabilise the sols and decrease their p_H values. Odén sulphur sol is neither sensitised nor protected by carbohydrates, but is stabilised by tannic acid.

O. J. WALKER.

Dispersoidological investigations on proteins. I. Influence of temperature on the dispersion and coagulation of egg-albumin. S. UTZINO (*Kolloid-Z.*, 1929, 47, 244—248).—The system albumin-water-alcohol, with and without addition of sodium chloride, has been studied. In absence of sodium chloride very stable dispersoid systems are produced, the opalescence and turbidity being more intense the higher is the temperature of preparation and the greater the amount of alcohol. With addition of sodium chloride, coagulation is the more complete the higher is the concentration of the salt. The turbidity is greater in systems prepared at higher temperatures, but, so long as the amount of sodium chloride is not too great, such systems are more stable than those prepared at lower temperatures. The solutions remain stable only at very low salt concentrations.

E. S. HEDGES.

Proteins. III. Proteins and the lyotropic series. R. A. GORTNER, W. F. HOFFMAN, and W. B. SINCLAIR (5th Coll. Symp. Mon., 1928, 179—198).—In order of ascending peptising effect on the proteins of wheat flour the following series were observed: fluoride, sulphate, chloride, tartrate, bromide, iodide, and (less pronounced) sodium, potassium, lithium, barium, strontium, magnesium, calcium. Alkali halides cause decreased, and alkaline-earth halides increased, peptisation with increasing concentration of salt. In neutral salt solutions, protein "solubility" is in reality peptisation.

CHEMICAL ABSTRACTS.

Colloid chemical reactions between sols of albumins and polymerised carbohydrates. I. W. OSTWALD and R. H. HERTEL (*Kolloid-Z.*, 1929, 47, 258—268).—A study has been made of the precipitation reactions between gelatin sols and sols of maize-, rice-, wheat-, and potato-starch, agar, and inulin. Potato-starch gives with certain concentrations of gelatin a liquid-liquid system, whilst the other starches and agar give a solid-liquid system. The influence of concentration and the relative proportions of the components has been investigated, and also the effect of time. In the formation of the solid-liquid system an optimum concentration of gelatin occurs at 2%, whilst in the liquid-liquid system (potato-starch) an optimum occurs at 5% of gelatin. Whilst the liquid-liquid system does not separate out until after about 3 hrs., separation of the solid-liquid system occurs in a few minutes after mixing.

E. S. HEDGES.

Caseinates and the theory of lyophilic colloids. M. H. FISCHER and M. O. HOOKER (*Kolloid-Z.*, 1929, 47, 193—206).—The system casein-water has been

studied with the object of applying a theory of lyophilic colloids previously advanced (cf. A., 1920, i, 215). The gels formed by the action of acids and bases of varying concentration on neutral casein are described. This action is specific and bears no relation to the hydrogen-ion or hydroxyl-ion concentration of the solutions. The substances formed are salts of the type of casein chloride or potassium caseinate, and their colloidal properties are conditioned by their solubility in water and their water-binding capacity. The effect of addition of a number of electrolytes to aqueous solutions of casein chloride and of sodium and potassium caseinate has been studied and two effects have been observed: (a) the electrolyte reacts with the casein compound to form a new substance with different solubility or degree of hydration; (b) a direct effect is excluded and the electrolyte combines with the solvent. These facts are considered to offer an explanation of the increase in viscosity, gelatinisation, syneresis, and final separation into solid and liquid phases.

E. S. HEDGES.

Denaturation of proteins. VIII. Effect of denaturation and coagulation on acid- and base-binding power of proteins. H. WU and T. T. CHEN (Chinese J. Physiol., 1929, 3, 7—27).—A solution of denatured egg-albumin containing sufficient acid to be on the acid side of the isoelectric point has a p_{π} greater than a solution of the native protein containing the same quantity of acid. Similarly, a solution of denatured egg-albumin containing alkali has a lower p_{π} than a solution of native protein containing the same quantity of alkali. Similar results are obtained with serum-globulin and haemoglobin. The greater buffering action of denatured as compared with native protein may be due to hydrolytic fission during denaturation. Coagulated protein has less buffering action than native protein. This may be due to molecular condensation during coagulation, but other possible explanations are given.

W. O. KERNACK.

Capillary structure of soft woods. A. J. STAMM (J. Agric. Res., 1929, 38, 23—67).—The limitations of microscopical methods for studying the structure of wood are indicated. Four dynamic physical methods have been developed and applied to the structure of soft woods. By the method of electro-osmotic flow the total effective capillary cross-sections have been measured for sections cut in each of the three structural directions. Further information on structure can be obtained by the method of hydrostatic flow, the method of overcoming surface tension of water in the capillary structure, and lastly the method of measuring the permeability to colloidal solutions.

R. A. MORTON.

Deduction of Einstein's formula for the Brownian movement from impulses of molecular collisions. V. POSPISIL (Physikal. Z., 1929, 30, 82—83).—The method used by Einstein in his later work in conjunction with the principle of superposition of motions leads to a deduction of the formula for the Brownian movement which is regarded as clear, brief, and suitable for teaching purposes.

R. A. MORTON.

Equilibrium in the system methyl alcohol-hydrogen-carbon monoxide. D. M. NEWITT, B. J. BYRNE, and H. W. STRONG (Proc. Roy. Soc., 1929, A, 123, 236—252).—Discrepancies between the recorded equilibrium data for the system methyl alcohol-hydrogen-carbon monoxide are discussed, and details are given of (a) a static method, and (b) an intermittent-flow method, by means of which the equilibrium constant K_p has been determined at eight temperatures within the range 280—340°, for pressures of about 100 atm. In each case, equilibrium was approached from opposite sides. The static method consists essentially in introducing an approximate equilibrium mixture into an evacuated vessel containing basic zinc chromate as catalyst. The rate of change of pressure is followed by a specially devised manometer until the attainment of equilibrium, when a sample of the contents of the vessel is analysed. Known quantities of the components are then added to displace the equilibrium in the required direction, and the pressure change is again followed until constant conditions are reached. In the intermittent-flow method, a mixture of the three components, in nearly equilibrium proportions, is passed over the catalyst maintained at the desired temperature, and the change in composition of the mixture determined by analysis. By varying the rate of flow from fast to slow through a series of experiments with a mixture of given composition, a series of apparent equilibrium constants is obtained approaching more closely to the true value as the velocity decreases. By plotting the apparent K_p values (obtained by synthesis and by decomposition) and the corresponding rates of gas flow two curves are obtained which meet at the true equilibrium value. The values obtained by the two methods show fair agreement among themselves, and when plotted against the absolute temperature lie on a curve rising steeply in the neighbourhood of 290°. The experimental figures are considerably lower than those found by calculation. The linear relation $\Delta F = 70.9T - 30500$ is found to hold between the free energy, calculated from the experimental K_p values, and the absolute temperature over the range studied. The following values of K_p are tabulated: 1.2×10^{-3} (260°), 4.5×10^{-4} (280°), 1.6×10^{-4} (300°), 6.7×10^{-5} (320°), 2.9×10^{-5} (340°), 1.3×10^{-5} (360°), 6.3×10^{-6} (380°).

L. L. BIRCHUMSHAW.

Heitler's theory of concentrated solutions. L. VIETH (Physikal. Z., 1929, 30, 126—139).—Heitler's theory has been subjected to a critical examination. Various assumptions, explicit and implicit, are not quantitatively in accord with experience. The theory nevertheless possesses great advantages, and the degree of agreement between experiment and theory in some instances lends support to the view that revision of the simple theory will lead to better agreement in other cases.

R. A. MORTON.

Equilibrium law for electrolytes. Association. K. JABŁCZYŃSKI (Rocz. Chem., 1929, 9, 97—110).—A study of the equilibrium constants given by various authors for concentrated solutions of alkali nitrates shows that K diminishes with increasing concentration, whence it is concluded that the anion to a certain

extent combines with undissociated molecules to give rise to complex ions of the type $(R \cdot N_2O_6)'$. The expressions $K_1 = \frac{1}{(N-2n_1)}$, and $K_2 = \frac{n_1(P)^{2/3}}{P^{2/3}(N-2n)}$ are derived, where K_1 and K_2 are respectively the dissociation constants of the nitrate in question and of the complex anion $(RN_2O_6)'$, n_1 is the concentration of the cation in each case, P the concentration of nitrate ions, and N the total number of molecules. In the case of nitric acid and of lithium nitrate association does not occur. K_1 decreases and K_2 increases along the series H, Li, Na, K, Rb, Cs. The cations are hydrated to the same extent in solutions of the alkali chlorides and nitrates.

R. TRUSZKOWSKI.

Effect of position of substitution on apparent dissociation constants of some amino-acids. C. L. A. SCHMIDT, W. K. APPLEMAN, and P. L. KIRK (J. Biol. Chem., 1929, 81, 723—726).— β -Aminopropionic acid has $K_a' 6.45 \times 10^{-11}$, $K_b' 3.98 \times 10^{-11}$; α -amino-*n*-valeric acid $K_a' 1.9 \times 10^{-10}$, $K_b' 2.3 \times 10^{-12}$; γ -amino-*n*-valeric acid $K_a' 3.99 \times 10^{-11}$, $K_b' 1.06 \times 10^{-10}$; δ -amino-*n*-valeric acid $K_a' 2.04 \times 10^{-11}$, $K_b' 1.62 \times 10^{-10}$. Curves obtained by plotting the negative logarithms of the above figures against the reciprocal of the distance between the carboxyl and amino-groups are straight lines (cf. MacInnes, A., 1928, 1326).

C. R. HARRINGTON.

Classical thermodynamics and the new problems of chemical dynamics. H. DAMIANOVICH (Anal. Soc. Cient. Argentina, 1928, 105, 255—271; Chem. Zentr., 1928, ii, 1067).

Entropy and heat of evaporation. W. HERTZ (Z. anorg. Chem., 1929, 179, 277—278).—The product of the entropy and the cube root of the latent heat of evaporation of the elements has an approximately constant value for each group of the periodic table, and also for certain groups of metallic halides.

H. F. GILLBE.

Thermodynamics of mixtures. V. FISCHER (Z. Physik, 1929, 53, 138—147; cf. A., 1928, 241).—Mathematical. The latent heat of fusion and of vaporisation of a binary mixture is calculated in terms of the latent heats of the pure materials. A general type of equation is derived for the equilibrium conditions for a binary mixture. An equation relating the m. p. of a liquid with the applied pressure is also developed, and the results deduced therefrom for the case of mercury were found to be in good agreement with the values measured by Bridgeman (Proc. Amer. Acad., 1911, 47, 432). J. W. SMITH.

Equilibria in systems containing surface distributed phases. N. VON RASCHEVSKY (Z. Physik, 1928, 51, 571—583).—The thermodynamics of the unimolecular films which form on the surface of some solutions has been developed by treating such films as separate phases.

R. W. LUNT.

Hysteresis phenomena in physico-chemical systems. N. VON RASCHEVSKY (Z. Physik, 1929,

It is shown that the state of any physico-chemical system which has several equilibrium states with fixed external conditions depends on the previous history of the system. Moreover, the state of such a system depends, not only on the path followed by such external conditions, but also

on the velocity with which the changes are carried out.

J. W. SMITH.

Equilibrium and reactions in systems with very large specific surface. N. VON RASCHEVSKY (Z. Physik, 1929, 53, 107—129; cf. A., 1928, 474, 690; and preceding abstracts).—The deductions drawn in previous papers concerning the conditions which exist in drops which gradually increase in size and then split are extended. It is also shown that in any system in which the surface energy is not negligible, the limitation of the number of phases demanded by the phase rule does not hold. Various general properties of such systems are treated, special reference being made to the case where the system has several equilibrium conditions and hence shows hysteresis phenomena.

J. W. SMITH.

Metastability of elements and compounds as a consequence of enantiotropy or monotropy. XII. **Heat of dissolution.** I. E. COHEN and J. KOOY (Z. physikal. Chem., 1928, 139, 273—350; cf. Person, Ann. Chim. Phys., 1851, 33, 437; Berthelot and Ilosvay, A., 1884, 704).—The effect of previous thermal history on the heat of dissolution of sodium and potassium chlorides, potassium sulphate and nitrate, and thallium sulphate has been investigated, the heats of dissolution being determined at 20.00° in the adiabatic calorimeter previously described (A., 1925, ii, 402). Details of the method and full data after various heat treatments and cooling are given, together with a discussion of previous investigations on each of the salts used.

Kahlbaum's potassium sulphate, dried at 300—350°, showed no change in the value of the heat of dissolution when recrystallised from water or when repeatedly heated below its transition temperature. Other heat treatments, however, show that potassium sulphate exists in two modifications, and the heat of dissolution of the α -form when diluted with 400 mols. of water is -6284 ± 4 g.-cal./mol. When heated above the transition temperature, initial deviations from this value occur to an extent which depends on the rate of cooling. The salt which had been melted and reacted neutral showed a deviation equal to that of the calcined salt, and potassium sulphate which reacted alkaline also showed a marked change in the heat of dissolution. Since deviation and decomposition do not run parallel, this behaviour cannot be ascribed to the presence, by itself, of the corresponding base, but it can be explained by the retarding influence of the base on the velocity of the change $\beta \rightarrow \alpha$ -K₂SO₄. On keeping, spontaneous stabilisation to the α -form occurs in all the cases examined.

Potassium nitrate also shows enantiotropy. The heat of dissolution of the form stable at the ordinary temperature and pressure on dilution to 200 mols. of water is -8336 ± 2 g.-cal./mol. at 20.00° and on dilution to 359 mols. of water -8426 ± 2 g.-cal. at 20.5° (cf. Roth, A., 1928, 22). When heated above the transition temperature, anomalous values, which return to the normal on stabilisation of the salt, are obtained. Melting and rapid cooling of the salt changes the heat of dissolution only slightly.

Thallium sulphate, prepared from Kahlbaum's pure metal and pure sulphuric acid with platinum as

catalyst, recrystallised from water and dried at 170° had d_4^{20} 6.765 and after melting, pulverisation, and heating at 170° , 6.771. The heat of dissolution of the rhombic form, diluted to 3200 mols. of water, is -7940 ± 60 g.-cal./mol., and in agreement with Tammann and von Sahmen (A., 1903, ii, 356) more than one modification of the salt is considered to exist. Crystallisation from aqueous or from pyridine-water solutions, melting, and subsequent quenching or slow cooling always yields a product which has the same heat of dissolution as that of the salt prepared by crystallisation from water and dried at 170° . Precipitation from aqueous solution by the addition of methyl or ethyl alcohol yields a product which gives a value initially different from the original. This product is concluded to be a mixture of polymorphic forms of thallium sulphate.

The heat of dissolution of potassium chloride diluted to 200 mols. of water is -4373 ± 2 g.-cal./mol. at 20.00° and -4191 ± 2 g.-cal. at 25.00° , and the former value is quite unchanged by various heat treatments. For sodium chloride diluted to 100 mols. of water, the values at the corresponding temperatures are -1100 ± 4 and -965 ± 2 g.-cal./mol., respectively, and, contrary to Person (*loc. cit.*) and Berthelot (*loc. cit.*), they are unaffected by the previous heat treatment. In both cases, the deviations from the values of other workers are so large that standard values for the heat of dissolution of these two salts cannot be given, but calorimetric processes and not polymorphism must be regarded as responsible for the lack of agreement between the published values.

Finally, it is re-emphasised that many physical constants are invalidated by insufficient physical purification of the substance investigated. This applies especially to potassium sulphate and nitrate, and to a smaller extent to thallium sulphate, and data relating to these substances have no significance unless the previous history of the salt has been taken into account. L. S. THEOBALD.

Transformation of the β -phase in zinc-copper alloys. Causes of the disagreement in the results of different investigators. P. SALDAU (Z. Metallk., 1929, 21, 97—98).—The widely different positions of the boundary line between the α and $\beta_1 + \gamma$ fields in copper-zinc alloys found by various investigators are ascribed to insufficient annealing; in the author's work (J. Inst. Metals, 1925, 34, 258) annealing was continued for 84 days at 440° (cf. also A., 1928, 955). A. R. POWELL.

System ferric oxide water. G. F. HUTTIG and H. GARSIDE (Z. anorg. Chem., 1929, 179, 49—76).—A study has been made of the vapour-pressure curves, X-ray diagrams, specific heats, chemical reaction velocities, velocities of dissolution, and catalytic activities of a number of preparations of hydrated ferric oxide, and the following conclusions are reached. The freshly-prepared hydrogel is amorphous, and although as regards the total composition the whole of the ferric oxide is chemically combined with water, probably as $\text{Fe}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3 \cdot \text{H}_2\text{O}$, at any given moment a certain fraction of the water molecules is mobile within the colloid and unattached to definite ferric oxide molecules. Careful desiccation of the gel

until the composition $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is reached results in an amorphous substance in which the greater number of molecules are of identical composition. Removal of the residual water is very difficult, and although this may be effected by warming, a partial conversion of the material into the crystalline form is unavoidable. The hydrogels may be kept for several months without crystallisation setting in, although changes take place in the activity and specific heat. The final product of ageing is goethite or crystalline ferric oxide with uncombined water; in presence of free water below a temperature somewhere between 77° and 228° , the former is the stable phase, whilst above this temperature the latter is stable. No crystalline hydrate other than goethite has been observed in an ageing gel. Although ageing at the ordinary temperature tends to the production of goethite, a certain fraction of the gel is converted into crystalline ferric oxide. Although the ferric oxide-water system is not stable at the ordinary temperature the velocity of formation of goethite is too slow to be observed in the laboratory. H. F. GILLBE.

Double sulphates of the rare-earth metals and the alkali metals. XII. Sulphates of cerium (cerous) and caesium. F. ZAMBONTINI and S. RESTAINO (Atti R. Accad. Lincei, 1929, 9, 131—133; cf. A., 1928, 957).—The system $\text{Ce}_2(\text{SO}_4)_3$ - Cs_2SO_4 - H_2O has been investigated at 25° . Only one compound was obtained, viz., $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$, which is stable at 25° in contact with solutions containing from 1.5% Cs_2SO_4 and 5.4% $\text{Ce}_2(\text{SO}_4)_3$ to about 46% Cs_2SO_4 . Some crystallographic data are given. O. J. WALKER.

Ternary system mercuric chloride-mercuric iodide-water. (MISS) R. SUGDEN (J.C.S., 1929, 488—491).—The system has been examined at 30° and 70° . The two salts are mutually soluble in the solid state. At the iodide end, two series of mixed crystals are obtained, corresponding with the two forms of the simple iodide. Their stability is dependent on temperature and chloride content. There is no evidence of compound formation (cf. Kohler, A., 1879, 1017). F. J. WILKINS.

Ternary system water-sodium nitrate-potassium nitrate. E. CORNEC and H. KROMBACH (Compt. rend., 1929, 188, 788—790).—Solubility measurements show the absence of mixed crystals between the ordinary temperature and 100° ; mixed crystals appear to be formed at 105° . J. GRANT.

Equilibria between metals and salts in fused masses. XVI. Disturbances of equilibria by additions, and their calculation by the new mass action law. R. LORENZ and G. SCHULZ [with M. HERING, P. WOLFF, and J. SILBERSTEIN] (Z. anorg. Chem., 1929, 179, 97—110).—Addition of inert miscible substances such as sodium chloride or antimony to the equilibrium $\text{Cd} + \text{PbCl}_2 \rightleftharpoons \text{Pb} + \text{CdCl}_2$ causes a displacement of the equilibrium which increases up to a certain limit as the quantity added increases. This limiting concentration is analogous to the infinite dilution of solutions, when the added substance is considered as the diluent, but the actual concentrations involved are much greater, and

although with increase of displacement the equilibrium isotherms approach those for an ideal system, there is always a certain deviation. The new mass action law, however, gives satisfactory results for such systems.

H. F. GILLBE.

Indirect analysis of a chemically single phase in a system composed of two phases. E. WEITZ [with H. STAMM] (*Z. anorg. Chem.*, 1929, 179, 193—210).—The composition of a compound A which constitutes phase A in a two-phase system, the other phase B being chemically complex, may be graphically determined by analysis of phase B and of a mixture of A and B if the number of components is not less than three.

H. F. GILLBE.

Heat of neutralisation of acetic acid. T. W. RICHARDS and B. J. MAIR (*J. Amer. Chem. Soc.*, 1929, 51, 737—740).—The heat of neutralisation of acetic acid with sodium hydroxide, each substance being at a dilution of 1 mol. in 100 mols. of water, was measured directly at 20°. With the aid of previously published data, the values at other concentrations were calculated. Graphical extrapolation yields the value 13,650 g.-cal./mol. at infinite dilution.

S. K. TWEEDY.

Thermochemical behaviour of sodium hydroxide solutions. T. W. RICHARDS and L. P. HALL (*J. Amer. Chem. Soc.*, 1929, 51, 731—736).—The heat of dilution of NaOH.10H₂O was determined at 16° and 20°. At 20° heat is evolved until the concentration NaOH.17.5H₂O is reached, after which heat is absorbed. The specific heats of some concentrated solutions are calculated. The earlier thermochemical data on sodium hydroxide solutions obtained by Richards and his co-workers are recalculated. Calculation yields the value 13,650 g.-cal./mol. as the heat of neutralisation of hydrochloric acid with sodium hydroxide at 20° at infinite dilution.

S. K. TWEEDY.

Heats of dissolution of some salts in water and ethyl alcohol solutions. J. R. PARTINGTON and W. E. SOPER (*Phil. Mag.*, 1929, [vii], 7, 209—247).—The heats of dissolution and dilution of potassium chloride, potassium thiocyanate, sodium thiocyanate, anhydrous cupric chloride, and anhydrous calcium nitrate in water, and of sodium thiocyanate, anhydrous cupric chloride, and anhydrous calcium nitrate in ethyl alcohol have been determined. The values for potassium chloride in water were determined to check the accuracy of the method adopted.

A. E. MITCHELL.

Heats of combustion of organic compounds. M. S. KHARASCH (*Bur. Stand. J. Res.*, 1929, 2, 359—430).—The literature on the heats of combustion of organic compounds is critically reviewed, and a table of best values compiled, containing all available data. The tables are arranged according to the types of the organic substances, and compounds are also indexed by formula. A full bibliography is given. A method for calculating the heats of combustion of organic compounds from the structural formulae is described. It is assumed that the heat generated is due to the displacement of the electrons between the carbon and oxygen atoms. When the initial and final states of the carbon atom correspond

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with methane and carbon dioxide the net energy liberated is taken as 26.05 kg.-cal.₁₅/electron/mole. The general formula for the heat of combustion, Q , is $Q=26.05N$, where N is the number of electrons, plus a structural correction factor when the electrons are displaced as compared with their position in methane. These correction factors are tabulated. The calculated values are given in the tables for comparison with the observed values.

C. J. SMITHELLS.

Specific heats and vapour pressures of systems formed from water and the oxides of zirconium, thorium, and tin. G. F. HUTTIG, S. MAGIER-KIEWICZ, and J. FICHMANN (*Z. physikal. Chem.*, 1929, 141, 1—34).—Changes in such systems which are usually attributed to "ageing" may be followed by means of specific heat measurements. Measurements made with preparations of varying water content in the systems ZrO₂-H₂O, ThO₂-H₂O, and SnO₂-H₂O by the method of Huttig and Wehling (*A.*, 1926, 1103) show that the relation between the specific heat and the water content is given as a first approximation by $\log_e c_0/c = k/N$, where c_0 is the molecular heat of pure water, c is the molecular heat of the hydrate containing N mols. of water to 1 mol. of oxide, and k is an empirical constant. Vapour-pressure measurements have also been made and a similar connexion is found to hold between the vapour pressure and water content. The changes in the "ageing" process are discussed.

O. J. WALKER.

Entropy decrease of a thermodynamic system by the intervention of an intelligent being. L. SZILARD (*Z. Physik*, 1929, 53, 840—856).—Theoretical.

W. E. DOWNEY.

Electrolytic transport of water in 0.1N-solutions of hydrobromic acid. J. BABOROVSKY and A. WAGNER (*Chem. Listy*, 1929, 23, 97—98).—When 96,490 coulombs are passed through a 0.1N-solution of hydrobromic acid 0.860 g.-mol. of water is transported. The transport number of the cation is 0.867. The value obtained is greater in the presence of a parchment-paper membrane than in its absence.

R. TRUSZKOWSKI.

Calibration of conductivity cells for use with dilute solutions. I. At 18°. C. W. DAVIES (*Trans. Faraday Soc.*, 1929, 25, 129—133).—The equation $\Lambda=129.85-79.8C^{1/2}$, where C is the equivalent concentration, is suggested for the determination of conductivity cell constants at 18° for concentrations up to 0.001N. Kohlrausch and Maltby's solvent correction for the conductivity data for potassium chloride is modified to take into account the interionic forces, and the conductivity values are thereby reduced by 0.06 unit or more. The differences between the calculated and the corrected experimental results are of the order of 0.02% (cf. following abstract).

J. GRANT.

Calibration of conductivity cells. II. Conductivity of potassium chloride at 25°. J. GRINDLEY and C. W. DAVIES (*Trans. Faraday Soc.*, 1929, 25, 133—137).—Corrected conductivity determinations (cf. preceding abstract) of aqueous potassium chloride solutions up to 0.0015N at 25° show an average deviation of 0.025% from the equation

$\Lambda = 150.59 - 109.0C^{1/2}$, where C is the equivalent concentration. The equation may therefore be used for cell constant determinations at 25°. J. GRANT.

Measurements of conductivities by means of oscillating circuits. S. D. GEHMAN and B. B. WEATHERBY (Phil. Mag., 1929, [vii], 7, 567—569).—The results of Burton and Pitt (A., 1928, 712) for the conductivities of various solutions by means of an oscillating valve circuit are vitiated by the changes in distributed capacity caused by the insertion of the tubes containing the liquids into the coils of the oscillating system; such capacity changes produce serious frequency changes in the circuit. Experimental results are described which indicate that the effects obtained by Burton and Pitt are due primarily to the dielectric constants of the liquids and not to their conductivities. A. E. MITCHELL.

Calculation of the conductivity of water. J. L. LINSCHOTEN (Chem. Weekblad, 1929, 26, 198—202).—Two methods are given for the construction of nomograms which permit the required conductivities to be obtained without calculation. S. I. LEVY.

Conductivity of strong electrolytes for high-frequency currents. H. ZAHN (Z. Physik, 1928, 51, 350—354).—The conductivities of magnesium sulphate and copper sulphate solutions for high-frequency current ($\lambda = 1$ metre) have been compared with the conductivities for direct current by determining the concentration of potassium chloride solution which has the same conductivity for the high-frequency current as the solution under investigation. The conductivities for direct current being known, and assuming the change for potassium chloride which was derived by Debye and Falkenhagen (A., 1928, 957), the changes in the conductivities of the other salts are deduced and found to be in good agreement with the theoretical values. J. W. SMITH.

High-frequency conductivity of aqueous solutions of electrolytes. H. RIECKHOFF and H. ZAHN (Z. Physik, 1929, 53, 619—627).—The increase in conductivity for alternating currents of high frequency of aqueous electrolytes has been further investigated over an extended range of concentrations. There is good agreement with the theory of Debye and Falkenhagen. A. J. MEE.

Conductance of mixed solutions of lead nitrate and ammonium nitrate. G. MALQUORI (Atti R. Accad. Lincei, 1929, [vi], 9, 231—233; cf. this vol., 141).—The conductance, corrected for viscosity effects, of lead nitrate solutions increases with rise of temperature from 10° to 60° for concentrations between 0.45 and 1.35 equiv./litre. The increase is rapid between 50° and 60°. For solutions of ammonium nitrate under similar conditions the conductance decreases. The conductance of mixed solutions with moderately high concentrations of ammonium nitrate decreases with temperature. A decrease is found also with solutions rich in lead nitrate excepting when the concentration of ammonium nitrate is rather low. In the latter case, $\text{Pb}(\text{NO}_3)_2$ 1.3525, NH_4NO_3 0.4773 equiv./litre, the conductance decreases up to 35°, and passes through a maximum at about 50°. This behaviour is attributed to com-

plex salt formation with the probable existence of a $\text{Pb}(\text{NO}_3)_4^{''}$ ion. F. G. TRYHORN.

Electrochemistry of ethereal solutions. II. System arsenic trichloride-ethyl ether. M. USSANOVITSCH (Z. physikal. Chem., 1929, 140, 429—434; cf. A., 1927, 315).—The electrical conductivities of 0—100% solutions of arsenic trichloride in ethyl ether have been determined at 18°. Up to 40% AsCl_3 the specific conductance is very small; the increased conductivity at higher concentrations shows a maximum at 94% AsCl_3 . The temperature coefficient of the conductivity is negative at all concentrations. The variation of the molecular conductivity with the dilution is abnormal when referred to arsenic trichloride as the electrolyte; taking ethyl ether as the electrolyte there is a steady rise in the conductivity with dilution. The conductivity curves are analogous to those of the system $\text{AsBr}_3\text{--Et}_2\text{O}$. The decomposition potential of a 68.81% solution of arsenic trichloride in ether at 18° is 1.22 volts. On electrolysis arsenic is deposited at the cathode in quantitative agreement with Faraday's law. O. J. WALKER.

Wien's voltage effect in electrolytes. M. BLUMENTRITT (Ann. Physik, 1929, [v], 1, 195—215).—Onsager's improved form of the Debye-Hückel theory has been applied to Wien's voltage effect, and good agreement with the experimental data is obtained for field strengths up to 25,000 volts/cm., the only exceptions being with ions of very high valency. R. A. MORTON.

Dielectric measurements as a rapid means of water determination. E. BERLINER and R. RUTER (Kolloid-Z., 1929, 47, 251—257).—A simple apparatus for the measurement of dielectric constants is described and it is shown that the measurement of dielectric properties can serve as a rapid means of determining water in other substances. The apparatus has been applied to the measurement of the dielectric constants of binary non-conducting liquid mixtures and aqueous solutions over a wide range of composition and results are given for aqueous solutions of methyl, ethyl, and isopropyl alcohols, glycol, glycerol, dextrose, sucrose, carbamide, acetone, and for the systems benzene-ethyl alcohol and benzene-nitrobenzene. E. S. HEDGES.

Deposition of radium and other alkaline-earth metals at the dropping mercury cathode. J. HEYROVSKY and S. BEREZICKY (J. Czechoslov. Chem. Comm., 1929, 1, 19—46).—Measurements of deposition potentials (i.e., the cathodic potentials, calomel electrode being zero, at which the slopes of the current-voltage curves are all 45°) during electrolysis, using a dropping mercury cathode (cf. A., 1923, ii, 119), have been increased in sensitivity partly by the introduction of an auto-registering apparatus (the "polarograph") and partly by other mechanical refinements.

The following deposition potentials for normal ionic concentrations are found: radium, -1.718 ; barium, -1.761 ; strontium, -1.964 ; magnesium, -1.996 ; calcium, -2.047 volts. Differences in the deposition potentials of alkaline-earth metals are large enough for the deposition of each of them from a mixture to

be followed. Thus the deposition of radium may be followed quantitatively for mixtures with barium when the ratio radium:barium falls between the limits 1:10 and 25:1 in $10^{-4}M$ concentrations. Traces down to 10^{-5} g.-equiv. per litre of radium or barium are likewise determinable in admixture with alkalis or alkaline earths, but strontium only in mixtures with alkaline earths or lithium.

The polarographic method has been used to obtain the solubilities of sparingly soluble salts; even in the presence of excess of other electrolytes it enables the concentrations of small quantities of certain ions to be determined. The following measurements are recorded: barium sulphate in $0.001N$ -lithium chloride, 3×10^{-5} g.-equiv. per litre (a marked ageing effect is observed, freshly-precipitated barium sulphate being eight times as soluble as a specimen 30 hrs. old); barium carbonate in $0.1N$ -lithium chloride, 8.2×10^{-4} g.-equiv. per litre, in water $5.7 \times 10^{-4}N$; strontium sulphate in $0.001N$ - and $0.01N$ -lithium chloride $1.1 \times 10^{-3}N$ and $1.8 \times 10^{-3}N$, respectively, in water $1.5 \times 10^{-3}N$; strontium carbonate in water $2.8 \times 10^{-4}N$; strontium oxalate in water $5.6 \times 10^{-4}N$; calcium oxalate in water $1 \times 10^{-4}N$ (all at 18°).

Evolution of hydrogen accompanies the deposition of magnesium and beryllium; by this means small quantities of magnesium can be determined.

"Adsorption currents" due to ionic adsorption at the cathodic mercury-solution interface were observed in all solutions more concentrated than $0.001N$ and were plainly indicated on current-voltage curves of solutions of the heavy alkaline earths. Illustrations of polarographic titrations of barium, strontium, and calcium ions are given. R. J. W. LE FÈVRE.

Electrolytic solution tension and the ionic state. V. Calculation of electrolytic solution tension. Mechanism of electrolytic dissociation. Nature of the ionic state. K. FREDENHAGEN (Z. physikal. Chem., 1929, 140, 435—474; cf. A., 1928, 1316; this vol., 397).—A theoretical discussion of the causes of electrolytic dissociation and of the nature of the ionic state. The thermodynamic treatment of electrolytic solution forces given in the previous papers is summarised and a mechanism of electrolytic dissociation is put forward. If KA represents a molecule of the solvent, then the chemical affinities of the two components K and A are not completely saturated by their union to form a molecule. The molecule KA will be partly dissociated into its constituents K and A , each of which will have a certain affinity for the dissolved substance and thereby decrease its chemical "activity." The solution tension of a substance depends on the difference of its affinities for the two constituents K and A , becoming zero when they are equal, and is therefore a function of the internal forces in the solvent molecule. The experimentally determined electrolytic solution tensions are of the order of magnitude required by the preceding assumptions. Further evidence for the theory is obtained from a consideration of the potential series of the elements in various solvents, of the dissociation of water and molten salts, and of the variation of solution tension and dissociation with the temperature. O. J. WALKER.

E.M.F. of uni-univalent halides in concentrated aqueous solutions. H. S. HARNED (J. Amer. Chem. Soc., 1929, 51, 416—427).—The *E.M.F.* at 25° are recorded for flowing amalgam cells of the type $Ag|AgX|MX(c)|M_2Hg|MX(0.1M)|AgX|Ag$ in which $M=K, Na, Li$, $X=Cl, Br$ and c varies between 0.05 and $4M$. For the less concentrated solutions, the results deviate uniformly from the additive relationship postulated by MacInnes and by Harned (A., 1920, ii, 664). The observed activity coefficients for the sodium and potassium salts agree well up to $2M$ with those calculated by Hückel's equation; above this concentration the calculated values become progressively smaller than the observed. The activity coefficients for the lithium salts are also recorded. A comparison of the activity coefficients obtained with those calculated from vapour pressure data is considered to confirm the accuracy of the *E.M.F.* method here employed. S. K. TWEEDY.

Oxidation-reduction potentials. I. Ferric-ferrous [iron] electrode. S. POPOV and A. H. KUNZ (J. Amer. Chem. Soc., 1929, 51, 382—394).—*E.M.F.* measurements were made on the cell $Pt, H_2|HCl|HCl+FeCl_2+FeCl_3|Pt$, the liquid junction potential being kept constant by the use of a flowing junction. By plotting a function of the potential against the concentration of the ferrous chloride for several values of the latter and extrapolating to zero concentration the junction potential is eliminated, and by plotting the potential for various acidities against the acid concentration and again extrapolating to zero concentration the influence of the acid is eliminated. The value obtained for the normal oxidation-reduction potential of the ferric-ferrous iron electrode is -0.7477 volt, in substantial agreement with the value derived from equilibrium measurements (cf. Noyes and Brann, A., 1912, ii, 916) and with the value calculated on the basis of ionic strength. S. K. TWEEDY.

Oxidation potentials of some hypochlorite solutions. V. H. REMINGTON and H. M. TRIMBLE (J. Physical Chem., 1929, 33, 424—434).—The oxidation potentials of hypochlorous acid and sodium hypochlorite solutions in various solutions have been determined. Reproducible results with smooth platinum wire electrodes could be obtained only after treating the electrode with hot, concentrated nitric acid for 10—15 min., cooling and washing with conductivity water, drying, and heating the wire electrically to dull redness for 1—2 min. and placing at once in the electrolyte. The passage of a current of carbon dioxide through sodium hypochlorite solution markedly increases the oxidation potential and even traces of this gas cause an increase of 0.05 — 0.1 volt. The oxidising power of hypochlorites in solution as measured potentiometrically increases with an increase in hydrogen-ion concentration, and the amount of added acid or base as well as the hypochlorite content can be approximately determined by electrometric titration. Solutions buffered with alkali phosphate, carbonate, or hydrogen carbonate are more stable and give potentials which are more readily reproduced than those of unbuffered solutions. L. S. THEOBALD.

Oxidation-reduction systems of biological significance. III. Mechanism of the cysteine potential at the mercury electrode. E. S. G. BARRON, L. B. FLEXNER, and L. MICHAELIS (J. Biol. Chem., 1929, 81, 743—754).—The behaviour of the mercury electrode in a solution of cyanide is closely similar to its behaviour in one of cysteine (cf. A., 1928, 1330); this is due to the fact that cysteine reacts with metallic mercury to form an undissociated compound which is apparently identical with that described by Brenzinger (A., 1892, 1111) in the same way that it reacts with cyanide to form undissociated mercuric cyanide. This accounts for the hitherto unexplained fact that the potential established at the mercury electrode in a solution of cysteine is independent of the concentration of the latter; it indicates further that observations made on the "cystine-cysteine" system at the mercury electrode are in reality applicable only to the "cysteine-mercuric cysteinate" system, and may not bear any relationship to the properties of the cystine-cysteine system under physiological conditions.

C. R. HARRINGTON.

Maxima on the current-voltage curves. III. Electrolysis of mercury salt solutions with dropping and steady mercury cathodes. P. HERASYMENKO, J. HEYROVSKY, and K. TANŌAKIVSKY (Trans. Faraday Soc., 1929, 25, 152—159).—Determinations of the current-voltage curve maxima and the corresponding changes in interfacial tension during the electrodeposition of mercury at a dropping mercury cathode (A., 1928, 372, 596) and at a stationary cathode formed by a large drop of mercury in the bottom of the cell, gave analogous results for both cathodes, but were least reproducible for the latter. According to Heyrovsky's theory (*loc. cit.*) the discontinuous decrease in current shown by the curves and the associated concentration polarisation are due to the formation of an interfacial layer free from mercury salts which prevents further adsorption at the cathode interface. Preferential adsorption is considered to explain the suppression of the maxima on the addition of adsorptive matter or of an indifferent electrolyte.

J. GRANT.

Inversion of the photovoltaic effect by hydroxyl and hydrogen ions. G. ATHANASIU (Compt. rend., 1929, 188, 786—788).—Addition of hydroxyl ions to photo-electric cells containing neutral potassium chloride as electrolyte destroys or inverts the positive photo-electric effect shown by the electrodes Ag|AgI, Ag|AgBr, Cu|Cu₂I₂, Cu|Cu₂Br₂, and Hg|Hg₂I₂, and increase the negative effect shown by the Ag|Ag₂S electrode. The positive effect of the oxidised copper electrode is increased by the addition of hydrogen ions. Halogens liberated at the electrode by the action of light are probably removed from the sphere of action by interaction with the ions of the electrolyte.

J. GRANT.

Becquerel effect. II. I. LIFSCHITZ and S. B. HOOGHOUTD (Z. physikal. Chem., 1929, 141, 52—70; cf. A., 1927, 423, 942).—The Becquerel effect is discussed from the point of view of Winther (A., 1928, 247), who suggested the necessity of distinguishing between the surface effects at light-sensitive electrodes

(effect of the first kind) and the volume effects in the electrolytic solution (effect of the second kind). It is shown that it is not easy to distinguish between these two effects. The effect of the second kind does not depend on a simple photochemical displacement of an equilibrium such as occurs in a cerous-ceric salt solution, for in the latter the changes in photochemical potential do not represent a true Becquerel effect.

The Becquerel effect occurs also with non-aqueous solutions, and is greatly dependent on the wavelength of the radiation and on the nature of the solvent and of the ions present, but the nature and size of the electrode have no appreciable influence. Measurements of the effect with open circuit give only the sign and order of magnitude of the effect. The mechanism of the Becquerel effect is discussed.

O. J. WALKER.

Theory of chemical reaction velocity. N. SEMENOV (Z. physikal. Chem., 1929, B, 2, 161—168).—Mathematical. The kinetics of chain reactions are considered, taking into account secondary activation of molecules taking part, as well as the primary activation. From the equations the theoretical conditions for explosion are calculated. Where experimental results are available they are in agreement with theory.

A. J. MEE.

Kinetics of combination of hydrogen and oxygen. N. SEMENOV (Z. physikal. Chem., 1929, B, 2, 169—180).—Mathematical. The kinetics of the reaction are developed on somewhat different lines from the treatment of Gibson and Hinshelwood (A., 1928, 960), use being made of the Einstein-Smoluchowski formula for calculating the length of the chain. The reactions which are supposed to occur are $H + O_2 = HO_2$; $HO_2 + H_2 = H_2O_2 + H$; $2H_2O_2 = 2H_2O + O_2$. The average number of elementary reactions in the chain is calculated when an inert gas is present, an increase in the reaction velocity being indicated in agreement with the experimental results of Gibson and Hinshelwood. The relationship between the number of elementary reactions and the partial pressure of the inert gas is calculated. It is necessary to make two assumptions, viz., that the diameters of all molecules concerned except HO_2 are equal, and that the diameter of the HO_2 molecule is much larger than that of the other molecules. With these assumptions, the relationship is calculated for nitrogen and helium. It is concluded that the effect of the inert gas is to increase the length of the chain. The temperature coefficient of the reaction and the conditions for explosion are worked out. The latter agree with experiment. The order of the reaction is also investigated. There are three ways in which the hydrogen molecule may be broken down into atoms: (1) by the absorption of radiation, (2) by collision with another molecule moving sufficiently rapidly, (3) by rebounding from the wall of the vessel with sufficient energy. These three are examined, and the first two are found to be insufficient to explain the reaction. Using the third method, the equation for the reaction velocity obtained is $w = e[H_2]^2([H_2] + [O_2])$, where w is the reaction velocity and $[H_2]$ and $[O_2]$ are the partial pressures of the gases. This is in fairly good agreement with experiment. The effect

of the addition of an inert gas on the secondary activation is also considered. The experimental curve between $\log p$ and $1/T$, where p is the minimum explosion pressure at a temperature T , is given and it is shown that below a certain temperature the curve can be explained on theoretical grounds.

A. J. MEE.

Thermal decomposition of ozone at low pressures. L. S. KASSEL (Z. physikal. Chem., 1929, B, 2, 264—265; cf. Riesenfeld and Schumacher, this vol., 146).—It has been shown that reactions which are of the second order at high pressures agree with the first order equations at low pressures, and for yet smaller pressures with the second order equations with increased velocity coefficient. Ozone shows this phenomenon in its decomposition at low pressures. The homogeneity of the reaction is still uncertain.

A. J. MEE.

Retardation period in spontaneous ignitions and explosions. M. BRUNNER (Helv. Chim. Acta, 1929, 12, 295—304).—The cause of the induction period, which is found to occur with certain gaseous mixtures before ignition or explosion after the ignition temperature has been reached, is discussed and an explanation is proposed based on recent theories of the mechanism of chain reactions (Semenov, Hinshelwood). During the retardation period ignition or explosion does not take place, because owing to the deactivating action of the walls of the vessel a sufficient number of reaction centres is not formed. The activity of the deactivating centres is gradually diminished through adsorption of the slowly-formed reaction products, until finally the formation of new reaction centres predominates, and ignition or explosion can occur. Experimental data on the effect of various factors on the induction period (*e.g.*, temperature, pressure, composition of the gaseous mixture, and nature of the surface of the vessel) support the proposed mechanism.

O. J. WALKER.

Kinetics of combustion of carbon monoxide. V. S. FINKELSTEIN and V. P. MASCHOVETZ (J. Russ. Phys. Chem. Soc., 1928, 60, 1601—1628).—The catalytic activity of oxides and silicates of iron, aluminium, and of other metals was investigated. The first silicate investigated was glass, either in the form of the walls of the containing vessel or as thin-walled tubes contained in a flask. All experiments were carried out at 500°, except those with ferric oxide, which was investigated at 300°. Results were calculated from a termolecular reaction equation, the concentrations being expressed in partial pressures. The velocity of the reaction was found to diminish, even under constant conditions, in successive experiments. The same was observed when carbon dioxide was passed through the reaction vessel for some time before combustion began. The surface could be reactivated by treating with nitric acid; exposure to air or washing with water is not so effective. Fall in activity is explained by assuming adsorption of the carbon dioxide by the glass surface on which it is held by chemical forces. All the results, together with those obtained with alumina, indicate termolecular reactions. The reaction mechanism assumed is that suggested by Langmuir (A., 1922, ii, 629), but it is assumed that

two molecules of carbon monoxide collide with one molecule of oxygen adsorbed on the glass. Ferric oxide as a catalyst was investigated with the view of determining the effect of temperature on the kinetics of the reaction. From k determined at different temperatures for the same composition of the reaction mixture, the mean energy of activation is determined and is found to be 23.9 kg.-cal. per mol.

A. FREIMAN.

Combustion of well-dried carbon monoxide and oxygen mixtures. III. W. A. BONE, F. R. WESTON, and D. A. WINTER (Proc. Roy. Soc., 1929, A, 123, 285—291).—In continuation of previous work (Bone and Weston, A., 1926, 480) a study has been made of the ignitibility of mixtures of (approximately) 2 vols. of carbon monoxide and 1 vol. of oxygen, dried over phosphorus pentoxide for 550—1000 days. The fact that practically no difference is observed between the present results and those recorded for a drying period of 120—240 days (*loc. cit.*) indicates that, under the given experimental conditions, the utmost limits of phosphorus pentoxide drying can be reached in about 6 months, and it is concluded that a highly purified, rigidly dried $2\text{CO} + \text{O}_2$ mixture will still explode and propagate flame if a sufficiently powerful igniting spark be used. The minimum spark energy required in any given case depends, not only on the character of the discharge, but also on the material and shape of the electrodes; with "pointed" platinum electrodes, a spark of smaller energy sufficed than when "balled" electrodes were used.

L. L. BIRCUMSHAW.

Kinetics in streaming reaction systems. H. SCHMID (Z. physikal. Chem., 1929, 141, 41—51).—A method of determining the speed of a chemical reaction in streaming reaction systems based on the procedure of Hartridge and Roughton (A., 1925, ii, 47; 1926, 1213) is described. The course of the reaction is followed, not by physical methods, but by "quenching" and subsequent analysis of the reaction mixture. It is claimed that the method is applicable to the investigation of the kinetics of rapid reactions in general and is not limited to a small number of relatively simple reactions. The accuracy of the method is illustrated from a study of the decomposition of nitrous acid in time intervals of less than 1 sec.

O. J. WALKER.

Decomposition of nitrogen pentoxide. II. H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1929, 140, 281—290; cf. A., 1928, 1099).—Contrary to the results of Daniels, Wulf, and Karrer (A., 1923, ii, 24), ozone is found to have no retarding effect on the decomposition of nitrogen pentoxide. The formation of nitrogen pentoxide from nitrogen peroxide and ozone has been investigated and the results support the following mechanism: $\text{NO}_2 + \text{O}_3 = \text{NO}_3 + \text{O}_2$, $\text{NO}_3 + \text{NO}_2 = \text{N}_2\text{O}_5$. It is shown that the oxide NO_3 is not formed as an intermediate product in the decomposition of nitrogen pentoxide.

R. N. KERR.

Reaction between nitrogen pentoxide and ozone. II. H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1929, B, 2, 267—281; cf. A., 1928, 1100).—The rate of the reaction between

nitrogen pentoxide and ozone at 20° and 36° is given, over a wide range of concentrations, by the equation $dp/dt = k[N_2O_5]^{-3}[O_3]^{-3}$, where k has the value 5.57×10^{-3} at 20° and 31.2×10^{-3} at 36°. This equation may be derived theoretically by postulating the following reaction mechanism: (1) $N_2O_5 \rightarrow 2NO_2 + 0.5O_2$; (2) $NO_2 + O_3 \rightarrow NO_3 + O_2$; (3) $NO_3 + NO_2 \rightarrow 2NO_2 + O_2$; (4) $NO_3 + NO_2 \rightarrow N_2O_5$. The results of Tolman and White (A., 1925, ii, 682) may be accounted for in the same way. It thus follows that the oxide of nitrogen which gives a characteristic absorption spectrum when nitrogen pentoxide and ozone are mixed (cf. Hautefeuille and Chappuis, A., 1882, 927) has the formula NO_3 . R. CUTHILL.

Reduction of permanganate ion by chromic ion in acid solution. H. A. FALES and P. S. ROLLER (J. Amer. Chem. Soc., 1929, 51, 345–359).—The above reduction was investigated at 25.1° in sulphuric acid solution. The initial slow oxidation is rapidly autocatalysed to an almost linear rate, which diminishes rapidly near the end of the reaction (cf. Schiloff, A., 1903, ii, 720). When the chromic ion is in excess the reaction is bimolecular: $MnO_4' + Cr^{+++} = CrO_4'' + Mn^{+++}$. In the presence of manganous ions the rate depends on the ratio Mn^{++}/MnO_4' ; the ions Mn^{+++} and Mn^{++} are formed [see eqn. (3) below], which, and especially the Mn^{+++} ion, oxidise the chromic ion more rapidly than the permanganate ion. With decrease in the ratio Mn^{++}/MnO_4' there is a large increase in the ratio Mn^{+++}/Mn^{++} . The Mn^{+++} ions are probably present in the form of complexes with sulphuric acid, and they oxidise indirectly through Mn^{+++} , e.g., (1) $Mn(HSO_4)_3 \rightleftharpoons Mn^{+++} + 3HSO_4'$; (2) $Mn^{+++} + Mn(HSO_4)_3 = Mn^{+++} + Mn^{++} + 3(HSO_4)'$; (3) $2Mn^{+++} = Mn^{+++} + Mn^{++}$; (4) $Mn^{+++} + Mn^{++} + Cr^{+++} + 4H_2O = CrO_4' + 2Mn^{++} + 8H'$. The unimolecular nature of (1) is demonstrated and its velocity coefficient calculated. S. K. TWEEDY.

Kinetics, quantum efficiency, and temperature coefficients of the decomposition of ferric thiocyanate and the bleaching of neocyanine and some other photochemical reactions in radiations of different frequencies. A. K. BHATTACHARYYA and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 143–154; cf. this vol., 37).—The order of reaction, temperature coefficient, and quantum efficiency of the following reactions have been determined in radiations of different wave-length: decomposition of ferric thiocyanate, bleaching of neocyanine by air, and reactions between sodium lactate and iodine, sodium tartrate and iodine, chromic acid and citric acid, chromic acid and tartaric acid, and chromic acid and lactic acid. The first two reactions are unimolecular and the two reactions with iodine are bimolecular. The Einstein photochemical equivalence law is not exactly applicable to these reactions. The quantum yield increases with the concentrations and temperature of the systems and with the frequency of the incident radiations. All these reactions are accelerated by radiations of wave-length 7304 Å. due to appreciable absorption of radiations around this wave-length. The temperature coefficients behave as in the case of the previous reactions studied. O. J. WALKER.

Kinetic salt effect. II. Velocity of ionic reactions at great dilutions. A. N. KAPPANNA (J. Indian Chem. Soc., 1929, 6, 45–52; cf. A., 1928, 962).—In order to test the validity of the Debye-Hückel equation for the activity coefficient of an ion as modified by Bronsted and by Soper, the velocity of reaction of sodium bromoacetate with sodium thio-sulphate has been studied at 30°, 40°, and 50° over the range of total ionic concentration between 0.0025 and 0.10 μ . So far as the ions involved in this reaction are concerned the Debye-Hückel equation accurately predicts the course of the reaction for ionic concentrations up to 0.015 μ . The temperature coefficient of the velocity has been found to be the same at all ionic concentrations, and this is in accordance with the equations of Debye and of Ghosh. O. J. WALKER.

Kinetic studies on ethylene oxides. J. N. BRONSTED, (MISS) M. KILPATRICK, and M. KILPATRICK, jun. (J. Amer. Chem. Soc., 1929, 51, 428–461).—Ethylene oxide may react with aqueous acid (e.g., HX) as follows: (I) $C_2H_4O + H_2O \rightarrow (CH_2OH)_2$; (II) $C_2H_4O + H_3O^+ \rightarrow (CH_2OH)_2$; (III) $C_2H_4O + X' + H_2O \rightarrow XC_2H_4OH + OH'$; (IV) $C_2H_4O + X' + H_3O^+ \rightarrow XC_2H_4OH + H_2O$. The kinetics of reactions I and II were investigated dilatometrically in solutions of perchloric acid, and the analogous reactions involving glycidic and epichlorohydrin were also examined in phosphate buffers, sodium hydroxide solutions, nitric acid, etc. In some of these cases reactions III and IV vitiated the results. In perchloric acid solutions the salt effect is positive and rather large; reaction II is determined by the hydrogen-ion concentration. *cyclo*Hexene oxide also takes up water rapidly. The apparent basicity of ethylene oxides is due to reaction III and not to reaction IV. Titrimetric methods which permit these reactions to be separately followed are described, although reaction IV is best followed by conductivity measurements. Reaction III exhibits a slight negative salt effect and proceeds at a rate which is proportional to the anion concentration; this rate increases in the order chloride, bromide, thiocyanate, iodide, and formate, benzoate, acetate, trimethylacetate. Reaction IV was investigated in detail for the addition of hydrobromic acid to glycidic. The general results indicate that the "basicity" of ethylene oxides is not a property inherent in the oxide molecule, but is exhibited in solutions of the substance under certain conditions, e.g., when acids are present (reaction III). Bases likewise are taken up from solution and the oxides then exhibit "acidity." Bronsted's general theory of reaction velocity is followed very closely by all four reactions. The velocity coefficients of the respective reactions, k_1, k_2, k_3, k_4 , are approximately related as follows: $k_1/k_2 = k_3/k_4$, and this is explained in terms of a mechanism which is suggested as the basis of all four reactions. S. K. TWEEDY.

Kinetics of the bromination and chlorination of aliphatic nitro-compounds in aqueous solutions of the hydrogen halides. R. JUNELL (Z. physikal. Chem., 1929, 141, 71–90).—The velocity coefficients have been determined for the bromination of β -nitropropane, dibromonitromethane, monobromonitromethane, and nitromethane in *N*-hydro-

bromic acid solution, and for the chlorination of nitromethane in *N*-hydrochloric acid solution. These reactions are all unimolecular with respect to the corresponding nitro-compound. With nitromethane three consecutive unimolecular coefficients have been determined. An electrometric method for the titration of bromine or chlorine in presence of aliphatic nitro-compounds is described. O. J. WALKER.

Rate of hydrolysis of ribonucleotides. P. A. LEVENE and E. JORPES (*J. Biol. Chem.*, 1929, 81, 575—580).—In the acid hydrolysis of adenylic and guanylic acids phosphoric acid and the base are liberated at similar rates; the same applies to hydrogenated cytidinephosphoric acid, whilst in cytidinephosphoric acid itself both groups are hydrolysed only with difficulty. In view of these results the earlier conclusion (A., 1920, i, 774) that in the pyrimidine nucleotides the phosphoric acid residue is attached to the terminal carbon atom of the pentose, is abandoned.

C. R. HARINGTON.

Rate of hydrolysis of casein in acid solution from formation of amino-nitrogen. E. S. NASSET and D. M. GREENBERG (*J. Amer. Chem. Soc.*, 1929, 51, 836—841).—The hydrolysis of casein in 2.5% solution in 0.5—1.0*N*-hydrochloric, 0.5—2.5*N*-sulphuric, and 2.5—3.0*N*-phosphoric acids at 105.5—127.5° has been followed by Van Slyke determinations of the amino-nitrogen. The results are in accordance with a reaction of the second order (cf. Dunn, A., 1925, i, 1477; Carpenter, A., 1926, 631) and the catalytic effect of the acid is proportional to its hydrogen-ion activity. An expression is given for the effect of temperature on the reaction velocity (cf. A., 1927, 213).

H. E. F. NOTTON.

Formation and decomposition of gallic acid, pyrogallolcarboxylic acid, phloroglucinolcarboxylic acid, and their potassium salts. O. WIDMER (*Z. physikal. Chem.*, 1929, 140, 161—193).—The rate of decomposition of pyrogallolcarboxylic acid and gallic acid by boiling with water has been measured. Both decompositions are first-order reactions. The thermal decomposition of both these acids in the dry state has also been studied; the pressure of carbon dioxide obtained is plotted against the time. The shape of the curve is dependent on the temperature, the preliminary treatment of the acid, the amount of acid present, and the addition of foreign substances. The decomposition is strongly accelerated by the products of decomposition and by impurities. The equilibrium constants for the reaction $\text{pyrogallol} + \text{KHCO}_3 \rightleftharpoons \text{potassium pyrogallolcarboxylate} + \text{H}_2\text{O}$ at 80° and 95° and for the reaction $\text{phloroglucinol} + \text{KHCO}_3 \rightleftharpoons \text{potassium phloroglucinolcarboxylate} + \text{H}_2\text{O}$ at 40°, 49°, and 60° have been determined. The rates of formation and decomposition of the potassium salts of pyrogallol- and phloroglucinol-carboxylic acids have also been measured. At equal stages from the equilibrium point the formation proceeds more quickly than the decomposition.

R. N. KERR.

Relation of structure to rate of hydrolysis of diketopiperazines. I. Hydrolysis of *N*-methyl-diketopiperazine by alkali. P. A. LEVENE, L. W. BASS, and R. E. STEIGER (*J. Biol. Chem.*, 1929, 81,

697—702).—Whilst glycine anhydride, glycylsarcosine anhydride, and sarcosylsarcosine anhydride are hydrolysed by sodium hydroxide at similar (rapid) rates, the hydrolysis, under similar conditions, of the anhydrides of *N*-methylalanylsarcosine, and still more of *N*-methylvalylsarcosine, proceeds much more slowly.

C. R. HARINGTON.

Some forms of carbon and their reactivity. R. V. WHEELER.—See B., 1929, 309.

Combustion of platinum. E. K. RIDGAL and O. H. WANSBROUGH-JONES (*Proc. Roy. Soc.*, 1929, A, 123, 202—216).—An investigation has been made of the loss of weight of platinum wire, enclosed in a bulb immersed in liquid air, when heated for different lengths of time over the temperature range 1400—1900° Abs. in varying pressures of oxygen (100—200 bars). At high temperatures, the loss of weight in oxygen is greater than in a vacuum (cf. Langmuir, A., 1915, ii, 467). The kinetics of the reaction were studied at various pressures and temperatures. The results are most readily interpreted by assuming a surface reaction of which the rate is proportional to the pressure and a zero order bulk phase reaction which occurs simultaneously, the combined effect being denoted by an equation of the type $-bt = \log_e(a + bp)/(a + bP_0)$, P_0 being the initial pressure. From the experimental data a and b are found, and from Langmuir's values for the rate of evaporation of platinum in a vacuum values for a are calculated (subject to certain assumptions) which agree well with those obtained in the present experiments. From the "clean up" of oxygen, and by actual analysis, the deposit on the bulb was found to be PtO_2 . From these results it appears that below 1700° Abs., and even above this temperature for pressures below 50 bars, the bulk reaction between platinum vapour and oxygen predominates. No experimental evidence could be found for Langmuir's suggestion that the alteration of reaction rate at high pressures and temperatures is due to the concentration of ozone or oxygen atoms, and it is considered that a surface reaction is more probable. A hypothesis is suggested for the mechanism of the surface action based on the thermionic work function of platinum, and it is shown that the oxidation of carbon and the catalytic decomposition of ammonia on certain metal surfaces are in accordance with this scheme. L. L. BIRCUMSHAW.

Oxidation of copper at high temperatures. W. FEITKNECHT (*Z. Elektrochem.*, 1929, 35, 142—151).—The velocity of oxidation of copper depends on the rate at which oxygen can diffuse through the surface film of oxide that is formed. The nature of the layer, produced at different temperatures, was investigated by means of X-rays, using the Debye-Scherrer method, and also with the microscope. The copper becomes covered with a cuprous oxide layer, having a structure similar to that of a metal, which is subsequently covered with a thin film of cupric oxide. For temperatures of 850—1020° the expression $x = Kt$ (x being the amount of oxygen taken up by the copper in t min. and K a constant) held only after some time had elapsed. The variation in the velocity coefficient, K , with temperature, T (Abs.), could not

be satisfactorily represented by $K - Ae^{-E/RT}$, A and E being constants, for it was found that K became smaller than that given by the formula for falling temperatures (cf. Dunn, A., 1926, 692). Experiments using oxygen-nitrogen and oxygen-carbon dioxide mixtures showed that, provided the partial pressure of the oxygen was greater than the dissociation pressure of copper oxide at the particular temperature, the velocity coefficient was independent of the oxygen pressure, but became approximately proportional to the logarithm of the partial pressure when it fell below the dissociation pressure. H. T. S. BRITTON.

Corrosion of iron in sodium chloride solution. W. VAN WULLEN-SCHOLTEN.—See B., 1929, 285.

Oxidation of ferrous hydroxide by air. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1929, 4, 65—68; cf. A., 1927, 425).—The disparity between the results obtained for the velocity coefficient of the above reaction by the author and those found by Krause (A., 1928, 1202) is attributed to the fact that whereas the coefficient measured by Krause refers to the rate of disappearance of ferrous iron, that of the author is in effect the velocity of dissolution of oxygen into the reaction mixture. According to the latter, the oxidation of the ferrous iron is an induced reaction, of which the velocity is dependent on the rate of dissolution of oxygen in the reaction mixture.

F. G. TRYHORN.

Acid and salt effects in catalysed reactions. XIX. **Catalytic activity of chloroacetic acid in the hydrolysis of ethyl acetate.** H. M. DAWSON and W. LOWSON (J.C.S., 1929, 393—401; cf. A., 1927, 1150).—In a study of the catalytic effect of chloroacetic acid and the corresponding acid-salt mixtures three factors have to be taken into account: (a) the chlorine hydrolysis of the catalyst, and the influence of ionic environment on (b) the catalytic coefficients and (c) the ionisation constant of chloroacetic acid. The disturbing effect of the first can be eliminated by suitable choice of the experimental conditions, and it is shown that the catalytic effect of the chloroacetic acid can be expressed by the formula $v = k_a[H^+] + k_m[HA]$, provided that suitable allowance is made for the factors (b) and (c). The chloroacetate ion has a negligible catalytic effect. In sodium chloride solutions of gradually increasing concentration, k_a increases continuously, whilst the ionisation constant of the acid passes through a maximum at about 0.5*M* concentration. F. J. WILKINS.

Activation of chemical reactions by neutral salts. III. **Activation of dissolution of nickel [in sulphuric acid].** N. ISGARISCHEV and S. SCHAPIRO (Z. physikal. Chem., 1929, 140, 223—226; cf. A., 1927, 945; 1928, 374).—The effect of various chlorides and potassium salts on the rate of dissolution of nickel in sulphuric acid has been studied. All salts accelerate the reaction and a highly specific action of the different ions is obtained. The order in which the bromate, iodate, and chlorate ions accelerate this reaction is the same as that found for the dissolution of aluminium (A., 1928, 486), but no connexion exists between the effect of the simple halide ions on the two reactions. R. N. KERR.

Activation of chemical reactions by neutral salts. IV. **Action of neutral salts on the potential of oxidation-reduction reactions.** N. ISGARISCHEV and A. TURKOVSKAJA (Z. physikal. Chem., 1929, 140, 227—234; cf. preceding abstract).—The oxidation-reduction potentials of the system Fe^{III}/Fe^{II} in presence of the chlorides and the nitrates of metals of the first two periodic groups and of sodium salts with different anions have been measured. The chlorides with the exception of those of zinc and cadmium lower, and the nitrates raise, the potential. For the cations of metals of the first group, the sequence is the same with the chlorides and the nitrates. The alteration of potential cannot be explained by the change in acidity of the solution or by the occurrence of complex formation with the ferric or ferrous ions. A parallelism exists between the sequence of the cations in their action on the potential and on the velocity coefficient of the oxidation of stannous chloride by ferric chloride (A., 1925, ii, 586).

R. N. KERR.

Activation of chemical reactions by neutral salts. V. **Action of neutral salts on cathodic polarisation.** N. ISGARISCHEV and H. RAVIKOVITSCH (Z. physikal. Chem., 1929, 140, 235—240; cf. preceding abstracts).—The effect of adding salts of metals of the first and second periodic groups and also of cobalt and aluminium on the current density-potential curve for the cathodic deposition of nickel from the chloride has been determined. A marked effect on the shape of the curve is obtained. The effect of the cation rises with the at.wt. throughout each periodic group. The polarisation changes are considered with reference to (a) the acidity of the solution and (b) the dehydrating action of the salt on the nickel ion. The action of the added salt on the yield and properties of the precipitated nickel has also been investigated.

R. N. KERR.

Catalytic effect of ruthenium salts on the reduction of perchloric acid by hydrobromic acid. W. R. CROWELL, D. M. YOST, and J. M. CARTER (J. Amer. Chem. Soc., 1929, 51, 786—794).—The reaction $ClO_4' + 8Br' + 8H^+ = Cl' + 4Br_2 + 4H_2O$, which proceeds only in the presence of ruthenium, was investigated. Tervalent ruthenium is far more effective catalytically than the quadrivalent form; the catalytic effect progressively slackens as the reaction proceeds, since the bromine liberated slowly oxidises tervalent ruthenium to the quadrivalent form. It is suggested that the perchloric acid first slowly oxidises the ruthenium from the tervalent to the hexa- or septavalent state, and that the latter is then almost instantaneously reduced by the bromide to the tervalent state. S. K. TWEEDY.

Catalytic power of medicinal mineral waters. O. FERNANDEZ (Anal. Fis. Quím., 1929, 27, 45—48).—Theories of the catalytic activity of mineral waters in decomposing hydrogen peroxide are reviewed. Bacteriological examination indicates that this effect is sufficiently explained by the catalase activity of bacteria originally present or acquired by contamination. R. K. CALLOW.

Autoracemisation. E. WEDEKIND (Naturwiss., 1929, 12, 199; cf. Kuhn and Wagner-Jauregg, this

vol., 425).—Examples in which autoracemisation is a catalytic process have already been quoted by Wedekind and Maiser (A., 1928, 898; this vol., 194).

R. N. KERR.

Theory of catalysis. A. BERTHOUD (J. Chim. phys., 1929, 26, 120—124).—A criticism of Dubrisay's thermodynamic theory of catalysis as applied to the Arrhenius conception of activated molecules (cf. A., 1928, 1334). The introduction of a small amount of a foreign substance into a chemical system cannot bring about a change in the concentration of the active molecules. Even if such a change is assumed it does not follow that the rate of the chemical reaction will be accelerated.

O. J. WALKER.

Theory of heterogeneous catalysed reactions. Multiplet hypothesis. Model of dehydrogenation catalysis. A. A. BALANDIN (Z. physikal. Chem., 1929, B, 2, 289—316).—Assuming that catalysed reactions at surfaces occur at active centres, the author suggests that in general such a centre will not attract every part of the reacting molecule with the same intensity, but will exert a preferential attraction on some part or parts of it. If all the centres attract by preference the same part of the molecule, there will be no tendency for the molecule to be broken up, and adsorption without reaction will occur. On the other hand, if there are present various types of centres, some attracting one part of the molecule and some attracting another part, decomposition becomes possible. For actual fission to take place, however, the different centres must not be too remote from each other, but should rather be arranged in groups, each group containing one or more centres of each type, and for such groups the term "multiplets" is proposed. Since catalysed reactions usually involve a synthesis as well as a decomposition, it is suggested that some centres may simultaneously attract two or more parts of the same molecule, or the same part of several molecules, and if decomposition occurs cause these fragments to unite by directing their valencies one to another. Thus in the reaction $C_2H_5 \cdot OH + C_2H_4 + H_2O$ it may be supposed that active centres of one kind preferentially attract the carbon atoms of $\cdot CH_2 \cdot CH_2 \cdot$ groups, whilst those of another kind attract both hydrogen and hydroxyl oxygen, which then unite to form water. If a foreign substance is adsorbed by one kind of centre only, leaving the others free, the surface will be largely poisoned without its adsorptive power being very much affected, whereas a substance which is able to give rise to active centres of a type in which the surface is deficient will act as a promoter. It is considered probable that the groups of active centres are densely packed, constituting small surface elements which are to be identified with crystallisation nuclei. If it is assumed that the arrangement of centres must be such as to correspond with the symmetry of the molecule in order for reaction to take place, it becomes possible to predict what kind of crystal lattice will catalyse a particular reaction and to calculate the extreme values of the distance between the various centres in order for the attractions to be great enough to dismember the molecule. In this way the theory becomes capable of accounting for many of the observations made in investigations of the catalytic

hydrogenation and dehydrogenation of organic compounds, and its application to the reactions of cyclohexane is discussed in detail.

R. CUTHILL.

Extension of the intermediate-compound theory of catalysis in gas reactions. H. H. STORCH (J. Physical Chem., 1929, 33, 456—458).—The function of intermediate compounds in gas-phase catalysis is to provide a complex, containing reactants and catalyst, of a sufficiently large number of degrees of freedom, so that the energy of these may be available for contribution to the energy of activation. The decomposition of hydrogen iodide at the surface of platinum, the catalytic effect of water vapour, and catalysis by gaseous ions are discussed in the light of this extension of the intermediate-compound theory.

L. S. THEOBALD.

Topochemistry of contact catalysis. G. M. SCHWAB and E. PIETSCH (Z. physikal. Chem., 1928, B, 1, 385—408).—Theoretical. An attempt has been made to evolve a theory of the surface catalysis of gas reactions which shall in itself achieve all that Langmuir's theory of a unimolecular adsorbed film and of reaction at a homogeneous surface and Taylor's theory of "active centres" (A., 1926, 365) achieve together. For this purpose, it is suggested that the centres of reaction are not distributed over the whole surface, or located at "active points," but rather lie on lines which are phase boundaries. The adsorbed molecules are assumed to be free to move over the surface (cf. Volmer, A., 1925, ii, 539), but they also undergo "adlineation," i.e., they crowd together at phase boundary lines in the surface in the same way as molecules in free space crowd together at a surface where they are adsorbed. By applying the methods of the kinetic theory it is possible to deduce an expression for the number of molecules adsorbed on the surface which impinge on unit length of a line in unit time, and this in its turn leads to the "adlineation isotherm." The same equations may be arrived at from thermodynamical considerations, which also afford a proof of the Langmuir adsorption isotherm, which, unlike that obtained by Volmer (*loc. cit.*), is quite rigid. By means of the new system of equations, formulæ for the velocities of the various types of gas reactions have been derived, and as these prove to be of the same form as those which are applicable to reactions at bounding surfaces, the new assumption as to the seat of reaction appears to be justified, and may be regarded as the basis of a truly comprehensive theory of surface catalysis.

R. CUTHILL.

Topochemistry of contact catalysis. II. Experimental case of alinement. G. M. SCHWAB and E. PIETSCH (Z. physikal. Chem., 1929, B, 2, 262—263; cf. preceding abstract).—Eisner's work on the adsorption of heavy metal ions on the edges of crystals (e.g., on crocoisite) and not on the whole surface is used as evidence for the theory of contact catalysis put forward in a previous paper.

A. J. MEE.

Topochemistry of contact catalysis. G. M. SCHWAB and E. PIETSCH (Z. Elektrochem., 1929, 35, 135—141).—An outline of a new theory of catalysis (cf. preceding abstracts) in which lines which are phase boundaries in the catalyst are considered to be the seats of the reactions as the result of "adlineation"

of the reacting molecules. The conceptions of heat of "adlineation" and the relative lengths of these lines of catalytic activity are believed to furnish a basis for the quantitative co-ordination of the various measurable properties of catalysts, *e.g.*, the increase or decrease in activity.

H. T. S. BRITTON.

Catalysis of decomposition of carbon monoxide. I. Iron as catalyst. H. TUTIYA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 69—82).—Iron and carbon have no catalytic action on the thermal decomposition of carbon monoxide; this reaction is, however, powerfully catalysed by ferric carbide formed in the presence of iron. The reactions taking place are: $3\text{Fe} + 2\text{CO} = \text{Fe}_3\text{C} + \text{CO}_2$ and $2\text{CO} = \text{C} + \text{CO}_2$. The carbon formed in the latter reaction acts anti-catalytically by covering the carbide surface. This carbon contains iron from which it is difficultly separable, even by prolonged extraction with concentrated acids. An X-ray examination of the deposit forming on iron wire shows that the "X-carbide" of Hofmann (A., 1928, 853) is in reality iron oxide.

R. TRUSZKOWSKI.

Thermal decomposition of ammonia on iron catalysts. II. C. H. KUNSMAN (J. Amer. Chem. Soc., 1929, 51, 688—695; cf. A., 1928, 1101).—The reaction, which was effected at the surface of platinum strips coated with catalyst by an ignition process, is uninfluenced by nitrogen and is retarded by hydrogen. No definite reaction order could be measured. The constants *A* and *E* in the Arrhenius equation vary with temperature for a given catalyst. The presence of a promoter displaces the activity curve towards a lower temperature, whereas a poison, or heat treatment, moves the curve towards a higher temperature, the general shape of the curve remaining unchanged.

S. K. TWEEDY.

[Platinum] gauze catalyst in ammonia oxidation. G. A. PERLEY and M. W. VARRELL.—See B., 1929, 321.

Decomposition of nitric oxide by platinum at elevated temperatures and its retardation by oxygen. P. W. BACHMAN and G. B. TAYLOR (J. Physical Chem., 1929, 33, 447—455).—The heterogeneous decomposition of nitric oxide on platinum wire at 1035°, and on platinum-rhodium wire at 1035°, 1210°, and 1385° is shown to be bimolecular with respect to nitric oxide (cf. Green and Hinshelwood, A., 1926, 915). It is retarded proportionally to the oxygen concentration. It is pointed out that bimolecular reactions retarded by a reaction product are similar to unretarded unimolecular reactions in that the fraction which reacts in a given time is independent of initial pressure. The apparent heat of activation on platinum-rhodium (10%) is approximately 24,000 g.-cal.; this indicates a large positive value for the heat of adsorption of nitric oxide on the metal. The suggested mechanism of decomposition is that two molecules of nitric oxide are adjacently adsorbed with oxygen towards the catalytic surface; the atoms of nitrogen combine, evaporate, and leave the oxygen to act as a retarding agent.

L. S. THEOBALD.

Topochemistry of catalysis of decomposition of hydrogen peroxide by mercury, and p_H for

pulsation. G. BREDIG and A. STARK (Z. physikal. Chem., 1929, B, 2, 282—286).—Von Antropoff's investigation of the decomposition of hydrogen peroxide in aqueous solution at a mercury surface (A., 1908, ii, 472) may now be considered to show that this is an example of catalysis at phase boundary lines (Schwab and Pietsch, this vol., 519). The p_H of the solution must lie between 6.65 and 7.05 for pulsations to occur.

R. CUTHILL.

Kinetics of the hydrogenation of ethylene using a copper catalyst of measurable surface. F. H. CONSTABLE (Z. Elektrochem., 1929, 35, 105—110).—Two series of experiments at 0°, 100°, and 200° on the hydrogenation of ethylene in presence of a copper catalyst, which was prepared by the repeated reduction of copper oxide with hydrogen, are described. In the first, equal volumes of hydrogen and ethylene were employed at pressures of 19, 38, 50, and 76 cm.; and in the second, the volumes of the reacting gases were varied but the pressure was kept constant at 76 cm. The first series showed that the surface of the catalyst was almost saturated with the gases at 0°, but was partly saturated at 100° and was very unsaturated at 200°. According to the second set, and with the particular catalyst used, the rate of production of ethane was at a maximum at 0° when the reaction mixture contained 18 vol.-% of ethylene; at 100°, 42%; and at 200°, approximately 50%.

The kinetics of the reaction at 0° were found to satisfy expressions previously derived (A., 1928, 718). The superficial area of the catalyst was ascertained by means of an interference method after coating the catalyst with a film of oxide by direct oxidation (A., 1928, 832). The interference method was also employed to investigate the nature of the gases adsorbed by the catalyst. At 0° much of the surface appeared to be covered with a unimolecular layer of hydrogen, whilst much of the remaining part was covered with ethylene.

H. T. S. BRITTON.

Indication of hydroxyl in a water-vapour discharge tube. G. I. LAVIN and F. B. STEWART (Nature, 1929, 123, 607).—The gas from a water-vapour discharge tube contains hydroxyl, indicated by the band at 3060 Å., the intensity of which is increased by the addition of a small quantity of oxygen. A larger amount produces the green oxygen afterglow. The active gas reduces copper sulphate and oxidises metallic silver.

A. A. ELDRIDGE.

Ozonisation under the action of high-frequency discharges. W. DANIEWSKI (Rocz. Chem., 1929, 9, 83—96).—The amount of ozone formed employing high-frequency alternating currents in an ozoniser without dielectric is constant at frequencies of 300,000, 1,700,000, and 12,500,000, being about 60 g./kw.-hr. This constancy is ascribed to the disproportion between the number of oscillations and the number of molecular collisions per unit time. The limiting concentration of ozone diminishes with increasing frequency from 6 g./m.³ at 300,000 to 14 g./m.³ at 12.5×10^6 ; this effect is due to the greater density of the sparks at higher frequencies.

R. TRUSZKOWSKI.

Chemical interaction of ions and the "clean up" of gases at glass surfaces under the influence of the electric discharge. J. TAYLOR (Proc. Roy. Soc., 1929, A, 123, 252—270).—By means of the arrangement previously described (J. Taylor and W. Taylor, A., 1928, 681) experiments have been carried out on the disappearance of gas in the electric discharge. Positive ions, obtained by means of an electrodeless discharge in hydrogen, oxygen, nitrogen, and helium at low pressures (down to 0.001 mm.), were pulled out by the action of an electric field and struck the walls of a thin-walled glass bulb immersed in a sodium nitrate bath maintained at a suitable temperature. A current usually traversed the walls of the bulb and in most cases a progressive diminution of the pressure of the gas in the discharge tube took place. For all the gases except helium, the quantity of gas disappearing was found to be directly proportional to the quantity of electricity transferred through the glass walls. It appears to be dependent on the previous treatment of the glass, but follows laws similar to the Faraday laws of electrolysis. For hydrogen, one molecule frequently disappeared for every electron charge passed, but with continued running one hydrogen atom disappeared for every electron transferred. For oxygen and nitrogen, every two electron charges passed usually involved the disappearance of one atom, but in some cases one oxygen atom disappeared for every four electron charges and one nitrogen atom for every three charges. For helium no progressive disappearance of gas occurred. Experiment showed that the gas which disappeared was not transferred through the glass by diffusion, and that the "clean up" was not of the nature of an occlusion of gas in the glass arising from the ions being driven with high velocity into the surface. Experiments were also made on the nature of the "clean up" in the electrodeless discharge alone and in the combined action of the electrodeless discharge and the direct current discharge through the glass walls. The spectrogram of the condensible product obtained in a liquid air trap was found, in the case of hydrogen, to be identical with the standard spectrum for water at low pressure, whilst with oxygen a condensible product was formed which gave a spectrogram similar to that obtained from a discharge in carbon dioxide. A theory is proposed to account for the observed phenomena. The clean up must be due to chemical interaction of the gaseous ions with the electrolytic products and ions of the glass. Regarding glass as a solution containing Na_2SiO_3 as electrolyte, then for every two electron charges transferred across the glass 2Na is liberated, the SiO_3 radical breaks down into $\text{SiO}_2 + \text{O}$, and the oxygen atom unites with a hydrogen molecule. Matters are, however, not so simple as this, and glass must be considered as a complex electrolytic solution containing carbon compounds and probably also peroxides.

L. L. BIRCUMSHAW.

Decomposition of nitrous oxide in the silent electric discharge. IV. Influence of the addition of foreign gases. S. S. JOSHI (Trans. Faraday Soc., 1929, 25, 137—143; cf. this vol., 404).—Measurements by the author's method (A., 1927, 635) of the

initial velocity of decomposition of mixtures of nitrous oxide and varying quantities of nitrogen, oxygen, and nitrogen peroxide by a silent discharge of 12.4 kilovolts applied for 50 min. show that the percentage decomposition is diminished by addition of these gases. The mean wattage consumed is also diminished and the minimum potential required to initiate decomposition is increased, the effect of nitrogen peroxide being greatest and that of nitrogen least. The relative influence of the foreign gases is explained in terms of their electron affinities, which follow the order $\text{N}_2 < \text{N}_2\text{O} < \text{O}_2 < \text{NO}_2$. Since addition of oxygen increases the nitrogen/oxygen ratio in the final mixture, it is suggested that the equation $4\text{N}_2\text{O} = 3\text{N}_2 + \text{N}_2\text{O}_4$ represents the main reaction, whilst oxygen is produced only by either or both of the reactions $\text{N}_2\text{O}_4 = \text{N}_2 + 2\text{O}_2$ and $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$.

J. GRANT.

Testing of electro-deposits on aluminium. G. B. BROOK and G. H. STOTT.—See B., 1929, 286.

Cathodic yield in nickel-plating with high current density. Influence of oxidising agents and hydrogen-ion concentration. BALLAY.—See B., 1929, 287.

Control of the current density in electrolytic baths. W. PFANHAUSER.—See B., 1929, 289.

Anodic behaviour of substituted acetic acids.

I. **Diphenylacetic acid.** H. KATAGISHI, Y. GINBAYASHI, and M. MATSUI (Mem. Coll. Sci. Kyoto, 1929, A, 12, 57—62).—On electrolysis between platinum electrodes of a solution of potassium diphenylacetate of concentration not less than about 35% and acidified with sulphuric or hydrochloric acid, diphenylmethyl alcohol and a little of its diphenylacetic ester are formed with evolution of carbon dioxide. Lead catalyses the formation of alcohol, but not of ester. If an alternating current is employed, the total yield, and also the relative amount of ester are increased.

R. CUTHILL.

Electrolytic reduction of aldehydes. V. Cinnamaldehyde. VI. Complete reduction of the carbonyl group. G. SHIMA (Mem. Coll. Sci. Kyotō, 1929, [A], 12, 69—72, 73—80).—V. The best yield (72%) of γ -phenylpropyl alcohol from cinnamaldehyde by electrolytic reduction was obtained by using a mercury cathode and adding the aldehyde slowly to a cathode solution containing saturated sodium hydrogen carbonate solution (50 c.c.) and alcohol (70 c.c.) at 20—22°, with a current density of 6 amp./100 cm.² The results of varying the conditions are tabulated. In alcoholic ethyl acetate solution the maximum yield was 50%.

VI. The use of a zinc amalgam cathode gives better results than cadmium (Schepss, A., 1913, i, 1154) in the complete electrolytic reduction of the aldehydo-group to methyl. The best yields of *p*-tolyl methyl ether from anisaldehyde (68%), and of *o*-cresol from salicylaldehyde (66%), were obtained by using a cathode solution containing 60% sulphuric acid (60 c.c.) and alcohol (20 c.c.) at 35—40° with a current density of 72 amp./100 cm.² The best yields of *p*-cresol from *p*-hydroxybenzaldehyde (58%), and of creosol from vanillin (75%), were obtained under

the same conditions, but in the absence of alcohol. The best yield of 3:4-methylenedioxytoluene from piperonal (55%) was obtained under the same conditions in a mixture of 60% sulphuric acid (50 c.c.) and alcohol (30 c.c.). The results of varying the conditions are tabulated. The effect of the presence of alcohol is discussed. Müller's theory (A., 1923, i, 90) does not account for the different behaviour of aldehydes and additive products.

R. K. CALLOW.

Photochemical properties of the halogens. J. PLOTNIKOV (J. Chim. phys., 1929, 26, 44—58).—From a critical review of the literature relating to the photochemical reactions of iodine and bromine, it is concluded that the experimental data are too incomplete and the discrepancies too pronounced for it to be possible to reach any conclusions as to the reaction mechanism. In experiments of this type, it is essential that monochromatic light shall be employed, and for regulating its intensity thin sheets of metal are recommended, the rotating-sector method being quite useless here.

R. CUTHILL.

Photosynthesis of hydrochloric acid at low pressures. G. K. ROLLEFSON (J. Amer. Chem. Soc., 1929, 51, 770—778).—The reaction was studied in white light with excess of chlorine; the equation which holds at high pressures, viz., $d[\text{HCl}]/dt = k[\text{H}_2][\text{Cl}_2]$, remains valid. The experimental results, considered in the light of previously published work, indicate that light dissociates chlorine molecules into chlorine atoms in the 2P_1 state (cf. Franck, A., 1925, ii, 1077) and also in the normal state. The mechanism of the reaction is discussed in detail and a series of chain reactions which accounts for the influence of water on the reaction is proposed.

S. K. TWEEDY.

Coloration of thin layers of silver iodide in light. E. JENCKEL (Z. anorg. Chem., 1929, 179, 89—96).—The alteration of colour exhibited by a thin film of silver iodide when exposed to light is due to the production of fine particles of silver.

H. F. GILLBE.

Inhibition of certain photochemical reactions by oxygen. H. B. DUNNICLIFF and J. N. JOSHI (J. Indian Chem. Soc., 1929, 6, 121—127).—The following photo-sensitive reactions are inhibited by oxygen or ozone or hydrogen peroxide: action of ammonium oxalate on mercuric chloride, oxidation of lactic acid by bromine water, reduction of ferric oxalate to ferrous oxalate and decomposition of silver halides. The mechanism of the inhibiting action is discussed.

O. J. WALKER.

Theory of the photographic process. H. KIESER (Z. wiss. Phot., 1929, 26, 321—340).—Based on the quantum theory, the secondary reactions produced by the photo-electric effect, and the probable alterations in the structure of the silver bromide crystal which accompany photolysis, a theory has been developed to account for the formation of the latent image. It has been employed to explain the following processes: solarisation, Clayden effect, Schwarzschild and intermittent exposure effects, sensitisation and desensitisation, and the Herschel effect.

H. T. S. BRITTON.

Photographic effects [with silver bromide emulsions]. H. TOLLERT (Z. physikal. Chem., 1929, 140, 355—378).—Using a specially prepared silver bromide emulsion in gelatin, determinations were made of (a) the amount of silver formed photolytically, (b) the amount of silver formed after developing, and (c) the amount of "blackening" of the developed silver. In the region of solarisation the amount of silver formed photolytically increases with the quantity of light used, whereas *b* and *c* do not increase. The sensitising action of erythrosin was examined by comparing the number of dye molecules adsorbed by the silver bromide with the number of silver atoms formed photolytically. The number of silver atoms is 64 times the number of adsorbed erythrosin molecules. Some experiments with other sensitisers and desensitisers are described. It is shown that the Herschel effect, i.e., the action of red light on photolytically formed silver before development, is due to a change not in the amount, but in the structure of the silver. A quantitative comparison is made of the energy necessary for direct blackening for blue and red light.

O. J. WALKER.

Effect of environment on photographic sensitivity. II. Effect of certain salts. S. E. SHEPARD and E. P. WIGHTMAN.—See B., 1929, 303.

Theory of the hydrogen peroxide effect, of physical development, and of the coloration produced by dyes and silver halides. A. STEIGMANN (Z. wiss. Phot., 1929, 26, 341—344).—The hydrogen peroxide effect is briefly discussed on the basis of the author's theory, according to which the number of reduction centres on the surfaces of silver halides diminishes in the order: chloride, bromide, iodide. The insensitivity of silver chloride in presence of silver bromide is considered to be due to the greater number of primary reduction centres on the surface of the chloride, which in the preparation of the plate causes enhanced adsorption to occur and so renders the subsequent action of light difficult. This inactivity to light is accompanied by an inactivity to hydrogen peroxide. Experiments are described on the action of dyes in solutions containing halides of alkali metals on silver halides. Erythrosin became bluish; pinachrome was almost decolorised in concentrated sodium chloride solution; fuchsin became blue and showed dichromatism; methylene-blue, pinakryptol-green, and phenolsafranin were each precipitated and their solutions bleached. Other experiments dealt with the probable chemical combination of methylene-blue with silver halides.

H. T. S. BRITTON.

Photochemical production of optically active substance. W. KUHN and E. BRAUN (Naturwiss., 1929, 17, 227—228).—The rotatory dispersion of ethyl α -bromopropionate in the ultra-violet discloses at first an increased rotation (specific rotation in alcohol of about 4000° at 2450 \AA .) followed by a reversal. The absorption bands in the near ultra-violet must therefore influence powerfully the optical activity. Solutions (4—8% in alcohol) of the racemic ester were exposed in quartz flasks to circularly polarised light. Monochromatic light (Mg line 2800 \AA .) was used. A solution of the active ester was simultaneously exposed to unpolarised light of corresponding inten-

sity, to provide control for the period of irradiation. The solutions exposed to dextro-circularly polarised light showed dextro-rotation, and *vice versa*. The greatest effect so far obtained is 0.05° on either side. The effect observed agrees in sign with theoretical predictions.

R. A. MORTON.

Transformation of cholesterol by X-rays. A. H. ROFFO and L. M. CORREA (Bol. Inst. Med. exp., 1925, No. 5, 3 pp.; Chem. Zentr., 1928, ii, 1671—1672).—The products resulting from the action of X-rays on cholesterol do not give colour reactions, and are not precipitable with digitonin. The double linking remains unaffected. The action consists in oxidation of the alcoholic carbon atom in Windaus' formula.

A. A. ELDRIDGE.

Development of chlorophyll in seedlings in different ranges of wave-lengths of light. J. D. SAYRE (Plant Physiol., 1928, 3, 71—77).—Wave-lengths longer than $680\text{ }\mu$ are not effective in the formation of chlorophyll in maize, wheat, oat, barley, bean, sunflower, or radish seedlings. The effectiveness of radiant energy appears to increase with wave-length to about $680\text{ }\mu$ and then to fall abruptly to zero.

CHEMICAL ABSTRACTS.

Change of conductivity of coloured substances during photochemical action. N. ZCHODRO (J. Chim. phys., 1929, 26, 59—64).—The conductivity of collodion films coloured with cyanine, pinaverdol, or pinachrome increases on illumination with white light; the increase is no longer obtained when the film has become decolorised. The conductivity increases with the duration of exposure until a maximum value is obtained; when illumination ceases the conductivity diminishes gradually. The effect of illumination by monochromatic light has also been studied and curves are given of change of conductivity against wave-length of light used. These curves resemble closely those obtained by Lasareff (Ann. Physik, 1907, 24, 661) for the energy of light absorbed by these coloured films, and the conclusion is reached that the increase of conductivity of the films during decolorisation is proportional to the energy of the light absorbed.

R. N. KERR.

Oxidations promoted by ultrasonic radiation. F. O. SCHMITT, C. H. JOHNSON, and A. R. OLSON (J. Amer. Chem. Soc., 1929, 51, 370—375).—Some ultrasonic radiation reactions were investigated in presence of oxygen and water, under conditions such that gas bubbles could be formed in the liquid. The reactions included oxidation of halide ions under various conditions, of hydrogen sulphide, and of carbon tetrachloride (chlorine is formed in presence of air and moisture). Some dye molecules are affected by the radiation and give rise to hydrogen ions. The reaction rate of ultrasonic reactions rises as the pressure is increased, but above a certain critical pressure the rate falls again. An explanation is suggested for this behaviour.

S. K. TWEEDY.

Is hydrogen peroxide formed in electrolytic gas by α -rays? B. M. MARKS (J. Physical Chem., 1929, 33, 381—383).—Contrary to the assumption of Scheuer (A., 1914, ii, 762), no hydrogen peroxide could be detected when electrolytic gas is acted on by

α -particles. Tests for ozone were also negative. The excess of hydrogen over that required for the formation of water reported by Scheuer is attributed to reaction of part of the oxygen with the mercury present in the system.

L. S. THEOBALD.

Pure hydrogen peroxide. VI. G. L. MATHESON and O. MAASS (J. Amer. Chem. Soc., 1929, 51, 674—687).—F.-p. curves are recorded for some binary hydrogen peroxide systems. Potassium chloride and sulphate and sodium fluoride are dissociated in solution, but methyl alcohol is associated. The eutectic point was always higher than that for the corresponding water systems; the eutectic for aqueous sodium fluoride solution lies at -2.9° , the composition being 1.4% of salt (cf. Guthrie, Phil. Mag., 1878, 5, 640). Potassium bromide decomposes hydrogen peroxide rapidly. Ether is only slightly soluble; a compound containing 48—55% of ether was isolated. Sulphur dioxide dissolves even in very cold peroxide to form sulphuric acid; compound formation occurs. Amines and hydrogen peroxide do not interact below 0° , but at the ordinary temperature the amine (e.g., piperidine) is often oxidised to the corresponding nitro-compound. Butylamine-hydrogen peroxide compounds were isolated; they probably represent the first stage in the oxidation to nitro-compounds. Evidence was obtained that the other amines also form compounds; the number of peroxide molecules in the ethylamine compound increases as the hydrogen atoms linked to nitrogen are replaced by ethyl groups. Dimethylaniline differs from aliphatic amines in being less soluble and associated in solution. Direct measurements gave 23,450 g.-cal. at 20° for the heat of the reaction $\text{H}_2\text{O}_2(l) = \text{H}_2\text{O}(l) + 0.5\text{O}_2$ (at 1 atm.). Vapour density measurements by the Victor Meyer method gave 34 as the mol. wt. of hydrogen peroxide vapour. The decomposition of the peroxide becomes explosive at 150 — 153° . This temperature is raised slightly by addition of water or of potassium chloride.

S. K. TWEEDY.

Action of helium on platinum. H. DAMIANOVICH (Compt. rend., 1929, 188, 790—792).—The action of pure helium on platinum under the influence of a moderate electric discharge at 0.75 — 3.5 mm. for 30 min. to 14 hrs. produces thin brown layers of the metal which is converted by heat into a mirror of ordinary platinum and retains large quantities of helium in the form of adsorption compounds or mixtures of such compounds with excess of metal.

J. GRANT.

Action of helium on platinum. H. DAMIANOVICH and J. J. TRILLAT (Compt. rend., 1929, 188, 991—992).—Products containing helium and platinum (preceding abstract) prepared under various conditions were examined by the Debye-Scherrer method and shown to have the same microcrystalline structure. The deposit obtained by the action of an alternating discharge (0.5 cm. spark) on platinum in helium at 3.5 mm. pressure contained a microcrystalline substance, possibly a compound of helium and platinum, which was not detectable in the other deposits.

J. GRANT.

Action of ozone on alkali azides. Pernitrous acid. I. K. GLEV and E. ROELL (Z. anorg. Chem.,

1929, 179, 233—266).—If oxygen containing about 10% of ozone be passed into an *N*-sodium azide solution an orange coloration is at first produced, but later the colour fades and the solution then contains nitrate and nitrite, but no azide. It has not been found possible to isolate the orange substance by freezing out the water, by precipitation with another solvent, or by effecting the reaction in non-aqueous solution; further, ozone does not appear to react with solid sodium azide. The orange substance is stable only in alkaline solution and decomposes below the b. p. with evolution of equal volumes of nitrogen, nitrous oxide, and oxygen; if no azide remains in the solution oxygen alone is evolved. Titrations with stannite, antimonite, and arsenite solutions yield concordant results for the oxidising power of the solution, but with formaldehyde anomalous results are obtained, which lead to the conclusion that this reducing agent is oxidised primarily to performic acid, which is then reduced by the nitrite present. Permanganate is reduced to manganate with vigorous evolution of oxygen. Quantitative titrations show that the nitrate and nitrite contents of the orange solution are equal, that the oxidation titre is equal to the reduction titre, and that the volume of oxygen produced by oxidation is double that resulting from decomposition of the orange substance. The latter is decomposed catalytically by manganese dioxide, and is reduced, although slowly, by hypobromite and hypochlorite solutions. The orange substance thus appears to be a derivative of hydrogen peroxide and is shown to react quantitatively as a pernitrous acid, isomeric with nitric acid, and having the structure $O:N\cdot O\cdot OH$. Its formation results from the production of an ozonide of azoimide, which then loses one molecule of nitrogen.

H. F. GILLBE.

New series of double sulphates of the copper-magnesium group and the phosphonium bases. I. P. C. RAY and N. RAY (J. Indian Chem. Soc., 1929, 6, 27—30; cf. A., 1928, 505).—The following *magnesium tetraethylphosphonium sulphates* have been obtained ($R=PEt_4$):—

$MgSO_4 \cdot R_2SO_4 \cdot 8H_2O$; $2MgSO_4 \cdot R_2SO_4 \cdot H_2SO_4$;
 $2MgSO_4 \cdot R_2SO_4 \cdot 2H_2SO_4 \cdot 2H_2O$;
 $2MgSO_4 \cdot R_2SO_4 \cdot H_2SO_4 \cdot H_2O$, and
 $2MgSO_4 \cdot R_2SO_4 \cdot H_2SO_4 \cdot 2H_2O$. Copper yields only the acid salt $2CuSO_4 \cdot R_2SO_4 \cdot H_2SO_4 \cdot 4H_2O$.

O. J. WALKER.

Spectro-analytical investigation of the dissolution of alloys and the Tammann resistance layer. VI. W. GERLACH (Z. anorg. Chem., 1929, 179, 111—112).—When alloyed with gold in absence of lead both copper and silver are protected from the action of nitric acid, but if lead be present the copper is dissolved simultaneously with the lead, as a result of compound formation between the two metals.

H. F. GILLBE.

Action of water on tricalcium silicate and β -dicalcium silicate. T. THORVALDSON and V. A. VIGFUSSON.—See B., 1929, 247.

Preparation of phosphorescent zinc sulphide. R. COUSTAL and F. PREVET (Compt. rend., 1929, 188, 703—705).—Phosphorescent zinc sulphide is obtained as a white, spongy mass of wurtzite crystals when

intimate and finely-powdered mixtures of zinc (particles of the order of 1 micron) and sulphur are exploded by shock, heat, or friction. In general, an excess of zinc decreases the persistence of the phosphorescence and displaces it towards the higher wave-lengths, the maximum intensity and explosive violence being obtained with 1.5—2 g. and 3.3 g. of zinc/g. of sulphur, respectively. Added copper, halogen, or phosphorus compounds increase or modify the colour of the phosphorescence, but metals (except uranium) have the reverse effect, and all diminish the violence of the explosion. Explosions carried out in nitrogen and sulphur dioxide give a less and more intense phosphorescence, respectively, than that produced in air, and the selenides and tellurides produced by the same method are less phosphorescent than the sulphides.

J. GRANT.

Mercurammonium iodides. M. FRANÇOIS (Ann. Chim., 1929, [x], 11, 22—43).—The existence of the two mercurammonium iodides, $HgI_2 \cdot 2NH_3$ and $3HgI_2 \cdot 4NH_3$, has been definitely established. Their vapour pressures at a series of temperatures have been measured and the conditions of stability in the dry state and in aqueous solution defined. The reaction between concentrated aqueous ammonia and $HgI_2 \cdot 2NH_3$ leading to dimercurammonium, Hg_2NI , and $3HgI_2 \cdot 4NH_3$ leading to $Hg_3N_4I_6$, has been fully investigated and details are given for the preparation of the final products in the pure state. Graphical formulæ for these mercurammonium compounds are described.

A. I. VOGEL.

Dehydration of kaolin. H. A. J. PIETERS.—See B., 1929, 323.

Wohler's titanium cyanonitride. V. M. GOLDSCHMIDT (Nachr. Ges. Wiss. Göttingen, 1927, 390—393; Chem. Zentr., 1928, ii, 1541—1542).—The substance has (E. BROCK) a crystal structure analogous to that of sodium chloride. Comparative measurements indicate that it consists of a solid solution of titanium carbide and nitride.

A. A. ELDRIDGE.

Compounds of tervalent cerium salts and thorium salts with sodium carbonate (sodium cericarbonate and thorcarbonate). L. LORTIE (Compt. rend., 1929, 188, 915—916).—*Sodium cericarbonate*, $Na_6[Ce(CO_3)_5] \cdot 12H_2O$, was prepared by gradual addition of a solution of 15 g. of ammonium cerinitrate in 25 c.c. of water to a cold 25% solution of sodium carbonate, the resulting precipitate, probably $CeCO_3(OH)_2$, being filtered. The yellow, prismatic crystals separate after some hours and are filtered and washed in ice water. The salt, which is dehydrated at 200°, is decomposed by water with the formation of the above hydroxycarbonate and by acids with the liberation of carbon dioxide. It is soluble in sodium carbonate solution, gives a blood-red colour with phenolic substances, and is isomorphous with the corresponding thorium salt. Determinations of active oxygen indicate that the cerium is quadrivalent.

J. GRANT.

Oxides of nitrogen. F. RASCHIG and W. PRAHL (Z. angew. Chem., 1929, 42, 253—257).—The evidence for the existence of higher oxides of nitrogen, based on oxidation of stannous chloride, has now been modified by experiments with titanous chloride; the

oxidation in this case indicated that no oxide higher than nitrogen peroxide was present, and the phenomena with stannous chloride are attributed to catalytic oxidation by free oxygen in presence of the nitrogen oxides. The dissociation constants of nitrogen peroxide into nitric oxide and oxygen, determined chemically, agree closely with those determined by Bodenstein by physical methods; the apparatus and methods employed are described. By reaction with potassium iodide, it is proved that an equimolecular mixture of nitric oxide and nitrogen peroxide behaves as a mixture, and not as a compound; the peroxide forms potassium nitrite with separation of iodine. S. I. LEVY.

Hypophosphoric acid. F. VOGEL (Z. angew. Chem., 1929, 42, 263).—Oxidation of red phosphorus with alkaline permanganate or peroxide yields hypophosphates, the yield being more than 80% on the phosphorus oxidised in the case of peroxide.

S. I. LEVY.

Preparation of hypophosphoric acid by the action of hypochlorite on red phosphorus. J. PROBST (Z. anorg. Chem., 1929, 179, 155—160).—Red phosphorus is added gradually to a well-stirred solution which is about 0.2M with regard to alkali and 1.5M with regard to hypochlorite. The initial temperature should be about 5° and the reaction vessel cooled in ice, when a yield of 25% of the salt $\text{NaHPO}_3 \cdot 3\text{H}_2\text{O}$, calculated on the phosphorus used, may be obtained. A new method for the determination of the hypophosphate ion is described: silver hypophosphate, quantitatively precipitated from a solution of the sodium hydrogen salt, is washed and dissolved in ammonium hydroxide solution, and the silver is reprecipitated with hydrogen chloride solution. The second precipitation is, when excess of chlorine ion is present, uninfluenced by the presence of hypophosphate ion. H. F. GILLBE.

Sulpho-salts. VII. Polysulphovanadates. L. FERNANDES [with C. ORLANDI] (Atti R. Accad. Lincei, 1928, [vi], 8, 234—238).—Polymerisation of normal orthovanadates may occur either as $\text{R}_3\text{VS}_4 \rightarrow \text{V}_2\text{S}_5$ in the presence of a relatively strong acid, or as $\text{R}_3\text{VS}_4 \rightarrow \text{RVS}_3 \rightarrow \text{R}_4[\text{H}_2(\text{VS}_3)_6]$ in the presence of hydrogen sulphide. To confirm the latter process the compounds $\text{NH}_4\text{VS}_3 \cdot 2\text{H}_2\text{O}$, $[\text{NH}_4\text{C}(\text{NH}_2)_2]\text{VS}_3 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_4[\text{H}_2(\text{VS}_3)_6] \cdot 18\text{H}_2\text{O}$, $[\text{NH}_4\text{C}(\text{NH}_2)_2]_4[\text{H}_2(\text{VS}_3)_6] \cdot 18\text{H}_2\text{O}$, and $\text{Ti}_4[\text{H}_2(\text{VS}_3)_6] \cdot 18\text{H}_2\text{O}$ have been prepared. The ammonium salts were obtained by the action of ammonium hydrosulphide and hydrogen sulphide on the orthovanadate, the other compounds being obtained from the corresponding ammonium salts by double decomposition. F. G. TRYHORN.

Reactions in liquid hydrogen sulphide. V. Reaction with furfuraldehyde. R. E. MEINTS and J. A. WILKINSON (J. Amer. Chem. Soc., 1929, 51, 803).—A monosulphur derivative of furfuraldehyde, $\text{C}_4\text{H}_3\text{O} \cdot \text{CHS}$, is formed by the spontaneous interaction under pressure of furfuraldehyde and liquid hydrogen sulphide. It forms yellow monoclinic needles, m. p. 95—98°, softening point 80°, soluble in hot ethyl acetate, which are converted in air into a black substance insoluble in liquid hydrogen sulphide. Since

furan, furfuryl alcohol, pyromucic acid, and its ethyl and nitroethyl esters do not react analogously with hydrogen sulphide, the sulphur must replace the aldehydic oxygen atom. Aldehydes as a class undergo this substitution when treated with liquid hydrogen sulphide. S. K. TWEEDY.

Sulphur. I. System sulphur-chlorine. M. TRAUTZ, H. ACKER, (FRL.) L. E. VON BROECKER, A. RICK, A. HOFFMANN, H. KLIPPEL, and O. LOTH (Z. Elektrochem., 1929, 35, 110—132).—Manometric measurements performed on various gaseous equilibria involving sulphur and chlorine at high temperatures indicate that the main reaction is: $\text{S}_2\text{Cl}_2 + \text{Cl}_2 \rightleftharpoons 2\text{SCl}_2$. Specific heat data show that other polythiochlorides exist in both the gaseous and liquid state, e.g., S_2Cl , S_3Cl_2 , and S_4Cl_2 . Heats of formation of the various chlorides are given, and equilibrium constants of reactions involving them at various temperatures have been calculated, using Nernst's theorem.

The change in colour, from yellow to red, which occurs when chlorine is passed into sulphur monochloride in the liquid form has been investigated by following changes in colour, in volume, and in the partial pressure of the chlorine in the gaseous phase. Difficulty was experienced in obtaining reproducible results, as the time when the sudden reddening occurred was found to be influenced by several factors, e.g., unless the liquid was "seeded" with sulphur dichloride the colour change did not occur until 3—4 hrs. had elapsed. The absorption of the chlorine by sulphur monochloride is represented by the scheme $\text{S}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow 2\text{SCl}_2$, the reaction being very slow except when the sulphur monochloride happens to be in the "active" state, or when a large amount of either sulphur dichloride or sulphur tetrachloride or stannic chloride or iodine has been previously added. The partition coefficients of chlorine between the gas phase and the solution, in both old and freshly-prepared samples of the pure monochloride, have been measured over wide ranges of temperature. Owing to an excess of chlorine being present in the reaction mixture when gaseous chlorine was allowed to act on rhombic sulphur to form sulphur monochloride, it was found necessary to extrapolate the heat of formation, which is given by: $2\text{S}(\text{rhombic}) + \text{Cl}_2(\text{gas}) = \text{S}_2\text{Cl}_2(\text{liquid}) + 14.5 \pm 0.4 \text{ kg.-cal.}$ The heat of dissolution of chlorine in sulphur monochloride was found to be represented by: $\text{S}_2\text{Cl}_2(\text{liquid}) + \text{Cl}_2(\text{gas}) = 2\text{SCl}_2(\text{dissolved in } \text{S}_2\text{Cl}_2) + 9.8 \pm 0.4 \text{ kg.-cal.}$, whilst $\text{S}_2\text{Cl}_2 + 3\text{Cl}_2 = 2\text{SCl}_4(\text{dissolved in a mixture of } \text{S}_2\text{Cl}_2 \text{ and } \text{SCl}_2) + 12—14 \text{ kg.-cal.}$ Chlorine reacts with sulphur dissolved in sulphur monochloride in accordance with the expression governing the rate of a reaction of the first order. Vapour pressure-temperature curves from 37° to 137° of sulphur monochloride are given, from which a value of 8.5 kg.-cal. for the heat of vaporisation was calculated. By long boiling at temperatures above 100°, but never below 100°, the colour may suddenly become red, through the formation of sulphur dichloride, which is accompanied by a lowering of the b. p. Vapour-pressure curves of sulphur monochloride solutions of sulphur of various concentrations are given, and the possibility of the existence of polythiochlorides is discussed.

The molecular heat of dissolution of sulphur in sulphur monochloride was found to lie between -1.3 and -3 kg.-cal. The specific heats of liquids having widely differing sulphur and chlorine contents were measured, and that of sulphur monochloride is given as $0.22 \pm 2.8\%$ at 22° . The sulphur-chlorine system was also studied as regards the composition of the corresponding gaseous and liquid phases, and attempts were made to correlate the vapour pressures with the compositions of the vapours on the supposition that they contained some S_2Cl . Numerous data, referring to the densities and viscosities of sulphur monochloride solutions in which either chlorine or sulphur was dissolved, are recorded. H. T. S. BRITTON.

Action of metals on persulphates. O. ASCHAN [with G. V. PETRELIUS] (Finska Kemistsamf. Medd., 1928, 37, 40—44; Chem. Zentr., 1928, ii, 1866—1867).—By the action of bivalent metals on cold aqueous solutions of potassium, sodium, or ammonium persulphate, the following double salts have been obtained: $M(KO)_2(SO_4 \cdot O)_2 \cdot 6H_2O$, where $M = Mg, Zn, Cd, Fe^{II}, Ni$, or Co ; $M(NaO)_2(SO_4 \cdot O)_2 \cdot 4H_2O$, where $M = Mg, Zn, Cd$, or Fe^{II} ; $M(NH_4O)_2(SO_4 \cdot O)_2 \cdot 6H_2O$, where $M = Mg, Zn, Cd, Fe^{II}, Ni$, or Co . A. A. ELDRIDGE.

Preparation of stable ammonium molybdate solution. J. P. MEHLIG (Chemist-Analyst, 1928, 17, No. 4, 6).—A solution of 380 g. of molybdenum trioxide in 550 c.c. of concentrated ammonia solution and 1030 c.c. of water is slowly dropped, through a filter, into 6 litres of 6*N*-nitric acid, which is continuously stirred. CHEMICAL ABSTRACTS.

Oxidations with fluorine. XII. Action of fluorine on nitric acid, perchloric acid, and related compounds. F. FICHTER and E. BRUNNER (Helv. Chim. Acta, 1929, 12, 305—313; cf. A., 1928, 973).—The action of fluorine on a 10% solution of sodium nitrite is extremely vigorous, but using a 2% solution cooled in ice a solution was obtained which showed the reactions of pernitric acid. Fluorine acts on a dilute solution of nitric acid and gives an appreciable yield of dinitrvi peroxide, which is hydrolysed by water in two stages to pernitric acid and hydrogen peroxide. By the action of fluorine on an alkaline solution of potassium chlorate a 25% yield of perchlorate was obtained. With fluorine and an aqueous solution of perchloric acid a solution was obtained which had the characteristic pungent odour of per-acids, liberated iodine from potassium iodide and bromine from potassium bromide, and contained hydrogen peroxide. It is considered probable that the peroxide Cl_2O_3 is first formed, and is then immediately hydrolysed, forming perchloric acid and per-perchloric acid, $HClO_5$, the latter reacting further to form perchloric acid and hydrogen peroxide. O. J. WALKER.

New isomorphous series of fluorine compounds. H. CARON and L. VANBOCKSTAEL (Compt. rend., 1929, 188, 869—871).—The triple salt $4CaSiF_6 \cdot 8CaF_2 \cdot Al_2(SO_4)_3 \cdot 45H_2O$ has been prepared by the action of 50 c.c. of hydrofluosilicic acid (d 1.075) on 10 c.c. of 10% aluminium sulphate solution, 100 c.c. of 15% calcium chloride solution,

and 200 c.c. of alcohol at 60° for 24 hrs. It forms fine octahedra insoluble in alcohol or ether, slightly soluble in water, and easily soluble in warm dilute acids, which lose water and silicon fluoride when heated. Strontium, but not barium, will replace calcium forming an isomorphous salt; iron or chromium will replace aluminium, whilst the sulphur may be replaced by selenium. J. GRANT.

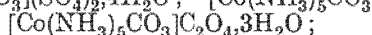
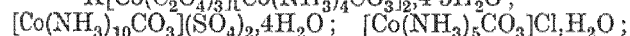
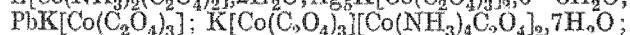
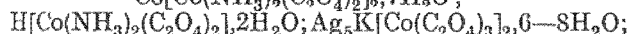
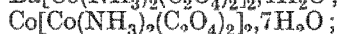
Univalent iron, nickel, and cobalt. V. Formation of nickel carbonyl. W. MANCHOT and H. GALL (Ber., 1929, 62, [B], 678—681; cf. A., 1927, 1157).—Nickel carbonyl is formed when carbon monoxide, saturated with methyl alcohol, is passed over the compound $Ni(NO) \cdot SEt$ at 100 — 140° . Preferably, an aqueous solution of nickel sulphate is mixed in an atmosphere of carbon dioxide with potassium hydroxide and ethyl mercaptan; after some time the pressure in the vessel rises owing to the production of nickel carbonyl. The gaseous products are driven successively through an aqueous suspension of mercury acetate and a calcium chloride tube, after which the carbonyl is condensed in acetone-carbon monoxide. The solution is again treated with carbon monoxide and the process repeated. Even better results are obtained by the action of carbon monoxide on nickel sulphate mixed with potassium hydroxide and hydrosulphide. If nickel sulphate is replaced by iron sulphate, the production of small amounts of a volatile iron carbonyl is observed. With cobalt salts a marked absorption of carbon monoxide occurs, but a volatile cobalt carbonyl is not produced; the action may be utilised for the detection of small amounts of nickel in cobalt salts. H. WREN.

Univalent iron, nickel, and cobalt. VI. Compounds of iron, sulphur, and nitric oxide. W. MANCHOT and S. DAVIDSON (Ber., 1929, 62, [B], 681—687; cf. preceding abstract).—A solution of ferrous sulphate in 50% alcohol is saturated with nitric oxide and then treated with potassium xanthate; the brownish-red precipitate, after crystallisation from carbon disulphide, yields almost black crystals of the compound $Fe(NO)_2(S \cdot CS \cdot OEt)_2$, which is readily auto-oxidised in benzene and evolves nitric oxide freely when decomposed with dilute sulphuric acid. The iron therefore appears bivalent.

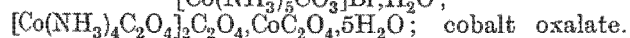
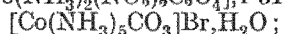
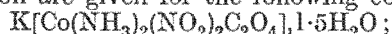
The assumption of univalent iron, nickel, and cobalt is justified by the following considerations. The arguments on which the bivalency of iron in the xanthate compound is based lead to the hypothesis of the univalent metal in the substances $Fe(NO)_2S \cdot R$, $Co(NO)_2S \cdot R$, and $Ni(NO)S \cdot R$. In these compounds the ability of iron to unite with nitric oxide finds expression. The preparation of these iron, cobalt, and nickel compounds has never been effected from a hyponitrite or a substance, $HS \cdot R$. A hyponitrite with tervalent iron should show the instability towards thiosulphate characteristic of ferric salts; actually with potassium thiosulphate the salts $Fe(NO)_2S \cdot SO_3K$ gives an additive compound, $Fe(NO)_2S \cdot SO_3K \cdot K_2S_2O_8$, and analogous compounds, $Co(NO)_2S \cdot SO_3K \cdot K_2S_2O_8$ and $Ni(NO)S \cdot SO_3K \cdot K_2S_2O_8$, have been prepared in well-defined form. The NO group in the sulphur-nitric oxide compounds is

characterised as neutral component by direct comparison with hyponitrites, since the former compounds yield nitric oxide with acids, whereas the latter decompose into nitrous oxide and water. The same substance is formed from nitric oxide and the cyanide in which nickel is certainly univalent as from the compounds $\text{Ni}(\text{NO})\text{S}\cdot\text{R}$ and potassium cyanide. Equivalent amounts of carbon monoxide and nitric oxide unite with ferrous xanthate. Cobalt and nickel salts with potassium xanthate unite with carbon monoxide and nitric oxide. H. WREN.

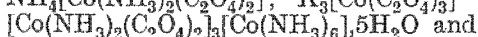
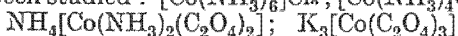
Complex oxalates and carbonates of trivalent cobalt. J. KRANIG (Ann. Chim., 1929, [x], 11, 44—103).—The following new complex compounds are described: $\text{CoK}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]_3\cdot 9\text{H}_2\text{O}$;



$[\text{Co}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2]_3[\text{Co}(\text{NH}_3)_6]_3\cdot 5\text{H}_2\text{O}$. New methods of preparation are given for the following compounds:



A new hexamminocobalt trioxalatocobaltate, $[\text{Co}(\text{C}_2\text{O}_4)_3][\text{Co}(\text{NH}_3)_6]$, was isolated. The absorption spectra in 0.02*N*-solutions of the following compounds have been studied: $[\text{Co}(\text{NH}_3)_6]\text{Cl}$; $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{Cl}$;



$[\text{Co}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2][\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\cdot 2\text{H}_2\text{O}$. The conductivities of aqueous solutions of the two last-named compounds were measured. A. I. VOGEL.

Ruthenium. H. REMY (Z. angew. Chem., 1929, 42, 289—290, 291). H. GALL (*ibid.*, 290—291).—Polemical. A discussion of the valency of ruthenium in the blue chloride solution and in solutions obtained by treating the tetroxide with hydrochloric acid (cf. Remy, this vol., 283). A. R. POWELL.

Displacement of metals and their oxides by hydrogen under pressure at high temperatures. Action of hydrogen at high temperatures and pressures on solutions of ruthenium salts. V. N. IPATIEV and O. E. ZVJAGINSTSEV (Ber., 1929, 62, [B], 708—710).—The ruthenium compounds investigated were $(\text{NH}_4)_2\text{RuCl}_5$, K_2RuCl_5 , Na_2RuCl_5 , and $\text{H}_2\text{Ru}(\text{OH})_2\text{Cl}_4$ in dilute aqueous solution acidified with hydrochloric acid. The same products are derived from all the salts. At 25° and 50 atm., reduction occurs slowly with decolorisation of the solution and formation of a slimy, black precipitate of ruthenium hydroxide which is gradually redissolved under atmospheric pressure. At 85°/65 atm., ruthenium hydroxide is formed as a heavy, black precipitate. At 160°/80 atm., a non-homogeneous precipitate of ruthenium oxide and hydroxide is produced. At 350°/125 atm., ruthenium, mixed with a small proportion of the oxide, is formed. H. WREN.

M M

Iridium fluorides. O. RUFF and J. FISCHER (Z. anorg. Chem., 1929, 179, 161—185).—Fluorine reacts with powdered iridium at 260° with the production solely of the hexafluoride, a yellow, vitreous substance which melts at 44° to a brownish-yellow liquid. After being kept at the ordinary temperature for some months crystal formation is evident, whilst at —150° X-ray investigation indicates a tetragonal structure. Approximate values of the density, b. p., heat of vaporisation, and heat of formation are 6.0, 53, 8.5, and 130 kg.-cal., respectively. Iridium hexafluoride is very volatile and highly reactive. Traces of moisture bring about decomposition. In air the substance volatilises completely on account of its high vapour pressure, and fumes are produced of hydrogen fluoride, iridium oxyfluoride, and ultimately lower fluorides. With an excess of water a violet to red colloidal solution of iridium tetrahydroxide is formed. Complex formation has not been observed. If iridium hexafluoride is prepared in glass vessels a greyish substance is formed simultaneously which is probably the oxyfluoride IrOF_4 ; in quartz vessels the oxyfluoride is stable at the ordinary temperature, but when gently heated or kept in glass vessels iridium oxide is produced. Iridium tetrafluoride may be prepared simply by heating powdered iridium with the hexafluoride at 150°. Continued heating removes the excess of hexafluoride, leaving the difficultly volatile tetrafluoride as a brown oil which is easily decomposed by water and, when moderately heated, decomposes with the production of a black, metallic substance. Similar black substances, obtained by reduction of the hexafluoride with excess of iridium, are of indefinite composition and insoluble in water, and are converted into the tetrafluoride when heated in an atmosphere of iridium hexafluoride. They probably consist of a mixture of lower fluorides. H. F. GILLBE.

Physical and chemical properties of the platinocyanides. I. Hydrates of lithium platinocyanide. F. E. E. GERMANN and O. B. MUENCH (J. Physical Chem., 1929, 33, 415—423).—Pure lithium platinocyanide has been prepared from lithium sulphate and barium platinocyanide; its hydrates have been studied by means of the vapour-pressure method previously described (A., 1928, 1203). The tetrahydrate crystallises from aqueous solutions as needles of a grass-green colour, and the equilibrium pressure of the system tetrahydrate-saturated solution at 25° is 14.14 mm. The anhydrous salt is formed at 25° over concentrated sulphuric acid or when the pressure of water vapour is less than 1.02 mm.; it is canary-yellow in colour. Exposure to a pressure of water vapour greater than 1.02 mm. at 25° yields a tan-coloured tetrahydrate. A black modification results, in turn, from this hydrate by exposure to bright sunlight, ultra-violet light, or to water vapour at low pressures above 10.2 mm. At high pressures, light brings about no change. Hydrogen and cyanide ions catalyse the change. The tetrahydrate is the only hydrate which exists. Previous work is summarised and discussed.

L. S. THEOBALD.

Spectrographic chemical analysis. H. RAMAGE (Nature, 1929, 123, 601—602).—By a modification of

the method of Hartley and Ramage (J.C.S., 1897, 71, 583, etc.) whereby the poles of an arc are placed horizontally in the flame above the burning filter-paper containing the material under examination, the delicacy and applicability of the test are increased. Rubidium is widely distributed in soils and in plants, and is particularly concentrated at the growing point; it is also present in most parts of the body, and in human and cow's milk.

A. A. ELDRIDGE.

Physical methods in the chemical laboratory.
IX. Use of radio-elements as indicators. F. PANETH (Z. angew. Chem., 1929, 42, 189—192).—A radioactive element when added to its more stable isotope causes no change in chemical properties, and by its radioactivity may be used as a very delicate means of detecting and determining small quantities of the element in question. A number of examples of the application of the method are described.

F. R. ENNOS.

Thermometric titration methods. C. MAYR and J. FISCH (Z. anal. Chem., 1929, 76, 418—438).—By conducting various titrations in small Dewar flasks provided with stirring apparatus and a Beckmann thermometer it is possible to determine the end-point by plotting the temperature against the c.c. of standard solution added; two straight lines are obtained the intersection of which occurs at the end-point. In this way sulphate may be determined by titration with barium chloride, chloride with silver nitrate, calcium, strontium (but not barium), mercurous, and mercuric nitrates with ammonium oxalate, lead with oxalic acid in acetate solution, arsenious acid with potassium bromate, sodium hypochlorite with arsenious acid, and potassium ferrocyanide, hydrogen peroxide, oxalic acid, and ferrous sulphate with potassium permanganate.

A. R. POWELL.

Glass electrode; its use in determining p_{H} . A. E. MIRSKY and M. L. ANSON (J. Biol. Chem., 1929, 81, 581—587).—A modification of the arrangement of Kerridge (A., 1925, i, 1201) is described.

C. R. HARRINGTON.

Effect of the method of preparation of quinhydrone on its value for analytical work. M. TRENEL and C. BISCHOFF (Z. angew. Chem., 1929, 42, 288—289).—The low p_{H} value of solutions of some samples of quinhydrone is shown to be due to the presence of iron salts. The following method of preparation is recommended: a solution of 115 g. of iron ammonium alum in 230 c.c. of water at 50° is poured into a solution of 25 g. of quinol in 100 c.c. of water at 60°, the solution is cooled in ice and the precipitate collected, washed seven times with ice-cold water, and recrystallised from water at 80°.

A. R. POWELL.

Tödt's simplified electrodes for the electrometric measurement of p_{H} . L. KÖHLER (Chem.-Ztg., 1929, 53, 69—70).—Combined calomel-quinhydrone and calomel-hydrogen electrodes, from which rapid readings may be obtained directly by means of tables supplied with the apparatus, are described. A micro-form of the former is also available.

S. I. LEVY.

Comparator for the colorimetric determination of the hydrogen-ion concentrations of

coloured solutions. D. McCANDLISH and G. HAGUES.—See B., 1929, 229.

Ultra-violet light in quantitative chemical examination. J. EISENBRAND (Pharm. Ztg., 1929, 74, 249—252).—Simple substances which show fluorescence in ultra-violet light sometimes show sufficient change in this property under the influence of variations in hydrogen-ion concentration. Both α - and β -naphthol show marked fluorescence in alkaline solutions, but are colourless in acid solutions; the transitions are extremely sharp, and very suitable for acid-alkali titrations. Quinine shows two sharp colour changes (p_{H} 6 and 9.5) and can be used for titration of strong and weak bases; it is suggested as a universal indicator in ultra-violet light. The changes in fluorescence may also be of use in determinations of dissociation constants. S. I. LEVY.

Potential gradient in titrations with acid and alkali and determination of reaction constants. F. L. HAHN (Ber., 1929, 62, [B], 727—736).—Mainly a theoretical paper in which precipitation analyses, titration of mono- and di-basic acids with alkali and ampholytes are considered. The possible accuracy and limits of applicability are discussed in detail. Measurements of the titration of pyridine with hydrochloric acid are cited. The original should be consulted for details.

H. WREN.

Determination of water by distillation with hydrocarbons. W. BOLLER (Chem.-Ztg., 1928, 52, 721; 1929, 53, 70).—An apparatus which avoids the difficulty due to adhering droplets of water is described. The vertical reflux condenser is drawn out into a capillary, which reaches to the bottom of the receiver, supported in the neck of the distillation flask, and vacuum-jacketed to prevent redistillation of the condensate by the ascending vapour. The calibrated receiver of the earlier form is later replaced by a detachable measuring vessel held in place by a spring.

S. I. LEVY.

Determination of halogen by Gasparini's method. K. HELLER (Z. anal. Chem., 1929, 76, 408—418).—Electrolytic oxidation of organic compounds containing bromine or iodine in concentrated nitric acid containing silver nitrate results in conversion of part of the halogen into silver halide and part into the corresponding halate, whilst some is sublimed in the elementary state. If the electrolysis is conducted in Gasparini's apparatus (cf. A., 1907, ii, 650) absorption bulbs should be provided to collect any bromine or iodine which may distil. After electrolysis for 4 hrs. the contents of the apparatus are treated with sodium sulphite to convert all the halogen into halide, hydrogen peroxide is added to oxidise the excess of sulphite, and the silver halide is collected and weighed or the excess of silver in the filtrate may be determined by Volhard's method. A. R. POWELL.

Determination of iodine in urine. H. BERNHARDT.—See this vol., 593.

Determination of sulphate in fluorides especially in cryolite. H. GINSBERG [in part with G. HOLDER] (Z. angew. Chem., 1929, 42, 314—317).—Digestion of the powdered substance with 10% sodium carbonate solution does not render all the

sulphate soluble when aluminium fluoride is present. Methods involving dissolution of the mineral in acids, with or without a previous treatment with alkali, removal of the alumina with ammonia, and precipitation of the sulphate in the usual way usually yield high results, as small amounts of aluminium fluoride escape precipitation with ammonia and subsequently contaminate the barium sulphate precipitate. Ignition of a mixture of the fluoride and zinc dust in hydrogen followed by determination of the sulphide formed by the evolution method gives good results and is the most rapid method available. Good results are also obtained by fusion with sodium carbonate, separation of the alumina with ammonia, expulsion of the fluorine by evaporation with hydrochloric acid and silica, and precipitation of the sulphate with barium chloride.

A. R. POWELL.

Determination of fluosilicate and fluorine ions.

E. BAYLE and L. AMY (Compt. rend., 1929, 188, 792—794).—The hydrofluosilicic acid is precipitated by addition of a few c.c. of ether and equal volumes of an excess of potassium chloride solution and 95% alcohol, the solution is neutralised to phenolphthalein with potassium hydroxide and heated on the water-bath with a few c.c. of 10% calcium chloride solution. The fluosilicate formed according to the equation $\text{H}_2\text{SiF}_6 + 2\text{KOH} = \text{K}_2\text{SiF}_6 + 2\text{H}_2\text{O}$ dissolves, and the colour is restored to the phenolphthalein by the addition of a measured amount of standard potassium hydroxide solution, $\text{K}_2\text{SiF}_6 + 4\text{KOH} = \text{Si}(\text{OH})_4 + 6\text{KF}$. Fluorides are heated in a 100 c.c. pyrex flask with a little silica and 10—20 c.c. of sulphuric acid (d 1.842) for several hours at 160° in a current of dry air, and the silicon fluoride produced is collected in distilled water and determined as hydrofluosilicic acid in the same way.

J. GRANT.

Determination of ozone in air. M. S. EGOROV.—See B., 1929, 282.

Automatic apparatus for determination of small concentrations of sulphur dioxide in air. II. M. D. THOMAS and J. N. ABERSOLD.—See B., 1929, 282.

Rapid volumetric determination of the sulphate content of drinking water by visual conductometric titration. H. FEHN, G. JANDER, and O. PFUNDT.—See B., 1929, 342.

Detection of sulphides and thiosulphates by the iodine-sodium azide reaction. L. METZ (Z. anal. Chem., 1929, 76, 347—348).—Thiosulphates, soluble and insoluble sulphides, tri-, tetra-, and pentathionates, but not dithionates or sulphites, catalyse the reaction between iodine and sodium azide (cf. Feigl, A., 1928, 1106).

A. R. POWELL.

Hydrogen peroxide as oxidation catalyst in the determination of nitrogen by Kjeldahl's method. E. GUBAREV (J. exp. Biol. Med. [Russia], 1927, 261—266; Chem. Zentr., 1928, ii, 1916).—Hydrogen peroxide is added after the substance has been heated for 10 min. with concentrated sulphuric acid.

A. A. ELDRIDGE.

Quantitative analysis of phosphoric acid. I. Determination as magnesium pyrophosphate. II. Gravimetric and volumetric methods. III.

Determination as zinc ammonium phosphate. M. ISHIBASHI (Mem. Coll. Sci. Kyoto, 1929, A, 12, 23—38, 39—47, 49—56).—I. In the gravimetric determination of phosphate by precipitation as magnesium ammonium phosphate, the magnesia mixture should be adjusted to a p_H of 5—6. The molecular ratio of ammonium chloride to magnesium chloride should be 5—15 : 1, and the ratio of magnesium chloride to phosphoric acid 1.3—10.5 : 1. If the p_H of the phosphate solution is 4.4—8.3, and the precipitation is effected below 35°, the precipitate will settle satisfactorily in 30 min. Sodium acetate, potassium chloride, and ammonium and sodium sulphates interfere.

II. The spontaneous oxidation of manganous ammonium phosphate in alkaline solution may be prevented by addition of hydroxylamine, so that it becomes possible to determine phosphate by precipitation as the double phosphate and weighing as pyrophosphate after ignition. Excess of a solution containing ammonium chloride and manganous chloride in the molecular ratio of 75—125 : 1 and a little hydroxylamine hydrochloride are added to the phosphate solution, which must be not too dilute and of such acidity that only a very slight precipitate results. The solution is then heated nearly at the b. p., precipitated by addition of ammonia, and filtered after 2 hrs. Ammonium citrate, tartrate, and oxalate interfere, and if ammonium molybdate is present it is necessary to precipitate from a strongly ammoniacal solution, then dissolve in acid and reprecipitate. The double phosphate may also be dissolved in acid and titrated with permanganate at 80—90°, the end-point being reached when the colour of the solution does not change for 2—3 min.; 2 g. of sodium acetate must be added for each 10 c.c. of 0.1N-permanganate.

III. Phosphate may also be determined by precipitating as zinc ammonium phosphate, igniting, and weighing as pyrophosphate. Excess of a solution containing ammonium chloride and magnesium chloride in the molecular ratio of 50—100 : 1, and 2.0—3.6N in respect of the former chloride, is added to the phosphate solution, the acidity of the mixture being so regulated that very little precipitation occurs. The solution is then heated nearly at the b. p., and ammonia slowly added until precipitation is complete, the p_H being kept at 5—6.5 during this process. Ammonium molybdate interferes. Instead of the precipitate being ignited, it may be converted into zinc oxalate by treatment with oxalic acid, and titrated with permanganate.

R. CUTHILL.

Determination of borate in natural waters. M. D. FOSTER.—See B., 1929, 304.

Determination of silicon in ferrosilicon and in other iron alloys. A. STADELER.—See B., 1929, 326.

Determination of small amounts of silica in orthophosphoric acid. P. ALBRECHT.—See B., 1929, 281.

Determination of carbon. D. STROHAL.—See this vol., 586.

Mercurimetry. E. VOTOCEK and J. KOTRBA (J. Czechoslov. Chem. Comm., 1929, 1, 165—172).—In

the authors' mercurimetric method for the determination of cyanide (A., 1921, ii, 238, 272) the action of mercuric cyanide on mercuric nitrate is found to be negligible, and a comparison of the method with gravimetric determinations shows that it is accurate to $\pm 0.25\%$. The Liebig-Deniges silver method gives results 0.8% low. The application of the method to the determination of chloride and cyanide in the presence of each other by removal of the cyanide with formaldehyde (which itself has no effect on the titration) is described. If at least five times the theoretical quantity of formaldehyde is used removal of the cyanide, as glycollonitrile, is quantitative and rapid (15 min. being allowed for safety) and the chloride is then determined mercurimetrically. Similar titration without the addition of formaldehyde determines the chloride and cyanide present, the latter being then obtained by difference. Alternatively, the cyanide may be determined by the silver method, providing a suitable correction is applied. Determination of alkali nitroprussides may also be effected by precipitation, from the solution acidified with nitric acid, with mercuric nitrate, filtering (with addition of a little infusorial earth) and washing (with water acidified with nitric acid) the precipitated mercuric nitroprusside, dissolving it in a known volume of $0.1N$ -sodium chloride solution, filtering, making up to 200 c.c., and titrating with $0.1N$ -mercuric nitrate. The method is not affected by the presence of cyanides, chlorides, and sulphates.

J. W. BAKER.

Mixed bromides in place of chlorides in alkali determinations. E. SPENCER and K. B. SEN (Analyst, 1929, 54, 224—226).—If ammonium bromide and hydrobromic acid be substituted for ammonium chloride and hydrochloric acid respectively in the Lawrence Smith method (Amer. J. Sci., 1871, 50, 269) for determining potassium and sodium in rocks and similar materials, the resulting mixed bromides are purer, less fusible, and less volatile than the mixed chlorides. In Berzelius' method (Pogg. Ann., 1824, 1, 169) barium bromide may be advantageously substituted for barium chloride for converting the alkali sulphates, and since the alkali platinibromides may be completely separated by 90% ethyl alcohol the above substitution still allows of the determination of potassium, but as platinibromide.

D. G. HEWER.

Separation of calcium and magnesium by the oxalate method. O. RØER (Tidsskr. Kjemi Berg., 1929, 9, 27—28; cf. Luff, A., 1925, ii, 438).—The usual method of precipitation with a large excess of ammonium oxalate in boiling solution gives a precipitate of calcium oxalate contaminated with magnesium salt. It is claimed that a perfect separation can be effected by a single precipitation according to the following methods, which are based on the stability of a supersaturated solution of magnesium oxalate at 70° . If up to 0.3 g. of lime is present, the feebly ammoniacal solution (containing ammonium chloride and having a volume of 200 c.c. for each 0.25 g. of magnesia present) is heated to boiling and 0.5*N*-ammonium oxalate solution added from a burette until no further precipitate forms. The solution is then cooled to 70° and an additional 4 c.c. of 0.5*N*-

ammonium oxalate per 100 c.c. of solution are added. With quantities of lime from 0.3 to 0.7 g. the liquid is neutralised with concentrated hydrochloric acid, and 2 c.c. in excess are added. After heating to boiling, a solution of *N*-oxalic acid in *N*-hydrochloric acid is added in quantity just equivalent to the lime present. The solution is neutralised with dilute ammonia, added drop by drop, cooled to 70° , and 4 c.c. of 0.5*N*-ammonium oxalate solution per 100 c.c. of liquid are added as in the previous method. For the determination of magnesia in limestones where very small amounts are present, it is recommended to effect a preliminary concentration of this constituent by boiling a solution of 10 g. of the limestone with 0.2 g. of pure lime, after previous neutralisation with sodium hydroxide. The precipitate, containing the whole of the magnesia together with alumina, ferric oxide, etc., is redissolved and the magnesia in it determined in the usual way.

H. F. HARWOOD.

Analysis of metals and ores by heating in a current of chlorine. R. WASMUTH.—See B., 1929, 328.

Spectrographic detection of beryllium. H. FESEFELDT (Z. physikal. Chem., 1929, 140, 254—262).—The beryllium lines given by mixtures of beryllium and aluminium oxides in the carbon arc have been measured. The most sensitive lines are 2348.62, 3130.42, and 3131.06 Å. These lines are obtained with a mixture containing only 0.0001% of beryllium oxide. The influence of adding impurities on the sensitiveness has been investigated. Addition of ferric oxide or a mixture of silica and sodium carbonate has no effect, but sodium carbonate alone or calcium oxide lowers the sensitiveness considerably.

R. N. KERR.

Detection of magnesium by means of dyes. E. EEGRIWE (Z. anal. Chem., 1929, 76, 354—359).—In the presence of excess of alkali hydroxide magnesium solutions give characteristic colours or, with larger quantities, precipitates with dilute solutions of certain disazo dyes. In the absence of nickel or cobalt the reactions are specific for magnesium and will detect 0.001 mg./c.c. In the presence of chromium the best results are obtained with diamine-blue FF, Chicago-blue 6B, and benzopurpurin 4B.

A. R. POWELL.

Quantitative emission spectrum analysis. II. **Determination of zinc in solution and of molybdenum in steel by the comparison method.** H. THURNWALD (Z. anal. Chem., 1929, 76, 335—347).—The intensity of the zinc line λ 3345 Å. is compared with that of the silver line λ 3383 Å. in solutions of known silver concentration. The intensities are equal when the zinc solution contains twenty times as much zinc as there is silver in the standard silver solution. For the determination of molybdenum in steel the alkaline molybdate obtained from the steel in the usual way is spectrographed and the intensity of the molybdenum line λ 2816 Å. is compared with that of the lead line λ 2832 Å. obtained with standard lead nitrate solutions; the intensities of these lines are equal when the same concentration of metal is present in each solution.

A. R. POWELL.

Analysis by electrolysis with a mercury cathode. W. MOLDENHAUER [with K. F. A. EWALD and O. ROTH] (*Z. angew. Chem.*, 1929, 42, 331—334).—A mercury cathode is conveniently contained in a glass spoon with platinum connexion immersed in the beaker in which electrolysis is carried out. Examples are given of its use in the determination of lead in nitric acid solution, of silver, nickel, and zinc in ammoniacal solution, and of silver in cyanide solution. Separations carried out by varying the *P.D.* include silver and copper or silver and lead in nitric acid solution, copper and nickel in sulphuric acid. Other separations are effected by precipitating one or other metal, *e.g.*, lead as sulphate, and then electrolysing. The use of a mercury electrode makes possible the separation of chromium and other metals which do not form a coherent deposit on platinum, and also the alkali and alkaline-earth metals. It is not suitable for platinum and its allies, antimony, or arsenic. C. IRWIN.

Electrometric determination of small quantities of lead ion. H. MILLET (*Trans. Faraday Soc.*, 1929, 25, 147—152).—Electromotive measurements at 25° of the cell $\text{Pb}|\text{Pb}(\text{NO}_3)_2|\text{saturated KCl}|\text{N-calomel electrode}$ have shown that the lead ion may be determined in concentrations of at least $10^{-8}M$ in solutions as strongly acid as 0.1*N*-hydrochloric acid. A lead-coated platinum electrode serves for neutral solutions, but in the presence of acid a liquid amalgam is prepared by heating the pure metals in an atmosphere of nitrogen, and oxygen is excluded throughout the determination. The modified Debye-Hückel formula (A., 1923, ii, 724), $-\log \gamma_{\text{Pb}^{2+}} = 0.48n^2\mu^{\frac{1}{2}}$, is suggested. J. GRANT.

Determination of small quantities of mercury in presence of organic and inorganic compounds. R. ROBINSON (*Analyst*, 1929, 54, 145—152).—In the presence of impurities such as copper, iron, zinc, sodium, and potassium, mercury may be determined by precipitation with hypophosphorous acid and the use of standard iodine solution. The mercury solution is diluted to 200 c.c. and the acidity adjusted with hydrochloric acid so that an excess of 5 c.c. of 2*N*-hydrochloric acid is present. Two g. of sodium chloride are added and 0.01 g. of paper pulp, followed by 30 c.c. of hypophosphorous acid (*d* 1.137), and the mixture is left over-night. After heating for 15 min., keeping for 20 min., and filtering by suction through a paper-pulp filter, the flask and filter are thoroughly washed, and 100 c.c. of water and 2 c.c. of 30% acetic acid are added to the pulp and mercury, followed by excess of 0.01*N*-iodine solution and 2 g. of potassium iodide. After keeping, 0.01*N*-sodium thiosulphate is added in excess and titrated with 0.01*N* iodine solution. A blank determination is necessary. The results are 0.3 mg. too low on the average, due to volatility of the mercury. The effects of excess of hydrochloric acid, different times of heating, and keeping after heating are discussed. Iron causes low results unless sodium chloride is present; copper does not affect the results unless too small an excess of hypophosphorous acid has been used. When organic compounds are present these may usually be satisfactorily destroyed by heating in a sealed tube at 180° with fuming nitric acid, but where a small amount of

sample is available 0.2—0.5 g. may be placed in a Kjeldahl flask connected with two wash-bottles and heated in a paraffin-bath at 130—150° with 10 c.c. of concentrated sulphuric acid with occasional addition of a crystal of potassium nitrate. The contents of the wash-bottles are added to the bulk, the solution is filtered, the filtrate neutralised below 50° with sodium hydroxide and rendered acid, and the original method employed. D. G. HEWER.

Determination of minute amounts of mercury. R. THILENIUS and R. WINZER (*Z. angew. Chem.*, 1929, 42, 284—288).—Stock's method (A., 1926, 814) is modified in that the mercury is collected on a gold wire or thin copper strip which is then heated in chlorine in a closed capillary tube at 250° for 2—3 hrs. The resulting mercuric chloride is dissolved in water, the solution treated with alcoholic diphenylcarbazone, and the blue colour compared with that produced by a standard mercuric chloride solution, using a 5% solution of potassium dichromate in a 1 cm. layer as a light filter. The dry chlorination is preferable to the treatment with chlorine water recommended by Stock, as it yields a neutral solution of mercuric chloride which gives the maximum intensity of colour with the reagent without further treatment. A. R. POWELL.

Oxidation of mercuric cyanide by sodium hypobromite. Application to the determination of cyanide and oxycyanide of mercury. J. GOLSE (*Bull. Soc. chim.*, 1929, [iv], 45, 177—183).—Quantitative oxidation of mercuric cyanide occurs in solution on the addition of alkaline sodium hypobromite solution according to the equation $\text{Hg}(\text{CN})_2 + 2\text{NaBrO} + 2\text{NaOH} = \text{HgO} + 2\text{NaCNO} + 2\text{NaBr} + \text{H}_2\text{O}$. The primary reaction is the oxidation of the cyanide to mercuric cyanate, which reacts with the free alkali to give mercuric oxide. The technique of the determination consists essentially in the addition of excess of a standard hypobromite solution, the portion remaining unchanged after oxidation of the cyanide being determined by titration with sodium thiosulphate solution, following the addition of excess of potassium iodide. The same reaction may be used for the determination of mercury; in this case the excess of hypobromite solution is decomposed by the addition of ammonia solution, the precipitated mercuric oxide dissolved in an excess of standard potassium cyanide solution, and the excess of the latter determined by titration with silver nitrate.

F. G. TRYHORN.
Detection of aluminium by dye reagents. E. EGGRIWE (*Z. anal. Chem.*, 1929, 76, 438—443).—The chloride solution is treated with one drop of a 0.1% solution of "eriochromecyanin R conc.," rendered just alkaline with 2*N*-sodium hydroxide solution, and reacidified with 0.2*N*-acetic acid added drop by drop until the colour changes to yellow, then, if aluminium is present, to an intense violet-rose; 0.0005 mg. of aluminium in 2 c.c. of solution produces a distinct colour. The morin test is rendered more sensitive by proceeding as follows: 1—2 drops of the chloride solution are treated with 0.1—0.2 c.c. of a cold saturated solution of morin in methyl alcohol and the mixture is saturated with sodium acetate; a green

fluorescence appears if the test solution contains more than 0.0003 mg. of aluminium in 0.5 c.c. These tests are almost as sensitive as the alizarin S and alizarin-red PS tests and are not affected by the presence of 0.1 mg. of cobalt, nickel, zinc, manganese, and chromium.

A. R. POWELL.

Determination of aluminium in steel. A. T. ETHERIDGE.—See B., 1929, 326.

Determination of manganese in water. J. DE GRAAF.—See B., 1929, 266.

Determination of iron and aluminium oxides, magnesium oxide, and calcium oxide in Portland cement. J. S. PIERCE and W. C. SETZER.—See B., 1929, 284.

Rapid determination of iron and uranium. G. SCAGLIARINI and P. PRATESI (*Annali Chim. Appl.*, 1929, 19, 85—90).—Ferric iron is reduced rapidly and quantitatively to the ferrous state by metallic copper in presence of sulphuric acid at the b. p. of the solution, no cuprous salt being formed, so that the iron may be subsequently determined by titration with permanganate solution. The liquid must be free from nitric and hydrochloric acids, and the copper is most conveniently used as a coil of fine electrolytic wire attached to a glass rod passing through a stopper so that it may be raised from the solution. The stopper is provided also with a Bunsen valve, and collapse of the flask by condensation of the steam is prevented by adding to the hot liquid a few crystals of pure sodium carbonate. The results are not affected by the presence of titanium, chromium, manganese, aluminium, or nickel. Uranyl compounds are similarly reduced to salts of quadrivalent uranium, which may be determined by re-oxidation with permanganate. Since ferric salts but not uranyl salts are reduced by hydrogen sulphide, it becomes possible to determine both uranium and iron in their mixtures.

T. H. POPE.

Fixation of phosphoric acid by ferric hydroxide in presence of varying amounts of ammonia. E. ANGELESCU and C. BALANESCU (*Kolloid-Z.*, 1929, 47, 207—221).—The complete simultaneous precipitation of iron and phosphoric acid is possible only when the ratio of iron to phosphorus is greater than 2 and at a p_H below 7. In acid solution, neither the temperature nor the nature of the anion has any effect. In alkaline solution, the phosphoric acid is incompletely retained by the ferric hydroxide, the amount of phosphoric acid going into solution depending on the ratio of iron to phosphorus and on the initial concentrations. The composition of the precipitate varies with the concentration of the ammonia and with the original iron to phosphorus ratio. In acid solution, various basic phosphates of definite chemical composition are formed, whilst in alkaline solution the fixation of the phosphoric acid proceeds in accordance with the adsorption equation. Two peptisation regions were observed, one in acid solutions at high iron to phosphorus ratios and the other in alkaline solutions at low iron to phosphorus ratios. The phenomena can be explained on the basis of a surface dissociation of the ferric hydroxide, which is influenced by the hydrogen-ion concentration. The

results of the investigation are applied to the determination of phosphoric acid, and a method is given for the determination of the oxides of iron, aluminium, and phosphorus in soils.

E. S. HEDGES.

Quantitative separation of nickel and calcium. G. W. KÜHL (*Chem.-Ztg.*, 1929, 53, 279).—Calcium is precipitated as oxalate from boiling ammoniacal solutions containing ammonium chloride and nickel determined in the filtrate as the dimethylglyoxime compound.

J. S. CARTER.

Determination of chromium, tungsten, molybdenum, vanadium, nickel, manganese, and cobalt in high-alloy steels. H. MENDE.—See B., 1929, 326.

Determination of molybdenum in steel in presence of tungsten and vanadium. I. KASSLER.—See B., 1929, 249.

Rapid determination of tin in tinplate. W. A. MASEL.—See B., 1929, 286.

Detection of small amounts of vanadium. A. FÖLSNER (*Chem.-Ztg.*, 1929, 53, 259).—The turbidity given by solutions of lead acetate is a much more sensitive reaction than the hydrogen peroxide test for the detection of vanadium.

J. S. CARTER.

Detection of vanadium and cerium by hydrogen peroxide. J. LUKAS and A. JILEK (*Z. anal. Chem.*, 1929, 76, 348—351).—In the colorimetric detection of vanadium by hydrogen peroxide, addition of oxalic acid to the sulphuric acid solution prevents bleaching by excess of hydrogen peroxide (cf. Meyer and Pawletta, A., 1926, 1020). The colour due to molybdenum in this test is bleached entirely by addition of boric acid, which does not affect the vanadium colour. Neutral cerous salt solutions are coloured yellow to orange by addition of quinine hydrochloride and hydrogen peroxide. Titanium and salts of metals which are readily hydrolysed interfere.

A. R. POWELL.

Evaluation of stibnite. I. Determination of sulphur. W. M. McNABB and E. C. WAGNER.—See B., 1929, 286.

Detection of gold and platinum metals [in ores]. SPORCQ.—See B., 1929, 286.

Potentiometric determination of gold and platinum with stannous chloride. E. MÜLLER and R. BENNEWITZ (*Z. anorg. Chem.*, 1929, 179, 113—124).—The gold is oxidised to the tervalent state by addition of chlorine water until the potential of the indicator electrode is about 1 volt, and the solution is then titrated with stannous chloride; the first break corresponds with the completion of the reaction $Cl_2 + Sn^{++} \rightarrow 2Cl^- + Sn^{+++}$, and the second with that of the reaction $2Au^{+++} + 3Sn^{++} \rightarrow 2Au + 3Sn^{+++}$. Platinum may be determined by oxidation to the tervalent state with potassium bromate solution and titration with stannous chloride at 75°; a break occurs when the platinum is reduced to the bivalent state, but no evidence is obtained of a second break such as would be expected if complete reduction to metal occurred; a complex ion is probably formed. If both gold and platinum are present a break occurs only after both metals have been

reduced, and for a constant total quantity of gold and platinum the position of the break varies with the ratio between the two metals. H. F. GILLBE.

Modified Pirani gauge for use in corrosive systems. G. K. ROLLEFSON (J. Amer. Chem. Soc., 1929, 51, 804).—A mercury thread contained in a thin-walled glass capillary is used as the hot filament in the gauge. It is then preferable to use the gauge by measuring the current necessary to keep the temperature of the mercury thread constant. The modified gauge responds to pressure change very rapidly.

S. K. TWEEDY.

Sensitive form of Pirani gauge for the measurement of high vacua. L. F. STANLEY (Proc. Physical Soc., 1929, 41, 194—203).—In a study of the factors affecting the sensitivity of the gauge it was found that the diameter of the manometer is without influence; rise in the temperature of the filament gives greater sensitivity up to about 100°, after which errors are introduced. The most important factor is the temperature of the walls of the manometer; the lower this temperature the more sensitive is the instrument. The construction of a manometer is described in which the length of the loop is 10 cm., the error due to loss of heat by conduction along the leads being minimised by the introduction of a 2 cm. subsidiary loop in both the manometer and the compensator. This gauge was used in conjunction with a Callendar-Griffiths bridge and was capable of measuring pressures between 2×10^{-3} and 4×10^{-6} mm. The accuracy of different forms of the McLeod gauge is discussed.

J. L. BUCHAN.

Laboratory apparatus for producing homogeneity. G. FRANK (Chem.-Ztg., 1929, 53, 259).—A helical stirrer operates in the vertical portion of a b-shaped vessel. The neck of the apparatus may be closed by a liquid seal. The apparatus is especially designed for producing homogeneity in small quantities of viscid liquids.

J. S. CARTER.

Reaction tube. C. DHERE (Bull. Soc. chim., 1929, [iv], 45, 183—184).—The two components of a reaction are separated by placing the one in a small test-tube which rests on three indentations inside a larger tube containing the other reactant. The larger tube is sealed off, and the reaction brought about by inverting the tube.

F. G. TRYHORN.

Efficiency of fractional distillation apparatus.
I. **Application of Brown's law to column distillations.** H. G. GRIMM (Z. physikal. Chem., 1929, 140, 321—341).—The equation which was found by Brown (1879) to represent the course of a distillation of binary liquid mixtures, in which reflux condensation was carefully prevented, has been shown to apply also in the case of distillation with rectifying columns. The three mixtures *i*-amyl bromide + ethyl butyrate, carbon tetrachloride + benzene, and cyclohexane + benzene were fractionally distilled by means of two types of rectifying column, and the weight and composition of the fractions and the speed of distillation determined at intervals. The composition of the mixtures was determined refractometrically. If L and M are the initial amounts of the two components, and ξ and η the respective

amounts remaining in the distillation flask at any given time, the course of the distillation is given by the linear relationship $\log \xi/L = (1+k)(P_1 - P_2)/P_2 \cdot \log \eta/M$, where P_1 and P_2 are the vapour pressures of the two components at the b. p. of the mixture. The constant k is a direct measure of the efficiency of the distillation apparatus. If k is determined for any given apparatus, the course of the distillation can be predicted by means of the above relationship. A modified form of fractionating column for use with small quantities of liquids is described.

O. J. WALKER.

Apparatus for fractional distillation. G. PICHARD (Ann. Sci. Agron. Franç., 1928, 45, 358—361; Chem. Zentr., 1928, ii, 1911).—The still-head is composed of three concentric tubes, whereby the path of the vapour is trebled.

A. A. ELDRIDGE.

Vacuum distillation. C. R. BURCH (Proc. Roy. Soc., 1929, A, 123, 271—284).—An apparatus consisting of an electrically heated copper tray (container) enclosed in a horizontal water-jacketed condensing tube is described. The latter can be evacuated by a mercury condensation pump, and distillations made in this manner are practically equivalent to evaporation into a perfect vacuum. Methods are given for the removal of gas from the apparatus. In most of the distillations an induction coil giving a 1.8 cm. spark between points produced no discharge at the electrode in the receiver chamber (the tray being earthed), this being the point of highest permanent gas pressure in the still. The differences between equilibrated and evaporation distillation are indicated and the theory of the latter is discussed. In the present apparatus the rate of evaporation is given by $0.382\sqrt{M}\sqrt{273/T} \cdot P$ g. per hr., where M is the mol. wt. of the chemical individual distilled at a temperature T° Abs., corresponding with a saturation pressure P microbars. This leads to a choice of about 20 c.c. per hr. as a maximum speed desirable in fractionations. Details are given of the distillation of a number of oils, and graphs showing the temperature-distillate yield relations are reproduced. This method enables distillations to be made which cannot otherwise be accomplished without decomposition and it is shown that a certain degree of fractionation is possible. A substance (grease) was prepared from petroleum jelly which had a vapour pressure as low as 10^{-3} microbar at 70° . Some experiments were made using such material instead of mercury in a condensation pump, and pressures of the order of $<2 \times 10^{-3}$ dyne/cm.² were obtained.

L. L. BIRCHUMSHAW.

Shaker for Clark hydrogen electrode vessel. D. M. CAMERON and R. SHEARER (J. Amer. Leather Chem. Assoc., 1929, 24, 130—133).—Two sheet-metal arms are mounted separately by their lower ends in a slantwise position to the side of a board by means of screws, which serve as pivots. A carriage for an electrode vessel is mounted to the upper end of each arm by means of two pivoting screws. The upper ends of the arms are connected by means of a horizontal rod from the middle of which a cord is attached to an eccentric pin on a pulley, whereby the driving force is applied.

D. WOODROFFE.

M.-p. apparatus. F. KERCKOW (Chem.-Ztg., 1929, 53, 219).—The apparatus consists of an L-shaped hard glass tube. The lagged horizontal limb contains an electrical heating spiral and an air inlet. Into the vertical limb, which is air-jacketed, is inserted a thermometer with a capillary m.-p. tube dipping into a small test-tube containing paraffin oil. The small oil-bath is heated by passing a current of air over the hot spiral. With a heating spiral of 7 ohms resistance and an air stream of 950 litres/hr. a temperature of 100° is reached with a current of 2.8 amp. and of 300° with 6 amp. in 4 and 16 min., respectively.

F. G. TRYHORN.

Tellurium-bismuth thermo-element and its applications. M. A. LEWITSKY and M. E. LUKOMSKY (Physikal. Z., 1929, 30, 203—205).—Methods and precautions for obtaining trustworthy data with the tellurium-bismuth thermo-element are indicated. The thermo-element is about six times as sensitive as the iron-constantan combination. For measuring the temperature decreases along an iron bar the ends of which are at 0° and 17.5°, respectively, the tellurium-bismuth thermo-element gives results slightly nearer the theoretical than does the iron-constantan element.

R. A. MORTON.

H-Particles made visible. H. PETTERSSON (J. Sci. Instr., 1929, 6, 130—132).—A modified cloud chamber for the observation of H-particles is described. A polonium point is enclosed in a thin glass tube coated inside with paraffin wax, the whole being placed in the cloud chamber. H-Particles are liberated from the paraffin wax by the α -particles from the polonium, and produce tracks in the cloud chamber. A spinthariscopes may be modified for the same purpose by placing a thin cutting of paraffin wax on a polonium source, and interposing a sheet of mica barely thick enough to stop the α -rays from reaching the zinc sulphide screen.

C. W. GIBBY.

Optical method for analysing photographs of α -ray tracks. L. F. CURTISS (Nature, 1929, 123, 529).—Two photographs are taken in directions at right angles; the developed negatives are then replaced in the cameras and images projected on to a screen which is so placed that no part of the composite image appears double. The screen may then be replaced by a photographic plate, whereby there is obtained a photograph of actual size, reproducing all angles of the track in the plane in which they occurred.

A. A. ELDRIDGE.

Self-adjusting pipette. E. G. BILHAM (J. Sci. Instr., 1929, 6, 119—120).—The discharge jet of an ordinary pipette is extended upwards inside the bulb, and retains a definite quantity of liquid, which is then poured out through the top of the pipette.

C. W. GIBBY.

Vacuum arc lamp for spectroscopic work. K. PROSAD (J. Sci. Instr., 1929, 6, 126—130).—The arc, which is started electromagnetically, is struck inside a brass cylinder and viewed through a quartz window. Vacuum-tightness is secured by wax joints, which are protected by water-cooling.

C. W. GIBBY.

Spectrography at the temperature of liquid air. G. BECK (Deut. Z. ges. gerichtl. Med., 1928, 12, 1—4;

Chem. Zentr., 1928, ii, 1918).—A tube for the spectrographic examination of alkaloid solution at -180° to -200° is described, and the eutectics of mixtures of ether, propyl alcohol, pentane, methylcyclohexane, and decahydronaphthalene have been examined in order to select a suitable solvent.

A. A. ELDRIDGE.

Measurement of flame temperatures. E. GRIFFITHS and J. H. AWBERY (Proc. Roy. Soc., 1929, A, 123, 401—421).—A "wire method" for measuring flame temperatures, in which the condition of thermal equilibrium is identified by the absence of energy interchange between the wire and the flame, has been devised. A platinum wire carrying electric current is immersed in the flame and the apparent temperature of the wire observed by means of a disappearing-filament optical pyrometer. The same wire is then set up in a vacuum and the temperature corresponding with various values of the current is determined. On plotting the data, two curves are obtained which intersect at a point giving the temperature of the flame. The absorption effect of the flame is so small that it may be neglected. The values obtained are independent of the diameter of the wire and agree with those found by the method of spectral line reversal. A description is given of the latter method, in which the source of the continuous spectrum is the incandescent sphere of a tungsten arc, the flame being coloured by sodium or lithium. The current in the arc is adjusted until the sodium or lithium lines just merge into the continuous background, when a reading of the temperature of the incandescent tungsten sphere taken on the optical pyrometer gives the flame temperature. It was found by experiment that the apparent temperature, obtained by the sodium line reversal method, of a column of sodium chloride vapour contained in an electrically heated carbon tube furnace is the same as the "black body" temperature of the furnace. The thickness of the flame has no influence on spectral line reversal, although it is advisable to use a thick flame to ensure sensitivity. This result is shown to be a consequence of theoretical deductions based on certain simplifying assumptions. The method has been successfully applied to the measurement of maximum temperatures in gaseous explosions, using a carbon monoxide, air, and nitrogen mixture; also to the study of combustion, using flames burning mixtures of carbon monoxide and air; and to the measurement of the temperature of the gases between the electrodes of the atomic hydrogen blow-pipe, for which a mean value of 2515° was obtained.

L. L. BIRCUMSHAW.

Platinising glass and other substances. G. F. TAYLOR (J. Opt. Soc. Amer., 1929, 18, 138—142).—Improved methods are described of preparing and applying a platinising solution of platonic chloride, oil of rosemary, and oil of lavender, so as to obtain either a surface which can be soldered or a fine, flawless mirror. Various properties of the films and applications of the method are described, and other materials which can be similarly treated are mentioned.

N. M. BLIGH.

Extrusive plastometer. P. M. GIESY and S. ARZOOMANIAN (5th Coll. Symp. Mon., 1928, 253—258).

Falling-sphere viscosimeter and plasticity measurements. H. E. PHIPPS (5th Coll. Symp. Mon., 1928, 259—266).

Manometer for determination of gases in vapours. D. F. OTHMER.—See B., 1929, 267.

Electric resistance furnace. W. ROSENHAIN and W. E. PRYTHERCH.—See B., 1929, 288.

Apparatus for testing liability to corrosion. V. DUFFEK.—See B., 1929, 289.

Improved Czapek apparatus for determining surface tension. V. I. KAMINSKI (Zhur. exp. Biol. Med., 1928, 10, 21—22). CHEMICAL ABSTRACTS.

Reduction of the time of photographic exposures, especially in X-ray work. F. EBERT (Z. anorg. Chem., 1929, 179, 279—280).—The time of exposure may be reduced by 50—70% by maintaining the film at about 40° during the exposure.

H. F. GILLBE.

Geochemistry.

Radiation in the upper atmosphere, and its bearing on physical and cosmic processes. L. MEITNER (Z. angew. Chem., 1929, 42, 345—351).—An account of the effects observed, the methods of measurement, and the theoretical significance of the results.

S. I. LEVY

Equivalent heights of the atmospheric ionised regions in England and America. E. V. APPLETON (Nature, 1929, 123, 445).

Earth's age by sodium accumulation. A. C. LANE (Amer. J. Sci., 1929, 17, [v], 342—346).—In determining solvent denudation by rivers, no account is usually taken of the fact that the greater part of the run-off of a river is in times of flood, when the amount of dissolved matter is much less, and that of sediment greater, than when the river is normal or low. Calculation of the amount of sodium carried off in solution gives lower values if weighted averages of the water analyses are used than if no allowance is made for the different amounts of water flowing at different times of the year.

C. W. GIBBY.

Thermal transformation of serpentine. H. HARALDSEN (Zentr. Min. Geol., 1928, A, 297—315; Chem. Zentr., 1928, ii, 1757).—When heated at 500—700°, serpentine loses most of its water, and the crystal structure of serpentine gives place at 700° to a structure analogous to that of olivine. At higher temperatures mixtures of olivine, free amorphous silica, and enstatite are obtained; the last increases with rising temperature at the expense of the silicic acid.

A. A. ELDRIDGE.

So-called "thermokalite" and the existence of sodium hydrogen carbonate as a mineral. F. A. BANNISTER (Min. Mag., 1929, 22, 53—64).—A white crystalline saline encrustation was found in 1888 on the walls of a Roman conduit at the Baths of Nero, which was exposed during the construction of the railway line from Baia to Naples. This material was provisionally called "thermokalite," evidently in the belief that it represented the potassium compound corresponding with thermonatrite. It, however, contains no trace of potassium, and analyses show varying amounts of sodium carbonate and sulphate with 7.48—8.45% H₂O. The analyses are interpreted as mixtures of thermonatrite (Na₂CO₃·H₂O), trona (Na₂CO₃·NaHCO₃·2H₂O), sodium hydrogen carbonate, and thenardite (Na₂SO₄), and each of these minerals was determined by the optical characters. The sodium hydrogen carbonate,

not hitherto definitely recognised as a mineral, is named *nahcolite* (from NaHCO₃) to distinguish it from the other sodium carbonate minerals. Its mode of origin and conditions of stability are discussed from a physico-chemical point of view. The reaction $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$ is much retarded by the formation of crusts, and even though it was collected forty years ago the material still contains about 20% of nahcolite.

L. J. SPENCER.

Tholeiite dikes of the north of England. A. HOLMES and H. F. HARWOOD (Min. Mag., 1929, 22, 1—52).—This set of basaltic dikes in the north of England and south of Scotland has a different direction from those associated with the Whin sill (A., 1928, 1211). They are of Tertiary age and radiate from the Mull volcanic centre. Eight detailed analyses of the different types show a range in silica from 50.07 to 57.57%.

L. J. SPENCER.

Deposition of sulphur at Monte Solfioroso near Scrofano in the province of Rome. E. ONORATO (Atti R. Accad. Lincei, 1928, [vi], 8, 243—251).—An investigation has been made of the minerals in the old and new workings of the sulphur mines of Monte Solfioroso. The tufa above the region of vegetation is clear reddish in colour, has little coherence, and is relatively acid, and probably trachitic, in nature. This type contains SiO₂ 47.47, Al₂O₃ 23.44%. A second variety which is perfectly white and trachitic in structure has the high silica content of 84.43%. The transformation of the former into the siliceous type is due to the extraction of sulphates by water circulating through the deposits. Goniometric measurements have been made of the sulphur crystals, some millimetres in length, which occur in the rocks. In the abandoned workings, where water has deposited stalactites and crystalline masses of sulphates, sulphur occurs in great masses of fibrous structure. In these deposits alum was recognised in distorted crystals, and alotrichite in a white, fibrous form of composition SO₃ 35.10, Al₂O₃ 10.61, FeO 9.10, CaO 2.33, MgO trace, H₂O 42.93%. A yellow form of alotrichite, deficient in iron and calcium, was also recognised (SO₃ 36.15, Al₂O₃ 10.84, FeO 4.98, CaO trace, H₂O, 46.99). Experiments were made on the action of hydrogen sulphide, sulphur trioxide, and sulphur dioxide on the tufa, the results of which appear to support the theory that the Monte Solfioroso deposits originated through the action of sulphur dioxide emitted during the acid period in this region.

F. G. TRYHORN.

Cinnabar from Idria. F. RODOLICO (Atti R. Accad. Lincei, 1929, [vi], 9, 176—179).—Crystallographic data are given of several samples of cinnabar obtained from Idria. O. J. WALKER.

Geology of the ball clays of South Devon. A. SCOTT (Trans. Ceram. Soc., 1929, 28, 53—61).

Application of isopycnometric analysis to auriferous rocks. E. CLERICI (Atti R. Accad. Lincei, 1928, [vi], 8, 251—254).—The isopycnometric method, employing liquids of d 3.03—4.19, is applicable for the separation of gold from auriferous rocks, and has been used successfully with minerals containing gold particles of 2—3 μ diameter. F. G. TRYHORN.

Natural etchings on Japanese pyrite crystals. S. ICHIKAWA (Amer. J. Sci., 1929, [v], 17, 245—257).—An illustrated description of natural etchings on pyrite crystals from various localities in Japan. The symmetry of the figures corresponds with the hemihedral symmetry of the crystals.

C. W. GIBBY.

Presence of a variety of jumillite near Calasparra (Murcia). (MME.) E. JEREMINE and P. FALLOT (Compt. rend., 1929, 188, 800—802).—The rock, which is black and compact, occurs in thin plates rich in phenocrysts of olivine and biotite, and contains (RAOULT) SiO_2 53.90, Al_2O_3 8.88, Fe_2O_3 1.78, FeO 4.16, CaO 3.76, MgO 13.24, Na_2O 1.17, K_2O 7.56, TiO_2 2.26, P_2O_5 0.65, $\text{H}_2\text{O} + 1.23$, $\text{H}_2\text{O} - 1.01$, MnO 0.13, CO_2 0.47, Cl 0.04, SO_3 0.24, total 100.48%. Compared with jumillite its silica, potassium, and magnesium contents are somewhat high and the alumina content is low. Unlike jumillite it is holocrystalline and rarely contains leucite. J. GRANT.

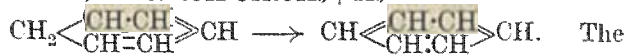
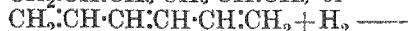
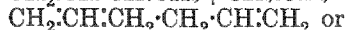
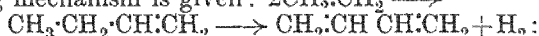
Presence of sulphur in the gaseous nebulae. I. S. BOWEN (Nature, 1929, 123, 450).—Wavelengths of lines due to transitions in singly-ionised sulphur correspond with those of lines observed in nebulae. All of the elements so far found in nebulae are gases or form stable compounds that are gases at low temperatures. A. A. ELDRIDGE.

Organic Chemistry.

Determination of the configuration of mirror-image isomerides. B. HOLMBERG (Svensk Kem. Tidskr., 1929, 41, 60—73).—A review of the various methods available for determining the configuration of compounds of the above type. The conclusion is reached that there is no general method which can be used in all cases. H. F. HARWOOD.

Mechanism of thermal decomposition of normal paraffins. E. N. HAGUE and R. V. WHEELER (J.C.S., 1929, 378—391).—The primary decompositions occasioned by the action of heat on the straight-chain hydrocarbons from ethane to n -hexane can be represented by a series of equations indicating the rupture of the chain at any position with production of an olefine and the complementary lower paraffin or, at the limit, hydrogen. As the series is ascended scission at the centre of the chain predominates and the tendency for hydrogen elimination to occur, leaving an olefine with the same number of carbon atoms as the original paraffin, rapidly diminishes.

Methane possesses a higher decomposition point than ethane: at comparatively low temperatures ethylene is formed. As with the other hydrocarbons, ethylene is regarded as the source, through butadiene, of the aromatic hydrocarbons obtained. In the case of methane, optimum benzene formation occurs over the range 1000—1100°; the remaining five hydrocarbons have optimum range 800—850°. The following mechanism is given: $2\text{CH}_3\cdot\text{CH}_3 \longrightarrow$



The formation of naphthalene, anthracene, phenanthrene, etc. may be analogously formulated by the condens-

ation of benzene with butadiene, naphthalene with butadiene, etc. Except in the cases of pentane and hexane, butadiene has been detected in the gaseous decomposition products obtained between 750° and 950°. The C_2 hydrocarbon which is evidently the precursor of the benzene obtained cannot be acetylene, since (a) this gas was absent from the gaseous products, (b) treatment of acetylene in a similar manner to the paraffins gave maximum yields of benzene over the range 650—700°, but is probably ethylene, which yields aromatic hydrocarbons above 700°. Further, in the decompositions of the paraffins ethylene yields are proportional to the yields (at a higher temperature) of aromatic hydrocarbons.

Addendum. T. M. LOWRY (*ibid.*, 392—393).—The degradation of the paraffins by the reversible elimination of a molecule HX is comparable with the elimination of an acid or water from any other additive compound of an olefine: the decomposition of the paraffins thus conforms to self-established precedents and depends on mechanism of a general character. Similarly, pyrogenic synthesis proceeds according to two well-established processes, viz., polymerisation (ethylene \longrightarrow butylene) and elimination of hydrogen (butylene \longrightarrow butadiene + H_2). A pyrogenic decomposition is a special case of reversible addition to an olefine of a hydride, either hydrogen or an olefine.

R. J. W. LE FÈVRE.

Decomposition of methane. I. C. W. H. JONES (J.C.S., 1929, 419—422).—Decomposition of methane by passage through a heated quartz tube is mainly into its elements. The temperature and pressure ranges investigated are 700—1080° and 10—70 cm., respectively. At 800—900° small traces of olefinic hydrocarbons are formed, at 1000° appreciable quantities are obtained (0.13—1.75% according to rate of flow and pressure).

The subjection of methane to the electric spark discharge results in an initially rapid formation of

olefines and acetylenes, the percentages of which tend to reach a steady level and the yields are proportional to the pressure of the gas during sparking. The maximum yield of acetylenes is obtained at $\frac{1}{2}$ atm. Small amounts of complex liquid and solid hydrocarbons are also formed. R. J. W. LE FEVRE.

Manufacture of olefines and diolefines [butadiene]. I. G. FARBENIND.—See B., 1929, 235.

Aliphatic diolefines. I. Behaviour of $\Delta^{\alpha\alpha}$ -hexadiene towards sulphuric acid. F. CORTESE (Ber., 1929, 62, [B], 504—509).— $\Delta^{\alpha\alpha}$ -Hexadiene is treated with 100% sulphuric acid at -15° to $+4^\circ$, whereby the production of diallyl ether is not noticeable. Addition of ice to the product causes separation of tar and production of a pale pink solution with marked odour of diallyl ether. Addition of ice-water to the tar yields a precipitate of the normal sulphate of hexane- $\beta\epsilon$ -diol, m. p. 90° (corr.). The pink solution, containing diallyl ether and a little tar, is neutralised with barium hydroxide, thus leading to the isolation of the very unstable barium $\beta\epsilon$ -hexyldisulphate, $[\text{CH}_2\text{CHMe}\cdot\text{O}\cdot\text{SO}_2\cdot\text{OBa}_{0.5}]_2$. If the reaction is effected below -10° , little tar is produced and the normal ester is readily precipitated; at 20 – 40° diallyl ether and the ester are not produced. With 60% sulphuric acid $\Delta^{\alpha\alpha}$ -hexadiene affords diallyl ether and a substance, $\text{C}_{12}\text{H}_{22}\text{O}$, b. p. 65 – $85^\circ/5$ mm., d_{25}^{25} 0.865, n_D^{25} 1.4536. 2:5-Dimethyltetrahydrofuran is converted by 67% sulphuric acid into a mixture of unsaturated hydrocarbons, the initial phase of the change consisting in the production of methyl *n*-butyl ketone. Similar treatment of acetone, methyl ethyl ketone, diethyl ketone, dipropyl ketone, or methyl *n*-butyl ketone results in the production of oils of agreeable odour and dark red, green, or purple colour, according to the structure of the initial material. H. WREN.

Reactions of olefines of high mol. wt. with sulphuric acid, hydrochloric acid, and air. W. E. MESSER (Abst. Thesis Mass. Inst. Tech., No. 3, Jan., 1929, 41—42).—The following olefines are prepared: cetene; Δ^8 -heptadecene, f. p. about -50° , b. p. $136^\circ/3.5$ mm., $173^\circ/16$ mm., d_{25}^{25} 0.795, obtained by distilling a mixture of sodium oleate and sodium ethoxide; a mixture of *eicosene* and *docosene* obtained from the mixed alcohols produced by the action of magnesium ethyl bromide on crude methyl stearate; and β -methylnonadecene, m. p. 11 – 12° , b. p. $146^\circ/2.2$ mm., $189^\circ/10$ mm., d_{25}^{25} 0.795, n_D^{25} 1.4504, obtained by dehydrating dimethylheptadecylcarbinol (Ryan and Dillon, A., 1913, i, 583) by oxalic acid. Cetene and heptadecene do not react appreciably with concentrated hydrochloric acid, with which, however, dimethylheptadecylcarbinol yields β -chloro- β -methyl-nonadecene, m. p. 19.6 – 20° , which can be hydrolysed by alcoholic alkali to the olefine and the alcohol. When any one of the above olefines is treated with sulphuric acid, very little organic matter passes into the acid layer; sulphur dioxide is produced in greatest amount with the branched-chain compounds, and when 100% or fuming sulphuric acid is used the formation of sulphur dioxide and tar occurs even at -15° (cf. Brooks and Humphrey, A., 1918, i, 286). Addition of sulphuric acid also occurs; *cetyl* and *heptadecyl*

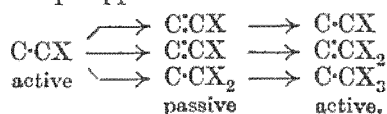
hydrogen sulphates, isolated from their barium salts, are found to be very easily hydrolysed, giving rise to alcohols. The alcoholic product from cetene is mainly *hexadecan- β -ol*, m. p. 41.5° ; that from heptadecene is a mixture of *heptadecan-0*- and *-1-ols*, m. p. 34° ; that from β -methylnonadecene has m. p. about 45° .

At the ordinary temperature, β -methylnonadecene is readily oxidised when exposed in a thin layer to the air. At 100° all the above olefines oxidise in the air, yielding acids. E. W. WIGNALL.

Polymerisation of acetylene by electric discharge. Synthesis of dipropargyl and its isomerides. G. MIGNONAC and R. V. DE SAINT-AUNAY (Compt. rend., 1929, 188, 959—961).—When acetylene is subjected to the electric discharge at -60° , a liquid, d_4^{25} 0.752, n_D^{25} 1.446, corresponding with a trimeride of acetylene, and a hydrocarbon, b. p. $-10^\circ/23$ mm., are obtained in small amounts. With a current of high frequency (d'Arsonval arrangement) and cooled electrodes a mixture of dipropargyl, γ -methyl- Δ^8 -pentadi-ene, and diethynylacetylene are formed. These last two hydrocarbons polymerise more readily than dipropargyl. Ethynylethylene is postulated as an intermediate product: addition of acetylene to it occurs in three different ways.

H. BURTON.

Law of periodicity. IV. P. PETRENKO-KRITSCHENKO [with V. OPOTZKY, M. DIAKOWA, and A. LOSOWOY] (Ber., 1929, 62, [B], 581—588; cf. A., 1928, 614).—The action of colloidal silver on halogeno-derivatives of methane which do not contain other different substituents is characterised by a uniform relationship, monohalogen derivative > dihalogen derivative < trihalogen derivative and a less uniform connexion between tri- and tetra-halogen derivatives; the rule $\text{CX} > \text{CX}_2$ is particularly important. In the presence of substituents (methyl, a different halogen, nitro-, carboxyl, phenyl), the influence of accumulation of the halogen towards silver is marked by the rule $\text{CX} < \text{CX}_2$. Silver nitrate behaves in the same manner as silver. Towards silver the methyl group changes its usual indifferent character and assumes pronounced chemical character. To eliminate the influence of conditions in the determination of activity coefficients of the dissimilarly substituted derivatives of methane, the ratios $\text{CH}_2\text{X}_2/\text{CH}_3\text{X}$ are adopted. The behaviour of a large number of di-derivatives towards silver, potassium hydroxide, piperidine, and silver nitrate has been examined. The graphs appear to fall into two groups: those characteristic of potassium hydroxide and piperidine are characterised by the relationship $\text{CX} > \text{CX}_2$, whereas with silver and silver nitrate the relationship $\text{CX}_2 > \text{CX}$ is maintained. Measurements are also recorded for a series of chlorostyrenes, bromoethylenes, chlorobenzene, α - and β -chloronaphthalene, and dichlorocyclopropanes. The following relationships appear to be established:



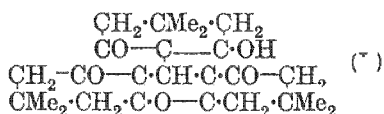
H. WREN.

Reaction of a mixture of methyl chloride and bromide with magnesium in ether. H. GILMAN

and R. J. VANDERWAL (Bull. Soc. chim., 1929, [iv], 45, 135—137).—Contrary to the observation of Rudd and Turner (A., 1928, 504), the authors affirm that a mixture of methyl chloride and bromide with magnesium in ether readily yields magnesium methyl chloride and bromide, the methyl bromide reacting the more rapidly.

R. BRIGHTMAN.

Action of alkali hydroxide on chloroform. D. VORLÄNDER and F. W. GUTHKE (Ber., 1929, 62, [B], 549—554).—The action of potassium hydroxide on chloroform in the presence of methone [5 : 5-dimethylhydroresorcinol] affords *anhydrotrimethoxymethane* (I), m. p. about 234° (corr. decomp.) after softening



[*acetyl* compound, m. p. 153°; *benzoyl* derivative, m. p. 258° (decomp.)], and a *substance*, m. p. 175—177°. The compound, m. p. 234°, is also obtained from formic acid but not from alkali formate in neutral or alkaline solution and methone. Since the compound is a derivative of formic acid and not of formaldehyde and methone is a specific reagent for aldehydes, the reducing action of chloroform and alkali hydroxide towards Fehling's solution cannot be attributed to the intermediate production of formaldehyde. The existence of hydroxyformaldehyde in equilibrium with formic acid, $\text{OH}\cdot(\text{C}^+\cdot\text{O})\cdot\text{H} \rightleftharpoons \text{H}\cdot\text{O}\cdot(\text{C}^+\cdot\text{O})\cdot\text{H}$, is therefore postulated. The action cannot be attributed to nascent formic acid, since a similar effect is not observed with formic esters and potassium hydroxide. Bromoform and iodoform (in boiling alcoholic-alkaline solution) and substances which form chloroform (such as chloral and trichloroacetic acid) behave similarly to chloroform towards Fehling's solution. Carbon monoxide or chloroform and alkali hydroxide reduce cold Fehling's solution and ammoniacal silver solution. Reaction does not appear to occur with ethylene chloride or bromide, ethylidene chloride, *s*-tetrachloroethane, or hexachloroethane. Carbon tetrachloride and alkali hydroxide do not produce cuprous oxide, although carbon monoxide and carbylamines are formed.

H. WREN.

Manufacture of isopropyl alcohol. G. O. CURME, jun., and E. W. REID.—See B., 1929, 275.

Preparation of allyl alcohol. R. DELABY and P. DUBOIS (Compt. rend., 1929, 188, 710—711).—The following method is based on the fact that allyl alcohol arises from the pyrolysis of glyceryl diformate (A., 1928, 767). Glycerol (184 g.) and 96% formic acid (300 g.) are heated at 65°/110—120 mm. for 2 hrs., after which the temperature is raised to 110°. After the first hour the pressure is reduced to 40 mm.; 96% formic acid (200 g.) is then added to the residue and the whole subjected to treatment similar to the first. Pyrolysis is effected at 200—250°/760 mm. over a period of 2 hrs. The yield is 435 g. from 1.0 kg. of glycerol.

G. A. C. GOUGH.

Aliphatic [open-chain] hydroterpenes. W. LONGUINOV and (MLE.) E. MARGOLISS (Bull. Soc.

chim., 1929, [iv], 45, 156—167).—Geraniol, b. p. 113.5—114°/12 mm., n_D^{20} 1.4762, on hydrogenation in 74% alcohol in presence of platinum-black (Vavon, A., 1914, i, 694) affords tetrahydrogeraniol, the properties of which, b. p. 110.5°/16 mm., b. p. 116—117°/25 mm., d_4^{20} 0.8341—0.8362, n_D^{20} 1.4398—1.4412, varied slightly with different preparations. 50% of the theoretical amount of hydrogen is rapidly absorbed, giving a dihydrogeraniol, b. p. 117—118°/15 mm., d_4^{20} 0.8560, 1.4543, the remainder being taken up much more slowly, especially in ethereal solution (cf. Grignard and Escourrou, A., 1925, i, 772). In ethereal solution the yield is lower and some $\beta\epsilon$ -dimethyloctane is formed. Geraniol from essence of palmarosa (Chiris), b. p. 110°/10 mm., d_4^{15} 0.8835, similarly gave a tetrahydrogeraniol, b. p. 108—109°/10 mm., d_4^{20} 0.8812, n_D^{20} 1.4772. With hydrobromic acid in a sealed tube at 100° tetrahydrogeraniol affords (yield 65—75%) a *bromide*, b. p. 91—92°/10 mm., d_4^{20} 1.0368, n_D^{20} 1.4534, which on distillation with quinoline gives $\beta\epsilon$ -dimethyl Δ^7 -octene, b. p. 154°/738 mm., d_4^{20} 0.7396, n_D^{20} 1.4212. Harries and Neresheimer's methylation method (A., 1911, i, 798) was unsuccessful, the quaternary base undergoing fission on distillation, probably with elimination of methyl alcohol, and not decomposition into trimethylamine and the unsaturated hydrocarbon. The constants of this tetrahydroterpene with a terminal double linking are lower than those of dihydrobupleurolene or $\gamma\epsilon$ -dimethyl- Δ -octene, which possess "internal" double linkings. When heated with hydrobromic acid in a sealed tube at 100°, β -dimethyl- Δ^7 -octene is converted into a *bromide*, b. p. 92°/10 mm., d_4^{20} 1.0743, n_D^{20} 1.4569, which with quinoline gives 70% of $\beta\epsilon$ -dimethyl- Δ^6 -octene, b. p. 161—162°/753 mm., d_4^{20} 0.7473, n_D^{20} 1.4272. Tetrahydrogeraniol could not be obtained by hydrogenation of citral, only 30% of the theoretical volume of hydrogen being absorbed.

R. BRIGHTMAN.

Pinacols and pinacolins. E. PACE (Atti R. Accad. Lincei, 1928, [vi], 8, 309—314; cf. A., 1928, 1113).—Treatment of diacetyl with magnesium alkyl bromide (2 mols.) and decomposition of the resulting compound with slightly acidified water yields α -di-tertiary alcohols (pinacols), which may be converted into the corresponding pinacolins by dehydration with dilute sulphuric acid (1 : 4) followed by steam distillation. $\alpha\beta$ -Dimethylbutane- $\alpha\beta$ -diol, m. p. 38°, b. p. 175°, or m. p. 47° (+6H₂O), gives acetone when oxidised with chromic acid mixture and bromoform (iodoform) when treated with alkaline bromine (iodine) solution. $\gamma\delta$ -Dimethylhexane- $\gamma\delta$ -diol has m. p. 51°, b. p. 216° (cf. Lawrinowitsch, A., 1877, ii, 427). $\delta\epsilon$ -Dimethyloctane- $\delta\epsilon$ -diol has m. p. 62°, b. p. 228—230° (cf. Friedel, Jahresber., 1869, 513). $\delta\delta$ -Dimethyloctane- ϵ -one, b. p. 185—187°, gives the iodoform reaction, combines with difficulty with sodium hydrogen sulphite, and forms an *oxime*, m. p. 152°. Acetylacetone fails to react with magnesium alkyl bromides, possibly owing to its existence in desmotropic forms.

T. H. POPE.

[**Configuration of pentaerythritol.**] A. SEMENZOV (Ber., 1929, 62, [B], 514).—The resolution of pentaerythritolderivatives, $\text{C} \left[\begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \cdot \text{O} \end{array} \right] \text{C} \left[\begin{array}{c} \text{R} \\ \text{R} \end{array} \right]$, into

optical isomerides does not necessarily establish that methane derivatives have a tetrahedral configuration under all conditions, since a plane of symmetry is not present in the *trans*-isomerides (cf. Boeseken and Felix, A., 1928, 1213; Kenner, this vol., 171).

H. WREN.

Catalytic elimination of alcohol from acetals. Preparation of unsaturated ethers. F. SIGMUND and R. UCHANN (Monatsh., 1929, 51, 234—252).—When acetals are passed over porous earth at 200° or a nickel catalyst (Sigmund and Marchart, A., 1927, 1054) at 160—200° in a current of nitrogen, elimination of alcohol occurs: $R\cdot CH_2\cdot CH(OR')_2 \longrightarrow R\cdot CH:CH\cdot OR' + R'\cdot OH$, and unsaturated ethers are obtained in good yield. Thus, heptaldehyde diethyl-acetal yields *ethyl Δ⁸-heptenyl ether*, b. p. 172—175°, and ethyl alcohol. Similarly, phenylacetaldehyde dimethylacetal gives styryl methyl ether; phenylacetaldehyde di-*n*-propylacetal affords styryl propyl ether; heptaldehyde di-*n*-propylacetal furnishes *propyl Δ⁸-heptenyl ether*, b. p. 184—187° (corr.), which does not react with semicarbazide acetate at the ordinary temperature, but after hydrolysis with 2*N*-sulphuric acid forms heptaldehydesemicarbazone (cf. Moureu, A., 1904, i, 285); acetaldehyde diethyl-acetal yields ethyl vinyl ether at 250°; benzaldehyde diethylacetal is unaltered at 250° owing to there being no available hydrogen atom for the elimination of the alcohol. Acetophenone dimethylacetal and di-*n*-propylacetal give *α*-methoxystyrene, b. p. 194—196°, and *α*-propoxystyrene, b. p. 214—219° (corr.), respectively. In these last cases hydrogen is eliminated from the methyl group: treatment of the styrenes with semicarbazide acetate yields acetophenonesemicarbazone.

With brass turnings as a catalyst elimination of methyl alcohol from phenylacetaldehyde dimethyl-acetal is incomplete even at 400—420°. With phenylacetaldehyde di-*n*-propylacetal partial elimination of propyl alcohol occurs and this is further dehydrogenated to propaldehyde.

H. BURTON.

Enzymic synthesis of β-hydroxyethyl dihydrogen phosphate. H. D. KAY (J.C.S., 1929, 524—527).—Aqueous sodium phosphate and ethylene glycol are smoothly converted at 38° by the catalytic action of a phosphatase preparation derived from duodenal mucosa of a cat into β-hydroxyethyl dihydrogen phosphate (isolated as the barium salt). The sodium salt is hydrolysed by enzymes at the same rate as a sample of the sodium salt isolated by Plimmer and Burch (this vol., 422).

R. J. W. LE FÈVRE.

Crystalline diglycide and its acetate. M. BATTEGAY, H. BUSER, and E. SCHLAGER (Compt. rend., 1929, 188, 796—798).—Treatment of glycerol with acetic acid and sulphuric acid at 135° affords monomeric acetins and a crystalline diglycide diacetate, $C_6H_{10}O_2(OAc)_2$, m. p. 138°, which, when hydrolysed with alcoholic hydrogen chloride, yields diglycide, $C_6H_{12}O_4$, m. p. 96—97°, b. p. 173°/16 mm.

G. A. C. GOUGH.

Synthetic glycerides. I. H. P. AVERILL, J. N. ROCHE, and C. G. KING (J. Amer. Chem. Soc., 1929, 51, 866—872).—In view of the uncertainty attaching to the properties of many glycerides the following

pure derivatives have been synthesised by methods which establish their constitutions (cf. Fischer, A., 1920, i, 805, 807): *α*-monoglycerides: palmito-, m. p. 77·0°; myristo-, m. p. 67·3°; *hexo*-, m. p. 51·4°; lauro-, m. p. 63·0°; stearo-, m. p. 81·1°; *αα*-diglycerides: lauro-, m. p. 56·6°; stearo-, m. p. 79·1°; palmito-, m. p. 69·5°; myristo-, m. p. 63·8—64·4°; also trilaurin, m. p. 45·6°; *β*-, m. p. 50·9°, and *α*-, m. p. 45·4°, -steardilaurins; *β*-, m. p. 49·2—49·5°, and *α*-, m. p. 48·5°, -lauro-, and *β*-, m. p. 59·8—60·0°, and *α*-, m. p. 53·0°, -palmito-dimyristins; *β*-, m. p. 64·8°, and *α*-, m. p. 62·6°, -stearo-; *β*-, m. p. 54·0°, and *α*-, m. p. 51—52°, -aceto-; *β*-, m. p. 66·0°, and *α*-, m. p. 60·0°, -*hexo*-; *β*-, m. p. 63·5—64·0°, and *α*-, m. p. 54·5°, -lauro-, and *β*-, m. p. 58·5—59°, and *α*-, m. p. 55·5°, -myristo-dipalmitins; *β*-, m. p. 62·7°, and *α*-, m. p. 56·6°, -aceto-, and *α*-lauro-, m. p. 50·9°, distearins. *Acetoneglyceryl hexoate*, *α*-iododilaurin, m. p. 23·5°, and *α*-iododimyristin were also obtained. In the nine pairs of isomeric triglycerides examined the symmetrical have all higher m. p. (mean difference, 4·7°) than the corresponding unsymmetrical derivatives.

H. E. F. NOTTON.

Chlorination products of ββ'-dichlorodiethyl sulphide. II. J. W. C. PHILLIPS, J. S. H. DAVIES, and S. A. MUMFORD (J.C.S., 1929, 535—549).—Chlorination of ββ'-dichlorodiethyl sulphide by 2 mols. of chlorine results mainly in the formation of *ααββ'*-tetrachlorodiethyl sulphide (d_4^{20} 1·53), which readily undergoes thermal decomposition, giving *β*-chloroethyl *αβ*-dichlorovinyl sulphide, b. p. 107°/15 mm., d_4^{20} 1·4315, n_D^{20} 1·5562. Chlorine reacts additively with the last compound, forming *ααβββ'*-pentachlorodiethyl sulphide, which easily loses hydrogen chloride, giving *β*-chloroethyl *αββ*-trichlorovinyl sulphide, b. p. 122—124°/15 mm., d_4^{20} 1·5425, n_D^{20} 1·5700, from which by further action of chlorine *ααββββ'*-hexachlorodiethyl sulphide, b. p. 158—159°/15 mm., d_4^{20} 1·6849, n_D^{20} 1·5683, and hexachloroethane are successively obtained.

Treatment of ββ'-dichlorodiethyl sulphide by 3 mols. of chlorine afforded *ααα'β*-pentachlorodiethyl sulphide, d_4^{20} 1·57, which decomposed when heated into *β*-chloroethyl *αββ*-trichlorovinyl sulphide and *β*-(*β*-chloroethylthiol)ethyl trichlorovinyl sulphide, m. p. 70·5°. Chlorination of ββ'-dichlorodiethyl sulphide by 3—4 mols. of chlorine led, after similar distillation, to *ααβ*-trichloroethyl *β*-chlorovinyl sulphide, b. p. 122—123°/15 mm., d_4^{20} 1·5404, n_D^{20} 1·5661. The two isomeric tetrachloro-sulphides have identical b. p.; the densities and physical properties of mixtures are approximately linear functions of the composition. In certain cases, however, a third isomeride appeared to be present, possibly *αβ*-dichloroethyl *αβ*-dichlorovinyl sulphide, b. p. 120—121°/15 mm., d_4^{20} 1·5378, n_D^{20} 1·5673. Chlorine reacted mainly additively with *ααβ*-trichloroethyl *β*-chlorovinyl sulphide, forming *ααα'*-hexachlorodiethyl sulphide, b. p. 159—160°/15 mm., d_4^{20} 1·6841, n_D^{20} 1·5681; the latter when heated lost hydrogen chloride and gave *αββ*-trichloroethyl *αβ*-dichlorovinyl sulphide, b. p. 134—135°/15 mm., d_4^{20} 1·6293, n_D^{20} 1·5778, from which, by addition of chlorine, *ααα'βββ'β'*-heptachlorodiethyl sulphide, b. p. 170—172°/15 mm., d_4^{20} 1·7473, n_D^{20} 1·5741, was obtained. By a similar

sequence of reactions, $\alpha\alpha'\beta\beta'$ -hexachlorodiethyl sulphide, b. p. 157—159°/15 mm., d_4^{20} 1.6825, 1.5681, $\alpha\beta$ -dichloroethyl $\alpha\beta\beta$ -trichlorovinyl sulphide, b. p. 133—134°/15 mm., d_4^{20} 1.6190, n_D^{20} 1.5770, and $\alpha\alpha'\beta\beta\beta'$ -heptachlorodiethyl sulphide, b. p. 132—134°/ca. 2 mm., d_4^{20} 1.743, n_D^{20} 1.5741, were prepared.

Maximum yields in the chlorination of $\beta\beta'$ -dichlorodiethyl sulphide were obtained when 3.5 mols. of chlorine were used. Further chlorination caused partial destruction of the hexachloro-sulphides already formed, chlorinated hydrocarbons of low b. p. and a residual tetrachloro-fraction being obtained on subsequent distillation; e.g., chlorination by 4.1 mols. of chlorine led to $\alpha\alpha\alpha\beta$ -tetrachloroethane, trichloroethyl sulphur chloride, b. p. 53.8°/3.5 mm., and $\alpha\beta$ -dichloroethyl $\alpha\beta\beta$ -trichlorovinyl sulphide. The last-named by chlorine addition yielded a heptachlorodiethyl sulphide, b. p. 144—146°/5.5 mm., d_4^{20} 1.7373, 1.5739, with a heavier isomeride, possibly either $\alpha\beta\beta$ -trichloroethyl $\alpha\beta$ -dichlorovinyl sulphide or $\alpha\alpha\beta$ -trichloroethyl $\alpha\beta$ -dichlorovinyl sulphide or both. The present work confirms the view that the $\alpha\beta\beta'$ -trichloro- and $\alpha\beta\beta\beta'$ -tetrachloro-diethyl sulphides of Mann and Pope (J.C.S., 1922, 121, 594) are β -chloroethyl $\alpha\beta$ -dichlorovinyl and $\alpha\beta\beta$ -trichlorovinyl sulphides, respectively, and that the formation of chloroethyl chlorovinyl sulphides is in all cases due to the loss of hydrogen chloride from saturated polychlorodiethyl sulphides—the first, but less stable, products of chlorination. Contrary to previous views, chlorination of $\beta\beta'$ -dichlorodiethyl sulphide is not confined to one chain.

In all cases chlorinations were effected in carbon tetrachloride solution and the removals of hydrogen chloride performed by heating at the b. p. under 15—20 mm. pressure. A mechanism of the course of chlorination is suggested. R. J. W. LE FÈVRE.

Modified Curtius reaction. III. Degradation of saturated fatty acids and benzoic acid. C. NAEGELI, L. GRUNTUCH, and P. LENDORFF (Helv. Chim. Acta, 1929, 12, 227—261; cf. A., 1928, 881).—In general, the acid chloride is treated, usually in benzene solution, with sodium azide, the course of the reaction being followed by measurement of the volume of nitrogen evolved, and the solution of the carbimide so obtained is treated with hydrochloric acid, calcium hydroxide solution, or acetic acid, and thus converted into the amine hydrochloride, the free base, or its acetyl derivative, respectively, this stage of the reaction being followed by measurement of the volume of carbon dioxide evolved. Thus stearyl chloride is converted into heptadecylamine hydrochloride, m. p. 158° (without decomp.; cf. lit.) (93% yield) (chloroplatinate), or acet-*n*-heptadecylamide, m. p. 62° (80%) (hydrochloride), accompanied by stearyl-*n*-heptadecylamide, m. p. 88° (20%), also obtained by the action of stearic acid on heptadecylcarbimide in benzene solution. Palmityl chloride similarly yields pentadecylamine (80%), its hydrochloride, m. p. 199° (without decomp.; cf. lit.) (95%), and acet-*n*-pentadecylamide, m. p. 72° (hydrochloride), together with palmitic acid. Palmityl-*n*-pentadecylamide, m. p. 93°, is obtained by the action of palmitic acid on pentadecylcarbimide. Lauryl chloride yields

undecylamine (71%), its hydrochloride, m. p. 190° (without decomp.; cf. lit.) (77—80%), together with a little diundecylcarbamide, and acetundecylamide (76%) (hydrochloride, m. p. 65—66°). *iso*Valeryl chloride yields *isobutylamine* hydrochloride (71%) and acetisobutylamide (79%), whilst from acetyl chloride is obtained methylamine hydrochloride (50—65%), according to experimental conditions, and acetmethylamide (72%) (hydrochloride, which is unstable and slowly loses 50% of its hydrogen chloride). Benzoyl chloride similarly yields aniline (79%), its hydrochloride (74%), and acetanilide (93%), although under certain experimental conditions diphenylcarbamide is the chief product. In no case were secondary or tertiary amines obtained. J. W. BAKER

Action of phosphorus trichloride on formic acid and acetic anhydride. A. VAN DRUTEN (Rec. trav. chim., 1929, 48, 312—323).—The reaction between formic acid and phosphorus trichloride in an atmosphere of nitrogen or carbon dioxide proceeds: $3\text{H}\cdot\text{CO}_2\text{H} + \text{PCl}_3 = 3\text{CO} + 3\text{HCl} + \text{H}_3\text{PO}_3$. When phosphorus trichloride reacts with acetic anhydride acetyl chloride is the main product, and after removal of this and any other liquid product by vacuum distillation, a solid product remains. This is hygroscopic, evolves hydrogen chloride when exposed to the air, dissolves in water forming an acid solution which reduces iodine, and from its high oxygen content does not appear to contain either phosphorous or phosphoric acid derivatives. No phosphorus trioxide was obtained in any experiment. H. BURTON.

Chloroacetic acids and zinc. H. W. DOUGHTY and D. A. LACOSS (J. Amer. Chem. Soc., 1929, 51, 852—855).—Trichloroacetic acid is quantitatively converted in aqueous solution by zinc (1 atom) into zinc dichloroacetate. The mechanism of the strongly exothermic reaction is probably similar to that suggested in the case of copper (cf. A., 1922, i, 427; 1925, i, 628). Dichloroacetic acid reacts less readily, 10% of the carboxylic hydrogen being liberated. Chloroacetic acid reacts slowly, even at 100°, evolving much hydrogen. H. E. F. NOTTON.

Products of the action of chlorosulphonic acid on propionyl chloride at the ordinary temperature. M. KRAJCINOVIC (Ber., 1929, 62, [B], 579—581; cf. A., 1926, 1125).—Propionyl chloride is converted by chlorosulphonic acid into α -sulphopropionic acid and 2:4-dimethyl- α -ethylpvernone, m. p. 151°.

H. WREN.

Configurative relationship of lactic and α -chloropropionic acids; relationship of lactic acid and *n*-pentan-3-ol. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, 84, 703—709).— Δ^7 -*n*-Penten-3-ol was converted into the hydrogen phthalate, m. p. 90°, which gave an insoluble *brucine* salt, $[\alpha]_D -13.7^\circ$, yielding a hydrogen phthalate, $[\alpha]_D +30.8^\circ$; the latter, on hydrolysis, gave the *l*-pentenol, $[\alpha]_D -3.7^\circ$ in ether ($c=24.8$) (α -*naphthyl*-carbamate, m. p. 130°, $[\alpha]_D +9.2^\circ$ in alcohol). The *l*-pentenol gave, with pyridine and phosphorus trichloride, 1- β -chloro- Δ^7 -pentene, $[\alpha]_D -9.1^\circ$ in ether, which, with ozone, yielded *d*- α -chloropropionic acid, $[\alpha]_D^{25} +2.0$ in water (sodium salt, $[\alpha]_D -0.48^\circ$). On reduction with hydrogen and palladium the *l*-pentenol

gave *d*-*n*-pentan- β -ol, and with ozone it yielded *d*-lactic acid. The latter is therefore configuratively related both to *d*- α -chloropropionic acid and to *d*-*n*-pentan- β -ol. C. R. HARRINGTON.

Constitution of glucic acid. E. K. NELSON and C. A. BROWNE (J. Amer. Chem. Soc., 1929, **51**, 830—836).—In 8% aqueous solution dextrose yields with calcium hydroxide in absence of air at 67° a mixture of calcium salts which readily absorbs oxygen and from which formic acid and glucic acid, $C_6H_{12}O_6$ (optical properties), darkens at 110°, but does not melt at 170°, are separated (cf. Winter, Z. Ver. Rübenzucker Ind., 1874, **44**, 1049). The latter is fairly stable when pure, absorbs 1 mol. of bromine, is readily oxidised to oxalic and formic acids, and shows typical enolic colour reactions. It is therefore probably 3-hydroxyacrylic acid (acrolactic acid; cf. Pinner, A., 1875, i, 554). When hydrogenated it appears to undergo polymerisation, yielding amorphous products. Its atmospheric oxidation to formic acid may account for the presence of the latter in molasses. Its transformation into Winter's *apoglucic acid* could not be repeated. H. E. F. NOTTON.

$\beta\lambda$ -Dihydroxypalmitic acid from rhamnoconvolvulic acid. E. VOTOČEK and V. PRELOG (J. Czechoslov. Chem. Comm., 1929, **1**, 55—64).—The dihydroxypalmitic acid obtained from commercial convolvuline (this vol., 544) is proved to be $\beta\lambda$ -dihydroxypalmitic acid, m. p. 83—84° (methyl ester, m. p. 81—82°, b. p. 140—150°/0.0001 mm., $[\alpha]_D^{20} +0.91^\circ$; ethyl ester, m. p. 72—73°). Reduction by hydriodic acid and red phosphorus gives palmitic acid. Treatment by sulphuric acid-potassium dichromate solution affords, by oxidative scission, acetic acid, pentadecane- $\beta\lambda$ -dione, m. p. 53.5—64° (disemicarbazone, m. p. 132—134°), and *l*-ketotetradecic acid, m. p. 69°. The *oxime* (an oil) of the last compound undergoes the Beckmann change with sulphuric acid giving, after hydrolysis etc., *n*-valeric acid, *n*-butylamine, sebacic acid, and *l*-aminononoic acid.

R. J. W. LE FÈVRE.

"Activated form" of oxalic acid. F. KRAUSS and E. BRUCHHAUS (Ber., 1929, **62**, [B], 487—489).—Aqueous solutions of oxalic acid which have been treated with a deficiency of potassium permanganate give a positive reaction for formic acid with mercuric chloride or resorcinol and sulphuric acid. If such solutions are distilled, formic acid may be identified in the distillate by the described tests or, analytically, as sodium formate. Aqueous solutions of oxalic acid do not yield formic acid when distilled under these conditions. The assumption of an activated form of oxalic acid (cf. Oberhauser and Hensinger, A., 1928, 505) appears unnecessary. H. WREN.

Complex scandium oxalates. J. ŠTERBA-BŮHM and Š. ŠKRAMOVSKÝ (J. Czechoslov. Chem. Comm., 1929, **1**, 1—18).—*Scandium oxalate*, $Sc_2(C_2O_4)_3 \cdot 6H_2O$, *d* 2.14 (obtained pure only in absence of sodium, potassium, and notably ammonium ions), is prepared by treating an acidified (hydrogen chloride) solution of scandium chloride at 60° with a slight excess of oxalic acid. On drying at 100° this hexahydrate forms a *dihydrate*; it readily absorbs

ammonia. Treatment of scandium chloride with slightly acid ammonium oxalate solutions or with oxalic acid in the presence of ammonium salts, or precipitation of scandium oxalate solutions by ammonium carbonate solutions or by ammonium oxalate solutions, results in the formation of *scandium ammonium oxalate dihydrate*, $NH_4Sc(C_2O_4)_2 \cdot 2H_2O$, *d* 1.75. Exposure of this to an ammoniacal atmosphere gives a salt, $(NH_4)_4Sc_2(C_2O_4)_3 \cdot 8H_2O$. Attempts to repeat preparations of higher complex scandium ammonium oxalates (Meyer and Wassjuchnow, A., 1914, ii, 369; Wirth, *ibid.*, 468) have failed.

Analogous procedures with potassium salts give *scandium monopotassium oxalate*, $KSc(C_2O_4)_2 \cdot 2H_2O$, *d* 1.90, which readily changes into *scandium tripotassium oxalate*, $K_3Sc(C_2O_4)_3 \cdot 4H_2O$, *d* 2.10, whilst, using sodium salts, *scandium monosodium oxalate*, $NaSc(C_2O_4)_2 \cdot 3H_2O$, *d* 1.94, and *scandium trisodium oxalate*, $Na_3Sc(C_2O_4)_3 \cdot 6H_2O$, *d* 1.84, are obtained. The last-named when dried at 100° gives a *monohydrate*.

The sodium salts are less stable than the corresponding potassium salts and these less so than the corresponding ammonium salts.

R. J. W. LE FÈVRE.

Butane- $\alpha\beta\delta$ -tricarboxylic acid. H. KILIANI (Ber., 1929, **62**, [B], 640—641).—The crystalline form of the acid is recorded. It does not appear to form well-characterised metallic salts; the barium and calcium compounds are less soluble in hot than in cold water. H. WREN.

Reaction of citric acid and its salts. V. ARREGUINE (Bull. Soc. Chim. biol., 1929, **11**, 242—245).—A dilute solution of citric acid (3—4 c.c.), when oxidised with 5% potassium permanganate, gives rise to acetonedicarboxylic acid, which condenses with resorcinol (0.1 g.) when concentrated sulphuric acid is added until a bright red colour is obtained. The phorone derivative thus formed affords an intensely blue, fluorescent solution in aqueous ammonia.

G. A. C. GOUGH.

Preparation of *d*-gluconic acid. H. KILIANI (Ber., 1929, **62**, [B], 588—592).—The following method avoids completely the use of silver or lead compounds. Dextrose in water is oxidised by liquid bromine and the product is treated with barium carbonate. The separation of barium *d*-gluconate from barium bromide is effected by dilute alcohol. The original memoir should be consulted for details.

In the application of oxalic acid to the determination of barium in salts of organic acids (A., 1928, 741) it has been overlooked that oxalic acid is slowly removed from barium oxalate by washing with 50% alcohol so that the filtrate is invariably acidic; the method is still valid if the oxalate is converted into the carbonate by gentle ignition. H. WREN.

***d*-Glycuronic acid.** II. F. EHRLICH and K. REHORST (Ber., 1929, **62**, [B], 628—634; cf. A., 1925, i, 1379).—Amended directions are given for the isolation of *d*-glycuronic acid from ammonium mentholglycuronate with the object of avoiding possible contamination of the product with ammonium sulphate and the too protracted action of barium carbonate. For the acid obtained by the action of

the requisite amount of sulphuric acid on the sodium salt the initial value $[\alpha]_D^{20} +3.61^\circ$ has been observed, but it has not been found possible to prepare an initially levorotatory acid. The following data are recorded: anhydrous and monohydrated sodium salt, $[\alpha]_D^{20} -0.56^\circ$ to $+22.51^\circ$ in water in 1.5 hrs.; anhydrous potassium salt, $[\alpha]_D^{21.5} -2.78^\circ$ to $+22.47^\circ$ in water in 2 hrs., and sesquihydrated salt, $[\alpha]_D^{20} +4.53^\circ$ to $+20.02^\circ$ in 1.5 hrs.; ammonium salt, $[\alpha]_D^{20} -4.05^\circ$ to $+23.17^\circ$ in water in 1.5 hrs.; barium salt, $[\alpha]_D^{20} +17.45^\circ$ in water (non-mutarotatory); brucine salt, $C_6H_{10}O_7 \cdot C_{23}H_{26}O_4N_2 \cdot H_2O$, m. p. 156—157°, $[\alpha]_D^{20} -15.08^\circ$ (non-mutarotatory). H. WREN.

Manufacture of substituted thiolacetic acids. I. G. FARBENTIND.—See B., 1929, 235.

Use of ozone for the determination of the constitution of unsaturated compounds. J. DEUVRE (Bull. Soc. chim., 1929, [iv], 45, 140—152).—A defence of the ozone method for the determination of the constitution of unsaturated compounds (cf. Verley, A., 1928, 1138, 1139). Samples of methylheptenone and citronellal giving 82% and 78% of acetone, respectively, gave 93% by the permanganate-chromic acid method and 84% by the ozone method, and the isomerising influence of ozone on the position of double linkings is therefore negligible. The failure of the method with eugenol is admitted. The ozonisation results (formaldehyde 25%, formic acid 106%) partly accord with Harries and Haarmann's theory (A., 1915, i, 133) of the formation of an unstable homovanillin peroxide, yielding vanillin and formaldehyde. The presence of acetone peroxide, which would be stable under the experimental conditions, or of pyruvic acid has not been detected in ozonisations by this method, and the formation of acetol in the ozonisation of citronellal dimethylacetal (Harries and Comberg, A., 1915, i, 966) is attributed to the formation of isoacetone under the enolising influence of the hexane.

Ozonisation is effected in acetic acid at about 0° with a current of oxygen containing 6—7% of ozone. Fresh controls confirmed the resistance of acetic acid (and acetone) to oxidation under these conditions. After diluting with water and leaving for 12 hrs. the formaldehyde in the decomposition products is determined with Grosse-Bohle's reagent (rosaniline hydrochloride 1 g., sodium sulphite 25 g., hydrochloric acid, d 1.12, 15 c.c., diluted to 1000 c.c.). Results are accurate only to 5—10%, a margin which has little effect on the total results for α - and β -isomerides, since the amount of formaldehyde is usually small. 3 C.c. of reagent are used for the test, the comparison being made 12 hrs. after mixing and diluting to 10 c.c. Formic acid is determined by Liebig's mercuric oxide method, after destroying oxygen present by boiling with sulphurous acid, and acetone by Messinger's method, using 15 min. reaction. In the latter case results are accurate to 5%. Acetaldehyde and glyoxylic acid also give a positive result with Grosse-Bohle's reagent and glycolaldehyde a violet coloration. Acetaldehyde, propaldehyde, isobutaldehyde, isovaleraldehyde, heptaldehyde, lævulaldehyde, β -dimethyl- Δ -heptenal, citral, citronellal, and benzaldehyde give no coloration. R. BRIGHTMAN.

Citronellal. H. I. WATERMAN and E. B. ELSBACH (Bull. Soc. chim., 1929, [iv], 45, 137—140).—The samples of citronellal examined by Verley (A., 1928, 1138, 1139) are regarded as impure, the density and refractive indices differing consistently from those given by the authors (cf. B., 1928, 654) and other workers, and the value given for the b. p., $82^\circ/2$ mm., is inconsistent with the b. p.-pressure curve based on the observations of Tiemann and others, and calculations after Clapeyron or Dühring's equation. Verley's equation, $1/n = k\lambda^2$, 1 is of doubtful value. Attention is directed to the inaccurate data for citronellal in current literature. R. BRIGHTMAN.

Chemistry of high molecular organic substances from the point of view of Kekule's theory.

XII. H. STAUDINGER (Z. angew. Chem., 1929, 42, 37—40, 67—73, 77).—Earlier work (cf. this vol., 49, 51, 53, etc.) is summarised in reply to Meyer (Z. angew. Chem., 1928, 41, 935). R. BRIGHTMAN.

Chemistry of high molecular organic substances. K. H. MEYER (Z. angew. Chem., 1929, 42, 76—77).—A reply to Staudinger (preceding abstract). In dispersions of highly polymerised substances groups or parts of the chains of indefinite size are present. The association of molecular groups as micelles in soap is not exceptional as Staudinger asserts but similar to the behaviour of tannin in water, substantive dyes, higher hydrocarbons, and fatty acids in phenol, lower fatty acids in water. Staudinger's views have been anticipated by Póányi and by Herzog (A., 1921, ii, 531). Later views of the latter author (A., 1925, ii, 942) are endorsed.

R. BRIGHTMAN.

Production of acetone. HOLZVERKOHLUNGS-IND. A.-G.—See B., 1929, 235.

Synthesis of α -dimethoxypentan- β -one. R. PAUL (Bull. Soc. chim., 1929, [iv], 45, 152—154).—Magnesium γ -methoxypropyl iodide with methoxyacetonitrile in ether affords α -dimethoxypentan- β -one, b. p. 98 — $99^\circ/23$ mm., d_4^{25} 1.001, n_D^{20} 1.42645 (semicarbazone, m. p. 88 — 5°). R. BRIGHTMAN.

Constitution of $\beta\gamma$ -diketones. II. Tendency and direction of enolisation. C. WEYGAND and H. BAUMGARTEL (Ber., 1929, 62, [B], 574—579; cf. 1927, 971).—In the series acetyl-, n -propionyl-, n -butyryl-, n -heptoyl-, and n -decoyl-acetone, the proportion of enol in the equilibrium mixture increases regularly with increasing mol. wt. until n -decoyl-acetone represents the first stable, homogeneous enol of the aliphatic series. Branching of the chain diminishes the proportion of enol, only 60% being present in pivalylacetone. Ozonisation of the diketones in ethyl chloride yields methylglyoxal (identified as the osazone) in the case of acetyl-acetone, probably a mixture of methyl- and n -propylglyoxals with n -propionylacetone, methylglyoxal and much butyric acid from n -butylacetone, much methylglyoxal and heptioic acid from heptoylacetone, impure methylglyoxal and large quantities of decioic acid from decoylacetone, which thus has the structure $CH_3 \cdot [CH_2]_8 \cdot C(OH) \cdot CHAc$. Distillation of the ketones isolated from the copper salts frequently appears to yield two distinct fractions of ketone which give rise

to two distinct copper salts; the isomerism does not appear to be of the enolic structural type, and based on observations of Harries (A., 1904, i, 427), is provisionally regarded as "mesityl oxide isomerism." The following observations are recorded: *n*-propionylacetone, b. p. 43°/12 mm., and b. p. 45°/12 mm., *n*-butyrylacetone, b. p. 57—61°/11 mm. (copper salt, m. p. 164—165°), and b. p. 64—68°/12 mm. (copper salt, m. p. 161—162°); *n*-heptylacetone, b. p. 108—112°/13 mm. (copper salt, m. p. 125—126°), and b. p. 114—118°/12 mm. (copper salt, m. p. 122—123°); *n*-decoylacetone, b. p. 150—152°/16 mm., m. p. 24—27° (copper salt, m. p. 110°) (cf. Morgan and Holmes, A., 1924, i, 496); pivalylacetone, b. p. 67—71°/18 mm. H. WREN.

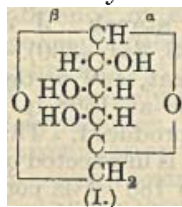
Complex salts of diacetyldioxime. J. V. DUBSKY and F. BRYCHTA (J. Czechoslov. Chem. Comm., 1929, 1, 137—154).—Various complex metallic derivatives of diacetyldioxime have been prepared. Interaction of equimolecular quantities of nickel chloride hexahydrate and diacetyldioxime in hydrochloric acid yields the complex chloride, $[\text{DH}_2\text{NiCl}_2] \cdot 2\text{H}_2\text{O}$ ($\text{D}=\text{NO}:\text{CMe}:\text{CMe}:\text{NO}$, $\text{DH}_2=[\text{CMe}:\text{N}:\text{OH}]_2$), which loses 2 mols. of water at 105°, yielding the same salt, DH_2NiCl_2 , as is obtained by dehydration of $[\text{DH}_2\text{NiCl}_2] \cdot \text{H}_2\text{O}$ (Paneth and Thilo, A., 1925, i, 1132). In water it decomposes thus: $2[\text{DH}_2\text{NiCl}_2] \cdot 2\text{H}_2\text{O} \rightarrow \text{Ni}(\text{DH})_2 + \text{NiCl}_2 + 2\text{HCl} + 4\text{H}_2\text{O}$. Similarly, the interaction of nickel carbonate and diacetyldioxime in hydrobromic acid furnishes the complex bromides $(\text{DH}_2)_2\text{NiBr}_2$ and DH_2NiBr_2 , the latter decomp. 200°, m. p. 225°, the hydrates of which could not be isolated. Similarly with hydriodic acid is obtained the periodide, $(\text{DH}_2)_2\text{NiI}_2 \cdot \text{I}_2$, which is instantly decomposed by water, alcohol, acetone, and ether to yield $\text{Ni}(\text{DH})_2 + 2\text{HI} + \text{I}_2$. It is assumed that the fixation of the oxime by the central atom depends on the anion, being weakest for the chloride ion. Analogous nitrates and sulphates could not be obtained. Similar methods yield the complex cobalt salts, $(\text{DH}_2)_2\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ [which loses its water above 100°, yielding $(\text{DH}_2)_2\text{CoCl}_2$ (Feigl and Rubinstein, A., 1924, i, 20)] and $\text{DH}_2\text{Co}(\text{DH})\text{Cl}$. Attempts to obtain the ethylenediamine compounds, $[\text{Co en}_2\text{DH}]\text{Cl}_2$ and $[\text{Co en}(\text{DH})_2]\text{Cl}$, failed owing to the great solubility of these derivatives. Similar attempts to isolate the complex $\text{DH}_2\text{CuCl}_2 \cdot x\text{H}_2\text{O}$ always yielded the anhydrous compound (Paneth and Thilo, *loc. cit.*), confirming the conclusion of the latter authors that the hydrate is probably incapable of existence. The chlorides of calcium and zinc do not form complexes with diacetyldioxime. J. W. BAKER.

Oxidative decomposition of sugars. II. Action of hydrogen peroxide on dextrose etc. in presence of calcium carbonate. K. BERNHAUER and J. NISLER (Biochem. Z., 1929, 205, 230—239; cf. this vol., 297).—The following products obtained by oxidation with hydrogen peroxide in presence of calcium carbonate are derived from glycerol: formaldehyde, formic, acetic, glyceric, and tartaric acids; from dextrose: formaldehyde, formic, acetic, oxalic, and *r*-tartaric acids, and pentoses; and from gluconic acid: formaldehyde, acetaldehyde, formic, acetic,

oxalic, *r*-tartaric, and polyhydroxy-acids. The mechanism of the reactions is discussed.

P. W. CLUTTERBUCK.

Sugar anhydrides. I. Galactosan (α 1:5) (β 1:6). F. MICHEEL (Ber., 1929, 62, [B], 687—693).—Acetobromogalactose is converted by trimethylamine in alcohol-benzene at 0° into *tetra-acetylgalactosidotrimethylammonium bromide*, m. p. 173° (decomp.), $[\alpha]_D^{20} + 31.1^\circ$ in chloroform, transformed by barium hydroxide into trimethylamine and *galactosan* (α 1:5) (β 1:6) (I), m. p. 220—221°, $[\alpha]_D^{20} - 21.9^\circ$ in water, which is not attacked by bromine, and only slowly oxidised by potassium permanganate or by boiling Fehling's solution. It is converted by acetic anhydride and pyridine into the corresponding *triacetate*, m. p. 73—



74°, $[\alpha]_D^{20} - 5.7^\circ$ in chloroform, and by acetone and anhydrous copper sulphate into the 3:4-*isopropylidene ether*, m. p. 151—152°, $[\alpha]_D^{20} - 61.7^\circ$ in water, $[\alpha]_D^{20} - 73.3^\circ$ in chloroform, from which the galactosan is regenerated by 1% aqueous hydrochloric acid. The 1:6-position of the bridge is established by considerations of strain and by the formation of the *iso*-propylidene ether. Galactosan is converted by 2% methyl-alcoholic hydrogen chloride into a mixture of α - and β -methylgalactosides. When heated in a vacuum at 270—360°, β -galactose yields small amounts of galactosan. *Galactosidotrimethylammonium bromide*, m. p. 162—164°, $[\alpha]_D^{20} + 37.6^\circ$ in water, is prepared by the action of hydrobromic acid on the tetra-acetyl derivative. β -Methylgalactoside is transformed by acetone and anhydrous copper sulphate into the 3:4-*isopropylidene ether*, m. p. 134—135°, $[\alpha]_D^{20} + 20.96^\circ$ in water, from which β -methylgalactoside is regenerated by 1% methyl-alcoholic hydrogen chloride. H. WREN.

Attempted transformation of α - into β -penta-acetylglucose. A. GEORG (Helv. Chim. Acta, 1929, 12, 261—263).—Since α -penta-acetylglucose is unchanged by heating with acetic anhydride and anhydrous sodium acetate, whilst this reagent converts α -glucose mainly into β -penta-acetylglucose, it is assumed that the conversion from α - into β -forms in the latter case must occur in the partly acetylated sugar before the terminal hydroxyl group is attacked.

J. W. BAKER.

Formula of digitalinum verum. A. WINDAUS and E. HAACK (Ber., 1929, 62, [B], 475—476).—Analyses of the crystalline *hexa-acetyl* derivative of digitalinum verum, $\text{C}_{36}\text{H}_{50}\text{O}_{14}\text{Ac}_6$, m. p. 212—213° after slight softening at 166° when slowly heated or m. p. 175—176° followed by re-solidification and re-melting at 212—214° when placed in a bath pre-heated to 160°, $[\alpha]_D^{20} - 18.1^\circ$ in chloroform, confirm the formula $\text{C}_{36}\text{H}_{56}\text{O}_{14}$ assigned to digitalinum verum on the basis of the products of its hydrolysis.

H. WREN.

Rhamnoconvolvulic acid. E. VOTOCEK and F. VALENTIN (J. Czechoslov. Chem. Comm., 1929, 1, 47—54).—Hydrolysis of commercial convolvuline with warm barium hydroxide gives *rhamnoconvolvulic acid heptahydrate*, $\text{C}_{52}\text{H}_{92}\text{O}_{32} \cdot 7\text{H}_2\text{O}$ (so named in contra-

distinction to the ether-soluble convolvulic acid which gives rhodose and isorhodose on hydrolysis), softening at 73–74° and effervescing at 104°. By drying at 100°, the anhydrous acid, m. p. 184° (decomp.) after softening at 137°, $[\alpha]_D -35.31^\circ$, is obtained. The last product yields, on hydrolysis by hot 10% oxalic acid, a *dihydroxypalmitic acid* (this vol., 541) and a mixture of sugars in which can be detected dextrose and *l*-rhamnose (yields 1:4:2 mols., respectively).
R. J. W. LE FEVRE.

Absorption of formaldehyde by starch. J. J. BLANKSMA (Rec. trav. chim., 1929, 48, 351–360).—When dry starch (potato, maize, wheat, and arrow-root) is heated with trioxymethylene at 160° in a sealed tube formaldehyde-starch is produced. This has the original starch structure, but it is unaffected by boiling with water. When heated to 180° it is converted into water-soluble dextrin, which, after a further treatment with trioxymethylene, affords an insoluble formaldehyde-dextrin. The composition of the formaldehyde-starch obtained depends on the weight of trioxymethylene used; with increasing weight of the last-named substance there is an increased formaldehyde content. Water is not eliminated during the reaction and the various products obtained are, therefore, absorption compounds. A very small formaldehyde content renders the product insoluble in water. When the capacity of the tube in which the reaction is carried out is small the formaldehyde content increases. The formaldehyde content of the reaction product is low when the heating is carried out below 160° or for less than 2–3 hrs. at 160°. In presence of water at 120–130° starch and trioxymethylene yield a gel, which when heated to 150–160° becomes a sol. The temperature at which liquefaction of formaldehyde-starch takes place rises with decrease in the amount of water added; the formaldehyde content of the product bears the same relationship.
H. BURTON.

Behaviour of polysaccharides in solutions. I. Solution of glycogen in resorcinol. R. O. HERZOG and W. REICH (Ber., 1929, 62, [B], 495–499).—Glycogen yields opalescent solutions in water which give a marked Tyndall effect. It is readily soluble in resorcinol at 120° and the solutions do not exhibit the Tyndall phenomena, thus indicating a molecular instead of a colloidal solution. Cryoscopic measurements point to the formula $(C_6H_{10}O_5)_4$, but these are considered to require confirmation. Removal of resorcinol from the solution by alcohol followed by repeated dissolution and precipitation of the residual glycogen by alcohol, purification by electrodialysis, and desiccation over phosphoric oxide at 78°/0.1 mm. gives 95% of the original glycogen, indistinguishable from the initial material in chemical or physical properties or in behaviour towards diastase.
H. WREN.

Absorption of formaldehyde by cellulose. J. J. BLANKSMA (Rec. trav. chim., 1929, 48, 361–362).—Treatment of dry cellulose (Swedish filter-paper, cotton-wool, wood, and viscose-silk) with trioxymethylene at 160° gives products containing amounts of formaldehyde varying according to the amount of trioxymethylene used. With large amounts of

trioxymethylene at 170° the cellulose swells, forming a transparent jelly. Water does not appear to be formed during the reaction.
H. BURTON.

Hydrolysis of cellulose. II. R. WILLSTATTER and L. ZECHMEISTER (Ber., 1929, 62, [B], 722–725).—Cellulose, dried at 115°, is treated with hydrochloric acid ($d_4^{25} 1.21$) at 19.5°; after 3 hrs., a portion of the hydrochloric acid is removed by evacuation and the residue is poured on to ice. The acid is removed by silver carbonate or by lead carbonate followed by hydrogen sulphide. The solution is treated fractionally with alcohol. The most sparingly soluble fractions are dextrin-like substances which swell in water, whereas the most freely soluble portions are cellobiose and dextrose. The intermediate fractions contain *cellotetraose*, $C_{24}H_{42}O_{11}$, m. p. (indef.) about 240° after softening at 205°, $[\alpha]_D +17.9^\circ$ to $+21.5^\circ$ for different specimens, soluble in water without swelling, and *cellotriose*, $C_{18}H_{32}O_{10}$, m. p. about 210° (decomp.), $[\alpha]_D +21.9^\circ$. The course of the hydrolysis of cellulose by hydrochloric acid is not in harmony with the conception of small units.
H. WREN.

Constitution of pine lignin. VIII. Investigation of pine sap. P. KLASON (Ber., 1929, 62, [B], 635–639).—The feebly acidic sap contains about 10% of dry material, including marked amounts of peptones and amino-acids. Sugars, probably including sucrose, are present in large quantity. The pentose is mainly xylose. Isolation of lignin from the sap is effected by treatment of the dried residue successively with 66% sulphuric acid and *N*-hydrochloric acid; the product is designated "protolignin." It is probably an intermediate product between pentoses and coniferyl alcohol. Coniferin appears to be present in the sap in amount varying very greatly with the season. Treatment of coniferin with emulsin affords coniferyl alcohol, which undergoes autoxidation at the atmospheric temperature to a trimeric form of coniferaldehyde identical with the lignin of wood. The protolignin of the sap, combined with sulphurous acid and condensed with naphthylamine, passes by loss of water into polymeric forms of coniferaldehyde; it can also lose water directly and pass into coniferyl alcohol, which appears as coniferin in the sap. It is highly probable that not only the coniferyl alcohol is united with sugar to coniferin but also that lignin is present in wood as a glucoside.

The observation of Pauly and Feuerstein (this vol., 446) that the author's synthetical naphthylamine salt of coniferylhydrosulphonic acid is derived from condensed acetaldehyde is not compatible with its very considerable methoxyl content. Coniferaldehyde exists in two forms, one of which is labile and combines with sulphurous acid and is found in living matter, whereas the other (Pauly's) is stable and does not unite with sulphurous acid.
H. WREN.

Catalytic reduction of dioximes. Preparation of β - γ -diaminobutane by reduction of dimethylglyoxime. J. FREJKA and (Mlle.) L. ZAHLOVA (J. Czechoslov. Chem. Comm., 1929, 1, 173–187).—A 50% yield of β - γ -diaminobutane, b. p. 60–64°/56 mm., $d_4^{20} 0.86011$, 1.44426 , $n_D^{20} = 0.00843$, is

obtained by catalytic reduction of diacetyldioxime with platinum-black in glacial acetic acid suspension. Under prescribed conditions the same catalyst can be used for eleven successive reductions. Distillation of the acetic acid solution of the products in a vacuum at 110°, redistillation in a vacuum of the residue saturated with potassium hydroxide, and a further vacuum distillation of the distillate after again treating with potassium hydroxide yields the diamine as a mixture of its mono- and hemi-hydrates, from which it is obtained anhydrous by distillation over sodium. No reduction occurs in alcoholic solution. The base is characterised by preparation of the following derivatives: *diacetyl*; *dibenzoyl*; *phenylurethane*, m. p. 230°; condensation product with ethyl acetoacetate [$\text{CHMe}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$]₂, m. p. 59° (coit.); hydrochloride; *hydrobromide*; *oily hydriodide*; *sulphate*; *chromate*; *chloroaurate*; *chloroplatinate*; *oxalate*, $+\text{H}_2\text{O}$ and anhydrous; *succinate*, *picrate*, and *picrolonate*. J. W. BAKER.

Cobaltic derivatives of $\beta\beta'\beta''$ -triaminotriethylamine. F. G. MANN (J.C.S., 1929, 409—411).—Mononuclear compounds of $\beta\beta'\beta''$ -triaminotriethylamine with cobalt are described in which co-ordination occurs at all four amine groups (cf. Jaeger and Koets, A., 1926, 697). Gentle boiling of an aqueous solution of roseo-cobaltic chloride and triaminotriethylamine trihydrochloride gave, after addition of potassium thiocyanate, *dithiocyanatotriaminotriethylaminocobaltic monothiocyanate monohydrate*, $[(\text{SCN})_2\text{Co tren}]\text{SCN}\cdot\text{H}_2\text{O}$, m. p. 208—210° (decomp.) [corresponding *mononitrate monohydrate*, m. p. 226° (decomp.); *anhydrous monochloride*, m. p. 225—226° (decomp.); *chloroplatinate*, m. p. 203—204° (decomp.)]. R. J. W. LE FEVRE.

Basic chlorides and additive compounds from metallic chlorides and hexamethylenetetramine. Exceptional behaviour of nickel chloride. J. C. DUFF and E. J. BILLS (J.C.S., 1929, 411—419).—Boiling hexamethylenetetramine solution does not react with chlorides of magnesium, calcium, strontium, or barium; zinc, ferric, chromic, aluminium, antimony, and tin chlorides all yielded the corresponding hydroxide; cadmium, lead, bismuth, manganese, ferrous, cobaltous, and cupric chlorides gave the respective basic chlorides [*basic ferrous chloride*, $3\text{Fe}(\text{OH})_2\cdot\text{FeCl}_2$]; nickel chloride gave a compound, $\text{N}(\text{CH}_2\cdot\text{OH})_3\cdot 3\text{Ni}(\text{OH})_2$. The following new additive compounds from metallic chlorides and hexamethylenetetramine, $\text{M}_2\text{C}_6\text{H}_{12}\text{N}_4\cdot x\text{H}_2\text{O}$, are described: $\text{M}=\text{ZnCl}_2$, $x=6$; $\text{M}=\text{CaCl}_2$, $x=10$; $\text{M}=\text{SrCl}_2$, $x=9$; $\text{M}=\text{FeCl}_2$, $x=9$; $\text{M}=\text{CuCl}\cdot\text{OH}$, CuCl_2 , $x=2$; $\text{M}=\text{Cu}_2(\text{SO}_4)_3$, $x=2$; $\text{M}=\text{SnCl}_4$, $x=0$; $\text{M}=\text{BiCl}_3$, $x=0$; $\text{M}=\text{ZnCl}_2$, $x=0$. The compounds $\text{SnCl}_4\cdot 4\text{C}_6\text{H}_{12}\text{N}_4$, $\text{SbCl}_3\cdot 3\text{C}_6\text{H}_{12}\text{N}_4$, and $\text{SbCl}_5\cdot 6\text{C}_6\text{H}_{12}\text{N}_4$ have also been prepared. R. J. W. LE FEVRE.

Nitrogen trichloride and unsaturated acids. G. H. COLEMAN and G. M. MULLINS (J. Amer. Chem. Soc., 1929, 51, 937—940).—The *hydrochloride of α -chloro- β -aminobutyric acid*, m. p. 161—161.5° (*benzoyl derivative*, m. p. 174—174.5°), slowly separates (9.3—19.7% of theory) from a solution of crotonic acid and nitrogen trichloride in carbon tetrachloride (cf. A., 1928, 1362). Nitrogen, chlorine, α ,3-dichlorobutyric

acid, and small amounts of ammonium chloride are also formed. The chloroamine is reduced by sodium amalgam in methyl alcohol to β -aminobutyric acid. Cinnamic acid and nitrogen trichloride yield the *hydrochloride*, m. p. 228—230°, of α -chloro- β -amino- β -phenylpropionic acid, m. p. 199—200°, which is reduced by sodium amalgam to β -amino- β -phenylpropionic acid (*benzoyl derivative*, m. p. 194—195°).

H. E. F. NOTTON.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on the decomposition of certain polypeptides. E. ABDERHALDEN and V. VLASSOPOULOS. **Specificity of enzymolytic degradation of polypeptides. Polypeptides containing *dl*-norleucine.** E. ABDERHALDEN and H. MAYER. **Specific action of enzyme complexes on fission of polypeptides.** E. ABDERHALDEN and F. REICH.—See this vol., 604, 605.

[Composition of] Buff's and Bunsen's salts. F. HOLZL [with W. KHUNL-BRADY] (Monatsh., 1929, 51, 157—168; cf. Bayer and Villiger, A., 1902, i, 355).—When the salt, $\text{H}_2\text{Fe}(\text{CN})_6\cdot 6\text{EtOH}\cdot 2\text{HCl}$ (I) (Buff, Annalen, 1854, 91, 253; cf. Freund, A., 1888, 571), obtained by the action of hydrogen chloride on an alcoholic solution of hydroferrocyanic acid, is allowed to decompose in a vacuum there is almost a complete loss of all the alcohol and hydrogen chloride after 34 hrs. Hydroferrocyanic acid remains as the end product (cf. Freund, *loc. cit.*). During the early stages (up to 10 hrs.) of the decomposition the ratio of the evolved hydrogen chloride and alcohol is approximately 1 : 2, hydroferrocyanic acid dialcoholate being a primary decomposition product: for longer times the ratio is 1 : 3. The existence of mono-, di-, tri-, and probably tetra-alcoholates of hydroferrocyanic acid is shown by vapour-pressure measurements. When Bunsen's salt, $(\text{NH}_4)_4\text{Fe}(\text{CN})_6\cdot 2\text{NH}_4\text{Cl}\cdot 3\text{H}_2\text{O}$ (II), is treated with silver nitrate, silver ferrocyanide and silver chloride (2 mols.) result. The same silver salts are obtained from silver nitrate and I, showing the similarity of the dissociation of I and II in aqueous solution.

H. BURTON.

Reaction between magnesium phenyl bromide and alkyl esters of acids of fifth group of elements. H. GILMAN and J. ROBINSON (Rec. trav. chim., 1929, 48, 328—331).—Magnesium phenyl bromide reacts with *n*-butyl nitrite yielding diphenyl, diphenylamine (formed presumably through the intermediate nitrosobenzene), and butyl alcohol. With methyl phosphite and magnesium phenyl bromide 42% of diphenylmethylphosphine oxide was obtained: ethyl phosphite gives 10% of triphenylphosphine oxide. Ethyl phosphate affords diethyl phenylphosphinate (16%) together with diphenylphosphinic acid (17%), whilst ethyl arsenite gives 85.3% of triphenylarsine. Ethyl arsenate and magnesium phenyl bromide yield an unidentified substance, m. p. 270°. Ethyl nitrate and methyl phosphate gave no definite products, and methyl vanadate afforded a quantitative yield of diphenyl. No alkylbenzene was produced in any experiment, as with alkyl sulphates.

H. BURTON.

Derivatives of trimethylethylstannane. R. H. BULLARD and R. A. VINGEE (J. Amer. Chem. Soc., 1929, **51**, 892—894).—Trimethylethylstannane (cf. Pope and Peachey, Proc. C.S., 1903, **19**, 290) prepared in 80% yield from sodium trimethylstannide and ethyl bromide in liquid ammonia, is converted by bromine in carbon tetrachloride into *dimethylethylstannic bromide*, b. p. 175—180°. *Sodium dimethylethylstannide* and ammonium bromide in liquid ammonia give *dimethylethylstannane*, b. p. 90°. This, unlike trimethylstannane (Kraus and Greer, A., 1923, i, 26), is oxidised by air to *dimethylethylstannic hydroxide*, also obtained from dimethylethylstannic bromide and 30% sodium hydroxide.

H. E. F. NOTTON.

Silver cacodylates. K. V. ZAPPI and (M.L.E.) A. MANINI (Bull. Soc. chim., 1929, [iv], **45**, 154—155).—Normal silver cacodylate, $\text{Me}_3\text{AsO}_2\text{Ag}$, is obtained by dissolving moist silver oxide in cacodylic acid. Double decomposition between silver nitrate and sodium cacodylate solutions always affords the double salt, $\text{Me}_3\text{AsO}_2\text{Ag}\cdot\text{AgNO}_3$. R. BRIGHTMAN.

Non-existence of isomerism among dialkyltelluronium dihalides. H. D. K. DREW (J.C.S., 1929, 560—569).—Absence of isomerism between the supposed isomeric dimethyltelluronium bromides and iodides of Vernon (*ibid.*, 1920, **117**, 86, 897; 1921, **119**, 105, 687) is demonstrated. Halides of the α -series are normal in type, non-polar, and have a tellurium atom with a tetrahedral valency distribution. The compounds of the β -series are salt-like complex substances having the same empirical formulæ as the corresponding substances in the α -series.

Vernon's β -base (new formula: $\text{TeMe}_3\cdot\text{O}\cdot\text{TeMeO}$) was treated in aqueous solution with hydriodic acid; the product contained trimethyltelluronium iodide (decomp. 240°) and the anhydride of methylhydroxytellurium oxide (telluracetic acid), blackens above 230°. The last-named product was easily converted by excess of hydriodic acid into methyltelluronium triiodide, decomp. 100°, m. p. 180°. Vernon's β -iodide was synthesised by mixing trimethyltelluronium iodide and methyltelluronium triiodide in acetone solution.

Similarly, the action of hydrobromic acid on the β -base gave trimethyltelluronium bromide, decomp. 250—280° (complex salts with ferric chloride and stannic bromide), accompanied by methyltelluronium triiodide, discoloured 140—150°, m. p. 156° (decomp.), and an anhydride of methyltellurium oxide or oxybromide (which accounts for traces of α -dibromide also isolated). Methyltelluronium tribromide and trimethyltelluronium bromide united, in acetone solution, to give Vernon's β -dibromide. In addition, the following mixed β -dihalides have been prepared from their constituents: $\text{TeMe}_3\text{I}\cdot\text{TeMeBr}_3$, m. p. 120° (decomp.), $\text{TeMe}_3\text{Br}\cdot\text{TeMeI}_3$, blackening below 90°. The following complex iodides are also described: $\text{TeMe}_3\text{I}\cdot\alpha\text{TeMe}_2\text{I}$, TeMe_2I_4 , m. p. about 80°, and $\text{TeMe}_3\text{I}\cdot 2\text{TeMe}_2\text{I}_2$.

The constitution of the β -salts is probably $[\text{Me}_3\text{Te}]^+[\text{TeMeX}_4]^-$, since the β -diiodide and potassium iodide gave, in acetone solution, trimethyltelluronium iodide and a substance (probably

$\text{K}^+[\text{TeMeI}_4]^-$). Attention is directed to the possible analogy between tellurium "β-dihalides" and the salts which trisacetylacetone silicon, germanium, and titanium halides form with metallic chlorides.

R. J. W. LE FÈVRE.

Ortho-para ratio in aromatic substitutions. A. LAPWORTH and R. ROBINSON (Mem. Manchester Phil. Soc., 1927—1928, **72**, 43—52).—The relation between constitutional conditions and the rate of substitution in the *o-p*-positions and allied phenomena in aromatic substitutions is discussed. Applied in the case of cationoid reagents, the hypothesis advanced, which is applicable to anionoid reagents in the opposite sense, is that the agent seeks a position of high electron density. This presupposes first a molecular polarisation, secondly a definite frequency of polar molecular phase. The disturbance of an *o-p* ratio in favour of increasing *p*-isomeride by augmenting the activity of the cationoid reagent is explained, on the activated phase hypothesis, as greater frequency of activation. Experimental confirmation is derived from the results of Gattermann and Liebermann (A., 1912, i, 1038) on the formation of azo-compounds. The electrical fields in the molecule or surrounding medium due to the presence of constituent groups control the availability of electrons, and hence the *o-p* ratio. The wide applicability is shown by numerous examples.

G. E. WENTWORTH.

Aromatic nitro-compounds and organomagnesium halides. H. GILMAN and R. McCracken (J. Amer. Chem. Soc., 1929, **51**, 821—830).—Previous work on this reaction is reviewed (cf. A., 1928, 530; Oddo, A., 1904, i, 862; Hepworth, J.C.S., 1920, **117**, 1004). Nitrobenzene reacts with 4 mols. of magnesium phenyl bromide in ether at the ordinary temperature, mainly according to the scheme $\text{PhNO}_2 + 4\text{MgPhBr} \rightarrow \text{NHPh}_2 + \text{PhOH} + \text{Ph}_2$. Traces of *p*-phenyldiphenyl and aniline are also obtained, but attempts to detect the intermediate formation of nitroso-, azoxy-, and hydroxylamino-derivatives and tetraphenylhydrazine were unsuccessful. Similar results are obtained with α -nitronaphthalene and *o*- and *p*-nitrotoluenes. Nitrobenzene and magnesium phenylacetylenyl bromide give, among other products, diphenyldiacetylene, m. p. 88° (previously obtained, but not identified, by Yocich, J., Russ. Phys. Chem. Soc., 1903, **35**, 555), and $\alpha\beta$ -diiodostyrene. Aliphatic Grignard reagents give hydrazines in addition to the above products. Thus, nitrobenzene and magnesium benzyl chloride give dibenzyl, aniline, *p*-ditolyl, and 1:2-diphenyl-1:2-dibenzylhydrazine. Diphenyldiethylhydrazine is similarly obtained with magnesium ethyl bromide. Tetraphenylhydrazine does not react with magnesium phenyl bromide, but dimethylaniline oxide gives phenol, diphenyl, and dimethylaniline, and ethyl nitrate at -80° gives phenol and diphenyl, but no nitrobenzene.

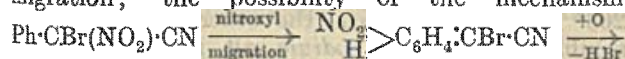
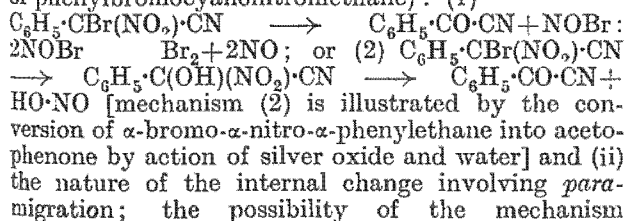
H. E. F. NOTTON.

Alternating effect in carbon chains. XXX. Nitration of phenylbromocyanonitromethane; an alleged example of intramolecular meta-rearrangement. J. W. BAKER and C. K. INGOLD (J.C.S., 1929, 423—447).—The speeds of the side

reactions which accompany the normal *meta*-nitration of phenylbromocyanonitromethane and lead to products giving by oxidation *p*-nitro- and *m*-bromobenzoic acids have been determined under formerly described conditions with nitric acid (d_4^{25} 1.490—1.517) and are found to be, unlike velocities of nuclear nitration, only comparatively slightly affected by the concentration of acid. Longer contact with more dilute acids increases lateral decomposition (as measured by brominated products) but decreases direct nitration (as measured by *meta*-nitration); *op*-nitro-derivatives arise partly by nitration and partly by side reactions.

The mechanisms advanced by Flürscheim and Holmes to explain the lateral decomposition process, namely, intramolecular *meta*-migration of bromine and extramolecular *para*-nitration of nucleus, are disputed, since (1) the former conception is foreign to a theory of aromatic substitution which postulates inductive *m*-deactivation in *m*-orientation, (2) free bromine (by elimination) is shown to be present in the reaction mixture under all conditions in which *m*-bromo-products, including *m*-bromophenylbromocyanonitromethane, are formed, (3) much evidence exists to show that the *m*-bromo-products are formed by extramolecular bromination of the nucleus by some external brominating agent which either is, or depends on, free bromine and that the *p*-nitro-derivatives are formed by an internal change involving group migration.

Tentative suggestions are made regarding (i) the form in which the bromine is originally eliminated; thus (since in absence of nitric acid benzoyl cyanide is found to be the main thermal decomposition product of phenylbromocyanonitromethane): (1)



$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CN}$ is enhanced by (a) the observation of the formation of *p*-nitrobenzoyl cyanide by the action of reagents known to be present in the original decomposition on *p*-nitrophenylacetoneitrile (by the action of bromine alone *p*-nitrophenylbromoacetoneitrile, m. p. 96°, is obtained), and (b) the isolation of dicyanostilbene by thermal decomposition of dry phenylbromocyanonitromethane.

An improved process for the preparation of phenylbromocyanonitromethane is described. *m*-Bromobenzyltrimethylammonium bromide, m. p. 216°, decomps. 220—225°, and the corresponding *picrate*, m. p. 150°, were prepared from *m*-bromotoluene by bromination and treatment of the resulting crude product with alcoholic trimethylamine. *Benzylmethylammonium bromide* has m. p. 235°. R. J. W. LE FEVRE.

Oxidation of unsaturated substances with perbenzoic and peracetic acids. II. J. BOESEKEN and G. ELSSEN (Rec. trav. chim., 1929, 48, 363—

369; cf. A., 1927, 39).—Oxidation of $\alpha\gamma$ -diphenylpropene, b. p. 164—168°/11 mm., d_4^{25} 1.0003, n_D^{25} 1.6010 (cf. von Braun and Köhler, A., 1918, i, 162), with peracetic acid gives $\alpha\gamma$ -diphenylpropane- $\alpha\beta$ -diol monoacetate. Similar oxidation of α -*p*-methoxyphenyl- Δ^a -propene and β -isosafole yields essentially the corresponding diol monoacetate. The above unsaturated hydrocarbons all have a double linking adjacent to the aryl group and are oxidised rapidly. When the double linking is further away from the aryl group as in allylbenzene and safole oxidation is slow. The former compound affords the corresponding diol diacetate, whilst the latter gives a complex mixture, presumably because of oxidation of the benzene nucleus. Eugenol, however, is rapidly oxidised and yields the diol monoacetate, and although indene is oxidised rapidly a mixture of the mono- and di-acetates results. Oxidation of cyclohexene with peracetic acid gives *trans*-cyclohexane-1 : 2-diol, separated by heating the oxidation mixture in a cathode vacuum, and a mixture of the diol mono- and di-acetates. H. BURTON.

Structure of certain phenylated olefines. K. VON AUWERS (Ber., 1929, 62, [B], 693—701).—On the basis of a rule that "an unsaturated carbon atom is capable of adding sodium only when it is united to aryl groups," Schlenk and Bergmann (A., 1928, 1031) have proposed alterations in the formulæ of various styrenes, for example, $\text{CHPh}\cdot\text{CMe}_2$, $\text{CMePh}\cdot\text{CMe}_2$, $\text{CPh}_2\cdot\text{CHMe}$, and $\text{CPh}_2\cdot\text{CMe}$, to $\text{CH}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{CH}_2$, $\text{CHMePh}\cdot\text{CMe}\cdot\text{CH}_2$, $\text{CHPh}_2\cdot\text{CH}\cdot\text{CH}_2$, and $\text{CHPh}_2\cdot\text{CMe}\cdot\text{CH}_2$, respectively. The mode of formation of the hydrocarbons renders the new constitution highly improbable, since they are uniformly produced by the loss of water or halogen hydride from carbinols or the corresponding halides containing the substituent in the α - or β -position to the benzene nucleus. The older formulæ are in complete harmony with spectrochemical behaviour as shown by a study of styrene, α -phenyl- Δ^a -propene, α -phenyl- β -methyl- Δ^a -propene, α -methylstyrene, α -phenyl- α -methyl- Δ^a -propene, α -phenyl- $\alpha\beta$ -dimethyl- Δ^a -propene, *as*-diphenylethylene, $\alpha\alpha$ -diphenyl- Δ^a -propene, $\alpha\alpha$ -diphenyl- β -methyl- Δ^a -propene, stilbene, 7-methylstilbene, triphenylethylene, and $\alpha\alpha\beta$ -triphenyl- Δ^a -propene. Schlenk's rule for the addition of alkali metal to the ethylenic linking does not appear generally applicable in its simple form.

The following data amongst others appear to be new: $\alpha\alpha$ -Diphenyl- Δ^a -propene, m. p. 51—52°, d_4^{25} 0.9710, n_D^{25} 1.57329; $\alpha\alpha$ -diphenyl- β -methyl- Δ^a -propene, b. p. 152—154°/14 mm., d_4^{25} 1.000, n_D^{25} 1.5875, which yields acetone when oxidised with chromic acid in glacial acetic acid; triphenylethylene, b. p. 219—221°/15 mm., m. p. 67—69°, d_4^{25} 1.0373, n_D^{25} 1.64012; $\alpha\alpha$ -diphenyl- γ -methyl- Δ^a -butene, b. p. 166—168°/18 mm., d_4^{25} 0.978, n_D^{25} 1.5753. $\delta\delta$ -Diphenyl- β -methylbutan- β -ol, from ethyl $\beta\beta$ -diphenylpropionate and magnesium methyl iodide, has b. p. 180—182°/12 mm., d_4^{25} 1.036, n_D^{25} 1.5636. H. WREN.

Orientation effects in the diphenyl series. VII. Effect of substituents in one nucleus on ratio of *ortho* : *para* nitration in the other. Nitration of 2- and 4-nitro- and of 2 : 4- and

2:4'-dinitro-diphenyl and of diphenyl-4-carboxylic acid. H. C. GULL and E. E. TURNER (J.C.S., 1929, 491—500).—Results of quantitative nitration experiments have confirmed the postulation (Le Fèvre and Turner, A., 1928, 630) of independent nuclear conjugation. 4-Nitrodiphenyl is nitrated by nitric acid (d 1.448) at 40—50° to the extent of 37% and 63% in the 2'- and 4'-positions, respectively, whilst 2-nitrodiphenyl (nitric acid, d 1.420 at 35°) gives 39% of the 2'-nitro- and 61% of the 4'-nitro-compound. Diphenyl by treatment with nitric acid (d 1.448 at 35—50°) undergoes nitration to the extent of 47% in the 4-position and 53% in position 2; further nitration of 4-nitrodiphenyl also occurs and 30% of the product is 4:4'-dinitrodiphenyl. 4:4'-Dinitrodiphenyl, by dissolution in boiling nitric acid (d 1.5), gives 2:4:4'-trinitrodiphenyl, m. p. 176°, which by further nitration by mixed acids at 100° gives 2:4:2':4'-tetranitrodiphenyl. 2:4-Dinitrodiphenyl, m. p. 110° (prepared by heating iodobenzene, chloro-2:4-dinitrobenzene, and copper bronze), is nitrated by dissolution for 1 min. in nitric acid (d 1.5) at 100° to the extent of 45% in position 2' and 55° in position 4'. Less than 1% of a third product is formed. Similar treatment of 2:4'-dinitrodiphenyl produces 47.5% of 2:4:2'- and 52.5% of 2:4:4'-trinitrodiphenyl. From 2:2'-dinitrodiphenyl (nitric acid, d 1.5 at 75—80°) 2:4:2'-trinitrodiphenyl, m. p. 150—151°, is formed to the extent of 80—85%. 2:4:6-Trinitrodiphenyl, m. p. 130°, is obtained by heating together picryl chloride, iodobenzene, and copper bronze.

Diphenyl-4-carboxylic acid (prepared by hypochlorite or permanganate oxidation of 4-acetyldiphenyl) is dinitrated by nitric acid (d 1.5) at —15°, giving 49% of 2:4'-dinitrodiphenyl-4-carboxylic acid (decarboxylation of which gives 2:4'-dinitrodiphenyl) and 51% of 2:2'-dinitrodiphenyl-4-carboxylic acid, m. p. 194—195° (decarboxylation of which gives 2:2'-dinitrodiphenyl) (all m. p. corr.).

R. J. W. LE FEVRE.

Pyrogenic decomposition of aromatic compounds under pressure of hydrogen in presence of a mixed catalyst. II. V. IPATIEV and N. ORLOV (Ber., 1929, 62, [B], 593—597; cf. A., 1927, 1060).—The experiments are performed at 440—465° under an initial pressure of about 70 atm. in the presence of a mixture of the oxides of aluminium and iron. α -Methylnaphthalene gives methane, naphthalene, benzenoid hydrocarbons, hydronaphthalene, and methylhydronaphthalene. β -Methylnaphthalene behaves similarly. The isolation of β -methylnaphthalene from 1:6- and 2:6-dimethylnaphthalenes is recorded. A technical paraffin, m. p. 25—56°, yielded exclusively paraffin hydrocarbons, b. p. 50—170°, d_4^{25} 0.7211, n_D^{25} 1.412. Carbazole is remarkably stable, whereas quinoline suffers partial decomposition into ammonia and hydrocarbons. Diphenylene oxide is completely unchanged. Indene is partly transformed into hydrindene, partly degraded to substituted benzenes, and partly polymerised to resin. 1:2:3:4-Tetrahydronaphthalene is dehydrogenated to naphthalene and decomposed in the hydrogenated nucleus. Dibenzyl is smoothly converted into toluene.

H. WREN.

Scission of certain sulphohydroxamic acids. A. ANGELI, D. BIGIARI, and Z. JOLLES (Atti R. Accad. Lincei, 1928, [vi], 8, 116—120).—According to Raschig ("Schwefel- und Stickstoffstudien," 89), the hydroxamic acid formed when sodium hydroxylaminosulphonate and benzaldehyde react in presence of alkali is difficult to detect by means of the violet coloration with ferric chloride because of the necessity of using a large proportion of alkali at 70° to effect the decomposition of the sulphonate. The authors find, however, that such decomposition occurs rapidly at the ordinary temperature and that the non-appearance of the coloration with ferric chloride is due to reduction of this reagent to the ferrous state by the sulphite formed. Angeli, Angelico, and Scurti's statement that the action of aqueous potassium hydroxide on naphthalene-1-sulphohydroxamic yields naphthalene-2-sulphinic acid (A., 1904, i, 310) requires correction, the compound formed being naphthalene-1-sulphinic acid, m. p. 103° (cf. Hinsberg, A., 1917, i, 328).

T. H. POPE.

Hydrogenation of phenanthrene. II. G. SCHROETER, H. MULLER, and J. Y. S. HUANG (Ber., 1929, 62, [B], 645—658; cf. A., 1925, i, 130).—Hydrogenation of phenanthrene, like that of anthracene, occurs in three distinct stages, 9:10-dihydro-, 1:2:3:4-tetrahydro-, and 1:2:3:4:5:6:7:8-octahydro-phenanthrenes being successively produced. Phenanthrene, purified from fluorene by distillation and from diphenylene sulphide by sodium, is partly hydrogenated in tetrahydronaphthalene. Tetrahydrophenanthrene is removed from the product as the picrate, leaving a mixture of *ms*-dihydrophenanthrene and octahydrophenanthrene which cannot be separated into its components by distillation. The mixture is treated with concentrated sulphuric acid, whereby octahydrophenanthrene is transformed into the sparingly soluble monosulphonic acid (corresponding chloride, m. p. 131°). The filtrate contains two isomeric *mesodihydrophenanthrenedisulphonic acids*, one of which gives a sparingly soluble *barium salt* (*sodium salt*), yielding a *disulphonyl chloride*, m. p. 263° (decomp.), whereas the other affords a freely soluble *barium salt*, a *sodium salt*, and a *disulphonyl chloride*, m. p. 184—185°. Treatment of the acids regenerated from the chlorides with fuming hydrochloric acid at 200° yields *ms*-dihydrophenanthrene, b. p. 168—169°/15 mm., m. p. 34.5—35°, d_4^{25} 1.0953, d_4^{20} 1.0757. Technical phenanthrene is converted by sodium and amyl alcohol into resinous products, *ms*-dihydro- and tetrahydro-phenanthrene; the latter compound partly forms mixed crystals with unchanged phenanthrene which can be separated from one another by fractional crystallisation. Octahydrophenanthrene is not produced. The synthesis of the *ms*-compound from 2:2'-dibromomethyldiphenyl and sodium is described. The compound described in the literature as *ms*-dihydrophenanthrene, m. p. 95° (picrate, m. p. 137°), is a mixture of phenanthrene and a small proportion of its tetrahydro-derivative. Tetrahydrophenanthrene has b. p. 173°/11 mm., m. p. 33—34°, d_4^{25} 1.0601 (picrate, m. p. 111°). Oxidation of 5:6:7:8-tetrahydrophenanthrene by chromic acid in 92% acetic acid affords 5-*keto*-

5:6:7:8-tetrahydrophenanthrene,

$$\begin{array}{c} \text{CH}_2\text{CH}_2\text{C}=\text{CH}\cdot\text{CH} \\ \text{CH}_2\text{CO}-\text{C}-\text{C}_6\text{H}_4 \end{array} \quad \text{m. p. } 69^\circ \quad [\text{semicarbazone},$$

m. p. 225° (decomp.); *oxime*, m. p. $172-173^\circ$; *picrate*, m. p. $101-102^\circ$]. With permanganate in the presence of acetone, tetrahydrophenanthrene gives a mixture of the 5-keto-compound and 8-keto-

5:6:7:8-tetrahydrophenanthrene,

$$\begin{array}{c} \text{CH}_2\text{CO}-\text{C}=\text{CH}\cdot\text{CH} \\ \text{CH}_2\text{CH}_2\text{C}-\text{C}_6\text{H}_4 \end{array} \quad \text{m. p. } 96-97^\circ \quad [\text{semicarbazone},$$

m. p. 247° (decomp.); *oxime*, m. p. $165-166^\circ$; *picrate*, m. p. $106-107^\circ$]. Oxidation of tetrahydrophenanthrene with boiling aqueous permanganate gives a mixture of *o*-phthalic acid and benzene-1:2:3:4-tetracarboxylic acid.

Synthesis of the two ketones is effected as follows. Naphthalene is converted by chloroacetyl chloride in presence of phosphoric oxide at $150-180^\circ$ into a mixture of unchanged naphthalene, 1-naphthacyl chloride (84%), and 2-naphthacyl chloride (16%). The chlorides are separated from one another by picric acid in alcohol. 1-Naphthacyl chloride has b. p. $203/12$ mm., m. p. $40-41.5^\circ$ (corresponding *picrate*, m. p. $94-95^\circ$), whilst 2-naphthacyl chloride has m. p. $67-68^\circ$ (corresponding *picrate*, m. p. $90-91^\circ$). 1-Naphthacyl chloride is transformed by methyl malonate and sodium in presence of benzene into methyl 1-naphthacylmalonate, which yields the corresponding dicarboxylic acid and β -1-naphthoylpropionic acid, m. p. $131-132^\circ$, reduced by amalgamated zinc and concentrated hydrochloric acid to γ -1-naphthyl-n-butyric acid, b. p. $217/15$ mm., m. p. $106-107^\circ$. Treatment of the last-named acid with phosphorus pentachloride followed by distillation of the product affords 8-keto-5:6:7:8-tetrahydrophenanthrene. Similarly, 2-naphthacyl chloride is converted successively into methyl 2-naphthacylmalonate, 2-naphthacylmalonic acid, m. p. 162° (which is monobasic towards methyl-orange in aqueous solution but dibasic towards phenolphthalein in alcohol), β -2-naphthoylpropionic acid, m. p. 174° , and γ -2-naphthyl-n-butyric acid, m. p. $94-95^\circ$. Distillation of the chloride of the last-named acid affords 5-keto-5:6:7:8-tetrahydrophenanthrene. H. WREN.

Pyrogenic dissociation of some condensed ring systems. N. A. ORLOV (Ber., 1929, 62, [B], 710-719).—Tetrahydrophenanthrene is converted by treatment with hydrogen at $450-470^\circ/70-75$ atm. (initial pressure) in the presence of the oxides of iron and aluminium (1:1) into benzenoid hydrocarbons, tetrahydronaphthalene, naphthalene, β -methylnaphthalene and its hydrides, and hydrogenated dimethyl-(or ethyl-)naphthalenes; the residue consists of phenanthrene and unchanged tetrahydrophenanthrene. The tetramethylene ring is thus ruptured with production of alkyl-naphthalenes, which then become de-alkylated and hydrogenated. Similarly, retene affords large amounts of saturated hydrocarbons formed by de-alkylation of the phenanthrene nucleus, naphthalene, (?) methylnaphthalene, and methylphenanthrene. The same products are derived under similar conditions from the resin oil of colophony which corresponds with a hydrogenated retene. With fluorene hydrogenation of the

aromatic ring takes place only to a limited extent, the main action consisting in fission of the molecule into benzene and toluene. Distillation of phenanthrene or anthracene with aluminium chloride yields an oil consisting mainly of hydronaphthalenes containing hydrogenated methylnaphthalenes and initial hydrocarbons. Similarly, fluorene affords hydrofluorenes and benzenoid hydrocarbons. The products are therefore identical with those obtained by "berginisation." The action of aluminium chloride consists of primary, intensive dehydrogenation with production of coke. The liberated hydrogen is added by the unchanged material in the same manner as in customary hydrogenation. Fission of the hydrides takes place between the methylene groups.

H. WREN.

Pyrogenic decomposition of chrysene under pressure of hydrogen. N. A. ORLOV and N. D. LICHATSHEV (Ber., 1929, 62, [B], 719-722).—Chrysene, m. p. 250° , is converted by exhaustive hydrogenation at $440-450^\circ/85-100$ atm. (initial pressure) in the presence of ferric chloride into coke and saturated gaseous hydrocarbons. The liquid product contains aliphatic and benzenoid hydrocarbons, and naphthalene; dehydrogenation of the higher fractions by platinised charcoal leads to a mixture of naphthalene, phenanthrene, α - and β -methylnaphthalenes.

H. WREN.

Action of acids on rubrene. C. MOUREU, C. DUFRAISSE, and E. ENDERLIN (Compt. rend., 1929, 188, 673-675).—Hydriodic acid reacts with rubrene in the presence of solvents to afford colourless ψ -rubrene, which first melts with loss of solvent of crystallisation and then remelts at $276-278^\circ$. A small amount of a substance, m. p. 230° , possibly a hydrogenated rubrene, is also produced in some cases. Hydrogen bromide, hydrogen chloride, and 98% sulphuric acid, but not fatty acids, effect the same change.

G. A. C. GOUGH.

Elimination of the nitroso-group from nitroso-amines. W. G. MACMILLAN and T. H. READE (J.C.S., 1929, 585-586).—Secondary amines, e.g., *m*- and *p*-nitromethylanilines, may be obtained in good yield from the nitroso-derivatives by heating with a solution of carbamide or thiocarbamide in 50% sulphuric acid. Nuclear nitroso-groups are unaffected.

R. K. CALLOW.

Nitration of *m*-acetamido-*tert*.-butylbenzene. J. B. SHOESMITH and A. MACKIE (J.C.S., 1929, 476-477).—Nitration of *m*-acetamido-*tert*.-butylbenzene with nitric acid (*d* 1.46) at $25-30^\circ$ gives 4-nitro-3-acetamido-*tert*.-butylbenzene, m. p. 116° , and not the 2-nitro-derivative as stated by Gelzer (A., 1889, i, 42). Hydrolysis of the nitro-compound with alcoholic potassium hydroxide yields 4-nitro-3-amino-*tert*.-butylbenzene, m. p. $91-92^\circ$ (cf. *loc. cit.*), which after reduction with stannous chloride and hydrochloric acid and subsequent condensation with phenanthraquinone affords the corresponding phenazine, m. p. $148.5-149^\circ$ (Gelzer gives m. p. 144° and 146.5°). The same phenazine is obtained from 3-nitro-4-amino-*tert*.-butylbenzene by the same reactions.

H. BURTON.

Nitration of phenylcyclohexane and its p-halogeno-derivatives. H. A. MAYES and E. E. TURNER (J.C.S., 1929, 500—508).—Nitration of phenylcyclohexane with nitric acid (*d* 1.5) at 0° gives *p*-nitrophenylcyclohexane (I), *b. p.* 198°/16 mm., *m. p.* 58.5°, together with 2:4-dinitrophenylcyclohexane, *m. p.* 57°. When nitration is effected with a mixture of nitric and acetic acids 62% of I and 38% of *o*-nitrophenylcyclohexane, *b. p.* 174°/16 mm., *d*₄²⁵ 1.111, 1.5472, are obtained. Nitration of *p*-aminophenylcyclohexane, *m. p.* 55° (acetyl derivative, *m. p.* 129°), with nitric and sulphuric acids affords 2-nitro-4-aminophenylcyclohexane, *m. p.* 66°, reduced by iron, water, and a small amount of hydrochloric acid to 2:4-diaminophenylcyclohexane, *m. p.* 108°. Nitration of *p*-chlorophenylcyclohexane, *b. p.* 145°/19 mm., *d*₄²⁵ 1.065, *n*_D²⁰ 1.5386 (obtained from cyclohexyl chloride and chlorobenzene in presence of aluminium chloride), with nitric acid at -5° to 0° gives 4-chloro-2:5-dinitrophenylcyclohexane (II), *m. p.* 92° (4-piperidino-derivative, *m. p.* 108°), reduced by iron and dilute acetic acid at 100° to 4-chloro-2:5-diaminophenylcyclohexane, *m. p.* 95—96°. The constitution of this last substance, and hence of II, follows from the observation that it gives the usual *p*-diamine reactions. Nitration of the chloro-compound in acetic acid solution yields 4-chloro-2-nitrophenylcyclohexane (45%), nitrated further to II, and 4-chloro-3-nitrophenylcyclohexane (55%); the amount of the latter is determined by the amount of piperidine hydrochloride obtained when the mixture of nitro-compounds is treated with piperidine. Similar analysis of the mixture produced by nitrating *p*-bromophenylcyclohexane, *b. p.* 160°/23 mm., *d*₄²⁵ 1.283, *n*_D²⁰ 1.5584, shows the presence of 61% of the 2-nitro- and 39% of the 3-nitro-isomerides. The main product formed by the action of nitric acid on *p*-iodophenylcyclohexane, *b. p.* 174°/11 mm., *d*₄²⁵ 1.448, *n*_D²⁰ 1.5900 (prepared by the Sandmeyer reaction from the corresponding amine), is *p*-iodonitrobenzene. Condensation of phenylcyclohexane with acetyl chloride in presence of aluminium chloride and carbon disulphide yields *p*-acetylphenylcyclohexane, *m. p.* 68—69° (phenylhydrazane, *m. p.* 103°), oxidised by acidified potassium permanganate to terephthalic acid, and by aqueous sodium hypobromite to *p*-cyclohexylbenzoic acid, *m. p.* 199° (sodium salt). This acid is also obtained by hydrolysis of the reaction product from diazotised *p*-aminophenylcyclohexane and sodium cuprocyanide.

H. BURTON.

Preparation of substituted diphenylamines. A. W. CHAPMAN (J.C.S., 1929, 569—572).—Diphenylamines with similar or different substituents may be prepared in good yield from substituted amines, R'·NH₂, and phenols, R'·OH, through the anilide-iminochlorides, R·CCl·NR', and benzimino-ethers, RC(OR'')·NR' (*ibid.*, 1922, 121, 1676). When heated these last yield benzoyldiphenylamines, R·CO·NR'·R'' (A., 1925, i, 1400; 1927, 874), which can be hydrolysed with alcoholic potassium hydroxide to the free bases. This method of synthesis has been employed to determine the constitution of the tetrachlorodiphenylamine obtained by chlorination of diphenylamine (Gnehm, A., 1876, i, 265), which is shown to be the 2:4:2':4'-

compound. The following substances are described: N-*o*-Chlorophenylbenzimidino-2:4:6-trichlorophenyl ether, *m. p.* 99—100°; benzoyl-2:4:6:2'-tetrachlorodiphenylamine, *m. p.* 131—132° (base, *m. p.* 87—88°); N-*p*-chlorophenylbenzimidino-2:4:6-trichlorophenyl ether, *m. p.* 121—122°; benzoyl-2:4:6:4'-tetrachlorodiphenylamine, *m. p.* 154° (base, *m. p.* 63—64°); N-2:4-dichlorophenylbenzimidino-2:4-dichlorophenyl ether, an oil; benzoyl-2:4:2':4'-tetrachlorodiphenylamine, *m. p.* 153—154° [base, identical with that prepared from diphenylamine, *m. p.* 141—142° (lit. 133—134°)]; 2:4:6-trichlorodiphenylamine, *m. p.* 43—44°. The final product of chlorination of diphenylamine is 2:4:6:2':4':6'-hexachlorodiphenylamine, *m. p.* 138—139°. The constitution, however, could not be confirmed, for the base could not be benzoylated, nor could the benzoyl derivative (A., 1927, 874) be hydrolysed.

R. K. CALLOW.

Perylene and its derivatives. XX. K. FUNKE, F. KIRCHMAYR, and H. WOLT (Monatsh., 1929, 51, 221—227).—Reduction of dinitroperylene (Zinke, Funke, and Lorber, A., 1927, 350) with phenylhydrazine, hydrazine hydrate at 170—180°, hydrazine hydrate in boiling xylene, or with sodium hydrogen sulphide in alcoholic sodium hydroxide affords diaminoperylene, crystalline, with dark green reflex, not melted at 400° [diacetyl, di(chloroacetyl), dibenzoyl, di-*p*-chlorobenzoyl, di-*p*-bromobenzoyl, di- α -naphthoyl, dibenzylidene, disalicylidene, phthaloyl, diphtaloyl, and phthaloyl-*p*-chlorobenzoyl derivatives], which reacts with ethyl chloroformate to give the corresponding urethane derivative.

H. BURTON.

Preparation of *p*-azoxyanisole and derivatives. W. DAVIES and R. A. R. DOWN (J.C.S., 1929, 586—587).—The preparation of *p*-azoxyanisole from *p*-chloronitrobenzene (cf. Jackson and Fiske, A., 1902, i, 362; Brand, A., 1903, i, 371) is best carried out under such conditions that substitution precedes reduction. This is accomplished by boiling with 0.86 mol. of 4*N*-methyl-alcoholic sodium methoxide for 12 hrs., adding a further 0.64 mol. of sodium methoxide, distilling off about half the methyl alcohol, and boiling for a further 12 hrs. *p*-Azoxyanisole was obtained in 64% yield. 1:2-Dichloro-4-nitrobenzene, obtained by chlorination of *p*-chloronitrobenzene at 100° in presence of antimony trichloride (cf. G.P. 167297), yields similarly 3:3'-dichloro-*p*-azoxyanisole, *m. p.* 182°, which does not form liquid crystals.

R. K. CALLOW.

Relationship between absorption spectra and constitution of azo- and azoxy-compounds. L. SZEGO (Ber., 1929, 62, [B], 736—744; cf. A., 1928, 1367, 1369).—Comparison of the absorption spectra in the ultra-violet of *p*-bromo-, *p*-nitro-, and *p*-methylazobenzene, *p*-methylazoxybenzene, azo- and azoxybenzene shows that the transformation of azo- to azoxy-compound causes no or only slight alteration in the frequency of the bands in the region examined. The bands of the azo-substances are usually more sharply defined and flatter than those of the azoxy-compounds. With the *p*-hydroxy- and *p*-amino-azo- and -azoxy-compounds, the α -form of the latter has two bands, whereas the β -isomeride has only one band and the common band is displaced by about

50 units towards the region of greater frequency. The β -*p*-amino-compound has a second band in the extreme ultra-violet. Similar observations are made with *m*-nitro-*p*-hydroxyazobenzene and the corresponding azoxy-derivatives. A close analogy exists therefore between the azo- and α -azoxy-compounds, whereas the β -azoxy-derivatives stand apart. The spectra of the 4-bromo-4'-nitroazoxybenzenes and the corresponding azo-compound, of 4-bromo-4'-methyl-azo- and -azoxy-benzene, and of 4:4'-dinitro- and 4:4'-dihydroxy-azo- and -azoxy-benzenes have been measured.

H. WREN.

Manufacture of azo-dyes [and new arylamido-sulpho-derivatives of anthranilic acid]. I. G. FARBERIND. A.-G.—See B., 1929, 239.

Decahydroquinoline derivatives. V. Synthesis of *trans*-1-dimethylamino-2-*n*-propylcyclohexane and elimination of water from 2-*n*-propylcyclohexanol. S. FUJISE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 83—89).—Reduction of *o*-allylphenol with hydrogen in presence of platinum-black and acetic acid affords 2-*n*-propylcyclohexanol, b. p. 84°/6 mm., d_4^{25} 0.9115, n_D^{25} 1.46036, oxidised by chromic acid in acetic acid solution to 2-*n*-propylcyclohexanone, b. p. 199°, d_4^{25} 0.9056, 1.45097 (cf. Vavon, A., 1928, 167). When 2-*n*-propylcyclohexanoneoxime, m. p. 67—68°, is reduced with sodium and alcohol, 2-*n*-propylcyclohexylamine results. Hydrolysis of the benzoyl derivative, m. p. 146—147°, of this with concentrated hydrochloric acid at 150—160° gives *trans*-2-*n*-propylcyclohexylamine, b. p. 193° (hydrochloride, m. p. 231°; hydrobromide, m. p. 229—230°; picrate, m. p. 168—169°), converted by heating with a mixture of formaldehyde and formic acid at 150—155° into *trans*-1-dimethylamino-2-*n*-propylcyclohexane, b. p. 205—207° (picrate, m. p. 114.5—115.5°; chloroaurate, m. p. 146—147°). This is identical with the product obtained by the degradation of *trans*-decahydroquinoline (A., 1928, 1022). Dehydration of 2-*n*-propylcyclohexanol by heating with potassium hydrogen sulphate yields Δ^1 -propylcyclohexene (Wallach, A., 1908, i, 429).

H. BURTON.

3:5-Diphenyl- Δ^2 -cyclohexenone. A. D. PETROV (Ber., 1929, 62, [B], 642—645).—3:5-Diphenyl- Δ^2 -cyclohexenone, m. p. 82—83°, dissolved in hexahydrotoluene, is hydrogenated under pressure in the presence of nickel at 240° to a mixture of 1:3-dicyclohexylcyclohexanes, m. p. 66° and b. p. 202°/14 mm., respectively. Dehydrogenation of the unsaturated ketone is effected by platinised charcoal at 300°, thus giving 3:5-diphenylphenol, m. p. 82—92° (phenylurethane, m. p. 180°). Reduction of the ketone with sodium and boiling alcohol affords 3:5-diphenylcyclohexanol, m. p. 127° (phenylurethane, m. p. 152°), oxidised to 3:5-diphenylcyclohexanone, m. p. 139—140° (oxime, m. p. 201°).

H. WREN.

Oxidising action of alkalis. R. LEMBERG (Ber., 1929, 62, [B], 592; cf. Lock, this vol., 67).—Fusion of sodium phenoxide with alkali containing water in a nickel apparatus in a current of nitrogen yields the same products as are derived from phenol and molten sodium hydroxide. Marked evolution of hydrogen is observed at a definite temperature.

H. WREN.

Thermal behaviour of phenols. A. HAGEMANN (Z. angew. Chem., 1929, 42, 355—361).—The effect of heat on phenol, cresol, the dihydroxybenzenes, and the naphthols, in presence of pumice, of nickel, and of active charcoal, has been examined. S. I. LEVY.

New condensation of ketones with phenols. II. "Cresol-phorones." J. B. NIEDERL and R. CASTY (Monatsh., 1929, 51, 86—92; cf. A., 1928, 1137).—Treatment of a mixture of *o*-cresol and acetone or phorone with cold concentrated sulphuric acid gives a condensation product, termed "*di-o-tolylphorone*" [*di*- β -(2-hydroxy-*m*-tolyl)- β -methyl-*n*-propyl ketone], m. p. 245° (dibenzoate, m. p. 130°, dimethyl ether, m. p. 154°), which gives sodium and potassium salts when treated with alcoholic alkali hydroxide solution. Bromination of the ketone in chloroform solution yields a dibromo-derivative, m. p. 220°. Similar treatment of *p*-cresol and acetone furnishes "*di-p-tolylphorone ether*" [anhydrodi- β -(6-hydroxy-*m*-tolyl)- β -methyl-*n*-propyl ketone], m. p. 137°. The constitution of "*di-m-tolylphorone ether*," namely, anhydrodi- β -(6-hydroxy-*p*-tolyl)- β -methyl-*n*-propyl ketone (cf. loc. cit.), follows from the production of thymol, menthol, and trimethylcoumaran from it, by successive oxidation, elimination of carbon dioxide or water, and hydrogenation (cf. B.P. 279,855, 279,857, and 280,924; B., 1929, 237, 316).

H. BURTON.

Scission of diaryl ethers and related compounds by means of piperidine. II. Nitration of 2:4:4'-trichlorodiphenyl ether, and of 2:4-dichlorophenyl *p*-toluenesulphonate and benzoate. L. G. GROVES, E. E. TURNER, and (in part) G. I. SHARP (J.C.S., 1929, 512—524).—Nitration of 2:4:4'-trichlorodiphenyl ether is found to take place successively in positions 2', 5, and 5', in accordance with Robinson's electron repulsion theory, with no subsidiary nitration in position 3', as might be expected on Flürscheim's theory. The nitration of analogous compounds was studied, and the constitution of certain of the products proved.

4:4'-Dichloro-2-nitrodiphenyl ether is prepared by fusion of 2:5-dichloronitrobenzene with potassium *p*-chlorophenoxide. Reduction yields the 2-amino-compound, m. p. 67°, converted by a Sandmeyer reaction into 2:4:4'-trichlorodiphenyl ether (I), b. p. 183°/11 mm., m. p. 54—55°. Mononitration of I in acetic acid yields 2:4:4'-trichloro-2'-nitrodiphenyl ether, m. p. 86—87°, which yields 2:4-dichlorophenol and 4-chloro-2-nitrophenylpiperidine when heated with piperidine. Dinitration of I in nitric acid yields 2:4:4'-trichloro-*o*:2'-dinitrodiphenyl ether (II), m. p. 103—104°, which gives with piperidine 2:4-dichloro-*o*-nitrophenol, m. p. 105—106° (see below), 4-chloro-2-nitrophenylpiperidine, and piperidine hydrochloride. The formation of the last compound is discussed. Reduction of II yields the 5:2'-diamino-compound, m. p. 93—94°, from which the pentachloro-derivative (III) could not be obtained. 4:5-Dichloro-2-nitrodiphenyl ether, m. p. 69—70°, is prepared from 4:5-dichloro-1:2-dinitrobenzene and potassium phenoxide. 4:5:4'-Trichloro-2-nitrodiphenyl ether, m. p. 77°, obtained similarly, yields on nitration 4:5:4'-trichloro-2:2'-dinitrodiphenyl ether, m. p. 131—132°.

which yields with piperidine 4-chloro-2-nitrophenylpiperidine. 4 : 5 : 2' : 4'-Tetrachloro-2-nitrodiphenyl ether, m. p. 125—126°, obtained similarly, is reduced to the 2-amino-compound, m. p. 97—98°, from which the pentachloro-compound (III) could not be prepared. Trinitration of I in fuming sulphuric acid yields the 5 : 2' : 5'-trinitro-compound, m. p. 155—157°, which gives with piperidine 2 : 4-dichloro-5-nitrophenol and 4-chloro-2 : 5-dinitrophenylpiperidine, m. p. 70—71°. 4-Chloro-2 : 6-dinitrophenylpiperidine (from piperidine and 4-chloro-2 : 6-dinitroanisole) has m. p. 165—166°.

2 : 4-Dichloro-2' : 4'-dinitrodiphenyl ether, m. p. 118—119° (from 1-chloro-2 : 4-dinitrobenzene and potassium 2 : 4-dichlorophenoxide), yields on nitration 2 : 4-dichloro-5 : 2' : 4'-trinitrodiphenyl ether, m. p. 128°, giving 2 : 4-dichloro-5-nitrophenol and 2 : 4-dinitrophenylpiperidine or 2 : 4-dinitrodiphenylamine, on scission with piperidine or aniline, respectively.

2 : 4-Dichlorophenol (best prepared from *p*-chlorophenol) yields the *p*-toluenesulphonate, m. p. 125°, which yields on nitration 2 : 4-dichloro-5-nitrophenyl *o*-nitro-*p*-toluenesulphonate (IV), m. p. 103°, reduced to the diamino-compound, m. p. 159—161°. The latter, by a Sandmeyer reaction, yields the tetrachloro-compound (not isolated), giving with piperidine 2 : 4 : 5-trichlorophenol, m. p. 66—67° [benzoate, m. p. 91—92° (Holleman, A., 1921, i, 102)], thus proving the occurrence of nitration in position 5 and, indirectly, the constitution of 2 : 4-dichloro-5-nitrophenol. The constitution of 2 : 4 : 5-trichlorophenol was confirmed by preparing it from 2 : 5-dichlorophenol by chlorination, and from 2 : 4 : 5-trichloroaniline by the method of Noelting and Kopp (A., 1905, i, 872). Scission of IV with piperidine yields 2 : 4-dichloro-5-nitrophenol and 1-*o*-nitro-*p*-toluenesulphonylpiperidine, m. p. 112°. The latter was also prepared from piperidine and *o*-nitro-*p*-toluenesulphonyl chloride. 1-*p*-Toluenesulphonylpiperidine has m. p. 103°.

2 : 4-Dichlorophenyl benzoate yields on nitration 2 : 4-dichloro-5-nitrophenyl *m*-nitrobenzoate, m. p. 154°, with traces of isomeric nitrobenzoates. It is best obtained pure by nitration of 2 : 4-dichlorophenyl *m*-nitrobenzoate, m. p. 115—116°, and is also prepared by nitration of 2 : 4-dichloro-5-nitrophenyl benzoate, m. p. 111—112°, or condensation of 2 : 4-dichloro-5-nitrophenol with *m*-nitrobenzoyl chloride. 2 : 4-Dichloro-6-nitrophenyl *m*-nitrobenzoate [from 2 : 4-dichloro-6-nitrophenol (Tarugi, A., 1901, i, 146)] has m. p. 149—150°.

The constitution of 2 : 4-dichloro-5-nitrophenol could not be proved directly. It is unaffected by thionyl chloride, and phosphorus pentachloride yields a substance, b. p. 150—160°/15 mm., m. p. 80—89°. Nitration of N-2 : 4-dichlorophenylphthalimide, m. p. 155° (from 2 : 4-dichloroaniline and phthalic anhydride), yields the 5-nitro-compound, m. p. 217—219°, which was hydrolysed to 2 : 4-dichloro-5-nitroaniline (Korner and Contardi, A., 1909, i, 220), but this could not be transformed into the phenol. Chlorination of *m*-nitrophenol yields 2 : 4-dichloro-3-nitrophenol, m. p. 85—87°. Reduction of the *p*-toluenesulphonyl derivative, m. p. 122°, yields 2 : 4-dichloro-3-aminophenyl *p*-toluenesulphonate, m. p.

113—114°. Diazotisation of this in concentrated sulphuric acid and a Sandmeyer reaction, followed by decomposition of the product with piperidine yields 2 : 3 : 4-trichlorophenol, m. p. 80—81° [benzoate, m. p. 143° (Holleman, *loc. cit.*)], also obtained by chlorination of 3 : 4-dichlorophenol (prepared by the method of Noelting and Kopp, *loc. cit.*).

R. K. CALLOW.

Rearrangement of phenyl benzyl ethers. W. F. SHORT and M. L. STEWART (J.C.S., 1929, 553—559).—Further evidence has been obtained that the rearrangement of phenyl benzyl ethers when heated with zinc chloride (van Alphen, A., 1928, 57; Short, *ibid.*, 516) takes place mainly, if not exclusively, by an intermolecular and not an intramolecular process, as stated by van Alphen.

Rearrangement of phenyl benzyl ether in presence of zinc chloride or zinc chloride and hydrogen chloride gives phenol, 2-hydroxydiphenylmethane (*benzyl ether*, m. p. 38°), 4-hydroxydiphenylmethane (*benzyl ether*, m. p. 49.5°), and 2 : 4-dibenzylphenol, b. p. 252—254°/10 mm. (α -naphthylurethane, m. p. 143—144°). When hydrogen chloride alone is used as catalyst, benzyl chloride is also present in the product. 2 : 4-Dibenzylphenol was synthesised from benzyl chloride and the sodium derivative of 4-hydroxydiphenylmethane in dry toluene (cf. Claisen, A., 1925, i, 655). 2-Hydroxydiphenylmethane and 2 : 6-dibenzylphenol, b. p. 237.5—238°/10 mm. (*benzyl ether*, m. p. 65°; α -naphthylurethane, m. p. 165—166°), are obtained from benzyl chloride and sodium phenoxide in dry toluene. Condensation of equimolecular quantities of phenol and anisole with benzyl chloride (1 mol.) yields 2- and 4-hydroxydiphenylmethanes, 2 : 4-dibenzylphenol, 4-methoxydiphenylmethane (oxidised by chromic anhydride to 4-methoxybenzophenone), and dibenzylanisole, the benzyl chloride being appropriated to an approximately equal extent by the phenol and anisole. Rearrangement of phenyl benzyl ether in presence of anisole (1 mol.) yields the same products. Quinol monomethyl ether and benzyl chloride with zinc chloride at 100° yield 2-hydroxy-4-methoxydiphenylmethane, m. p. 77°.

R. K. CALLOW.

Condensation products of dextrose and *p*-anisidine. M. AMADORI (Atti R. Accad. Lincei, 1929, [vi], 9, 226—230).—Like *p*-phenetidine (this vol., 439), *p*-anisidine condenses with dextrose giving two isomeric compounds, C₁₃H₁₉O₆N : (1) a glucosidic compound, m. p. 86°, [α]_D —86°, and (2) a compound, m. p. 140°, [α]_D —28°, having the constitution of a Schiff's base.

T. H. POPE.

2 : 5-Dichlorophenetidine. G. BARGELLINI and (SIGNA.) L. MONTI (Atti R. Accad. Lincei, 1928, [vi], 8, 590—593; cf. this vol., 438).—The dichlorophenetidine obtained by treating phenacetin in acetic acid solution with nascent chlorine and hydrolysing the resulting dichlorophenacetin (cf. Reverdin and Düring, A., 1899, i, 266) yields 2 : 5-dichlorobenzoquinone, m. p. 161° (cf. Levy and Schulz, A., 1882, 509), when converted into the 2 : 5-dichloro-4-aminophenol, m. p. 178—179°, and then oxidised, so that it is the 2 : 5-dichloro-compound. 2 : 5-Dichlorophenetidine condenses with 2 : 4-dinitrochlorobenzene,

giving 2:5-dichloro-2':4'-dinitro-4-ethoxydiphenylamine, m. p. 136—138°, and gives a piperonylidene derivative, m. p. 148°. T. H. POPE.

Constitution of some dichlorophenetidines. G. BARGELLINI (*Gazzetta*, 1929, 59, 16—32).—See this vol., 438, and preceding abstract.

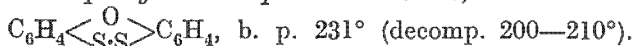
6-Amino-m-cresol and derivatives. M. T. BOGERT and G. H. CONNITT (*J. Amer. Chem. Soc.*, 1929, 51, 900—915).—Acetylation of 6-amino-m-cresol [hydrochloride; *salicylidene*, m. p. 111—111.5° (+EtOH, m. p. 92.5°), *N-chloroacetyl*, m. p. 133°, and *phthalyl*, m. p. 204°, derivatives] in presence of water gives 6-acetamido-m-cresol (Staedel and Kolb, A., 1891, 186), converted by hypochlorite into 2:4-dichloro-6-acetimidotoluquinone, m. p. 159—159.5°, from which 2:4-dichloro-*p*-toluquinone and 2:4-dichloro-6-acetamido-m-cresol were prepared (cf. Rairford, A., 1914, i, 524). Nitration of 6-acetamido-m-tolyl acetate, m. p. 127.5—128°, in acetic anhydride below 5° gives (a) a 5-nitro-derivative, m. p. 190—190.5°, hydrolysed by potassium carbonate to 5-nitro-6-acetamido-m-cresol, m. p. 188.5°, and (b) a little 2:4-dinitro-6-acetamido-m-cresol (I), m. p. 231°, hydrolysed by hydrochloric acid to 2:4-dinitro-6-amino-m-cresol, m. p. 166.5—167.5° (hydrochloride, decomp. 200°; diacetyl derivative, m. p. 170.5°; cf. Nietzki, A., 1891, 308). The sodium salt of 6-benzylidenemino-m-cresol, m. p. 135.5°, gives with ethyl bromide or sulphate an ethyl ether, b. p. 215—217°/20 mm., hydrolysed by acid to 6-amino-m-tolyl ethyl ether, b. p. 253—255° (hydrochloride, m. p. 212°, decomp. from 200°; *salicylidene*, m. p. 48.5°, *chloroacetyl*, m. p. 140.5—141°, *salicyl*, m. p. 153.4—154°, *oxalyl*, m. p. 205°, and *phthalyl*, m. p. 140.5°, derivatives), which gives an acetyl derivative, m. p. 118.5° (*N-carbethoxymethyl* derivative, b. p. 210—212.5°/22 mm.). This yields with hypochlorite a 2:4-dichloro-derivative, m. p. 162.5—163°, hydrolysed to 2:4-dichloro-6-amino-m-tolyl ethyl ether, m. p. 244°, darkening from 220°, and with nitric and acetic acids 4-nitro-, m. p. 192.5—193°, and a little 5-nitro-, m. p. 160°, derivatives, which are hydrolysed, respectively, to 4-nitro-, m. p. 86—87° (hydrochloride, decomp. 249°, darkening from 240°), and 5-nitro-, m. p. 101—101.5° (hydrochloride, decomp. 200—240°), -6-amino-m-tolyl ethyl ethers. Further nitration of the acetyl derivative affords 4:5-dinitro-6-acetamido-m-tolyl ethyl ether, m. p. 257—258°. The sodium salt of I (above) is converted by ethyl sulphate into 2:4-dinitro-6-acetamido-m-tolyl ethyl ether, m. p. 167—167.5°, hydrolysed to the 6-amino-compound, m. p. 96—97° (hydrochloride, decomp. 195—197°). 4:6-Diacetamido-m-tolyl ethyl ether, m. p. 200—200.5°; 3-hydroxy-3'-ethoxy-6:6'-azotoluene, m. p. 132.5°; 3:3'-diethoxy-6:6'-azotoluene, m. p. 149.5°, and 2-acetamido-5-β-hydroxyethoxytoluene, m. p. 117—117.5° (acetyl derivative, m. p. 117°), are described. Unsuccessful attempts have been made to convert these derivatives, many of which are of therapeutic interest, into heterocyclic compounds. H. E. F. NORRIS.

Reduction of naphthol-yellow by stannous chloride. J. G. F. DRUCE (*Chem. News*, 1929, 138, 209).—When naphthol-yellow is reduced by a hot solution of stannous chloride in hydrochloric acid, the

3-chlorostannate, m. p. about 112°, of 3:4-diamino-β-naphthol-6-sulphonic acid is produced.

H. BURTON.

o-Thiolphenylhydrazine. P. C. GUHA and T. N. GHOSH (*J. Indian Inst. Sci.*, 1929, 12A, 31—35).—Attempts to convert o-aminothiophenol into o-thiolphenylhydrazine through 2:2'-diaminodiphenyl disulphide by reduction of its bisdiazonium chloride failed. The latter does not interact with aniline or potassium ethyl xanthate, but decomposes in presence of water, giving 2:2'-dihydroxydiphenyl disulphide and diphenylene disulphide 2:2'-oxide,



Failure to nitrosate 2:2'-diacetamidodiphenyl disulphide, m. p. 154°, is recorded. 2-Phenyl-5:6-benzo-1:3:4-thiadiazine, m. p. 109°, obtained by fusing together sulphur and benzoylphenylhydrazine, decomposes when fused with potassium hydroxide, hydrogen sulphide and benzoic acid being among the reaction products. R. J. W. LE FÈVRE.

Condensation products from m- or p-cresol and aliphatic ketones. Alkylisopropylphenols and alkylated coumarans. CHEM. FABR. AUF ACTIEN (VORM. E. SCHERING).—See B., 1929, 236.

Introduction of thiocyno-groups into organic compounds. I. G. FARBENIND. A.-G.—See B., 1929, 236.

Production of N-monoalkyl derivatives of aminophenols. W. TRAUBE and E. HELLRIEGEL.—See B., 1929, 236.

Manufacture of halogenated organic compounds [aromatic sulphonarylamides and arylamines]. COMP. NAT. MAT. COL.—See B., 1929, 276.

Manufacture of 2:3-aminonaphthol and derivatives. I. G. FARBENIND. A.-G.—See B., 1929, 276.

Importance of acetone and boric acid methods in the study of alicyclic 1:2-diols. C. J. MAAN (*Rec. trav. chim.*, 1929, 48, 332—350).—Oxidation of substituted cyclohexenes with potassium permanganate in presence of alcohol and magnesium sulphate solution at -50° to -40° gives the corresponding cis-1:2-diols in 20—30% yield. When the cyclohexenes (or cyclopentenenes) are oxidised with perbenzoic acid in chloroform solution the corresponding oxides result. These are hydrated (usually by shaking with cold 0.02N-hydrochloric acid) giving the corresponding trans-1:2-diols. 1-Phenylcyclohexene-1:2-oxide yields a mixture of the cis- and trans-glycols when hydrated with 0.05N-sulphuric acid. 1-Phenylcyclopentene-1:2-oxide could not be converted into the diol. Condensation of cis-1:2-diols with acetone in presence of concentrated sulphuric acid affords the isopropylidene ethers. The following are described: 1-methylcyclopentane-1:2-diol isopropylidene ether, b. p. 157.5—157.8°/760 mm., *d*₄²⁵ 0.9469, *n*_D²⁵ 1.4300; 1-phenylcyclopentane-1:2-diol isopropylidene ether, m. p. 52.5—53.5°; 1-methylcyclohexane-1:2-diol isopropylidene ether, b. p. 183.5—

184°/760 mm., d^{20}_D 0.9701, n^{20}_D 1.4496; 1-phenylcyclohexane-1:2-diol isopropylidene ether, b. p. 155—157°/18 mm., d^{20}_D 1.066, n^{20}_D 1.5304. The *trans*-diols do not furnish isopropylidene derivatives. The specific conductivity of boric acid is increased by the addition of *cis*-1-methylcyclopentane-1:2-diol, but is lowered by the *trans*-derivatives. The conductivity is also lowered by addition of either the *cis*- or *trans*-forms of 1-methyl- and 1-phenylcyclohexane-1:2-diols. Treatment of *cis*-1-methylcyclopentane- and 1-methylcyclohexane-1:2-diols with a saturated aqueous solution of boric acid and 50% potassium hydroxide solution gives the potassium salts of the resulting boric acid complexes, $C_6H_{10}\langle O \rangle B \cdot OK, 4H_2O$ and

$C_7H_{10}\langle O \rangle B \cdot OK, 4H_2O$, respectively. In aqueous solution these salts undergo hydrolysis, since continuous extraction with chloroform furnishes the free diol. The degree of hydrolytic dissociation is, however, much smaller for the cyclopentane than for the cyclohexane derivative: the same relationship is also found for the corresponding 1-phenyl derivatives. Addition of *trans*-1-methylcyclopentane- and -1-methylcyclohexane-1:2-diols to potassium borate does not result in the formation of any complex. *cis*-1-Phenylcyclopentane-1:2-diolboric acid, $C_{11}H_{12}O_2B \cdot OH$, m. p. 107—110°, is obtained by treating the diol with boric acid in aqueous solution. The boric acid complex from the same diol described by Coops (Diss., Delft, 1928, 91) has the composition $[(C_{11}H_{12}O_2)_2B]H$. Neither of the 1-phenylcyclohexane-1:2-diols gave boric acid complexes.

It is shown that the decomposition constant of the diol-borate complex is smaller in borate solution than in boric acid, and conductivity measurements should be carried out in the former. H. BURTON.

Action of sulphites on aromatic amino- and hydroxy-compounds. XIII. Action of sulphites on resorcinol (synthesis of *m*-hydroxyazo-dyes), *p*-phenylenediamine and its derivatives. H. T. BUCHERER and E. HOFFMANN (J. pr. Chem., 1929, [ii], 121, 113—152).—By prolonged heating of resorcinol with sodium hydrogen sulphite solution, a sodium sulphurous ester of resorcinolsulphonic acid (I) is formed. This reacts very slowly with aqueous ammonia, forming probably a sulphite compound of sodium *o*-hydroxysulphanilate. Interaction of resorcinol, sodium hydrogen sulphite, and phenylhydrazine in boiling aqueous solution gives, in small yield, a hydrogen sulphite compound of 3-hydroxyazobenzene-4-sulphonic acid (sodium salt). The yellowish-red dye is turned blue by mineral acid. It is decomposed by boiling sodium hydrogen sulphite solution into aniline and (?) *m*-aminophenol-6-sulphonic acid. It is obtained in better yield from phenylhydrazine and I. When *p*-phenylenediamine is boiled with an equivalent of resorcinol in sodium hydrogen sulphite solution or with a solution of I good yields of *p*-amino-*m*-hydroxydiphenylamine-*p*'-sulphonic acid, darkening at 180° and charring at 270° (benzoyl derivative, m. p. 107°), are obtained, from which, by diazotisation and coupling, various azo-dyes were prepared.

No reaction occurs between acetyl-*p*-phenylenedi-

amine, *p*-aminophenol, or *p*-aminosalicylic acid and resorcinol-sodium hydrogen sulphite mixture.

m-Phenylenediamine by interaction with aqueous sodium hydrogen sulphite loses ammonia giving the same product as is obtained directly from resorcinol. *m*-Tolylenediamine also loses ammonia, but from the character of the azo-dye obtained by coupling the product with diazotised *p*-nitroaniline, does not appear to form a sulphonic acid. Phenol is unattacked by sodium hydrogen sulphite solution even in the presence of *p*-phenylenediamine.

By the action of *p*-phenylenediamine on 1:4-, 1:5-, and 1:6-naphthylaminesulphonic acids and 1:2:4-aminonaphtholsulphonic acid in the presence of sodium hydrogen sulphite solution the corresponding *p*-aminophenyl-naphthylaminesulphonic acids and 1-*p*-aminophenylamino-2-naphthol-4-sulphonic acid (which readily undergoes oxazine ring formation by oxidation) respectively are obtained. The benzoyl derivative of *p*-aminophenyl- α -naphthylamine-6-sulphonic acid couples with diazotised *p*-nitroaniline to give a bluish-violet dye. R. J. W. LE FÈVRE.

Cholesterol and phytosterol and the spectroscopy of the colour reactions of the sterols in general. J. MORRIS (J. S. African Chem. Inst., 1929, 12, 16—20).—Spectroscopic examination of the closely similar colour reactions of cholesterol and sitosterol shows that there is a slight difference in the position of the bands; these sterols are therefore not exactly isomeric. The reactions of ergosterol, zymosterol, and coprosterol are also described.

F. R. ENNOS.

Oxidation of cholesterol. Mechanism of oxidation with chromic acid. S. MINOVIĆ and M. VANGHELOVIĆ (Bull. Acad. Sci. Roumaine, 1929, 11, 20—25).—See this vol., 440.

Transformation of cholesterol by X-rays. A. H. ROFFO and L. M. CORREA.—See this vol., 523.

Mobile anion tautomerism. III. Activation of three-carbon anionotropic systems by alkyl and aryl groups. H. BURTON (J.C.S., 1929, 455—458).—When a solution of α -methylallyl *p*-nitrobenzoate, m. p. 43—44°, in acetic anhydride is boiled for 24 hrs. no interconversion into the γ -substituted allyl ester occurs, as with the corresponding phenyl derivative (A., 1928, 880). The activation of the three-carbon anionotropic system by the methyl group is, therefore, small. Magnesium phenyl bromide reacts with crotonaldehyde yielding α -phenyl- γ -methylallyl alcohol, b. p. 121.5—123.5°/14 mm., which when acetylated with boiling acetic anhydride affords γ -phenyl- α -methylallyl acetate (I), b. p. 141—144°/15 mm., showing that activation by the phenyl group predominates. Hydrolysis of I with alcoholic potassium hydroxide gives γ -phenyl- α -methylallyl alcohol [phenylcarbimide derivative, m. p. 92—93° (lit. 94—95°)], also acetylated to I, whilst treatment with ozone in chloroform solution, and subsequent decomposition of the ozonide with boiling water, affords benzoic and pyruvic acids. The activation of three-carbon prototropic systems by the phenyl group (Ingold and Shoppee, this vol., 556) in addition to the anionotropic systems shows that the phenyl

group is able, by tautomeric electron-displacements of either sign promoted by the requirements of the system, to absorb an electric charge of either sign produced by the ionisation of an attached atom or group.

H. BURTON.

Dehydration of s-disubstituted $\alpha\beta$ -glycols and the isomerisation of the corresponding ethylene oxides. Influence of the affinity capacities of cyclic and aliphatic radicals. (MLLE.) J. LÉVY and F. GOMBINSKA (Compt. rend., 1929, 188, 711—713).—In continuation of previous work (A., 1927, 662), the following pairs of glycols and ethylene oxides are found each to yield the same ketone in accordance with theory: γ -phenylpropane- $\beta\gamma$ -diol and α -phenyl- Δ^a -propylene oxide give benzyl methyl ketone; δ -phenylbutane- $\gamma\delta$ -diol and α -phenyl- Δ^a -butylene oxide give benzyl ethyl ketone; ϵ -phenylpentane- $\delta\epsilon$ -diol and α -phenyl- Δ^a -n-amylene oxide give benzyl propyl ketone; δ -phenyl- β -methylbutane- $\gamma\delta$ -diol and α -phenyl- γ -methyl- Δ^a -n-butylene oxide give benzyl isopropyl ketone; $\alpha\gamma$ -diphenylpropane- $\alpha\beta$ -diol and $\alpha\gamma$ -diphenylpropylene oxide give dibenzyl ketone; α -p-methoxyphenylpropane- $\alpha\beta$ -diol and α -p-methoxyphenyl- Δ^a -propylene oxide give p-methoxybenzyl methyl ketone; α -p-methoxyphenylbutane- $\alpha\beta$ -diol and α -p-methoxyphenyl- Δ^a -n-butylene oxide give p-methoxybenzyl ethyl ketone; α -p-methoxyphenylpentane- $\alpha\beta$ -diol and α -p-methoxyphenyl- Δ^a -n-amylene oxide give p-methoxyphenyl propyl ketone.

G. A. C. GOUGH.

Stovaine. I. RIBAS and A. RANCAÑO (Anal. Fis. Quím., 1928, 26, 430—434).—The relationship of the optically inactive "stovaine" (hydrochloride of methylethylidimethylaminomethylcarbinol benzoate) to the d- and l-forms (A., 1928, 49) has been investigated. Inactive stovaine is found to be a true racemic compound. The saturated solution of the racemate in brine readily dissolved either active form. The m. p. curve of mixtures of the d- and l-forms is of the characteristic symmetrical type corresponding with the formation of a racemate, m. p. 175°, with eutectics at 172°. r-Stovaine has d_{25}^{20} 1.1860, whereas l-stovaine has d_{25}^{20} 1.1698. Dilatometric measurements show that the racemate is stable between -10° and 170°, the range of observation.

R. K. CALLOW.

Di- and tetra-hydro- β -naphthoic acids obtained by catalytic hydrogenation. A. LEÓN and A. CHARRO (Anal. Fis. Quím., 1928, 26, 423—429; cf. Ranedo and León, A., 1928, 173).—Catalytic hydrogenation of β -naphthoic acid was carried out in acetic acid solution in presence of platinum oxide-platinum-black. Using 1 mol. of hydrogen, two new dihydro- β -naphthoic acids were obtained, one, m. p. 140—141° (chloride, b. p. 181—182°/29 mm., amide, m. p. 191°), and, in small quantity, a second, m. p. 132—133° (chloride, b. p. 182°/25 mm., amide, m. p. 133—134°). Hydrogenation by 2 mols. of hydrogen yielded a single product, a new tetrahydro- β -naphthoic acid, m. p. 153° (chloride, b. p. 196—197°/50 mm.; amide, m. p. 139°), which was also obtained by hydrogenation in aqueous alkaline solution and by further hydrogenation of the dihydro-acid of m. p. 132—133°. Hydrogenation of Sowinski's tetrahydro- β -

naphthoic acid, m. p. 97° (A., 1891, 1380), or of the new tetrahydro-acid yielded decahydro- β -naphthoic acid, m. p. 72—76°, identical with the product of complete hydrogenation of β -naphthoic acid (*loc. cit.*).

R. K. CALLOW.

ζ -Phenyl- $\Delta^{a\gamma\epsilon}$ -heptatrienoic acid. D. VORLÄNDER and E. DAHN (Ber., 1929, 62, [B], 545—549; cf. Engelberg, Diss., Berlin, 1914).— δ -Phenyl- $\Delta^{a\gamma}$ -pentadienal is converted by malonic acid in presence of aqueous-alcoholic ammonia or pyridine into ϵ -phenyl- $\Delta^{a\beta\epsilon}$ -pentadienylidenemalonic acid, Ph·[CH:CH]₂·CH:C(CO₂H)₂, m. p. about 191° (corr. decomp.) according to the rate of heating, which passes in acetic anhydride at 120—130° into ζ -phenyl- $\Delta^{a\gamma\epsilon}$ -heptatrienoic acid, m. p. I about 199°, II 189—190° (corr.). In chloroform the acid absorbs 3 mols. of bromine without marked evolution of hydrogen bromide. The potassium, sodium, and ammonium salts, methyl ester, m. p. 114° (corr.), ethyl ester, m. p. 91° (corr.), chloride, anilide, m. p. 213° (corr.), p-toluidide, m. p. 209° (corr.), p-anisidide, m. p. 203—204° (corr.), and p-phenetidide, m. p. 210—211° (corr.), are described. Reduction with sodium amalgam appears to give a tetrahydro-product.

Luminescence phenomena do not appear definitely related to the more or less saturated state of the compounds. The tetrabromide of p-methoxyphenylpentadienoic acid phosphoresces almost more strongly than the doubly-unsaturated acid. Anisic acid phosphoresces at least as strongly as p-methoxycinnamic acid or methyl phenylheptatrienoate, whereas benzoic acid is less powerful than cinnamic acid. The luminescence phenomena vary with the position of the double linking. Complete hydrogenation has a weakening effect, but the rule is not without exception. The condensation products of amines and aldehydes appear black in the light of the quartz-mercury lamp whether they contain more or fewer C:C linkings or methoxy-groups. Ethyl p-azoxycinnamate appears black. Phenylhydrazones shine brightly and anilides and anisidides of acids appear more or less bright.

H. WREN.

Amino-derivatives of hydroxybenzoic acids.

E. PUXEDDU (Gazzetta, 1929, 59, 10—15).—The preparation of 5-aminosalicylic acid by the reduction of benzeneazosalicylic acid (acetyl derivative, m. p. 145°) by phenylhydrazine (cf. A., 1906, 8, 995) is repeated; o-tolueneazosalicylic acid, m. p. 186° (obtained from diazotised o-toluidine and salicylic acid) is also used, with advantage. 5-Aminosalicylic acid (diacetyl derivative, m. p. 184°) can be converted into the 5-hydroxy-compound (gentisic acid) by preparing diazosalicylic acid (explodes at 162°; cf. Goldberg, A., 1879, 928), and heating this in dilute sulphuric acid. Similarly, 6-benzeneazo-m-hydroxybenzoic acid is reduced by phenylhydrazine to 6-amino-m-hydroxybenzoic acid (darkens 235°, decomp. 252°; cf. Limpricht, A., 1891, 1037), which may be converted into the diazo-compound (explodes 169°); this also when heated in dilute sulphuric acid gives rise to gentisic acid.

E. W. WIGNALL.

Syntheses in the amino-acid group. II. α -Anisylideneamino- β -lactones. G. MINUNNI and S. D'URSO (Gazzetta, 1929, 59, 32—39).—The con-

densation of aldoximes with β -ketonic esters in the presence of phosphoric acid (cf. A., 1928, 1245) is effected with α -anisaldoxime.

[With V. BELLECCI.]—With ethyl acetoacetate, this gives α -anisylideneaminocrotono- β -lactone, m. p. 179–180°, which is readily decomposed by phenylhydrazine or by alkali.

[With I. OTTAVIANO.]—With ethyl benzoylacetate, the product is α -anisylideneaminocinnamo- β -lactone, m. p. 166–166.5°, which is similarly decomposed.

E. W. WIGNALL.

Syntheses in the amino-acid group. III. Behaviour of α -arylideneaminocinnamo- β -lactones with phenylhydrazine and with hydroxylamine. New method for the replacement of hydrogen by the amino-group. G. MINUNNI [with I. OTTAVIANO and V. SPINA] (Gazzetta, 1929, 59, 116–128).—In an attempt to hydrolyse off the arylidene group from α -arylideneaminocinnamo- β -lactones, it was found that the lactone ring was also affected. Thus the product from the benzylidene derivative is α -amino- β -hydroxycinnamic acid phenylhydrazide, m. p. 148–149° (decomp.), which has the formula $C_{15}H_{15}O_3N_3$ (cf. A., 1928, 1245); benzaldehydephenylhydrazine is also formed. The anisylidene derivative (cf. preceding abstract) gives rise to the same phenylhydrazide, with anisaldehydephenylhydrazone.

Hydroxylamine, on the other hand, does not open the lactone ring, and when it reacts with a suspension of α -benzylidene- or α -anisylidene-aminocinnamo- β -lactone in alcohol, α -aminocinnamo- β -lactone, m. p. 154–154.5° (after darkening), is produced, together with the oxime of the respective aldehyde. Condensation with an araldoxime and treatment with hydroxylamine thus gives a new method by which, in certain compounds, hydrogen may be replaced by the amino-group.

E. W. WIGNALL.

Mobility of symmetrical triad (prototropic) systems. IV. Mobility in simple three-carbon system terminated by aryl groups. C. K. INGOLD and C. W. SHOPPEE (J.C.S., 1929, 447–455).—Condensation of sodium β -*p*-methoxyphenylpropionate with benzaldehyde in presence of acetic anhydride at 150–170° gives a mixture of α -*p*-methoxybenzylcinnamic acid (Ia), m. p. 165.5°, and γ -phenyl- α -*p*-methoxyphenyl- Δ^{β} -propene (IIa), having b. p. 179–180°/3 mm., $n_{D_{441}}^{20}$ 1.60246, when regenerated from its dibromide, m. p. 94° (cf. Ingold and Piggott, J.C.S., 1922, 121, 2381). by treatment with zinc dust and alcohol. Similar condensation of sodium β -phenylpropionate and anisaldehyde yields *p*-methoxy- α -benzylcinnamic acid (Ib), and α -phenyl- γ -*p*-methoxyphenyl- Δ^{β} -propene (IIb), b. p. 185–186°/3 mm., $n_{D_{441}}^{20}$ 1.60598 (dibromide, m. p. 119°). Interconversion of Ia and Ib occurs when either substance is boiled with alcoholic sodium ethoxide and the equilibrium values are 44% of the former and 56% of the latter. Similar equilibration of IIa and IIb with 1.45*N*-alcoholic sodium ethoxide at 85° gives a mixture containing 29.5% of the former and 70.5% of the latter, the proportions being determined refractometrically. The coefficient of the velocity of interconversion ($k_1 + k_2$) is 0.79 hr.⁻¹, and the equilibrium ratio k_1/k_2 is 0.42.

Methyl α -p-methoxybenzylcinnamate, b. p. 237–238°/14–15 mm., $n_{D_{441}}^{20}$ 1.60221, and *methyl p-methoxy- α -benzylcinnamate*, b. p. 245°/11–12 mm., m. p. 55°, are only slowly interconverted by methyl-alcoholic sodium methoxide at 100°, but *ethyl α -p-methoxybenzylcinnamate* (IIIa), b. p. 235°/13–14 mm., 1.58972, and *ethyl p-methoxy- α -benzylcinnamate* (IIIb), b. p. 240–241°/10–11 mm., m. p. 45°, are equilibrated by heating with 1.45*N*-alcoholic sodium ethoxide into 43.5% of IIIa and 56.5% of IIIb. The velocity coefficient is 0.0585 hr.⁻¹, and the equilibrium ratio (k_1/k_2) is 0.770. The above substances are not interconverted by boiling with alcoholic potassium hydroxide (cf. Ingold and Piggott, loc. cit.).

H. BURTON.

Goldschmiedt's condensation products of 2-hydroxy-3-naphthoic acid with aromatic aldehydes and their relationships to the triphenylmethane group. M. REBEK and V. KRAMARŠIĆ (Ber., 1929, 62, [B], 477–487).—In presence of dry hydrogen chloride, methyl 2-hydroxy-3-naphthoate and *p*-dimethylaminobenzaldehyde condense in ether, affording the hydrochloride of *methyl 2-hydroxy-1- α -chloro-*p*-dimethylaminobenzyl-3-naphthoate*, $CO_2Me \cdot C_{10}H_5(OH) \cdot CHCl \cdot C_6H_4 \cdot NMe_2 \cdot HCl$, decomp. above 200°; attempts to isolate the corresponding dye salt were unsuccessful. The chlorine atom is unusually mobile. The compound is converted by successive treatment with aqueous acetone and sodium hydrogen carbonate into *methyl 2-hydroxy-1- α -hydroxy-*p*-dimethylaminobenzyl-3-naphthoate*, m. p. 152–154° after becoming discoloured at about 140° (picrate); separation of the hydrochloride, m. p. 173–175°, from acid solutions of the ester could not be achieved, but the compound is prepared by the action of a small proportion of water on the chloro-compound dissolved in acetone. Methyl alcohol followed by sodium hydrogen carbonate converts the chloro-compound into *methyl 2-hydroxy-1- α -methoxy-*p*-dimethylaminobenzyl-3-naphthoate*, m. p. (indef.) 190°, whereas methyl alcohol alone affords the corresponding *hydrochloride oxonium chloride*, $C_{22}H_{25}O_4NCl_2$, m. p. 155–160° (decomp.), whilst in presence of benzene the compound, $C_{22}H_{25}O_4NCl_2 \cdot C_6H_6$, m. p. (indef.) 82° (decomp.), is produced. Spontaneous loss of hydrogen chloride from the oxonium compound leads to *methyl 2-hydroxy-1- α -methoxy-*p*-dimethylaminobenzyl-3-naphthoate hydrochloride*, m. p. 150–160° (decomp.), preferably prepared by the successive action of methyl alcohol and acetone on the chloro-compound. Triphenylmethyl chloride appears to be transformed by slightly aqueous acetone into a very labile oxonium chloride and by methyl alcohol and acetone into a somewhat more stable methyl-oxonium chloride. *Methyl 2-hydroxy-1- α -methoxybenzyl-3-naphthoate hydrochloride*, m. p. 169°, is described. Pyridine and aniline with methyl 2-hydroxy-1- α -chlorobenzyl-3-naphthoate afford the compounds $(C_5H_5N)Cl \cdot CHPh \cdot C_{10}H_5(OH) \cdot CO_2Me$ and $(NHPh, HCl) \cdot CHPh \cdot C_{10}H_5(OH) \cdot CO_2Me$, m. p. 179°. The action of water on triphenylmethyl chloride in pyridine, of hydrogen chloride on triphenylcarbinol in pyridine, and of anhydrous pyridine on triphenylmethyl chloride gives a product identical with the

"triphenylcarbinol hydrochloride" of Helferich and others (A., 1925, i, 790, 1269) which is shown to be triphenylmethylpyridinium chloride.

The action of copper powder on methyl 2-hydroxy-1- α -chlorobenzyl-3-naphthoate in absence of oxygen and moisture gives the dimeride, $C_{38}H_{30}O_6$, m. p. 223—224°, in about 70% yield. The compound $[CO_2Me \cdot C_{10}H_5(OH) \cdot CH(C_6H_4 \cdot NO_2)]_2$, m. p. 185—195°, is prepared similarly. H. WREN.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on polypeptides and related compounds. E. ABDERHALDEN and H. BROCKMANN. Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on polypeptides and related compounds. E. ABDERHALDEN and E. SCHWAB. Specific action of enzyme complexes in fission of polypeptides. E. ABDERHALDEN and F. SCHWEITZER. Behaviour of N-sodium hydroxide, erepsin, and trypsin-kinase towards polypeptides containing a 3:5-halogen-substituted tyrosine residue, glycyl-*d*-tyrosine, glycyl-*dl*-nitrotyrosine, and glycyl-*dl*-*o*-tyrosine. E. ABDERHALDEN and A. SCHMITZ.—See this vol., 604, 605.

Synthesis of homogentisic acid. G. HAHN and W. STENNER (Z. physiol. Chem., 1929, 181, 88—100).—A synthesis of homogentisic acid in 26% final yield is described. Quinol monobenzoate (Witt and Johnson, A., 1893, i, 571) is converted by shaking with allyl bromide in acetone solution in the presence of anhydrous potassium carbonate into its allyl ether, m. p. 71—72° (quinol itself yields mainly the diallyl ether, m. p. 36—37°). This is converted by distillation in a vacuum (bath temperature 130—280°) into a mixture of 2-allylquinol, and its mono- and di-benzoate (I), m. p. 107—108°, the latter (57% of the theoretical) being separated by utilising its smaller solubility in ether. Benzoylation of the mixture of the other two products yields a further quantity of I, which is converted (yield 83%) by ozonolysis in acetic acid at 80° into dibenzoylhomogentisic acid (II), m. p. 180—181° (methyl, m. p. 125°, and ethyl, m. p. 130—131°, esters). Hydrolysis of II with 2*N*-sodium hydroxide in an atmosphere of nitrogen gives a 90% yield of homogentisic acid.

J. W. BAKER.

Anomalies of condensation and ring-formation. R. CORNUBERT and C. BORREL (Compt. rend., 1929, 188, 919—921).—Two isomerides of α -benzyl- α -methyladipic acid, m. p. 103—106° and 133—135°, when treated with acetic anhydride, yield samples of 2-benzyl-5-methylcyclopentanone which afford the same semicarbazone, m. p. 188—189°, and the same tetrahydropyrynone derivative, m. p. 156.5°, when heated with benzaldehyde and hydrochloric acid. It was observed by Mohr (A., 1901, i, 364) that the corresponding dimethyladipic acids appear to form an equilibrium mixture.

G. A. C. GOUGH.

Synthesis of γ -phenylglutamic acid. A. VON BEZNAK (Biochem. Z., 1929, 205, 414—419).—Ethyl β -chloro- α -phenylpropionate was condensed with ethyl sodiomalonate and the resulting ester, a viscous oil, b. p. 215°/15 mm., converted by ethyl nitrite in the cold into the ethyl ester (crystallised with difficulty)

of α -oximino- γ -phenylglutaric acid, m. p. 143.5° (benzoyl derivative, m. p. 173—175°). Reduction with sodium amalgam gave γ -phenylglutamic acid, m. p. 185° (decomp.). J. H. BIRKINSHAW.

β -Amino- β -aryl-aliphatic acids from aromatic aldehydes and malonic acids. W. M. RODIONOV and E. A. POSTOVSKAJA (J. Amer. Chem. Soc., 1929, 51, 841—847).—The view that the amino-acids formed in Knoevenagel's cinnamic acid synthesis (cf. A., 1927, 137, 451) are produced by the condensation of malonic acids or esters with aldehyde-ammonias, and not from ammonia and the cinnamic acids, is supported by the observation that the latter reaction (cf. Engel, A., 1887, 793) can be effected only under much more drastic conditions and that alkylmalonic esters also give amino-derivatives, although they cannot give cinnamic acids. Thus ethyl α -amino- α -phenylpropane- $\beta\beta$ -dicarboxylate hydrochloride, m. p. 158°, is obtained almost quantitatively from benzaldehyde, ethyl methylmalonate, and alcoholic ammonia at 100°. Hydrochlorides of the following are obtained similarly: ethyl α -amino- α -piperonylpropane- $\beta\beta$ -dicarboxylate, m. p. 125—127°; ethyl α -amino- α -phenyl- and - α -piperonyl-butane- $\beta\beta$ -dicarboxylates, m. p. 166° and 157°. The β -aminopropionic acids obtained by hydrolysing these esters are also formed, together with unsaturated acids of uncertain constitution, from the alkylmalonic acids, aldehydes, and alcoholic ammonia at 100—145°. The following hydrochlorides of β -aminopropionic acid derivatives have been prepared by the latter method, other reaction products being given in parentheses: γ -amino- γ -phenylpropane- β -carboxylic, m. p. 225° [acid, $C_9H_{10}O_2$, m. p. 173° (decomp.)]; γ -amino- γ -piperonylpropane- β -carboxylic (acid, $C_{10}H_{12}O_4$, m. p. 201—202°); δ -amino- δ -phenyl-n-butane- γ -carboxylic, m. p. 249° (acid, $C_{11}H_{12}O_2$, m. p. 107°); δ -amino- δ -piperonyl-n-butane- γ -carboxylic, m. p. 215° (decomp.) (acid, $C_{12}H_{12}O_4$, m. p. 135°); γ -amino- $\alpha\gamma$ -diphenylpropane- β -carboxylic, m. p. 222° [acid, $C_{16}H_{14}O_2$, m. p. 160°, also hydrocinnamic acid and (?) α -amino- $\alpha\gamma$ -diphenylpropane], which is also obtained from benzhydramide and benzylmalonic acid in alcohol at 100—125°; and γ -amino- α -phenyl- γ -piperonylpropane- β -carboxylic acids, m. p. 203—205° (acid, $C_{17}H_{14}O_4$, m. p. 205°). H. E. F. NOTTON.

β -Amino- β -arylethane- $\alpha\alpha$ -dicarboxylic acids; mechanism of Knoevenagel synthesis of cinnamic acids. W. M. RODIONOV [with V. B. ZENKOVICH and J. A. HOLMOGORZEVA] (J. Amer. Chem. Soc., 1929, 51, 847—852).—Primary amines may be substituted for ammonia in the synthesis of β -aminopropionic acids described in the preceding abstract, but secondary amines give mainly unsaturated acids. At the ordinary or reduced temperatures benzaldehyde gives with malonic acid and amines high yields of β -amino- β -phenylethane- $\alpha\alpha$ -dicarboxylic acids, which decompose when warmed into mixtures of cinnamic acid and β -amino- β -phenylpropionic acids in proportions varying widely with the conditions. Piperonal gives smaller yields of the primary products and veratraldehyde only the cinnamic acid. β -Amino- β -arylpropionic acid hydrochlorides also decompose when heated with hydrochloric acid into β -arylalanines and with sodium acetate into cinnamic acids.

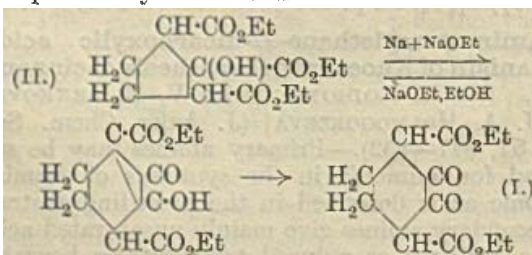
Reactions of this kind may account for the presence of these last in natural products. The following are described: β -ethylamino- β -piperonylpropionic acid, m. p. 198—200° (nitroso-derivative, m. p. 136—138°); β -dimethylamino- β -piperonylpropionic acid hydrochloride; β -amino- β -phenyl-, m. p. 148°; β -piperidyl- β -phenyl-, m. p. 163—164° (decomp.); β -piperidyl- β -piperonyl-, m. p. 150—152°; β -ethylamino- β -phenyl-, m. p. 163—164°, and β -ethylamino- β -piperonyl-, m. p. 155—157°, -ethane- α -dicarboxylic acids.

H. E. F. NOTTON.

Phenylhydroxymaleic anhydride. J. BOUGAULT and (MLLE.) B. LEROY (Compt. rend., 1929, 188, 921—923).—Ethyl phenylcyanopyruvate when treated with sulphuric acid at 0° affords ethyl β -carboxylamido- β -phenylpyruvate as well as phenylhydroxymaleic anhydride (A., 1914, i, 839). The latter combines with equimolecular amounts of primary or secondary amines to form unstable additive compounds which possess definite m. p. and pass, when heated, into the corresponding amides of phenylpyruvic acid. The additive compounds, together with those formed from tertiary amines, are insoluble in ether and yield the parent anhydride on treatment with dilute hydrochloric acid.

G. A. C. GOUGH.

Action of sodium ethoxide on ethyl cyclohexane-2 : 3-dione-1 : 4-dicarboxylate. L. DE DUSENKO (Acta Univ. Asia Med., 1928, 6, 3—16).—In the presence of an excess of alcohol ethyl cyclohexane-2 : 3-dione-1 : 4-dicarboxylate (I) is converted by the action of sodium ethoxide into ethyl 2-hydroxycyclopentane-1 : 2 : 3-tricarboxylate (II), the reverse change being effected by the action of sodium ethoxide and metallic sodium in absence of alcohol. Condensation of ethyl adipate with ethyl oxalate yields, in addition to ethyl cyclopentanone(? ol)carboxylate, I, ethyl Δ^1 -cyclopentene-1 : 2 : 3-tricarboxylate (III), and ethyl oxaladipate. The mechanism of the production of the cyclopentene ester is thus left undecided, but it is considered probable that the primary product of the rearrangement of ethyl oxaladipate is II, which then, under the influence of dry sodium ethoxide and excess of sodium, may either eliminate water to yield III, or alcohol to yield I. Conversion of II into I is explained by the scheme

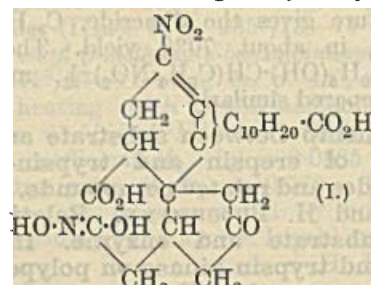


I being in equilibrium with its various mono- and dicyclic enol forms. The reverse conversion of I into II is explained by a benzil-benzilic acid type of change, $-\text{CO}\cdot\text{CO}- + \text{EtOH} \rightleftharpoons >\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$, occurring in the presence of alcoholic sodium ethoxide.

J. W. BAKER.

Bile acids. XXIII. M. SCHENCK and H. KIRCHHOFF (Z. physiol. Chem., 1929, 181, 185—198).—Treatment of deoxybilanic acid oxime with nitric acid (d 1.4) gives deoxybilanic acid together with an

amorphous substance. Similar treatment of dehydrocholic acid trioxime affords a compound (I), $\text{C}_{24}\text{H}_{34}\text{O}_5\text{N}_2$, decomp. about 280° after previous sintering and darkening. This is soluble in sodium hydroxide solution, does not give hydroxylamine by



heating with 20% hydrochloric acid probably because of its insolubility, when heated with diphenylamine and concentrated sulphuric acid gives a blue coloration, and with phenol and concentrated sulphuric acid a dark green coloration. Hydrolysis of I with hot 5% sodium hydroxide solution yields bilanic acid, the nitro-group being replaced by hydroxyl and subsequent ketonisation.

The nitro-compound, $\text{C}_{24}\text{H}_{36(\text{or } 34)}\text{O}_{10}\text{N}_2$ (A., 1928, 1008), is unaffected by treatment with hot sodium hydroxide solution and does not give a colour reaction either with diphenylamine or phenol and sulphuric acid.

H. BURTON.

Manufacture of new carboxylic acids of the fatty-aromatic series. I. G. FARBENIND. A.-G.—See B., 1929, 237.

Manufacture of alkoxynaphthamides. I. G. FARBENIND. A.-G.—See B., 1929, 276.

Dehydration of cyclohexene oxide and transformation of the cyclohexane to the cyclopentane ring. P. BEDOS and A. RUYER (Compt. rend., 1929, 188, 962—964).—When cyclohexene oxide is passed over thorium oxide at 330°, $\Delta^{1:3}$ -cyclohexadiene (I), b. p. 81°/755 mm., and cyclopentanealdehyde (II), are formed. The amounts vary greatly with small variations in experimental procedure. Dehydration is also effected with boiling phthalic anhydride, and in one experiment 15% of the theoretical amount of I and 40% of II were obtained. Similar treatment of cyclohexane-1 : 2-diol gives the same products. The formation of II is also effected by using potassium hydrogen sulphate or anhydrous oxalic, sulphuric, and phosphoric acids as dehydrating agents.

H. BURTON.

Action of semicarbazide hydrochloride and 2 : 4-dinitrophenylhydrazine hydrochloride on aldoximes and their derivatives. O. L. BRADY and F. H. PEAKIN (J.C.S., 1929, 478—479).—When a solution of an aldoxime is treated with a solution of semicarbazide hydrochloride at the ordinary temperature, the aldehydesemicarbazone is precipitated. Both α - and β -forms of three substituted benzal-oximes examined gave only one form of the semicarbazone in each case. No reaction occurs if semicarbazide is used, indicating that the oxime is first hydrolysed to the aldehyde. The *N*-methyl ethers react more rapidly than the *O*-methyl ethers presumably because of the greater ease of hydrolysis of

the former. An analogous change occurs when oximes and their *N*- and *O*-ethers are treated with a solution of 2:4-dinitrophenylhydrazine in 2*N*-hydrochloric acid. The sparing solubility of the resulting aldehyde-2:4-dinitrophenylhydrazone allows this change to be used as a convenient method for the determination of small amounts of oximes.

H. BURTON.

α -Phenyl- Δ^{88} -pentadienal and γ -phenyl- Δ^{82} -heptatrienal. II. D. VORLÄNDER and E. DAEHN (Ber., 1929, 62, [B], 541—545).—The aldehydes (cf. A., 1925, i, 1068) are known to some extent in the perfume industry and have been examined by Engelberg (Diss., Berlin, 1914). Re-investigation of the products derived from the residues obtained from the fractionation of synthetic cinnamaldehyde establishes the identity of all the specimens of the phenylpentadienal, but the data for derivatives of phenylheptatrienal are not in harmony with those of Engelberg. The following data are new or amended. α -Phenyl- Δ^{88} -pentadienal yields compounds with aniline, m. p. 112° (corr.); *p*-toluidine, m. p. 105° (corr.); *p*-anisidine, m. p. 147° (corr.); *p*-phenetidine, m. p. 137° (corr.); *p*-aminoazobenzene, m. p. I 168°, II 163° (corr.); β -naphthylamine, m. p. 145° (corr.), and *p*-aminoacetophenone, m. p. 154—155° (corr.). The phenylhydrazone, m. p. 178° (corr.), and dimorphous hydrazone, m. p. 210° (corr.) or 217° (corr.) are described. The condensation products with acetone, acetophenone, cyclopentanone, and cyclohexanone have m. p. 189°, 79°, 203—204°, and 202° (corr.), respectively. Isolation of γ -phenyl- Δ^{82} -heptatrienal from the residues of the technical cinnamaldehyde synthesis appears difficult. The products derived from a suitable fraction with phenylhydrazine [m. p. 189° (corr.)], *p*-phenetidine [m. p. I 188° (corr.), II 164° (corr.)], and *p*-aminoazobenzene [m. p. I 250—252° (corr.), II 208—210° (corr.)] have uniformly lower m. p. than those recorded by Vorländer and Kunze (*loc. cit.*). The possibility therefore exists that the properties assigned previously to the trienal actually belong to a higher homologue. The difficulty cannot be elucidated analytically.

H. WREN.

Salicylaldehyde and its methyl ether. M. COPISAROW (J.C.S., 1929, 588—589).—*o*-Tolyl carbonate is prepared in 83% yield by the action of carbonyl chloride on *o*-cresol in aqueous sodium hydroxide solution. Chlorination (Raschig, G.P. 233631) and hydrolysis of the product by methyl-alcoholic sodium hydroxide gives salicylaldehyde in 50% yield. The action of methyl sulphate on the reaction mixture obtained by hydrolysis of the chlorination product gives *o*-anisaldehyde in 38% yield. R. K. CALLOW.

Influence of substituents on Reimer-Tiemann reaction. H. H. HODGSON and T. A. JENKINSON (J.C.S., 1929, 469—471).—A standardised Reimer-Tiemann reaction has been carried out with seven phenols, and the amounts of the corresponding *o*- and *p*-hydroxybenzaldehydes produced were determined as *p*-nitrophenylhydrazones. The *o/p* ratios show that with phenol, *o*- and *m*-cresols, *m*-chloro-, -bromo-, and -iodo-phenols the *para* position is more reactive than the *ortho*, and a preponderance of the *p*-hydroxy-aldehyde results: if the reaction mixture is acidified

with mineral acid the yield of the *p*-hydroxy-aldehyde is considerably reduced. The *m*-halogenophenols give higher *o/p* ratios (0.71—0.78) than phenol (0.6), the 4-position being deactivated more than the 2-position owing to the direct and inductive effects of the halogen atom: deactivation is in the order Cl > Br > I. With *m*-cresol the *o/p* ratio (0.46) is smaller, activation of the 4-position being increased by the direct and inductive effects of the methyl group. *o*-Chlorophenol gives a ratio of 1.6, and it is assumed that the positive field of the chlorine atom attracts the negative field of the oxygen sufficiently to relieve the 2-position of a considerable amount of steric hindrance due to the oxygen. With *o*-cresol (ratio 0.46) the reverse influence is shown.

H. BURTON.

Coupling of diazonium salts in the side-chains of unsaturated compounds. II. A. QUILICO and E. FLEISCHNER (Gazzetta, 1929, 59, 39—49).—The reaction of unsaturated phenol ethers with diazonium salts (cf. A., 1928, 997) is extended to *isoeugenol*. This, in contrast to its behaviour in aqueous solutions (cf. Oddo and Puxeddu, A., 1905, i, 492; Puxeddu, A., 1906, i, 774), in alcoholic or acetic acid solutions reacts in the side-chain, which is partly eliminated. Thus with *p*-nitrobenzenediazonium sulphate, vanillin-*p*-nitrophenylhydrazone is formed, identical with a synthesised specimen; the substance forms an *acetyl* derivative, m. p. 151°, also obtained by acetylation of *acetylvanillin-p-nitrophenylhydrazone*, m. p. 179°. Reduction of the substance yields a *hydrazo*-compound (?), C₁₄H₁₅O₄N₃, m. p. 192° (decomp.). The product from 2:4-dinitrobenzenediazonium sulphate is similarly identified with *vanillin-2:4-dinitrophenylhydrazone*, m. p. 250° (decomp.). The difference in behaviour between unsaturated phenol ethers containing the $\cdot\text{CH}:\text{CHMe}$ and the $\cdot\text{CH}_2\text{CH}:\text{CH}_2$ groupings, respectively, is discussed with reference to Angeli's rule (A., 1924, i, 626). For piperonal-*p*-nitrophenylhydrazone, obtained from either *isosafole* (A., 1928, 997) or piperonal, the new m. p. 208° is given.

E. W. WIGNALL.

[Hadromal, lignin, and coniferaldehyde, preparation and identification.] Coniferaldehyde. A. HILLMER and E. HELLRIEGEL (Ber., 1929, 62, [B], 725—727; cf. Pauly and Feuerstein, this vol., 446).—Coniferaldehyde is yellow when dissolved in water, lower alcohols, glycol, and glycerol, very pale yellow in *isoamyl* alcohol, benzyl alcohol, and pyridine, colourless in ether, acetone, methyl ethyl ketone, hexane, carbon tetrachloride, carbon disulphide, benzene, and xylene. It may be used as indicator in alkalimetry, the end-point lying at *p_H* 7.6. The absorption spectra of coniferaldehyde and of its methoxymethyl ether are quite distinct from that of vanillin. The maximum of absorption of coniferaldehyde lies at $\lambda=321$ and 301 μ , of methoxymethyl-coniferaldehyde at $\lambda=312$ and 292 μ , and of vanillin at $\lambda=303$ and 282 μ . The characteristic absorption minima of the compounds lie at $\lambda=262$, 257, and 248 μ . The extinction values ϵ of coniferaldehyde and its methoxymethyl ether in the mid ultra-violet are about three times that of vanillin. The absorption spectrum of lignin resembles those of coniferyl

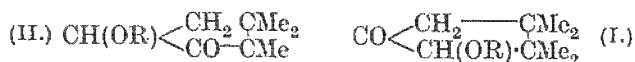
alcohol and certain of its derivatives but not that of coniferaldehyde.

H. WREN.

The keto-group. R. CORNUBERT and C. BORREL (Compt. rend., 1929, 188, 798—800).—A series of 5-substituted 2-methylcyclopentanones was prepared to investigate the influence of the substituting group on the ease of formation of the "tetrahydropyrone derivatives" (cf. A., 1926, 953). Tetrahydropyrone derivatives of the following ketones are prepared under standardised conditions by condensation with benzaldehyde (the m. p. and yield of the derivative are given in parentheses): 2:5-dimethylcyclopentanone (127°; 73%); 2-methyl-5-ethylcyclopentanone, b. p. 164—165° (98—99°; 59%); 2-methyl-5-n-propylcyclopentanone, b. p. 78—79°/18 mm. (116—116.5°; 59%); 2-methyl-5-isopropylcyclopentanone, b. p. 178° (125.5°; 10%); 2-methyl-5-n-butylcyclopentanone, b. p. 93—94°/16 mm. (101—102°; 54%); 2-methyl-5-isobutylcyclopentanone, b. p. 82—83°/13 mm. (118°; 35%); 2-methyl-5-benzylcyclopentanone, b. p. 150°/16 mm. (156.5°; 77%). 2:6-Dibenzylcyclohexanone affords a semicarbazone, m. p. 190—191°, and two oximes, m. p. 90° and 188°.

G. A. C. GOUGH.

Mobile hydrogen tautomerism analogous to the Wagner-Meerwein rearrangement. II. Tautomerism of 1(or 5)-hydroxy-2:2:3:3-tetramethylcyclopentan-5(or 1)-one and its derivatives. C. W. SHOPPEE (J.C.S., 1928, 1662—1670; cf. A., 1928, 414).—When α -acetoxy-2:2:3:3-tetramethylcyclopentanone is hydrolysed with aqueous-alcoholic sodium hydroxide, the *hydroxy-ketone* named in the title, m. p. 142° [p-nitrobenzoyl derivative, m. p. 85°; p-nitrophenylhydrazine, m. p. 223—224° (decomp.)], is obtained. With acid reducing agents it affords a mixture of 2:2:3:3- and 3:3:4:4-tetramethylcyclopentanones, and must be represented by both I and II (R=H). Similarly, by benzylation



in pyridine solution it yields a mixture of 1-benzoyloxy-2:2:3:3-tetramethylcyclopentan-5-one, m. p. 105° (I, R=Bz) [oxime, m. p. 115° (III)], and α -benzoyloxy-2:2:3:3-tetramethylcyclopentan-1-one, m. p. 60° (II, R=Bz) [oxime, oily (IV)]; III (benzoyl derivative, m. p. 135°) by reduction with sodium amalgam in glacial acetic acid gives 3:3:4:4-tetramethylcyclopentylamine, whilst IV (benzoyl derivative, b. p. 200—215°/15 mm.), similarly reduced, yields 2:2:3:3-tetramethylcyclopentylamine. When oxidated the hydroxy-ketone yields a mixture of the oximes of I and II, converted by benzylation with excess of benzoyl chloride in pyridine solution into the benzoyl derivatives of III, m. p. 135°, and IV, b. p. 200—215°/14 mm. Methylation with methyl sulphate and 10% sodium hydroxide at 100° yields mainly 5-methoxy-2:2:3:3-tetramethylcyclopentan-1-one, b. p. 88—90°/10 mm., 1.4574 (II, R=Me), reduced by hydriodic acid d 1.7 to 3:3:4:4-tetramethylcyclopentanone, and giving an oily oxime which affords 2:2:3:3-tetramethylcyclopentylamine by reduction; the isomeric 1-methoxy-ketone (I, R=Me) may be present in small quantity.

C. W. SHOPPEE.

Methylation of cycloheptanone. M. GODCHOT and (Mlle.) CAUQUIL (Compt. rend., 1929, 188, 794—796).—Methylation of cycloheptanone by the action of methyl iodide on an ethereal suspension of its sodium derivative (prepared by Haller's method), followed by separation of the resultant products by means of their semicarbazones, affords small amounts of 2:2-dimethylcycloheptanone, b. p. 191—192° (corr.)/770 mm. (semicarbazone, m. p. 174—175°; cf. Tarbouriech, A., 1913, i, 181), and 2-methylcycloheptanone, b. p. 185—186° (corr.)/760 mm., d_{20}^{25} 0.9395, n_D^{25} 1.461 (semicarbazone, m. p. 117—118°; oxime, b. p. 126°/16 mm.; oxime phenylcarbamate, m. p. 96—97°). The last-named ketone on oxidation with aqueous potassium permanganate yields ε -acetyl-n-hexoic acid (semicarbazone, m. p. 113—114°, cf. Wallach, A., 1906, i, 370).

G. A. C. GOUGH.

Three-carbon system. XX. cyclopentylidenemethyl ethyl ketone. A. H. DICKINS, W. E. HUGH, and G. A. R. KON (J.C.S., 1929, 572—580).—The interconversion of cyclopentylidenemethyl ethyl ketone (I) and Δ^1 -cyclopentenylmethyl ethyl ketone (II) and of cyclopentylidenemethyl ethyl ketone (III) and Δ^1 -cyclopentenylacetone (IV) has been studied in the same way as the interconversion of the cyclohexane analogues (A., 1928, 887). Equilibrium is attained much more rapidly in the cyclopentane compounds, and is on the side of the $\alpha\beta$ -forms instead of the $\beta\gamma$ -forms.

cyclopentylidenemethyl ethyl ketone is prepared from cyclopentylidenemethyl ethyl ketone (loc. cit.) and purified by conversion into the semicarbazone, m. p. 174°, which is accompanied by the semicarbazido-semicarbazone, m. p. 215°. The ketone regenerated from the semicarbazone has b. p. 96°/20 mm., d_{20}^{25} 0.93179, n_D^{25} 1.47801, $[R_L]_D$ 41.96. Δ^1 -cyclopentenylacetic acid is prepared from its ester or by dry distillation of cyclopentylidenemethyl ethyl ketone under reduced pressure. The acid chloride and zinc diethyl or magnesium methyl iodide yield only the $\alpha\beta$ -compound (I); the Blaise-Maire reaction under carefully controlled conditions gives a low yield of cyclopentenylmethyl ethyl ketone, which, regenerated from the semicarbazone, m. p. 135°, has b. p. 90°/21 mm., d_{20}^{25} 0.92429, n_D^{25} 1.46509, $[R_L]_D$ 41.31. Condensation with ethyl sodiomalonate, followed by hydrolysis, yields cyclopentane-spiro-4-methylcyclohexane-3:5-dione, m. p. 174—175°. The equilibrium between I and II in presence of N-alcoholic sodium ethoxide is practically reached after 20 min., and the mixture contains about 85% of I. The compounds III and IV were previously obtained as an equilibrium mixture (Kon, J.C.S., 1921, 119, 810; Kon and Linstead, A., 1925, i, 633). cyclopentylidenemethyl ethyl ketone is prepared from cyclopentylidenemethyl ethyl ketone and purified by conversion into the semicarbazone, m. p. 189°. The regenerated ketone has b. p. 70°/12 mm., d_{20}^{25} 0.94205, n_D^{25} 1.47937, $[R_L]_D$ 37.16. The iodine absorption of this material corresponds with a higher percentage of $\beta\gamma$ -compound than the equilibrium mixture, an effect which is attributed to the action of acid, and the ketone was best purified by repeated fractionation. Δ^1 -cyclopentenylacetone (from Δ^1 -cyclopentenylacetyl chloride), best purified by regeneration from the

semicarbazone and subsequent treatment with aluminium amalgam, has b. p. 69—70°/16 mm., d_4^{20} 0.93568, n_D^{20} 1.46211, $[R_L]_D$ 36.58. The ketone obtained by distillation of calcium cyclopentanediacetate (Kon, *loc. cit.*) contains only 64% of the $\alpha\beta$ -form. Distillation of calcium acetate and calcium cyclopentenylacetate yields a similar product. The equilibrium between III and IV with *N*-alcoholic sodium ethoxide is practically established after 10 min., and the mixture contains 84% of III.

Examination of cyclopentylidenecyclopentanone indicates that the point of equilibrium lies near the $\alpha\beta$ -compound. The iodometric method breaks down in the case of cyclohexenylcyclohexanone.

R. K. CALLOW.

Transposition and purity of naphthyl methyl ketones. L. CHOPIN (Bull. Soc. chim., 1929, [iv], 45, 167—168).— β -Naphthyl methyl ketone is slowly transformed into the α -isomeride at the ordinary temperature, the isomerisation being, however, dependent on the initial presence of traces of the α -isomeride. The isomerisation is accelerated by heat and acids, especially by warm concentrated hydrochloric acid. Sulphuric acid and phosphoric acid are much less effective. Solvents used in the synthesis are without influence. The β -isomeride is usually contaminated with aniline or phenylcarbimide, and in contrast to the α -ketone darkens on keeping. Treatment with phosphoric acid effects partial purification.

R. BRIGHTMAN.

Use of magnesium and methyl alcohol as reducing agent. L. ZECHMEISTER and P. ROM (Annalen, 1929, 468, 117—132).—Benzophenone gives a 90% yield of benzhydrol when reduced by absolute methyl alcohol and magnesium (small pieces of ribbon). A quantitative yield is obtained by the ammonium chloride method (A., 1926, 720). Using the new method of reduction, dibenzyl ketone gives dibenzylcarbinol (90% yield), whilst acetophenone gives phenylmethylcarbinol (45% yield), acetophenone pinacol (11%) and tarry by-products. *p*-Methoxyacetophenone gives 47% of carbinol and some pinacol. Phenacyl bromide is converted (68% yield) into phenylmethylcarbinol. Styryl methyl ketone gives β -phenylethylmethylcarbinol in 77% yield, whilst distyryl ketone gives di- β -phenylethylcarbinol (71%) and a small amount of a substance, m. p. 279°. $\alpha\alpha'$ -Dichloroethylbenzene gives an 86% yield of $\alpha\alpha'$ -dimethoxyethylbenzene, also obtained from the dichloro-compound and magnesium methoxide. Magnesium and moist methyl alcohol convert the dichloro-compound into benzhydrol, benzpinacol, etc.

Chlorobenzene is unaffected by magnesium and methyl alcohol. Bromobenzene is to a large extent dehalogenated, but gives no diphenyl. Iodobenzene gives an 80% yield of benzene, α -bromonaphthalene gives a 96% yield of naphthalene, and α -chloronaphthalene is largely dehalogenated.

Nitrobenzene, according to conditions, may give β -phenylhydroxylamine, azoxy-, azo-, or hydrazobenzene, or aniline, but some usually escapes reduction. The nitrotoluenes are reduced more smoothly. Some unchanged material is usually recovered, and some of the hydroxylamine and the toluidine is formed.

The main product is in each case, however, the azoxy-compound (yields: *o*, 57%; *m*, 70%; *p*, 61%).

Magnesium and methyl alcohol convert *o*-, *m*-, and *p*-chloro- or -bromo-nitrobenzenes into the corresponding dihalogenoazoxybenzenes, the yields being of an order similar to that using the ammonium chloride method (*loc. cit.*). Some dehalogenation also occurs. During the reduction of all compounds with halogen *ortho* to a nitro-group, intense colorations are observed. 2:5-Dibromonitrobenzene gives a 30% yield of 2:5:2':3'-tetra bromoazoxybenzene, m. p. 166°.

E. E. TURNER.

Nitration of 4-chloro-4'-bromo-benzophenone and -diphenylsulphone, and attempted nitration of 4-chloro-4'-bromodiphenyl. L. G. GROVES and E. E. TURNER (J.C.S., 1929, 509—511).—4-Chloro-4'-bromobenzophenone, m. p. 150° (corr.), was obtained by a Friedel-Crafts reaction from chlorobenzene and *p*-bromobenzoyl chloride. In sulphuric acid it is nitrated to the extent of 51% in position 3 and 49% in position 3', as determined by the mixed halogen displaced from the product by piperidine. 4-Chloro-4'-bromodiphenylsulphone, m. p. 157° (corr.) (from bromobenzene and *p*-chlorobenzenesulphonyl chloride), is mononitrated to the extent of 34% in position 3 and 66% in position 3'. Dinitration yields the 3:3'-dinitro-compound, m. p. 219° (corr.). The results are concordant with the behaviour of benzophenone and diphenylsulphone and of bromo- and chloro-benzene on nitration. 4-Chloro-4'-bromodiphenyl, m. p. 147° (corr.), was obtained from 4-chloro-4'-aminodiphenyl by diazotisation and decomposition of the diazonium perbromide in hot acetic acid. Attempted nitration yielded only decomposition products.

R. K. CALLOW.

Relative ease of formation of 5-, 6-, and 7-membered carbon rings. J. VON BRAUN and G. MANZ (Annalen, 1929, 468, 258—277).—The preparation of $\beta\gamma$ -diphenylpropyl chloride described previously (A., 1928, 174) is unsuitable for obtaining large quantities, for a considerable amount of α -methylstilbene is also produced. $\beta\gamma$ -Diphenylbutyric acid is therefore more conveniently prepared as follows: Reduction of ethyl α -phenylcinnamate with alcohol and a large excess of sodium gives some $\alpha\beta$ -diphenylpropane, b. p. 145—148°/13 mm., m. p. 50° (cf. Klages and Heilmann, A., 1904, i, 487, who describe it as a liquid), but mainly $\beta\gamma$ -diphenylpropyl alcohol, b. p. 185—188°/13 mm. (yield 60%). The latter is converted by fuming hydrobromic acid at 130° into $\beta\gamma$ -diphenylpropyl bromide, b. p. 188—190°/13 mm., which with aqueous-alcoholic potassium cyanide gives some methylstilbene, but a 50% yield of $\beta\gamma$ -diphenylbutyronitrile, b. p. 204—206°/13 mm. The corresponding acid, obtained by heating the nitrile with concentrated hydrochloric acid at 120°, is converted by thionyl chloride into a chloride (not isolated) which with aluminium chloride in carbon disulphide gives 1-keto-3-phenyl-1:2:3:4-tetrahydronaphthalene, m. p. 65—66° (yield 75%) (oxime, m. p. 190°; semicarbazone, sinters 204°, m. p. 208°), reduced by Clemmensen's method to 2-phenyltetrahydronaphthalene, b. p. 180—181°/13 mm., d_4^{25} 1.0579, n_D^{25} 1.5980. The constitution of the last-named follows

from its oxidation (heated litharge) to β -phenyl-naphthalene.

γ -Phenylpropyl bromide and ethyl sodiobenzylmalonate give a 70% yield of *ethyl benzyl- γ -phenylpropylmalonate*, b. p. 244—247°/13 mm., hydrolysed to the acid, which begins to lose carbon dioxide at 96°, and, when heated in a vacuum, gives *8-phenyl- α -benzyl-n-valeric acid*, b. p. 243—245°/13 mm. (yield 80%). Thionyl chloride gives the acid chloride (not isolated), which is converted by carbon disulphide and aluminium chloride into *2- γ -phenylpropyl-1-hydrindone*, b. p. 227—229°/13 mm. (yield 60%) (*semicarbazone*, m. p. 172°; *p-nitrophenylhydrazine*, m. p. 161°; *oxime*, oily, reduced to 1-amino-2- γ -phenylpropylhydrindene, b. p. 217°/13 mm., which forms a *hydrochloride*, m. p. 169°, and a *picrate*, m. p. 203°). Clemmensen reduction of the ketone gives *2- γ -phenylpropylhydrindene*, b. p. 197°/13 mm., d_4^{25} 1.0128, n_D^{25} 1.5667. Bromine converts the hydrindone in chloroform solution into a *bromo-derivative*, m. p. 82°, presumably the 2-compound. The constitution of the hydrindone follows from its formation by reducing *2-cinnamylidene-1-hydrindone*, m. p. 124° (from α -hydrindone and cinnamaldehyde), with palladised charcoal.

When anhydrous ethyl sodiobenzylmalonate is heated at 100° with ethyl β -iodo- or β -chloro-propionate, an 85% yield of *ethyl α -phenylbutane- $\beta\beta\delta$ -tricarboxylate*, b. p. 219—221°/13 mm., is obtained. The ester is hydrolysed by aqueous-alcoholic alkali to *α -phenylbutane- $\beta\beta\delta$ -tricarboxylic acid*, m. p. 166° (decomp.), together with some *α -phenylbutane- $\beta\delta$ -dicarboxylic acid*. The tricarboxylic acid, when heated in a vacuum, gives *α -benzylglutaric acid*, b. p. 231—236°/0.5 mm., m. p. 76° (not an oil, as lit.). Thionyl chloride converts this acid into the *anhydride*, m. p. 81°, which with aluminium chloride in nitrobenzene gives (yield 30%) *2-ethyl-1-hydrindone- ω -carboxylic acid*, m. p. 238—243°/14 mm. (*oxime*, m. p. 145°; *semicarbazone*, m. p. 244—246°), converted by heating with soda-lime into *α -hydrindone* (yield 50%).

Reduction of *o*-phenylbenzonitrile with hydrogen (15—20 atm.) in presence of nickel at 120—130° gives a 45% yield of *o*-phenylbenzylamine, b. p. 163°/12 mm. (*hydrochloride*, m. p. 212°; *picrate*, m. p. 188°; *acetyl derivative*, m. p. 125°; *benzoyl derivative*, m. p. 95°), which is converted by sodium nitrite and acetic acid into *o*-phenylbenzyl alcohol, b. p. 174°/13 mm. Concentrated hydrochloric or hydrobromic acid at 100° converts this into *o*-phenylbenzyl chloride, b. p. 154°/12 mm., or *o*-phenylbenzyl bromide, b. p. 166°/12 mm. The latter is converted (1) by ammonium dithiocarbamate into the *dithiourethane*, $C_6H_4Ph \cdot CH_2 \cdot S \cdot CS \cdot NH_2$, m. p. 106°, hydrolysed to *o*-phenylbenzylmercaptan, b. p. 160°/12 mm., (2) by sodium in presence of ether into *2:2'-bisdiphenylethane*, b. p. 260°/12 mm., (3) by aqueous-alcoholic potassium cyanide into *ω -cyano-2-methyldiphenyl*, b. p. 182°/12 mm., which is readily hydrolysed to *2-methyldiphenyl- ω -carboxylic acid*, m. p. 114°, and (4) by sodiomalonic ester into *ethyl 2-ethyldiphenyl- $\omega\omega$ -dicarboxylate*, b. p. 245—258°/12 mm. (yield 80%). The latter is readily hydrolysed to the acid, which loses carbon dioxide in hot aqueous solution to give *β -2-diphenylpropionic acid*, m. p. 125°. The latter is converted by thionyl chloride into the chloride (not

isolated), which with aluminium chloride in light petroleum gives *4-phenyl-1-hydrindone*, b. p. 200—205°/11 mm. (*semicarbazone*, m. p. 192°). When heated with 30% nitric acid at 200° the latter gave a crude product containing no diphenic acid (proof of constitution).
E. E. TURNER.

Ease of substitution of aromatically bound hydrogen atoms. J. VON BRAUN, G. MANZ, and E. REINSCH (Annalen, 1929, 468, 277—303).—Phenyl *m*-tolyl ketone, b. p. 183—185°/16 mm., reacts with zinc and ethyl bromoacetate to give crude *ethyl β -m-tolylcinnamate*, b. p. 208—210°/16 mm., which cannot be freed from unchanged ketone. Hydrolysis of the product gives *β -m-tolylcinnamic acid*, m. p. 114°, b. p. 229—232°/17 mm. Hydrogenation of the latter affords *β -phenyl- β -m-tolylpropionic acid*, m. p. 109°, b. p. 206—210°/13 mm., the *chloride*, b. p. 200°/16 mm., of which is converted (yield 60%) by aluminium chloride in carbon disulphide into *3-phenyl-5-methyl-1-hydrindone*, b. p. 210—215°/16 mm. (*oxime*, formed slowly, m. p. 163°, is difficult to hydrolyse, but gives the hydrindone as a solid, m. p. 61°). Oxidation of the hydrindone with alkaline permanganate gives *benzophenone-2:5-dicarboxylic acid*, m. p. 285°, which establishes the constitution.

From ethyl *m*-methylbenzylmalonate and benzyl chloride may be obtained *ethyl benzyl-m-methylbenzylmalonate*, b. p. 231—233° (?), hydrolysed to *benzyl-m-methylbenzylmalonic acid*, melting at 168° to give *benzyl-m-methylbenzylacetic acid*, $C_6H_4Me \cdot CH_2 \cdot CH(CH_2Ph) \cdot CO_2H$, m. p. 67—68°. Aluminium chloride converts the chloride of the latter into *2-benzyl-5-methyl-1-hydrindone*, m. p. 87—89° (*oxime*, m. p. 103°; *semicarbazone*, m. p. 196°), and a liquid which appears to be mainly the same hydrindone (oxidation gives benzoic and trimellitic acids). The constitution of the hydrindone follows from the following synthesis: the chloride of *β -m-tolylpropionic acid* is converted by aluminium chloride into the known *5-methyl-1-hydrindone*, oxidised to trimellitic acid and therefore not a mixture, as thought by Young (A., 1892, i, 1221). *5-Methyl-1-hydrindone* readily condenses with benzaldehyde in presence of alkali. The *2-benzylidene-5-methyl-1-hydrindone*, m. p. 134°, so obtained is hydrogenated in methyl alcohol in presence of palladium to give the above benzylmethylhydrindone.

Phenyl *o*-tolyl ketone, zinc, and ethyl bromoacetate give *ethyl β -o-tolylcinnamate*, b. p. 160—180°/14 mm. (about 35% of unchanged ketone is present), hydrolysed to *β -o-tolylcinnamic acid*, m. p. 114°, b. p. 218—220°/14 mm. The latter when reduced affords *β -phenyl- β -o-tolylpropionic acid*, m. p. 129°, and the *chloride*, b. p. 189°/16 mm., of the latter is converted (80% yield) by aluminium chloride into *3-o-tolyl-1-hydrindone*, m. p. 87°, b. p. 195—196°/14 mm. (*oxime*, m. p. 166°; *semicarbazone*, m. p. 267°), oxidised to *benzophenone-2:2'-dicarboxylic acid*, m. p. 148—150° (*anhydride*, m. p. 212°). Clemmensen reduction of the hydrindone gives *1-o-tolylhydrindene*, m. p. 57°, b. p. 160—162°/14 mm.

From phenyl *p*-tolyl ketone, *β -p-tolylcinnamic acid*, m. p. 140° (*ethyl ester*, b. p. 205—210°/14 mm.) is obtainable in good yield. The derived *β -phenyl- β -p-*

tolylpropionic acid, m. p. 140°, b. p. 230—232°/14 mm., forms a *chloride*, b. p. 194°/14 mm., which is converted in 70% yield into 3-*p*-tolyl-1-hydrindone, m. p. 92°, b. p. 202—204°/14 mm. (*oxime*, m. p. 200°; *semicarbazone*, m. p. 219°). The constitution of this ketone follows from its oxidation to benzophenone-2:4'-dicarboxylic acid, m. p. 241° (lit. 235°). Reduction affords 1-*p*-tolylhydrindene, b. p. 168—170°/14 mm., d_4^{20} 1.0455, n_D^{20} 1.5878.

ω -Bromo-*p*-xylene and ethyl benzylmalonate give rise to the *ethyl ester*, b. p. 232—235°/14 mm., of benzyl-*p*-methylbenzylmalonic acid, melting and decomposing at 155—157° to give β -*p*-tolyl- α -benzylpropionic acid, m. p. 88—89°, b. p. 235—237°/13 mm. (*amide*, m. p. 131°). The chloride of the latter is converted by aluminium chloride in carbon disulphide mainly into 2-*p*-methylbenzyl-1-hydrindone, b. p. 221—223°/14 mm. [*oxime* (not pure), m. p. 131—142°; *phenylhydrazone* (not pure), decomp. 105—113°; *semicarbazone*, m. p. 195—197°], but also some (?) 2-benzyl-6-methyl-1-hydrindone. The composition of the product is deduced as follows: α -Hydrindone readily condenses with *p*-tolualdehyde to give 2-*p*-methylbenzylidene-1-hydrindone, m. p. 138°, reduced to 2-*p*-methylbenzyl-1-hydrindone, b. p. 223—226°/15 mm. (*oxime*, m. p. 132°; *phenylhydrazone*, m. p. 109°, both depressing the m. p. of the corresponding derivatives of the Friedel-Crafts product). 6-Methylhydrindone and benzaldehyde give 6-methyl-2-benzylidene-1-hydrindone, m. p. 165°, reduced to 2-benzyl-6-methyl-1-hydrindone, m. p. 38—39°, b. p. 206—210°/12 mm. (*oxime*, m. p. 130—143°, depressing the m. p. of the Friedel-Crafts product). Moreover, oxidation of the Friedel-Crafts ketone mixture gives terephthalic, trimellitic, and benzoic acids. A limited amount of ring-closure must therefore occur in the tolyl nucleus *meta* to the methyl group.

Catalytic reduction of the above ethyl β -*p*-tolylcinnamate in an autoclave in presence of nickel gives ethyl β -phenyl- β -*p*-tolylpropionate, m. p. 41°, b. p. 205—207°/14 mm., reduced by sodium and alcohol to γ -phenyl- γ -*p*-tolyl-*n*-propyl alcohol, b. p. 210—215°/20 mm. The latter is converted by fuming hydrobromic acid at 100° into γ -phenyl- γ -*p*-tolyl-*n*-propyl bromide, b. p. 202—203°/14 mm., and thence into γ -phenyl- γ -*p*-tolyl-*n*-butyronitrile, b. p. 211—222°/14 mm., and γ -phenyl- γ -*p*-tolyl-*n*-butyric acid, b. p. 238—239°/14 mm. The chloride, b. p. 205—208°/14 mm., of the latter is converted (yield 70%) by aluminium chloride in carbon disulphide into 4-*p*-tolyl-1-keto-1:2:3:4-tetrahydronaphthalene, m. p. 75°, b. p. 198—200°/14 mm. (*semicarbazone*, m. p. 204°), oxidised to benzophenone-2:4'-dicarboxylic acid (proof of constitution), and containing a small quantity of 4-phenyl-7-methyl-1-ketotetrahydronaphthalene.

Zinc, ethyl bromoacetate, and phenyl β -naphthyl ketone produce the *ethyl ester*, b. p. 250—260°/13 mm., of β -2-naphthylcinnamic acid, m. p. 217°, reduced to β -phenyl- β -2-naphthylpropionic acid, m. p. 132°. The chloride of this acid is converted by aluminium chloride in carbon disulphide into 3-phenyl-6:7-benzhydrindone, m. p. 119°, b. p. 257—259°/13 mm. [*oxime*, m. p. 190—192°; *semicarbazone*, m. p. 235—238° (decomp.)], reduced to 3-phenyl-6:7-benzhydr-

indene, m. p. 79°, b. p. 226—229°/13 mm. The constitution of the product follows from its oxidation by alkaline permanganate to 2-benzoyl- α -naphthoic acid (converted by alkali fusion into α -naphthoic and benzoic acids), and from the fact that the hydrindene is different from 1- β -naphthylhydrindene, m. p. 47°, b. p. 229—230°/13 mm., obtained by hydrogenation (palladium) of 1- β -naphthylindene, m. p. 88°, b. p. 246—250°/14 mm., which is obtained by treating α -hydrindone with magnesium β -naphthyl bromide.

From ethyl benzylmalonate and ω -bromo- β -methyl-naphthalene is obtainable (60% yield) the *ethyl ester*, b. p. 225—230°/0.3 mm., of α -phenyl- γ -2-naphthylpropane- β - β -dicarboxylic acid, melting at 111—113° to give β -2-naphthyl- α -benzylpropionic acid, m. p. 103—104°, b. p. 235—240°/vac. The chloride of the latter is converted by aluminium chloride in nitrobenzene into 2-benzyl-6:7-benzhydrindone, m. p. 72—74°, b. p. 205—210°/0.5 mm., identical with the product of reducing 2-benzylidene-6:7-benzhydrindone, m. p. 166°, with hydrogen and palladium in methyl-alcoholic solution.

α -Phenyl- γ -1-naphthylpropane- β - β -dicarboxylic acid (*ethyl ester*, b. p. 225—230°/0.5 mm.) decomposes when heated in a vacuum to give β -1-naphthyl- α -benzylpropionic acid, m. p. 101—103°, b. p. 245—250°/0.8 mm. The chloride of this acid undergoes Friedel-Crafts ring closure to give (not less than 50% yield) 2-benzylperinaphthindanone, b. p. 205—210°/4 mm. (*oxime*, m. p. 163—164°). The other product is apparently not 2- α -naphthylmethylhydrindone, m. p. 87—88° (obtained by reducing 2- α -naphthylidene-1-hydrindone, m. p. 128°, from α -hydrindone and α -naphthaldehyde), but is apparently formed by ring-closure in the β -position in the naphthalene nucleus. The constitution of the *periketone* follows from its synthesis: perinaphthindanone (from β -1-naphthylpropionyl chloride and aluminium chloride in light petroleum or in carbon disulphide, but not in nitrobenzene, which gives rise to perinaphthindone, m. p. 130—143°, reducible to the indanone) condenses with benzaldehyde to give benzylidene-perinaphthindanone, m. p. 163°, reduced to the above ketone formed in the ring-closure.

From ω -bromo-2-methylnaphthalene and ethyl α -naphthylmethylmalonate, $C_{10}H_7 \cdot CH_2 \cdot CH(CO_2Et)_2$, is obtainable the *ethyl ester*, b. p. 255—260°/0.05 mm., of α -naphthylmethyl- β -naphthylmethylmalonic acid, an oil, decarboxylation of which produces α -1-naphthyl- γ -2-naphthylpropane- β -carboxylic acid, b. p. 280—290°/0.8 mm. Aluminium chloride converts the chloride of the latter in nitrobenzene solution into a mixture of 2- α -naphthylmethyl-6:7-benzhydrindone, m. p. 139°, b. p. 250—255°/0.1 mm. (also obtained by reducing α -naphthylidenebenzindanone, m. p. 189—190°), and another product or products formed by β - or *peri*-ring-closure (?).

The ring-closures effected with the benzene derivatives show that the *para*-hydrogen atom in toluene is more reactive than a hydrogen atom in benzene, the latter hydrogen atom being in turn more reactive than a *meta*-hydrogen atom in toluene. The ring-closures with the naphthalene derivatives show that an α -hydrogen atom in naphthalene is more reactive than a benzene hydrogen atom, and that the latter

is (probably) less reactive than a β -hydrogen atom in naphthalene. E. E. TURNER.

Manufacture of hydroxydiaryl ketones. I. G. FARBERIND. A.-G.—See B., 1929, 276.

Isomeric relationships in the chalkone series. VI. **Relationships between polymorphism and ethylenic isomerism.** C. WEYGAND [with E. BAUER and H. HENNIG] (Ber., 1929, 62, [B], 562—573; cf. A., 1928, 180).—The known forms of β -hydroxychalkone and its methyl and ethyl ethers are summarised as follows: β -Methoxychalkone (*o*-methyl ether), m. p. 65°, 78°, 81°, ?; series III. β -Ethoxychalkone (*o*-ethyl ether), m. p. 63°, 74°, 78°, 81°; series II. β -Hydroxychalkone (dibenzoylmethane), m. p. ?, 73°, 78°, 81°; series I. All the forms which exist in a number of closely allied substances are termed a "family." The hylotropic-isomeric varieties of a single structurally homogeneous compound are designated a "series," whilst the members of two or more series arranged in the same vertical column are "corresponding members." It is proposed to designate the individual members for the time being by a figure based on the m. p.; thus the variety m. p. 72—73° is known as form 73. Dibenzoylmethane, m. p. 72—73°, is not identical with the variety m. p. 70—71° of Dufraisse and Gillet (A., 1927, 58). The scheme of the polymorphic family is based on the following observations. (i) The m. p. serve as criteria for the mutual relationship of individual members; the scheme is complete except for the absence of two extreme members and the absence of a place for the very unstable variety 71. (ii) A second criterion is to be sought in the stability relationships of the individual members. The expectation that the most stable members of related series must be corresponding forms is not completely realised, but the relationships support rather than condemn the internal justification of the scheme. (iii) The third criterion is purely chemical and demands the hydrolysis of the corresponding members of the alkoxy-series II and III by acids to the corresponding members of the enol series I. The ethyl ether 81 gives the corresponding dibenzoylmethane 81. The stable dibenzoylmethane 78 is derived from the methyl ether 81 and the ethyl ether 78. From the methyl ether 65 the corresponding (unknown) dibenzoylmethane is not produced, its place being taken by the metastable form 73. The stable dibenzoylmethane 78 is derived from the ethyl ether 63. Conversely, dibenzoylmethane 78 yields mainly the corresponding methyl ether 81 and the ethyl ether 78. (iv) Corresponding forms may be expected to be crystallographically similar. According to Dufraisse and Gillet (*loc. cit.*), the methyl ethers 65 and 81 are to be regarded as very labile, ethylenic stereoisomerides. The corresponding members of the ethyl series, 63 and 78, lie on the boundary between isomerism and polymorphism. The more freely soluble, metastable compound can be extracted by light petroleum from the conglomerate. They give mixed m. p. but no depression. The supercooled mixture can be caused to crystallise as either variety by suitable inoculation and the metastable 63 form passes either spontaneously or on contact with the

78 variety into the latter. With the methyl ethers 65 and 81, this is not the case. These observations are confirmed by microscopic observation of the solidification mechanism of molten preparations. In two pairs of corresponding members of a polymorphic family, the one pair appears to behave as labile stereoisomerides, whereas the other consists of monotropic, polymorphic forms. The boundaries between ethylenic isomerism and polymorphism in the classic sense are therefore ill-defined. H. WREN.

Green varieties of *p*-dihydroxydibenzylidene ketones. D. VORLANDER and O. KOCH (Ber., 1929, 62, [B], 534—540).—Contrary to the previous observation that the green varieties of di-*p*-hydroxystyryl ketone are free from halogen (A., 1925, i, 1106), it is found that the presence of a minute amount of strong acid is necessary for the production of the green colour; the Beilstein test is much less sensitive than is supposed. Decolorisation of the green forms in solution or transition from green to yellow variety when preserved is not due solely to loss of the minute amount of hydrogen chloride, but also to transition from the colloidal state of the green form into the more coarsely crystalline condition of the yellow variety. If the black hydrochloride *A* is dissolved in cold, dilute alkali hydroxide and the solution is immediately acidified with acetic acid a green precipitate results; if, however, the solution is preserved for some time and then acidified, the yellow ketone separates. Explanation is found in the markedly colloidal condition of aqueous alkaline solutions of the hydroxy-ketones which causes retention of small amounts of adsorbed hydrogen chloride for variable periods even in the presence of excess of hydroxyl ions. Precisely similar phenomena are shown by other hydroxybenzylidene ketones, the behaviour of divanillylideneacetone being described in detail. The green coloration of the yellow preparations depends on the concentration and strength of the aqueous acid. In addition to the halogen acids, nitric, perchloric, and sulphuric but not acetic acids give green products. Both forms yield the same *dibenzozate*, m. p. 191° (corr.). Solutions of the green variety are markedly colloidal, whereas those of the yellow form are almost optically empty; in excess of alkali hydroxide all preparations give identical colloidal red solutions of the alkali salts. The "time reaction" is dependent on the concentration of alkali hydroxide and the temperature. *Divanillylidene*cyclohexanone has m. p. 179° (corr.). H. WREN.

Oximes of the three methylbenzils. J. MEISENHEIMER, O. BEISSWENGER, H. O. KAUFFMANN, U. VON KUMMER, and J. LINK (Annalen, 1929, 468, 202—258).—Benzaldehyde and *o*-tolyl nitromethane condense in alcoholic methylamine to give a small amount of a compound, $C_{21}H_{17}O_2N$, m. p. 195° (decomp.), but mainly (98% yield) α -nitro-2-methylstilbene, $C_{17}H_{17}C(NO_2)CHPh$, m. p. 92°. The latter is converted by methyl-alcoholic potassium hydroxide (cf. A., 1907, i, 860) into α -2-methylbenzil-7-monoxime dimethylacetal (the α_2 -acetaloxime), m. p. 179°, hydrolysed by glacial acetic acid at 100° to α -2-methylbenzil-7-monoxime, $\begin{array}{c} \text{COPh} \cdot \text{C} \cdot \text{C} \cdot \text{H}_7 \\ | \\ \text{N} \cdot \text{OH} \end{array}$ (the α_2 -monoxime),

m. p. 117—118° (*benzoyl* derivative, m. p. 110°; *o*-*toluoyl* derivative, m. p. 82—83°). The monoxime is far more stable than any α -benzilmonoxime previously described, is partly decomposed when heated for a short time with concentrated hydrochloric acid, giving *o*-toluonitrile and benzoic acid, and is almost unaffected when heated under pressure with alcohol at 100°. Aqueous sodium hydroxide at 100° gives *o*-toluamide and benzoic acid, whilst the aqueous-alcoholic alkali gives the latter and *o*-toluonitrile (showing an α -configuration). The effects produced by these reagents correspond with a Beckmann change of the second order (Werner and Piguet, A., 1905, i, 66), usually observed only with acyl derivatives. This removes the doubts raised by Brady and Bishop (A., 1925, i, 930) in connexion with the relation between the configuration of benzilmonoximes and of their acyl derivatives. The tendency to undergo Beckmann changes of the second order is characteristic of the α -benzilmonoximes.

Cold or hot oximation of the α -oxime gives the α -dioxime, $\text{Ph}\cdot\text{C}\begin{smallmatrix} \text{---} & \text{C}\cdot\text{C}_6\text{H}_5 \\ \text{OH}\cdot\text{N} & \text{N}\cdot\text{OH} \end{smallmatrix}$, m. p. 250° (taken slowly) or 260° (taken quickly) (decomp.). The dioxime undergoes no transformation when heated with alkali or with alcohol; the *diacetyl* and *dibenzoyl* derivatives melt respectively at 139° and 162—163°. The former is readily, and the latter with difficulty, hydrolysed to the parent substance.

Condensation of *o*-tolualdehyde with phenylnitromethane gives β -*nitro-2-methylstilbene*, m. p. 99°, together with a small quantity of a substance, $\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}$, m. p. 195° (decomp.), apparently different from, but not depressing the decomp. point of, the above compound, $\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}$. From the stilbene is obtained α -2-methyl-7'-benzilmonoxime dimethylacetal (the α_1 -acetaloxime), m. p. 174°, and thence α -2-methylbenzil-7'-monoxime (the α_1 -monoxime),

$\text{Ph}\cdot\text{C}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, m. p. 119° (*benzoyl* derivative, m. p. 87—88°, hydrolysing normally). Concentrated hydrochloric acid converts the α_1 -acetaloxime into β -2-methylbenzil-7'-monoxime (the β_1 -monoxime),

$\text{Ph}\cdot\text{C}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, m. p. 121° (with or without $0.5\text{C}_6\text{H}_6$) (*benzoyl* derivative, m. p. 129°, hydrolysing normally). Oximation of the β_1 -monoxime in alcoholic alkali

gives γ -2-methylbenzildioxime, $\text{Ph}\cdot\text{C}\begin{smallmatrix} \text{---} & \text{C}\cdot\text{C}_6\text{H}_5 \\ \text{N}\cdot\text{OH} & \text{N}\cdot\text{OH} \end{smallmatrix}$, m. p. 188.5° (decomp.) (rapid heating; slow heating produces the α -dioxime) (*dibenzoyl* derivative, m. p. 127—128°; acetylation produces much α -derivative). The γ -dioxime is converted by alkali at 100° into the α -dioxime and 3-phenyl-4-*o*-tolylfurazan, m. p. 49°, also formed in the hot oximation of the β_1 -monoxime, or, together with benzoic acid, by the action of boiling alkali on the dibenzoate. Sodium hypochlorite converts the γ -dioxime into α -3-phenyl-4-*o*-tolylfurazan oxide, $\text{CPh}\cdot\text{C}\cdot\text{C}_6\text{H}_5$, m. p. 103°, also formed, together with the β -isomeride, by oxidising α -2-methylbenzildioxime, and reducible to the γ -dioxime. Reduction of a mixture of α - and β -furazan oxides gives a mixture of the two *amphi*-dioximes, benzoylated to a mixture of γ - and δ -dioxime benzoates.

The above α -nitro-2-methylstilbene is converted by 50% aqueous sodium hydroxide at 150—160° into 4-phenyl-3:5-di-*o*-tolylisooxazole, m. p. 111.5°, oxidised by ozone to the *o*-toluate, $\text{C}_7\text{H}_7\cdot\text{CBz}\cdot\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, m. p. 114°, of β -2-methylbenzilmonoxime (the β_2 -monoxime), m. p. 124°, which is not appreciably affected by acid or alkali, whilst the β -nitrostilbene similarly affords 3:5-diphenyl-4-*o*-tolylisooxazole, m. p. 126°, oxidised to the benzoate, m. p. 192° (above), of the β_1 -monoxime. Oximation of the β_2 -monoxime affords δ -2-methylbenzildioxime (*dibenzoyl* derivative, m. p. 112—113°), melting at 184°, then solidifying and passing into the α -dioxime. The δ -dioxime is oxidised to β -3-phenyl-4-*o*-tolylfurazan oxide, $\text{CPh}\cdot\text{C}\cdot\text{C}_6\text{H}_5$, m. p. 86—87°.

Benzaldehyde and *m*-tolylnitromethane undergo condensation in presence of aliphatic amines, and phenyldi-*m*-tolylisooxazole, m. p. 170° (indef.), is produced in addition to the desired α -nitro-3-methylstilbene, but this substance, m. p. 82°, once nuclei have been obtained by careful procedure in absence of light, is readily prepared. Methyl-alcoholic potassium hydroxide converts it into α -3-methylbenzil-7-monoxime dimethylacetal (the α_2 -acetaloxime), m. p. 176°, hydrolysed by cold concentrated hydrochloric acid (10 min.) to α -3-methylbenzil-7-monoxime (the α_2 -monoxime), m. p. 83°, much β_2 -oxime also being produced. The β_2 -oxime (β -3-methylbenzil-7-monoxime, m. p. 122°; *benzoyl* derivative, m. p. 136°, hydrolysed partly to oxime; *acetyl* derivative, m. p. 67°, readily hydrolysed to the oxime) is formed when the α_2 -oxime is boiled with alcohol, and is prepared by treating the α_2 -acetaloxime with cold concentrated hydrochloric acid for 24 hrs.

Cold alkaline oximation of the α_2 -monoxime produces α -3-methylbenzildioxime, m. p. 216° (rapid heating) [*benzoyl* derivative, m. p. 185° (decomp.)], hydrolysed mainly to oxime, converted in 2 hrs. at 170—175° (more rapidly when impure) into the β -dioxime. Hot alkaline oximation of the β_2 -monoxime gives α - and β -dioximes (method of preparing latter) and some phenyltolylfurazan. The β -dioxime has m. p. 150°, and may crystallise $+1\text{C}_6\text{H}_6$ (exchanged for $1\text{H}_2\text{O}$ by air-drying) (*dibenzoyl* derivative, m. p. 141.5°, partly hydrolysable to oxime). Cold oximation of the β_2 -monoxime gives δ -3-methylbenzildioxime (the δ -dioxime), m. p. 135° (decomp.) or ($+x\text{C}_6\text{H}_6$) m. p. 70—75° and 135°. The readily obtained *disodium* salt gives a δ -dioxime of m. p. 141° (hydrated). Both preparations appear to contain some of the next-mentioned furazan. The *di*-benzoyl derivative, m. p. 152°, is very slowly hydrolysed by cold alkali, but the hot reagent produces 3-phenyl-4-*m*-tolylfurazan, m. p. 37°, b. p. 175—185°/vac., also formed, together with the α -dioxime, by boiling the δ -dioxime with alkali. Sodium hypochlorite oxidises the δ -dioxime to β -3-phenyl-4-*m*-tolylfurazan oxide, m. p. 77.5°, reduced by zinc dust and methyl-alcoholic acetic acid to the δ -dioxime.

The preparation of β -nitro-3-methylstilbene, m. p. 51°, b. p. 195°/14 mm., requires great attention to detail. The crude material is converted by methyl-alcoholic alkali etc. into a little 3:5-diphenyl-4-*m*-tolylisooxazole, m. p. 156°, much α -nitro- β -methoxy-

α -phenyl- β -m-tolylethane, m. p. 89° (also obtained by dissolving the pure nitrostilbene in methyl-alcoholic alkali), and a stereoisomeride (?), m. p. 129° , of the ethane. Reduction of these two stereoisomerides gives two bases, the hydrochlorides of which melt respectively at 235° (becoming brown) and 223° , and may be those of the two stereoisomeric α -amino- β -methoxy- α -phenyl- β -m-tolylethanes.

3-Methylbenzil-7'-monoxime dimethylacetal (the α_1 -acetaloxime), decomp. 214° , is obtained from the nitrostilbene or from the ethane, and, when crystallised from methyl alcohol, is partly converted into the above isooxazole, m. p. 156° . The α_1 -acetaloxime is readily converted into α -3-methylbenzil-7'-monoxime (the α_1 -monoxime), m. p. 113° (benzoyl derivative, m. p. 91° , hydrolysed to benzonitrile, and benzoic and m-toluic acids), together with some β -3-methylbenzil-7'-monoxime (the β_1 -monoxime), m. p. 134° (benzoyl derivative, m. p. 120° , hydrolysable to the oxime), which is best obtained by treating the above acetal-oxime with concentrated hydrochloric acid.

Cold oximation of the β_1 -monoxime gives γ -3-methylbenzildioxime (the γ -dioxime), m. p. 126.5° or $(+1C_6H_6)$ 118° (benzoyl derivative, m. p. 108 — 116° , converted by hot alkali into the furazan, m. p. 37°). Crystallisation of the dioxime from benzene produces the β -dioxime, whilst boiling benzene slowly converts it into the α -dioxime, also formed (together with the furazan) by the action of hot alkali. Sodium hypochlorite converts the γ -dioxime into β -3-phenyl-4-m-tolylfurazan oxide, m. p. 75.5° , reducible to the γ -dioxime (trace of α -dioxime).

p-Tolylnitromethane and benzaldehyde condense readily in aqueous-alcoholic methylamine to give α -nitro-4-methylstilbene, m. p. 75 — 76° , convertible into 4-methylbenzil-7-monoxime dimethylacetal (the α_2 -acetaloxime), m. p. 217° , which in turn gives α -4-methylbenzil-7-monoxime (the α_2 -monoxime), m. p. 115° (benzoyl derivative, m. p. 118° , hydrolysed mainly to *p*-toluonitrile, *p*-toluic acid, and benzoic acid). Concentrated hydrochloric acid slowly converts the α_2 -monoxime or the acetaloxime into β -4-methylbenzil-7-monoxime (the β_2 -monoxime), m. p. 134° (benzoyl derivative, m. p. 156° , hydrolysed to the oxime).

Cold alkaline oximation of the α_2 -monoxime affords α -4-methylbenzildioxime (the α -dioxime), m. p. 223 — 224° (dibenzoyl derivative, m. p. 184° , hydrolysed to dioxime) (cf. Ponzio and Bernardi, A., 1924, i, 293, who named it β -phenyl-*p*-tolylglyoxime). The α -dioxime is converted by alcohol at 150° under pressure into β -4-methylbenzildioxime (the β -dioxime), m. p. 184° $(+0.5C_6H_6)$ (dibenzoyl derivative, m. p. 140° , hydrolysed to dioxime), also obtained in appreciable quantities by oximation of the α_2 -monoxime. Cold alkaline oximation of the β_2 -monoxime gives δ -4-methylbenzildioxime (δ -dioxime), m. p. $(+0.5C_6H_6)$ 160° , which with hot alkali passes into the β -dioxime. The dibenzoyl derivative, m. p. 119° , is converted slowly by cold alkali into β -phenyl-4-*p*-tolylfurazan, m. p. 80° , and benzoic acid. Oxidation of the δ -dioxime with sodium hypochlorite gives β -3-phenyl-4-*p*-tolylfurazan oxide, m. p. 117° , reducible to the δ -dioxime.

p-Tolualdehyde and phenylnitromethane condense

in presence of methylamine to give β -nitro-4-methylstilbene, m. p. 79° , together with a substance, $C_{21}H_{19}O_2N$ (cf. the 2-methyl series), and α -nitro- β -methoxy- α -phenyl- β -*p*-tolylethane, m. p. 93° . The last, converted by alkali into the nitrostilbene, is different from the products, m. p. 101 — 102° and 95 — 96° , respectively, of dissolving the nitrostilbene in methyl- or ethyl-alcoholic alkali (stereoisomerides?), and is converted by methyl- or ethyl-alcoholic alkali into the substance, m. p. 101 — 102° . 4-Methylbenzil-7'-monoxime dimethylacetal (the α_1 -acetaloxime), decomp. 215° , obtained normally from the nitrostilbene, is converted by concentrated hydrochloric acid into β -4-methylbenzil-7'-monoxime (the β_1 -monoxime), m. p. 120 — 121° (benzoyl derivative, m. p. 94° , hydrolysed to oxime). The latter is oximated to give γ -4-methylbenzildioxime (the γ -dioxime) (amphi), m. p. 150° or $(+xH_2O)$ 142° (sintering at 110°) or $(+CHCl_3)$ 146° (dibenzoyl derivative, m. p. 137° , hydrolysed to the furazan, m. p. 80°), which with sodium hypochlorite gives α -3-phenyl-4-*p*-tolylfurazan oxide, m. p. 121° , reduced to the γ -dioxime. E. E. TURNER.

Constitution of oximes. X. J. MEISENHEIMER and W. THEILECKER (Annalen, 1929, 469, 128—146).—A reply, in support of the Hantzsch-Werner view of the isomerism of oximes, to Ponzio (A., 1928, 888). α -4'-Methoxybenzil-7-monoxime (Meisenheimer and Lange, A., 1924, i, 433) when pure has m. p. 95 — 96° (*loc. cit.* 88 — 89°) and the dioxime obtained from this specimen has m. p. 218° and is identical with the " β "-phenyl-*p*-anisylglyoxime obtained by Ponzio and Bernardi (A., 1924, i, 293). (To avoid confusion the symbols in inverted commas apply to the nomenclature of Ponzio.) This does not vitiate the authors' conclusions that the isomerism is explained by the Hantzsch-Werner theory, since the existence of four dioximes is based on differences in chemical behaviour. Ponzio's view regarding the nature of " β "-methylphenylglyoxime (*loc. cit.*) is criticised on the grounds (1) that as a single crystalline substance it cannot be an equilibrium mixture of " α " and " γ " forms, and (2) that it gives a red nickel salt sparingly soluble in acetic acid, whilst the nickel salts of the " α " and " γ " oximes are greenish-yellow and readily soluble in acetic acid. The authors consider that the " β " oxime has the α -(anti)structure, giving, by oxidation, two structurally isomeric furazans, $\begin{array}{c} \text{CR}-\text{CR}' \\ \text{O:N}-\text{O:N} \end{array}$ and $\begin{array}{c} \text{CR}-\text{CR}' \\ \text{N:O}-\text{N:O} \end{array}$, the peroxide

formulation of Ponzio, even if correct, being no evidence of configuration, since oxidation must involve a rearrangement. The " α " dioxime is regarded as the γ - or δ -(amphi)oxime, $\begin{array}{c} \text{MeC}-\text{C}^{\text{Ar}} \\ \text{HO:N} \quad \text{HO:N} \end{array}$. In agreement with the known attraction of the methyl for the oximino-hydroxyl group, both these forms are stable. The forms $\begin{array}{c} \text{MeC}-\text{C}^{\text{Ar}} \\ \text{N:OH} \quad \text{N:OH} \end{array}$ and $\begin{array}{c} \text{MeC}-\text{C}^{\text{Ar}} \\ \text{N:OH} \quad \text{HO:N} \end{array}$ are regarded as unstable and are either not obtained, or obtained only in an impure condition, and thus is explained the existence of Ponzio's " γ " glyoxime which has not been obtained pure, being always contaminated with the " β " form into which it passes. Similarly with the monoarylglyoximes, only two forms

are stable, " β "-phenylglyoxime having the *anti*-structure and " α "-phenylglyoxime the *amphi*-structure $\begin{array}{c} \text{H}-\text{C}=\text{C}-\text{Ph} \\ \text{HO}-\text{N} \quad \text{HO}-\text{N} \end{array}$ or $\begin{array}{c} \text{H}-\text{C}=\text{C}-\text{Ph} \\ \text{N}-\text{OH} \quad \text{N}-\text{OH} \end{array}$. Contrary to Ponzio, the authors consider that the action of benzenediazonium chloride on " α "-phenylglyoxime does involve a rearrangement (*e.g.*, the " α "-glyoxime yields a nickel salt, whilst the resulting β -benzildioxime does not), the resulting β -benzildioxime being formed by a rearrangement of the unstable γ -(*amphi*)-benzildioxime, which is considered to be the primary product, since hydrolysis of its acetyl derivative yields a trace of diphenylfurazan, showing the presence of a trace of the γ -compound. In attempts to prepare a stable *amphi*-derivative condensation with *o*-, *m*-, and *p*-toluenediazonium chlorides was attempted. In the first two cases the evidence is doubtful, since mainly unchanged " α "-phenylglyoxime and resinous products are obtained, but with the *p*-compound there results a mixture containing β - (14%), α - (0.7%), and *amphi*- (0.5%) dioximes and it is believed that the α - and β - are produced from the *amphi*-form which is the primary product of the reaction. The discrepancies between the results of Russanoff (A., 1892, 321) and of Ponzio and Avogadro (A., 1923, i, 472) relating to " β "-phenylglyoxime are explained by the fact that the product designated " β " by the former author is really the unchanged " α "-compound, the true " α " and " β " compounds giving different and not identical diacetyl derivatives. The sufficiency of the Hantzsch-Werner view in explaining oxime isomerism is maintained and the untrustworthiness of physical properties for the determination of configuration is discussed. J. W. BAKER.

Perylene and its derivatives. XXI. A. PONGRATZ and E. POCHMULLER (Monatsh., 1929, 51, 228—233).—When 4 : 10-dichloro- or 4 : 10-dibromo-3 : 9-dibenzoylperylene is heated with cuprous cyanide in presence of quinoline, 4 : 10-dicarbylamino-3 : 9-dibenzoylperylene, not melted at 360°, is obtained; hydrolysis of this with concentrated sulphuric acid gives 4 : 10-diamino-3 : 9-dibenzoylperylene, not melted at 360° (*dibenzoyl* derivative, sinters at 350° without melting) (*cf.* A., 1927, 1190).

Perylene reacts with *p*-bromobenzoyl chloride in presence of aluminium chloride and carbon disulphide forming 3 : 9-di-*p*-bromobenzoylperylene, m. p. 308°, which when treated with cuprous cyanide in boiling quinoline gives the corresponding dicarbylamino-derivative, m. p. 293°. Hydrolysis of this with concentrated sulphuric acid yields an uncrystallisable product, insoluble in alkali. Distillation of *dipropionyl*- and *dibutyl-yl*-perylene, m. p. 247° and 253°, respectively (obtained by the Friedel-Crafts reaction), with zinc dust gives perylene as the chief product. H. BURTON.

Triquinoyl. F. BERGEL (Ber., 1929, 62, [B], 490—491).—Intensive desiccation of triquinoyl octahydrate, $\text{C}_6\text{O}_6 \cdot 8\text{H}_2\text{O}$ (*cf.* Henle, A., 1907, i, 144), by phosphoric oxide at 78° causes almost complete removal of water. The constitution of the yellowish-brown product as a polymeric carbon monoxide appears established by its behaviour towards barium chloride; it cannot, however, be re-converted into the octahydrate. H. WREN.

Differently coloured conditions of anthraquinolcarboxylic acids and anthraquinol- α -carboxylactones. R. SCHOLL, O. BOTTGER, and S. HASS (Ber., 1929, 62, [B], 616—628).—Sodium anthraquinone-1-carboxylate is reduced by sodium hyposulphite in aqueous solution to *anthraquinol-1-carboxylic acid*, permanganate-like crystals which dissolve in alkaline solution in the absence of air to red solutions from which mineral acids precipitate the organic acid as a red gel which passes in 10—15 min. into a violet, readily-filterable condition. The acid is converted by short treatment with boiling acetic anhydride into *anthraquinol-1-carboxylactone* and by more protracted treatment into the corresponding *acetyl* derivative, $\text{C}_{17}\text{H}_{10}\text{O}_4$, m. p. 196°. Anthraquinone-1 : 5-dicarboxylic acid dissolved in sodium hydroxide is reduced by sodium hyposulphite at the atmospheric temperature to a red vat from which hydrochloric or sulphuric acid immediately gives a violet precipitate. The sparing solubility of the violet acid in organic media at the ordinary temperature and its instability at higher temperature inhibit its preparation in the crystalline condition. The quantitative reduction of sodium anthraquinone-1 : 5-dicarboxylate to a dark red solution requires 2.09 atoms of hydrogen in the presence of spongy platinum, whilst the oxidation of the vat (obtained with zinc dust and alkali) by sodium hypochlorite is effected by 2 atoms of oxygen. There can therefore be no doubt that the violet compound is pure *anthraquinol-1 : 5-dicarboxylic acid* and that the colour is not due to radical- or quinhydrone-like impurities. Solutions obtained from sodium anthraquinone-1 : 5-dicarboxylate or from free anthraquinone-1 : 5-dicarboxylic acid with sodium hyposulphite yield a violet precipitate when shaken with air; this is attributed to oxidation of the excess of hyposulphite to hydrogen sulphite and sulphate which thereby causes acidification of the solution. If the solution obtained by the action of anthraquinol-1 : 5-dicarboxylactone on methyl-alcoholic potassium hydroxide is acidified with not too dilute sulphuric acid previous to dilution with water a gelatinous red acid is precipitated which usually passes into the violet form but can occasionally be dried as the red variety. The latter, in contrast to the violet form, is readily soluble in nitrobenzene, acetic anhydride, dioxan, etc., but, like the violet acid, gives red solutions in alkali hydroxide from which the violet form is precipitated. The red and violet acids are converted by acetic anhydride into *anthraquinol-1 : 5-dicarboxydilactone*, decomp. about 380°. The differences in colour are attributed to difference in the size of particles. The violet powder gives a reddish-brown mark when rubbed with a glass rod on porous earthenware; in thin layers it appears under the microscope to be violet-red in transmitted light, otherwise black. The violet colour is therefore a surface effect.

H. WREN.

Derivatives of 3 : 4-phenanthraquinone. L. F. FIESER (J. Amer. Chem. Soc., 1929, 51, 940—952).—4-Amino-3-phenanthrol hydrochloride is oxidised by chromic anhydride in glacial acetic acid, or by nitrous acid (*cf.* Werner, A., 1902, i, 437), to 3 : 4-phenanthraquinone (*cf.* Barger, J.C.S., 1918, 113, 218) (char-

acteristic blue to green colour reaction with sulphuric acid). This is converted by concentrated aqueous sodium hydrogen sulphite into sodium 3 : 4-dihydroxyphenanthrene-1-sulphonate (I) (corresponding *p*-toluidine salt, decomp. 182°), oxidised by chromic and sulphuric acids to sodium 3 : 4-phenanthraquinone-1-sulphonate (ammonium salt), which gives with *p*-toluidine in hot aqueous solution red 1-*p*-toluidino-3 : 4-phenanthraquinone, m. p. 260° (decomp.), reduced by zinc, acetic anhydride, and sodium acetate to 1-*p*-toluidino-3 : 4-diacetoxypheanthrene, m. p. 208°. Orange-yellow 3-hydroxy-1 : 4-phenanthraquinone, m. p. 230°, sintering from 200° (sodium and ammonium salts; methyl ether, m. p. 170°; 1 : 4-diacetoxy-3-methoxypheanthrene, m. p. 168.5°), is best obtained by oxidising I with hydrogen peroxide and alkali. Its silver salt yields with allyl bromide in boiling benzene 1-allyloxy-3 : 4-phenanthraquinone (17% of the theoretical), m. p. 161°, and 3-hydroxy-2-allyl-1 : 4-phenanthraquinone (63%), m. p. 155°, which is converted by cold sulphuric acid into a compound, $C_{17}H_{12}O_3$, red needles, m. p. 198—199°. 3-Hydroxy-1 : 4-phenanthraquinone behaves like a β -diketone towards boiling 6*N*-sodium hydroxide, being hydrolysed to 2-acetyl-1-naphthylglyoxylic acid, m. p. 196° (decomp.) (methyl ester, m. p. 181°). This is converted by hydrogen peroxide and alkali into naphthalene-1 : 2-dicarboxylic acid, and by potassium dichromate and acid into 1 : 3-diketo- α -naphth-hydrindene, m. p. 174—175° (benzylidene derivative, m. p. 179°; cf. Noto, A., 1915, i, 973), and gives with aniline at 175° 2-acetyl-1-naphthylideneanil, m. p. 202°.

H. E. F. NOTTON.

Perylene and its derivatives. XIX. A. ZINKE, W. HIRSCH, and E. BROZEK (Monatsh., 1929, 51, 205—220).—Reduction of 3 : 4 : 9 : 10-tetranitroperylene (Zinke and Unterkreuter, A., 1920, i, 541) with alkaline sodium hyposulphite, sodium sulphide, or stannous chloride gives the corresponding tetra-amino-derivative (dibenzylidene derivative), which in view of its intense colour is probably admixed with some diaminoperylenequinonedi-imine. The tetra-amino-compound reacts with 2 mols. of oxalyl chloride forming a dioxalyl derivative, not melted at 360°, and with acetic anhydride, benzoyl, *p*-bromobenzoyl, and *p*-chlorobenzoyl chlorides, forming the corresponding benziminazole derivatives (annexed formula, $R=Me, Ph, C_6H_4Br, C_6H_4Cl$, respectively), all of which have m. p. above 360°.

When 3 : 9-dichloro-4 : 10-dinitroperylene is heated with concentrated sulphuric acid at 150—160°, perylene-3 : 4 : 9 : 10-diquinone (I) results. The same diquinone is obtained also from dinitroperylene and 3 : 4 : 9 : 10-tetranitroperylene by similar treatment with sulphuric acid. Reduction of this with alkaline sodium hyposulphite and subsequent treatment with the appropriate acyl chloride gives the tetrabenzoate and tetra-*p*-bromobenzoate of 3 : 4 : 9 : 10-tetrahydroxyperylene. The tetrabenzoate is hydrolysed and oxidised at the same time by warm concentrated sulphuric acid, yielding I. Bromination of I in nitrobenzene suspension affords a tetrabromo-derivative, whilst chlorination furnishes

a product, probably a mixture of di- and tetra-chloro-derivatives, which after reduction and benzylation yields a dichlorotetrabenzyloxyperylene. The halogenated derivatives of perylenediquinone are mordant dyes.

H. BURTON.

Manufacture of benzanthraquinone derivatives and substitution products. I. G. FARBENIND. A.-G.—See B., 1929, 237.

Manufacture of vat dyes [of the dibenzanthrone series] and intermediate products thereof. I. G. FARBENIND. A.-G.—See B., 1929, 238.

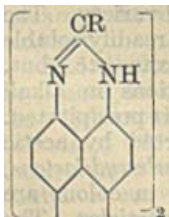
Euphorbons from euphorbium resin. J. A. MULLER (J. pr. Chem., 1929, [ii], 121, 97—112).—By the process of extraction described a sterol-free preparation of euphorbon, sintering at 118°, melting at 121.5—122.5° to a cloudy liquid which becomes clear at 125°, $[\alpha]_D^{20} +16.58^\circ$, is obtained. This, like all hitherto believed uniform specimens, is a mixture, since acetylation (acetic anhydride alone or in presence of anhydrous sodium acetate or pyridine) leads to the simultaneous formation of vitorbol acetate (yield 60%), sintering at 85°, melting to a cloudy liquid at 90—91°, which becomes clear at 98°, $[\alpha]_D^{20} +11.34^\circ$, and novorbol acetate, m. p. 123—124° (clear liquid), $[\alpha]_D^{20} -12.52^\circ$. Each of these compounds may have either of two formulæ: $C_{26}H_{41}OAc$ or $C_{27}H_{43}OAc$. Similarly, treatment of euphorbon with *p*-bromobenzoyl chloride gives vitorbol *p*-bromobenzoate, m. p. 132—133° (cloudy liquid), 137° (clear), $[\alpha]_D^{20} +20.45^\circ$, accompanied by novorbol *p*-bromobenzoate, which exists in two crystalline forms, both with m. p. 183.5—184.5°, $[\alpha]_D^{20} +18.88^\circ$.

Hydrolysis of the foregoing acyl derivatives yields vitorbol, m. p. 120.5°, 122.5—123.5°, 125°, $[\alpha]_D^{20} +11.34^\circ$, and novorbol, m. p. 123.5—124.5°, $[\alpha]_D^{20} +29.61^\circ$. Vitorbol gives no digitonin precipitate.

Dibromovitorbol acetate, m. p. 163—164° (decomp.), after sintering at 156°, $[\alpha]_D^{20} -5.615^\circ$, is formed by addition of bromine in chloroform solution. All rotations were taken in benzene solution.

R. J. W. LE FEVRE.

Saponin of the sugar beet. K. REHORST (Ber., 1929, 62, [B], 519—534).—Dried beetroot shavings are extracted with cold 0.5% sodium hydroxide and the extract is acidified with hydrochloric acid. The crude saponin is dried, extracted with boiling ethyl alcohol, and the extract evaporated to dryness. The solution of the residue in methyl alcohol is treated with ether, the precipitate is removed, and the filtrate again evaporated. Further purification of the residue is effected by dialysis and treatment with methyl alcohol and ether. Final extractions with light petroleum and water leave a product which cannot be separated into appreciably different portions by fractional extraction with ether. The saponin, $C_{37}H_{56}O_9$, has m. p. 215—216°, $[\alpha]_D^{20} +31.07^\circ$ in methyl alcohol. It has strongly hæmolytic properties which are not inhibited by addition of cholesterol. Hydrolysis affords 30% of *d*-glycuronic acid and 68.67% of sapogenin. The latter compound, which appears saturated, after desiccation at 105° has m. p. 301—302°, $[\alpha]_D^{20} +78.82^\circ$ in 96% alcohol. Analyses and determinations of mol. wt. agree better with the formula $C_{31}H_{48}O_3$ than with $C_{31}H_{50}O_3$, and the



amended composition appears to accord better with the recorded analyses of oleanol and caryophyllin, which are identical with beetroot sapogenin. The proportion of water of crystallisation in the air-dried substance varies somewhat with the mode of preparation, 2, 1.5 and 1 mol. being recorded. Specimens which have been preserved for a considerable period and then dried at 140° appear to have the composition $C_{31}H_{48}O_3 \cdot 0.5H_2O$, but the observations may be caused by partial autoxidation. Distillation of the sapogenin with zinc dust affords carbon dioxide, water, substances with an odour of petroleum, and a viscous, fluorescent oil which can be separated by steam into a volatile and a non-volatile portion. The most volatile fraction from the former portion appears to be a sesquiterpene, $C_{15}H_{24}$, d 0.9079, n_D^{25} 1.5126, $[\alpha]_D^{25}$ +3.75°, which absorbs 1 mol. of hydrogen in presence of palladium chloride. Dehydrogenation with selenium affords an oil which partly crystallises. The crystalline portion, m. p. 273—275°, is a largely dehydrogenated product, $C_{30}H_{20}O$ or $C_{30}H_{18}O$, in which the carbon skeleton of the sapogenin remains almost intact. The oil gives a yellow product with picric acid, the first portions of which have m. p. 114—116°, whereas later fractions have a lower and less distinct m. p. Regeneration of the hydrocarbon and treatment of it with trinitroresorcinol permits the isolation of a styphnate, m. p. 119—123°; the observations agree moderately well with the recorded m. p. of cadalene picrate (114—115°) and eudaline styphnate (119—120°). It is concluded with reserve that two hydrogenated naphthalene hydrocarbons are present in beetroot sapogenin.

The scheme $C_{37}H_{56}O_9 + H_2O = C_{31}H_{48}O_3 + C_6H_{10}O_7$ is suggested for the hydrolysis of the saponin.

H. WREN.

Plant colouring matters. XI. Lycopin. P. KARRER and W. E. BACHMANN (Helv. Chim. Acta, 1929, 12, 285—291).—When lycopin is shaken with lithium, sodium, or potassium powder in a mixture of dry ether and benzene, intensely coloured solutions of *lithium*, *sodium*, and *potassium additive* compounds are obtained and, in the first two cases, separation of the metal additive compound ultimately occurs. Titration of the solution of the potassium compound shows that two atoms of the metal are taken up. The action of dry, oxygen-free carbon dioxide on the sodium compound gives a *lycopincarboxylic acid* which, after being freed from non-acidic impurities by dissolution in ammonia, has a composition corresponding with $C_{40}H_{56}(CO_2H)_4$, but titrates as a dibasic acid, and with diazomethane yields an *ester* which contains only 6.1% OMe (the dimethyl ester requires 8.6%). Decomposition of the lithium or sodium compound with water yields an orange-yellow, amorphous *substance* (C, 86.4; H, 10.5%) containing some oxygen, which is autoxidisable. By the action of methyl iodide on the solution of the potassium compound, lycopin is not regenerated, and hence it is improbable that the two potassium atoms are attached to adjacent carbon atoms. The action of dry oxygen on the potassium compound regenerates lycopin, accompanied by an amorphous (? oxidation) product. Ozonolysis of lycopin yields acetaldehyde, acetic acid, acetone, and a substance which gives the

reactions of lævulic acid; the structure $CMe_3 \cdot CH \cdot [CH_2]_2 \cdot [CMe \cdot CH \cdot CH \cdot CH]_5 \cdot CMe \cdot CH \cdot [CH_2]_2 \cdot CMe \cdot CHMe$ is suggested for lycopin (cf. Karrer and others, this vol., 49). No metallic derivatives could be obtained from carotin, xanthophyll, γ -crocetin, or bixin methyl ester.
J. W. BAKER.

Constituents of red sandal wood. Homopterocarpin and pterocarpin. H. DIETERLE and H. LEONHARDT (Arch. Pharm., 1929, 267, 81—116; cf. A., 1926, 618).—Fifty kg. of red sandal wood furnished 214 g. of homopterocarpin, $C_{17}H_{16}O_4$, m. p. 83—84°, $[\alpha]_D^{25}$ —216.3° in chloroform, and 44 g. of pterocarpin, $C_{14}H_{12}O_4$, m. p. 162.5—163°, $[\alpha]_D^{25}$ —220.1°, the two constituents being separated by fractional crystallisation from chloroform and alcohol. Homopterocarpin reacts abnormally with hydriodic acid and red phosphorus, but it contains two methoxyl groups. The remaining two oxygen atoms are not present as hydroxyl groups, since, although acetyl chloride in hot benzene solution affords *acetyldihydrohomopterocarpin*, $C_{19}H_{20}O_5$, m. p. 130—131°, and *acetyldemethylhomopterocarpin*, $C_{18}H_{16}O_5$, darkening at 205°, decomp. 220°, the one derivative is a reduction product and the other a demethylated compound. Homopterocarpin appears to be a lactone of a phenolic acid, since treatment with methyl sulphate and potassium hydroxide solution furnishes a *monomethyl ester*, which affords another lactone, *acetylhomopterocarpin*, m. p. 195°, when acetylated. The lactone ring is reduced by hydrogen in presence of palladised charcoal at 76°, with the formation of *1-dihydrohomopterocarpin*, m. p. 153—154°, $[\alpha]_D^{25}$ —12.8° in chloroform, which contains two methoxyl groups and a phenolic hydroxyl group, although it is insoluble in alkalis (*monoacetyl* derivative, m. p. 130.5—131°, $[\alpha]_D^{25}$ +18.8°; *benzoyl* derivative, m. p. 99—100°, $[\alpha]_D^{25}$ +34.0°; *methyl ether*, m. p. 57—58°), and an optically inactive isomeride, *i-dihydrohomopterocarpin*, yellowish-red, m. p. 76°, soluble in alkalis (*benzoyl* derivative, m. p. 67—70°). These compounds are saturated, bromination of homopterocarpin and of *i-dihydrohomopterocarpin* by means of pyridine perbromide affording *dibromohomopterocarpin*, m. p. 184—185°, $[\alpha]_D^{25}$ —273.0°, and *dibromodihydrohomopterocarpin*, m. p. 199—200° (decomp.), respectively, both of which furnish a mixture of homopterocarpin and its dihydro-derivatives when reduced with sodium and alcohol. Homopterocarpin is resistant to potassium permanganate and unidentified complex products result from oxidation with chromic acid or ozone. Dehydrogenation with molten selenium under pressure, however, produces a *substance*, $C_{34}H_{34}O_8$, m. p. 110° (decomp.) (*diacetyl* derivative, m. p. 132°), containing two phenolic hydroxyl groups, whilst concentrated nitric acid in boiling glacial acetic acid solution affords *dinitrohomopterocarpin*, m. p. 136—138°, a *compound*, m. p. 122°, a *substance*, $C_{16}H_{13}O_9N_3$, m. p. 244° (decomp.), oxalic acid, and styphnic acid. Homopterocarpin is resistant towards molten potassium hydroxide, the only insoluble products, besides a considerable amount of unchanged material, being resorcinol and phloroglucinol, whilst resorcinol dimethyl ether and a *methylanthracene*, m. p. 167°, are obtained on distillation with zinc dust.

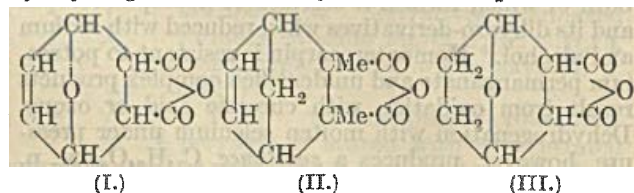
Pterocarpin, which contains only one methoxyl group, is insoluble in alkalis; it cannot be acetylated, and reduction with hydrogen and palladised charcoal affords *dihydropterocarpin*, m. p. 141—142°. Bromine gives *monobromopterocarpin*, m. p. 143—144°, and methyl sulphate and potassium hydroxide have no action. Most of the above compounds give characteristic colour reactions with 65% nitric acid, concentrated sulphuric acid, and mixtures of these.

S. COFFEY.

Optical activity and polarity of substituent groups. X. Influence of ionisable groups on rotatory power of *l*-menthyl benzoate. H. G. RULE and W. E. MACGILLIVRAY (J.C.S., 1929, 401—409).—The influence of the groups NH_2 , NMe_2 , OH , and CO_2H on the rotatory power of *l*-menthyl benzoate has been studied. The most definite variations were found with the *o*-substituted esters; increase in the rotatory power occurs with the *m*-orienting groups CO_2H , NMe_2H^+ , and NH_3^+ , whilst a decrease was observed with the *o*-*p*-orienting groups CO_2^- , NMe_2 , and O^- . *l*-Menthyl salicylate and anthranilate give an unexpected increase in rotatory power, which is attributed to their chelated condition. The following are described: *l*-menthyl salicylate (from acid chloride and menthol), b. p. 156°/0.5 mm.; *l*-menthyl *m*-hydroxybenzoate (from acid chloride and menthol in pyridine), b. p. 182°/1.2 mm.; *l*-menthyl *p*-hydroxybenzoate, b. p. 178°/0.1 mm.; *l*-menthyl anthranilate, b. p. 156°/0.33 mm., m. p. 62.5—63.5° (hydrochloride, m. p. 150—170°); *l*-menthyl *m*-aminobenzoate (by reduction of *l*-menthyl *m*-nitrobenzoate with titanous chloride and alcohol), b. p. 168°/1.8 mm.; *l*-menthyl *p*-aminobenzoate, b. p. 175°/0.2 mm. (decomp.); *l*-menthyl *o*-dimethylaminobenzoate, b. p. 170°/0.2 mm., m. p. 36—37°.

A. I. VOGEL.

Syntheses in the hydroaromatic series. II. Cantharidin. O. DIELS and K. ALDER [with E. NAUJOKS] (Ber., 1929, 62, [B], 554—562; cf. A., 1928, 1018).—Maleic anhydride is quantitatively converted by furan in the presence of ether into the compound I, m. p. 125° (decomp.) with regeneration of its components. Similarly, cyclopentadiene and dimethylmaleic anhydride in benzene at 100° afford the substance II, m. p. 155°. The compound I is converted by hydrogenation in ethyl alcohol in presence of



colloidal palladium into ethyl hydrogen 3:6-endoxyhexahydrophthalate, m. p. 107—108°, and by similar treatment in aqueous alkaline solution into 3:6-endoxohexahydrophthalic anhydride (norchantharidin), III, m. p. 116—117° (cf. von Bruchhausen and Bersch, this vol., 192). 3:6-Endoxohexahydrophthalic acid ($+1\text{H}_2\text{O}$), m. p. 122—123° (decomp.), and its methyl hydrogen ester, m. p. 146° (decomp.), are described. The constitution of norcantharidin is established as follows. The substance is converted by concentrated hydrochloric acid at 100° into 3:6-

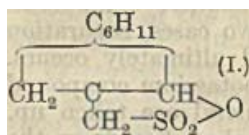
dichlorohexahydrophthalic acid, m. p. 111°, and by glacial acetic and hydrobromic acids at 100° into α -3:6-dibromohexahydrophthalic acid, m. p. 218—219° (decomp.), whereas aqueous hydrobromic acid at 100° affords β -3:6-dibromohexahydrophthalic acid, m. p. 177° (decomp.). The β -dibromo-acid is transformed by 25% potassium hydroxide into $\Delta^{1:3}$ -cyclohexadiene, identified as its additive compound, m. p. 147°, with maleic anhydride. Reduction of the dibromo-acid with sodium amalgam in alkaline solution affords *trans*-hexahydrophthalic acid, m. p. 219—220° after softening. Maleic anhydride and 2:5-dimethylfuran afford 3:6-endoxy-3:6-dimethyl- Δ^4 -tetrahydrophthalic anhydride, catalytically hydrogenated to 3:6-endoxy-3:6-dimethylhexahydrophthalic anhydride (isocantharidin), m. p. 121.5°. Concentrated hydrochloric acid at 100° transforms the anhydride into 3:6-dimethyl-6-dihydrophthalic anhydride, m. p. 159° after softening, oxidised by nitric acid (*d* 1.4) at 100° to 3:6-dimethylphthalic acid, m. p. 142—143°.

H. WREN.

Constitution of isoborneol. E. PUXEDDU (Gazzetta, 1929, 59, 59—69).—Ordinary methods of oxidation are too violent to distinguish between borneol and isoborneol. Oxidation by an ethereal solution of ferric chloride exposed to light (cf. A., 1920, ii, 406; 1922, ii, 415) furnishes, however, a delicate method, by which borneol is oxidised to camphor, with a dark brown precipitate, whilst isoborneol furnishes other, unidentified, products, including an oil containing chlorine, but not including camphor. It is concluded that isoborneol may be I.

E. W. WIGNALL.

Problem of addition in the camphene series. P. LIPP and M. HOLL (Ber., 1929, 62, [B], 499—504; cf. Lipp and others, A., 1927, 883).—Camphene, $[\alpha]_D^{20} +82^\circ$ in alcohol, is converted by sulphur trioxide in glacial acetic acid at 100° into a mixture of isobornyl acetate and 2-hydroxycamphane- ω -sulpholactone (I), b. p. 147.5—148° (corr.)/0.6 mm., m. p. 133.5° (corr.), $[\alpha] \pm 0$; the compound is obtained with greater difficulty from nearly optically inactive camphene. It is converted by alkali hydroxides



into the salts of 2-hydroxycamphane- ω -sulphonic acid, of which the sodium, barium, and ammonium, decomp. 186°, compounds are described. The constitution of the sulpholactone is elucidated as follows. Reyckler's camphorsulphonic acid is reduced by sodium and alcohol to a mixture of 2-hydroxycamphane- ω -sulphonic acids, which is treated with ammonia in ether, whereby the ammonium salt of the "endo" acid, decomp. 232°, is precipitated; the filtrate from the salt contains 2-hydroxycamphane- ω -sulpholactone, identical with that described above; the *p*-toluidine salts of endo-2-hydroxycamphane- ω -sulphonic acid and of *d*-camphorsulphonic acid, m. p. 152—153° (decomp.) and 161—162° (corr.) after softening, are described. Treatment of the "endo" acid with glacial acetic and fuming hydrochloric acids at 70° causes formation of 2-hydroxycamphane- ω -sulpholactone in 73% yield.

H. WREN.

Manasse's α - and β -hydroxycamphors (*ortho-exo-* and *ortho-endo*-hydroxycamphors). II. J. BREDT [and in part H. AHRENS and P. SCHOLL] (J. pr. Chem., 1929, [ii], 121, 153—172).—The crude hydroxycamphor obtained by reduction of camphorquinone by zinc dust and acetic acid or by aluminium amalgam and ether was resolved, by treatment with methyl-alcoholic hydrogen chloride, into *ortho-exo*-hydroxycamphor [acetate, m. p. 61—62° (lit. 63—64°); benzoate, b. p. 168°/0.33 mm.; benzenesulphonate, m. p. 79—80°; sulphite (obtained by treatment with thionyl chloride in the presence of pyridine), m. p. 130°; semicarbazone, m. p. 183—184°] and bis-*ortho-endo*-hydroxycamphor methyl ether. The last compound gave by boiling with methyl-alcoholic hydrogen chloride monomeric *ortho-en-hydroxycamphor methyl ether*, m. p. 37—38°, b. p. 81°/4 mm., 105—106°/12 mm., d_{20}^{25} 0.9996, n_D^{25} 1.4636 (semicarbazone, m. p. 124°). The corresponding monomeric *ortho-exo-hydroxycamphor methyl ether*, b. p. 105—107°/15 mm., d_4^{20} 1.0202, n_D^{20} 1.47426 (semicarbazone, m. p. 204°), was obtained by direct esterification. Magnesium methyl iodide and *ortho-endo*-hydroxycamphor interacted in ethereal solution to give *allomethylbornylene glycol*, C_8H_{14} $\begin{smallmatrix} \text{CH}\cdot\text{OH} \\ \diagup \\ \text{CMe}\cdot\text{OH} \end{smallmatrix}$, m. p. 163—164°.

The following derivatives of *ortho-endo*-hydroxycamphor are also described: semicarbazone, m. p. 215—216°, 210—211° (according to rate etc. of heating); benzoate, m. p. 84—85°; benzenesulphonate, m. p. 110°.

R. J. W. LE FEVRE.

New camphor bases. H. W. EGLI (Helv. Chim. Acta, 1929, 12, 270—277).—I. Two isomeric ketimides of camphoric acid imide. The base $C_{10}H_{16}ON_2$ obtained by the action of methyl-alcoholic potassium hydroxide on α -camphoronitrile acid amide (Tiemann and Kerschbaum, A., 1901, i, 19), or as a by-product in the preparation of isonitrosocamphor, is probably the α -ketimide of camphoric acid imide,

C_8H_{14} $\begin{smallmatrix} \text{C}\cdot\text{NH} \\ \diagup \\ \text{CO} \end{smallmatrix} \text{NH}$, m. p. 278° (hydrochloride, $-2H_2O$,

and anhydrous, m. p. 250°; picrate, m. p. 269°; benzoate, m. p. 230°; hydrogen tartrate, m. p. 180°; hydrogen oxalate, m. p. 146°; corresponding phenylthiocarbamate, m. p. 234°; benzoyl derivative, m. p. 204°), which may be tautomeric with the form

C_8H_{14} $\begin{smallmatrix} \text{C}\cdot\text{NH} \\ \diagup \\ \text{CO} \end{smallmatrix} \text{N}$. It is readily converted by nitrous

acid into camphoric acid imide. Similarly, β -camphoronitrile acid amide with methyl-alcoholic potassium hydroxide gives the isomeric β -ketimide, m. p. 238° (hydrochloride, m. p. 230°; picrate, m. p. 293°).

II. Condensation of α -aminocamphor with γ -diketones and γ -keto-esters. α -Aminocamphor (I) condenses with acetylacetone in glacial acetic acid to yield α -2:5-dimethylpyrrolycamphor (II), b. p. 176°/10 mm., m. p. 90°, reduced by tin and alcoholic hydrogen chloride to the double stannochloride, m. p. 149°, of α -2:5-dimethyl-2:5-dihydropyrrolycamphor, $[C_{10}H_{15}\cdot N < \begin{smallmatrix} \text{HMeC} \\ \text{CHMe}\cdot\text{CH} \end{smallmatrix} \cdot \text{HCl}]_2$, SnCl_2 , which with hydrogen sulphide gives the hydrochloride, m. p. 232°, of the dihydro-base (picrate, m. p. 194°). Similar con-

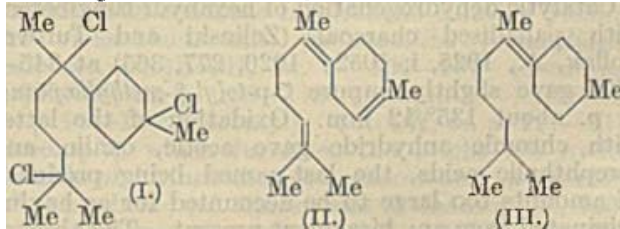
densation of I with ethyl acetylacetoacetate yields the corresponding 3-carbethoxy-derivative, m. p. 139°, of II, which is hydrolysed to the free acid, m. p. 232°. The latter, when heated above its m. p., gives carbon dioxide and II. With ethyl laevulate I condenses to give a poor yield of a substance, m. p. 150°, probably $C_{10}H_{15}\cdot O\cdot N\cdot CMe\cdot [CH_2]_2\cdot CO_2Et$. Molten zinc chloride converts I into a double zincchloride, $(C_{10}H_{15}\cdot O\cdot NH_2)_2\cdot ZnCl_2$, m. p. 217—234°, whilst monochloroacetone and I yield a neutral substance, m. p. 226°, and a basic substance, m. p. 186°.

J. W. BAKER.

Fenchene. J. L. KONDAKOV (Chem. Listy, 1929, 23, 49—54).—*D-l*-Fenchyl alcohol, m. p. 45°, $[\alpha]_D -12.3^\circ$, when heated at 180° with potassium hydrogen sulphate yields fenchene and α -fenchyl alcohol, m. p. 48.5—49°. The latter alcohol, submitted to similar treatment, gives a product, m. p. 47°, which after repeated heating with potassium hydrogen sulphate gives finally an alcohol, m. p. 49°. The alcohol, m. p. 48.5—49°, differs from that of Kenyon and Priston (A., 1925, i, 941) in its rotatory power, as does also its hydrogen phthalate. Two urethanes, having m. p. 84° and 82—83°, are prepared from α -fenchyl alcohol at the ordinary temperature and at 100°, respectively. α -Fenchyl chloride, b. p. 90°/13 mm., prepared from the alcohol, m. p. 48.5—49°, was converted by alcoholic potassium hydroxide into *D-l*- α -fenchene, b. p. 157.5—160°/752 mm., $[\alpha]_D -34.5^\circ$. Oxidation of the fenchene so obtained with cold alkaline permanganate yields *D-l*- α -fenchylcamphorone (semicarbazone, m. p. 210—211°) and α -oxyfenchenic acid. The above results indicate that Kenyon and Priston's alcohol was contaminated with the β -isomeride, and consequently that the hydrogen phthalate method of separation of the α - and β -forms is imperfect.

R. TRUSZKOWSKI.

Higher terpene compounds. XXXV. Constitution of bisabolene. L. RUZICKA and A. G. VAN VLEEN (Annalen, 1929, 468, 133—143).—An investigation of bisabolene, obtained either from opopanax oil by redistillation or from the trihydrochloride (I). The hydrocarbon has the constitution (II) for the following reasons: ozonolysis of bisabolene in carbon



tetrachloride or in glacial acetic acid produces acetone and laevulinic and succinic acids. This agrees with II but could be accounted for on the two other possible formulæ. Reduction of bisabolene in cyclohexane solution, using platinum-black and hydrogen, gives the tetrahydro-derivative, also obtained using platinum oxide. On the other hand, using platinum oxide in glacial acetic acid, hexahydrobisabolene is formed (cf. Semmler and Rosenberg, A., 1913, i, 377). The slow addition of the last two atoms of hydrogen is best explained by formula III for tetrahydrobisabolene, corresponding with II for bisabolene.

Tetrahydrobisabolene is III, since when it is submitted to ozonolysis a mixture of β -methylheptan- ζ -one and 4-methylcyclohexanone results, recognised by oxidation to a mixture of δ -methylhexoic and β -methyladipic acids.

The absence of diacetylvaleric acid and of formaldehyde or formic acid in the products of ozonolysis of bisabolene excludes the possibility of the sesquiterpene being a mixture of II (the γ -form) with the α - and β -forms.

Dehydrogenation of bisabolene using 2 atoms of sulphur gives a benzene derivative (oxidised to terephthalic acid, which is not obtained when bisabolene itself is oxidised) and not a naphthalene derivative. Selenium gives results similar to those obtained using sulphur.

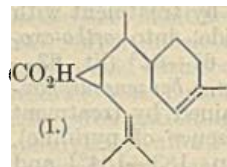
E. E. TURNER.

Higher terpene compounds. XXXVI. Constitution of zingiberene. L. RUZICKA and A. G. VAN VEEN (Annalen, 1929, 468, 143—162).—Crude zingiberene from ginger oil is a mixture of zingiberene and γ -bisabolene (preceding abstract), for when it is treated with hydrogen chloride in anhydrous ethereal solution, bisabolene trihydrochloride separates. If moisture is not rigorously excluded, some *isozingiberene* dihydrochloride is also formed. When crude zingiberene is treated with glacial acetic and sulphuric acids, *isozingiberene* is produced, converted by absolute ether and hydrogen chloride into *isozingiberene* dihydrochloride. Ozonolysis of crude zingiberene gives acetone and lævulic and succinic acids (once, a trace of formaldehyde was observed). The yield of the acids shows that the amount of bisabolene present in the mixture does not exceed 20—30%, a fact in accord with the possibility of isolating analytically pure dihydrozingiberene by a reduction process (sodium and alcohol) which does not affect bisabolene.

Crude zingiberene undergoes catalytic hydrogenation in presence of platinum-black to give *tetrahydrozingiberene*, b. p. 130—135°/18 mm., d_4^{25} 0.842, n_D^{25} 1.463. Ozonolysis of the crude reduction product gave methylheptanone (from the tetrahydrobisabolene) as the only recognisable product.

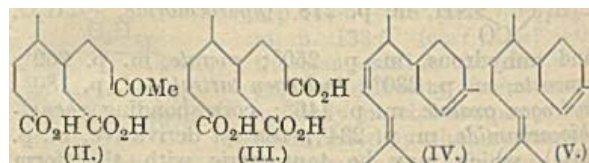
Catalytic dehydrogenation of hexahydrozingiberene with palladised charcoal (Zelinski and Turova-Pollak, A., 1925, i, 1052; 1926, 277, 365) at 345—360° gave slightly impure ζ -p-tolyl- β -methylheptane, b. p. about 135°/12 mm. Oxidation of the latter with chromic anhydride gave acetic, oxalic, and terephthalic acids, the last-named being produced in amounts too large to be accounted for as having originated from any bisabolene present. The absence of a tri- or tetra-carboxylic acid of benzene in the oxidation mixture shows that the skeleton of zingiberene is similar to that of bisabolene. The above heptane, b. p. 135—136°/15 mm., d_4^{25} 0.8524, n_D^{25} 1.4832, was synthesised by treating methylheptenone with magnesium *p*-tolyl bromide, heating the resulting mixture of hydrocarbon and carbinol with potassium hydrogen sulphate at 200°, and reducing the product catalytically (platinum-black). Chromic acid oxidation of the heptane gave terephthalic acid in yield similar to that obtained from the naturally-derived heptane.

Since bisabolene does not react with ethyl diazoacetate, which adds readily to conjugated double linkings, crude zingiberene was treated with this ester. Hydrolysis of the product gave an oily acid, $C_{17}H_{26}O_2$, b. p. 170—180°/0.3 mm. (alkaline solution is a soap), together with a little dizingiberene (?). The acid is regarded as being I. It is converted by ozone into much acetone. Catalytic reduction of the crude ester obtained from ethyl diazoacetate and crude zingiberene underwent catalytic hydrogenation in presence of



platinum oxide, but the product decomposed when distilled. It was therefore heated with selenium at 270—300°; the dehydrogenation product (b. p. 140—180°/12 mm.) so obtained gave some terephthalic acid on oxidation, proving that zingiberene is a 1:4-substituted cyclohexane derivative.

Reduction of crude zingiberene with sodium and absolute alcohol (Semmler and Becker, A., 1913, i, 742) gave dihydrozingiberene, having b. p. 135—136°/15 mm., d_4^{25} 0.865, and n_D^{25} 1.4881. It was unaffected by ethyl diazoacetate, gave an amorphous product when treated with hydrogen chloride, and gave some cadalene when heated with sulphur at 180—250°. Ozonolysis of dihydrozingiberene gave merely acetone and succinic and lævulic acids, but oxidation of the ozonide with permanganate gave a mixture of acids, converted into a mixture of two esters, $C_{14}H_{24}O_5$, A, b. p. 145°/0.3 mm., and B, b. p. 150°/0.3 mm., corresponding with a dicarboxylic acid of the formula $C_{12}H_{20}O_5$ (exclusion of one possible formula for dihydrozingiberene). Oxidation of the ester mixture with sodium hypobromite gave a mixture of two esters, $C_{14}H_{24}O_6$, A', b. p. 140—145°/0.3 mm., and B', b. p. 145—150°/0.3 mm., corresponding with a tricarboxylic acid, $C_{11}H_{18}O_6$. The C_{12} acid is therefore II, the C_{11} acid is III, zingiberene is IV, and dihydrozingiberene is V.



The fact that bisabolene does not and zingiberene does give cadalene when heated with sulphur or selenium is clearly due to hindrance of dehydrogenation by the hemicyclic double linking in bisabolene. Similarly, it is possible to account for the fact that zingiberene is much more readily converted, by acids, into a hydrogenated naphthalene hydrocarbon (*isozingiberene*).

E. E. TURNER.

Higher terpene compounds. XXXVII. Agathidicarboxylic acid, the crystalline resin acid, $C_{20}H_{30}O_4$, of kauri, hard and soft Manila copals. L. RUZICKA and J. R. HOSKING (Annalen, 1929, 469, 147—192; cf. Tschirsch and Koch, A., 1902, i, 478).—The isolation of the ether-soluble crystalline resin acids from the above copals by the method of Horrmann and Kroll (B., 1927, 609) and careful fractionation of the product with ammonium

carbonate, sodium carbonate, and sodium hydroxide is described. From each copal is isolated the same crystalline dibasic acid, $C_{20}H_{30}O_4$, m. p. 203—204°, $[\alpha]_D$ varying from +52° to +56° in alcohol, for which the name *agathidicdicarboxylic acid* (I) is suggested. The various dibasic acids isolated from different copals and described under various names in the literature are probably more or less impure forms of this acid. By a large number of analyses and direct comparison of the acids (crystallographic data by GOEDHART) and the derivatives described below, the identity of the parent acids from various sources is definitely established and the above composition assigned in preference to the alternative $C_{20}H_{28}O_4$. Molecular refractivity data of the various derivatives support this conclusion. The systematic nomenclature used throughout this abstract is that suggested by the authors to replace the various names occurring in the earlier literature. By the silver salt method I yields a *dimethyl ester*, b. p. 196—198°/0.6 mm., $[\alpha]_D$ +61.2° to +54.6° in alcohol, d_4^{25} 1.076, n_D^{25} 1.5178. Catalytic reduction (by various methods) of I yields the saturated *tetrahydroagathidicdicarboxylic acid*, purified through its *dimethyl ester*, b. p. 189—190°/1 mm., 165—166°/0.1 mm., $[\alpha]_D$ +47.9° to +42.2° in alcohol, d_4^{25} 1.040, n_D^{25} 1.4910. By heating it above its m. p. I is converted (17—20% yield) by loss of carbon dioxide into *noragathic acid*, $C_{18}H_{30}O_2$, b. p. 195—197°/0.9 mm., 180—183°/0.4 mm., m. p. 146—147° [Hornmann and Kroll (*loc. cit.*) describe it as a glass, m. p. 60°], $[\alpha]_D$ +59.3° in alcohol (*methyl ester*, b. p. 151—152°/0.6 mm., $[\alpha]_D$ +57.02° in alcohol, d_4^{25} 1.002, n_D^{25} 1.5087), which is reduced catalytically to *tetrahydronoragathic acid*, m. p. 133°, $[\alpha]_D$ +50.3° in alcohol (*methyl ester*, b. p. 141—142°/0.3 mm., m. p. 52—53°, $[\alpha]_D$ +53.7° in alcohol, d_4^{25} 0.9411, n_D^{25} 1.4693). I thus contains two double linkings which, unlike those in abietic acid, exhibit no difference in reactivity and the molecular refractivity data are in good agreement with the bicyclic structure thus required. Evidence to be published later shows that I is a reduced naphthalene derivative which is isomerised by strong acids to a hydrophenanthrene derivative. Catalytic dehydrogenation of the amorphous, ether-soluble resin acids from kauri copal with selenium (Diels and others, A., 1928, 169) yields the methyl-ethylnaphthalene obtained similarly from soft Manila copal (Ruzicka, Steiger, and Schinz, A., 1927, 60), a *hydrocarbon*, $C_{17}H_{20}$ (*picrate*, m. p. 138°), and some retene, but no pimarane. Similarly, dehydrogenation of the pure acid I (subsequent communication) yields the same *hydrocarbon* $C_{17}H_{20}$, and pimarane, but no retene.

J. W. BAKER.

[Acid from] Finnish pine resin. A. M. NORDSTROM (J. pr. Chem., 1929, [ii], 121, 204—222).—The acid fraction of the resin, obtained by extraction with sodium carbonate solution and subsequent acidification, gives after extraction with ether and light petroleum, followed by ten-fold crystallisation from alcohol, 14% of an *acid* (I), $C_{20}H_{30}O_2$, m. p. 142—143°, $[\alpha]_D^{18}$ —102.73° in alcohol, —71.8° in benzene, $[\alpha]_D^{19}$ —14.7° in acetic acid (*silver salt*). This furnishes a crystalline *ammonium salt*, and belongs therefore to the pimaric acid group. The acid is practically

unaffected by repeated crystallisation from alcohol (cf. Dupont, A., 1921, i, 510), but prolonged heating of an alcoholic solution causes a diminution in the rotation; in acetic acid-alcohol solution the change is more rapid. When fused at 150°, I is converted into an isomeric *acid*, m. p. 144—145°, $[\alpha]_D$ +56.59° in benzene, +35.83° in alcohol; at 180—205° this change is followed by the production of a *laevo-acid* (cf. Ruzicka, A., 1923, i, 818). Both of the above acids are isomerised by treatment with a 2.6% alcoholic hydrogen chloride solution (cf. Kesler, Lowy, and Faragher, A., 1928, 60), or by heating above 150° into abietic acid, m. p. 166—167°, $[\alpha]_D^{18}$ —92.54° in alcohol (gelatinous ammonium salt).

The neutral constituents of the resin are a turpentine oil (3%), b. p. 156—158°, $[\alpha]_D^{18}$ —8.35° when distilled over sodium, and small amounts of a monoterpene *alcohol*, b. p. 90—95°/9 mm. (*phenylcarbamide* derivative, m. p. 110°), and a *hydrocarbon*, $C_{20}H_{34}$, b. p. 178°/9 mm., n_D^{25} 1.52307, $[\alpha]_D^{18}$ +77.24°, easily oxidised by air.

H. BURTON.

Preparation of 1:3-benzdioxin. F. D. CHATTAWAY and F. CALVET (Anal. Fis. Quím., 1928, 26, 417—422).—1:3-Benzdioxin, the parent substance of the condensation products of formaldehyde, chloral, dichloroacetaldehyde, and butylchloral with *p*-substituted phenols (A., 1926, 1242; 1927, 458, 967; 1928, 632, 750; this vol., 65), could not be obtained from the product of condensation of phenol and formaldehyde. It was, however, obtained indirectly from 6-nitro-1:3-benzdioxin (Borsche and Berkhout, A., 1904, i, 415), prepared by the condensation of formaldehyde and *p*-nitrophenol. When reduced with zinc in aqueous-alcoholic hydrochloric acid this yielded 6-amino-1:3-benzdioxin, isolated as the *hydrochloride*, m. p. 230° (decomp.). Diazotisation and heating with potassium stannite solution and steam-distillation of the reaction mixture yielded 1:3-benzdioxin, b. p. 211—212°/758 mm., a colourless liquid with a peculiar odour.

R. K. CALLOW.

Reactions between furfuraldehyde, aniline, and malonic acid. T. BOEHM (Arch. Pharm., 1929, 267, 129—141).—Furfuraldehyde, aniline, and malonic acid condense in alcoholic solution yielding the violet-black salt, *furfuraniline furfurylidene-malonate*, $[+\frac{1}{2}\text{EtOH}]$, m. p. 106—107° (decomp.); $+\frac{1}{2}\text{MeOH}$, m. p. 109—110° (decomp.); $+\frac{1}{2}\text{Pr}^n\text{OH}$, m. p. 99—100° (decomp.); $+\text{AcOH}$, m. p. 117—118° (decomp.), which furnishes the bright red hydrochloride of furfuraniline (ϵ -anilino- α -anilo- β -hydroxy- $\Delta^{2,5}$ -pentadiene) (cf. Zincke and Mülhausen, A., 1906, i, 33; Dieckmann and Beck, *ibid.*, 109; König, *ibid.*, 109), m. p. 173—174° [H_2O , m. p. 167—169° (decomp.)], when treated with hydrochloric acid. Similar compounds are produced when the aniline is replaced by other amines (given in parentheses): (*p*-toluidine) $\frac{1}{2}\text{EtOH}$, greenish-violet, m. p. 128—129° (decomp.); (*m*-toluidine) $\frac{1}{2}\text{EtOH}$, violet, m. p. 98—100°; (*p*-chloroaniline), black, m. p. 120—121°; (*p*-bromoaniline), greenish-black, m. p. 121—122°; (*p*-phenetidine), dark blue, m. p. 135—136°; (ψ -cumidine), $\frac{1}{2}\text{EtOH}$, dark green, m. p. 97—99°. The following salts of furfuraniline are obtained when aniline and furfuraldehyde are allowed to react in molecular

proportions with the appropriate acid: *oxalate*, violet, m. p. 138—139° (EtOH), red, m. p. 135—136° (decomp.); *acetate*, bluish-violet, giving blood-red solutions (AcOH), m. p. 63°; *fumarate* ($\frac{1}{2}$ EtOH), m. p. 137—138°; *tartrate* ($\frac{1}{2}$ EtOH), reddish-violet, m. p. 159—162° (decomp.); *citrate* ($\frac{1}{2}$ EtOH), dark violet, m. p. 130—131°. The *malonate* ($\frac{1}{2}$ EtOH), wine-red, m. p. 107—108°, is obtained by treating the furfurylidenemalonate with ammonia and dissolving the precipitated base in an alcoholic solution of malonic acid.

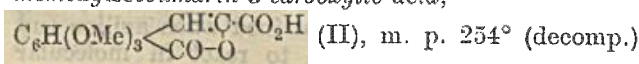
S. COFFEY.

Manufacture of alkylisopropenylphenols and alkylated coumarans. CHEM. FABR. AUF ACTIEN.—See B., 1929, 236, 237.

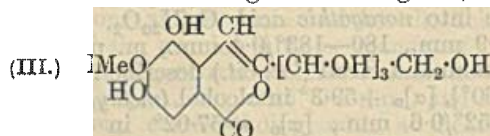
Coumarin condensations. I. Condensation of ethyl allylacetoacetate with phenols. K. G. NAIK, R. D. DESAI, and H. R. DESAI (J. Indian Chem. Soc., 1929, 6, 83—87).—Ethyl allylacetoacetate condenses with resorcinol in presence of cold concentrated sulphuric acid, yielding 7-hydroxy-4-methyl-3-allylcoumarin, m. p. 221—222° (acetyl derivative, m. p. 152—153°), since hydrolysis with boiling 50% aqueous potassium hydroxide gives resorcinol. When this condensation is carried out in presence of glacial acetic acid and dry hydrogen chloride the product formed is 7-hydroxy-4-methyl-3-chloropropylcoumarin, m. p. 200—201° (acetyl derivative, m. p. 122—123°; benzoyl derivative, m. p. 193°). This substance is unaffected by boiling with sodium acetate solution. Condensation of ethyl allylacetoacetate with α -naphthol, *m*-cresol, and phloroglucinol in presence of concentrated sulphuric acid gives 4-methyl-3-allyl-1:2- α -naphthopyrone, m. p. 155—156°, 4:7-dimethyl-3-allylcoumarin, m. p. 126—127°, and 5:7-dihydroxy-4-methyl-3-allylcoumarin, m. p. 207—208° (acetyl derivative, m. p. 130—131°), respectively. With phosphoryl chloride as the condensing agent pyrogallol furnishes 7:8-dihydroxy-4-methyl-3-allylcoumarin, m. p. 175—176° (acetyl derivative, m. p. 145—146°). A definite product was not isolated using phenol, and condensation did not proceed with pyrocatechol, guaiacol, thymol, quinol, and β -naphthol.

H. BURTON.

Non-tannin substances in the extract of the root of badan (*Saxifraga crassifolia*). I. **Bergenin.** A. E. TSCHITSCHIBABIN, A. V. KIRSSANOV, A. J. KORELEV, and N. N. VOROSCHZOV, jun. (Annalen, 1929, 469, 93—127; cf. Garreau and Machelart, Compt. rend., 1880, 91, 942).—Bergenin, $C_{14}H_{16}O_9$ (also $+H_2O$ which is lost at 100°), $[\alpha]_D -37.25^\circ$ in alcohol (mono- and di-sodium, and potassium salts), isolated from the acetone extract of badan roots after removal of tannins, contains six hydroxyl groups (by Zerevitinov's method) and one methoxyl group, but no carbonyl or free carboxyl groups. With excess of acetic anhydride it yields a *penta-acetyl* derivative, m. p. 199—203°, which still contains one hydroxyl group. Methylation of bergenin with diazomethane yields *dimethylbergenin*, $+2H_2O$, m. p. 80°, anhydrous, m. p. 194—196°, which when oxidised with alkaline potassium permanganate yields 5:6:7-trimethoxysocoumarin-3-carboxylic acid, (I), m. p. 84°, 5:6:7-trimethoxysocoumarin-3-carboxylic acid,



(silver salt which yields I by distillation in a vacuum; methyl ester, m. p. 155—156°), and 3:4:5-trimethoxyphthalic acid, b. p. 226°/17 mm., m. p. 139—140° with conversion into its anhydride, but in a bath at 170° it has m. p. 176—177° (decomp.). By the action of the theoretical quantity of boiling 0.1*N*-sodium hydroxide I is converted into a substance, m. p. 129°, probably $C_6H(OMe)_3(CO_2H) \cdot CH_2 \cdot CHO$ or $CH:CH \cdot OH$ (resinous derivative with phenylhydrazine), whilst with excess of 0.5*N*-sodium hydroxide it yields a substance, m. p. 185—186° (cf. Bamberger and Frew, A., 1894, i, 192). Further oxidation of I with alkaline potassium permanganate converts it into 3:4:5-trimethoxyhomophthalic acid, m. p. 145—146° (converted by distillation at 14 mm. into its anhydride, m. p. 124—125°). This acid is synthesised from 4-hydroxy-3:5-dimethoxyphthalide-2-carboxylic acid (Alimchandani and Meldrum, J.C.S., 1920, 117, 964) by reduction with hydriodic acid and red phosphorus and rapid methylation (in an atmosphere of hydrogen) of the resulting trihydroxyhomophthalic acid with methyl sulphate. By fusion with potassium hydroxide at 200° bergenin is converted into 3:5-dihydroxy-4-methoxybenzoic acid. On the basis of these results the structural conclusions of Sadikov and Guthner (A., 1928, 207) are criticised and the structure III is assigned to bergenin, and in

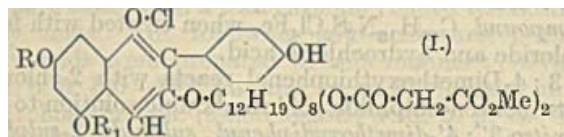


agreement with this it titrates as a lactone. The following reactions are rather less readily explained. Bergenin couples normally in alkaline solution with one molecule of benzenediazonium chloride to yield *benzeneazobergenin*, decomp. 200°, which, however, can couple with a second molecule of the diazonium salt to yield the substance $C_{14}H_{14}O_9(N_2Ph)_2$. The monoazo-derivative is reduced by stannous chloride to yield (3-)aminobergenin, $+3H_2O$ and anhydrous, m. p. 244° (decomp.) (yielding a *diazo-oxide*, $+2H_2O$ with nitrous acid). Like the parent isocoumarin, I and II are converted by ammonia under suitable conditions into the corresponding trimethoxysocoumarin-3-carboxylic acid, m. p. 165—167° (reduced by hydriodic acid to tetrahydroxyisoquinoline), and trimethoxysocoumarin-3-carboxylic acid, m. p. 280° (decomp.). The possible biosynthesis of bergenin from gallic acid and dextrose and its relationship to glucogallic acid (Feist, A., 1913, i, 70; Fischer and Bergmann, A., 1918, i, 224) are discussed.

J. W. BAKER.

Plant colouring matters. XII. Constitution of monardæin and salvianin. P. KARRER and R. WIDMER (Helv. Chim. Acta, 1929, 12, 292—295).—Monardæin (A., 1928, 1255) is shown to be identical with salvianin (Willstätter and Bolton, A., 1917, i, 42) on the basis of the following evidence. Like salvianin, hydrolysis of monardæin with 20% hydrochloric acid yields 24—26% of malonic acid, whilst hydrolysis of salvianin chloride with 10% sodium hydroxide yields *p*-hydroxycinnamic acid and salvianin chloride, m. p. 184° (lit. 168°), $[\alpha]_D -236^\circ \pm 20^\circ$, identical with monardin chloride, m. p. 184° (mixed

m. p.), $[\alpha]_D -241^\circ \pm 20^\circ$. The identity of these two compounds is confirmed by a comparison of their colours at various p_H values (Robinson). The structure



I is provisionally assigned to salvianin (monardæin) chloride (R and R_1 = either H or $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}$).
J. W. BAKER.

Bixin. F. FALTIS and F. VIEBOCK (Ber., 1929, 62, [B], 701—708).—In reply to Kuhn and Winterstein (A., 1928, 644), who, on the basis of microanalyses, have regarded the formula $\text{C}_{25}\text{H}_{30}\text{O}_4$ as correct for bixin (cf. Heiduschka and Panzer, A., 1917, i, 408), the analyses on which the authors base their formula $\text{C}_{26}\text{H}_{30}\text{O}_4$ are tabulated. If Kuhn's formula be correct, completely hydrogenated bixin and norbixin must have the compositions $\text{C}_{25}\text{H}_{48}\text{O}_4$ and $\text{C}_{25}\text{H}_{46}\text{O}_4$, respectively, and the latter substance must be a purely aliphatic, dicarboxylic acid. If, however, the formula $\text{C}_{26}\text{H}_{30}\text{O}_4$ be retained for bixin, perhydronorbixin has the composition $\text{C}_{25}\text{H}_{46}\text{O}_4$, which permits the presence of a ring system in the molecule, thus accounting better for the intense colour of bixin for which the structure

$\text{CH} \begin{cases} \text{CMe}\cdot\text{C}\cdot\text{CH}\cdot[\text{CH}\cdot\text{CMe}]_3\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Me} \\ \text{CH}=\text{C}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H} \end{cases}$ is suggested.

Bixin, dissolved in glacial acetic acid, is converted by hydrogen in presence of palladised barium sulphate into perhydrobixin, transformed by methyl-alcoholic hydrogen chloride into *perhydromethylbixin*, b. p. 278—285°/12 mm. The last-named compound is hydrolysed to perhydronorbixin, in which the presence of two carboxyl groups is established by conversion into the corresponding chloride and thence into the *diamide*, $\text{C}_{25}\text{H}_{18}\text{O}_2\text{N}_2$, m. p. 107—109° after softening at 100°, and (?) the *imide*, $\text{C}_{23}\text{H}_{44} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NH}$.

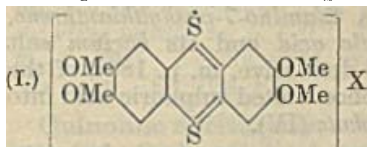
Treatment of perhydronorbixin with red phosphorus and bromine and subsequently with methyl alcohol yields an ester which appears to contain 5 atoms of bromine.
H. WREN.

Thianthrene. III. K. FRIES, H. KOCH, and H. STUKENBROCK (Annalen, 1929, 468, 162—201).—I. 2:3:6:7-Tetramethoxythianthrene and its oxidation products. An improved method is given for preparing 4-aminoveratrole, the *acetyl* derivative, m. p. 135°, of which is converted by phosphorus pentasulphide and potassium sulphide in boiling toluene into 4:5-dimethoxythioacetanilide, m. p. 114° (yield 55%). Oxidation of the latter with alkaline ferricyanide gives 4:5-dimethoxy-1-methylbenzthiazole, p. 75°, b. p. 184°/11 mm. (yield 40%). This substance is converted by alcoholic potassium hydroxide at 100° (pressure) into the *sodium* derivative of 2-amino-4:5-dimethoxythiophenol, which with nitrous acid gives 4:5-dimethoxybenzthiodiazole, m. p. 138°, converted by heat into 2:3:6:7-tetramethoxythianthrene, m. p. 174°, b. p. 280—300°/14 mm.

P F

The conditions for converting veratrole into potassium 3:4-dimethoxybenzenesulphonate and thence into 3:4-dimethoxybenzenesulphonyl chloride (yield 50—60%) are given. Reduction of the chloride with zinc dust and hydrochloric acid in presence of ether gives 3:4-dimethoxythiophenol, b. p. 138°/14 mm., converted by alcoholic hydrogen peroxide into 3:4:3':4'-tetramethoxydiphenyl disulphide, m. p. 89°. When the thiophenol is treated with sulphuric acid and then with stannous chloride, there again results tetramethoxythianthrene (m. p. 176°). Oxidation of the latter with dilute nitric acid in acetic acid gives the *monosulphoxide*, m. p. 196°, whilst concentrated nitric acid and acetic acid gives the *disulphoxide*, m. p. 259°, converted into the thianthrene by hydrobromic and acetic acids and sodium hydrogen sulphite. When chlorine is passed into an aqueous-acetic acid solution of tetramethoxythianthrene, the *sulphonesulphoxide*, m. p. 275°, is formed. This is converted by sulphuric acid into the monosulphone, m. p. 253° (below), together with a red compound which with sodium hydrogen sulphite and glacial acetic acid gives the *trimethyl ether*, m. p. 270°, of 2:3:6:7-tetrahydroxythianthrenesulphonesulphoxide. Tetramethoxythianthrenesulphonesulphoxide when treated first with hydrogen bromide and acetic acid and then with sodium hydrogen sulphite gives 2:3:6:7-tetramethoxythianthrenemonosulphone, m. p. 253°, converted into the former compound by nitric and acetic acids. Oxidation of tetramethoxythianthrene with hydrogen peroxide and glacial acetic acid gives 2:3:6:7-tetramethoxythianthrenedisulphone, m. p. 296°, which with boiling alcoholic potassium hydroxide affords 4:5-dimethoxy-2-ethoxybenzenesulphinic acid, sintering at 75°, m. p. 118—120° (decomp.). This substance is converted by hydrogen bromide and glacial acetic acid, followed by sodium hydrogen sulphite, into 3:4:3':4'-tetramethoxy-2:2'-diethoxydiphenyl disulphide, m. p. 84°, reduction of which or of the sulphinic acid (stannous chloride, glacial acetic acid) produces the readily oxidised 3:4-dimethoxy-2-ethoxythiophenol (not isolated).

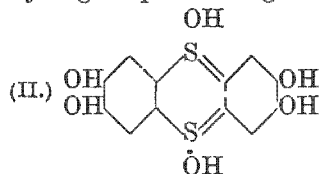
When a solution of tetramethoxythianthrene in concentrated sulphuric acid is allowed slowly to absorb atmospheric moisture, the deep blue *meriquinonoid dithionium* salt (I, $\text{X}=\text{SO}_4\text{H}$), m. p. 230—232° (decomp.), is formed. This is (1) reduced by stannous chloride or hydriodic acid to the thianthrene and (2) slowly hydrolysed by water or more rapidly by hot dilute acetic acid to a mixture of the thianthrene and its sulfoxide. The corresponding *perchlorate* (I, $\text{X}=\text{ClO}_4$) explodes at 245°, and the *chloride* (I, $\text{X}=\text{Cl}$) has m. p. 164—166° (decomp.). The *perbromide* (I, $\text{X}=\text{Br}_3$), m. p. 220—



222° (decomp.), results when excess of bromine is added to a solution of the thianthrene in carbon disulphide. So great is the tendency for the formation of the perbromide that the latter is formed when the monosulphoxide or the disulphoxide is treated with hot hydrogen bromide and glacial acetic acid.

Tetramethoxythianthrene is converted by boiling hydriodic and acetic acids into 2:3:6:7-tetra-

hydroxythianthrene, m. p. 273° (tetra-acetyl derivative, m. p. 224°), which, when treated in acetic acid with hydrogen peroxide gives the blue anhydride of



2:3:6:7-tetra-acetoxythianthrene sulphoxide, m. p. 213°, hydrolysable to the blue substance.

When tetramethoxythianthrenemonosulphone is heated with hydriodic and acetic acids, 2:3:6:7-tetrahydroxythianthrenemonosulphone, charring above 300°, results (tetra-acetate, m. p. 203°). Similar treatment of the disulphone produces 2:3:6:7-tetrahydroxythianthrenedisulphone, m. p. above 310° (tetra-acetate, m. p. 245°). Bromination of the latter gives the 1:4:5-tribromo-derivative, m. p. above 340°, or the 1:4:5:8-tetrabromo-derivative, m. p. above 350° (tetra-acetate, decomp. 300°).

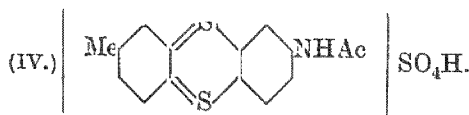
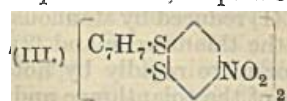
When a solution of tetrahydroxythianthrene in concentrated sulphuric acid is allowed to absorb moisture, a meriquinonoid dithionium sulphate is formed (I, OH instead of OMe and X=SO₄H). This is reducible to the thianthrene and is hydrolysed in excess of water. The corresponding perchlorate, bromide, and chloride are described.

Nitric and acetic acids convert tetramethoxythianthrene into 1:8(?)-dinitro-2:3:6:7-tetramethoxydiphenylenesulphone, m. p. 238°, also formed when tetramethoxythianthrene-monosulphone or -sulphonoxide (?) is treated with cold nitric acid.

4-Bromo-5-nitroveratrole is converted by alcoholic sodium sulphide into 2:2'-dinitro-4:5:4':5'-tetramethoxydiphenyl sulphide, m. p. 209° (60% yield), reduced by stannous chloride in hydrochloric and acetic acids to 2:2'-diamino-4:5:4':5'-tetramethoxydiphenyl sulphide, m. p. 110°, which could not be converted into the diphenylene sulphide.

II. Amino-derivatives of thianthrene. From thio-*p*-cresol and 2-chloro-5-nitrobenzenesulphinic acid may be obtained 4-nitro-4'-methylthianthrene 2-sulphinic acid, m. p. 123°, converted by hot hydrogen

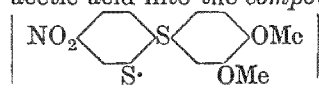
bromide and acetic acid into the compound (III), m. p. 154° (yield 60%), or, by cold concentrated sulphuric acid into 2-nitro-7-methylthianthrene, m. p. 157°, which when reduced affords 2-amino-7-methylthianthrene, m. p. 130° (1-sulphonic acid and its barium salt described). The acetyl derivative, m. p. 180°, of the base is converted by concentrated sulphuric acid into the half-quinonoid sulphate (IV).



2-Chloro-5-nitrobenzenesulphinic acid condenses with 4-acetamidothiophenol in alkaline solution to give 4-nitro-4'-acetamidodiphenyl sulphide 2-sulphinic

acid, converted by concentrated sulphuric acid into the acetyl derivative, m. p. 205°, of 2-nitro-7-aminothianthrene, m. p. 198°. This when reduced affords 2:7-diaminothianthrene, m. p. 192°, giving a deep blue compound, C₁₂H₁₀N₂S₂Cl₄Fe, when treated with ferric chloride and hydrochloric acid.

3:4-Dimethoxythiophenol reacts with 2-chloro-5-nitrobenzenesulphinic acid in alkaline solution to give 4-nitro-3':4'-dimethoxydiphenyl sulphide 2-sulphinic acid, m. p. 131°, converted by hydrogen bromide and acetic acid into the compound



, m. p. 196°, and by concentrated sulphuric acid into 2-nitro-6:7-dimethoxythianthrene, m. p. 194°, b. p. 192—196°/14 mm., also formed from the compound, m. p. 196°, and the same reagent. Reduction of the nitro-compound gives 2-amino-6:7-dimethoxythianthrene, m. p. 149° (acetyl derivative, m. p. 180°). When 2-bromo-5-nitroaniline is heated with alcoholic sodium disulphide and sulphur, there results 4:4'-dinitro-2:2'-diaminodiphenyl sulphide, m. p. 211° (diacetyl derivative, m. p. 245°), which could not be obtained when sodium sulphide was used, whilst if excess of sulphur were taken the product was 4-nitro-2-aminothiophenol, m. p. 108°, oxidised by air to 4:4'-dinitro-2:2'-diaminodiphenyl disulphide, m. p. 178°. The diacetyl derivative, m. p. 263°, of the latter is converted by sodium sulphide or dextrose in alkaline-alcoholic solution into 4-nitro-2-methylbenzthiazole, the corresponding dibenzoyl derivative, m. p. 225°, similarly giving 4-nitro-2-phenylbenzthiazole, m. p. 193°, also obtained by benzoylating 4-nitro-2-aminothiophenol in presence of alkali or from 2-bromo-5-nitrobenzanilide, m. p. 166°, and sodium disulphide. Thianthrene derivatives could not be obtained from the dinitrodiaminodiphenyl sulphide or from the related compounds.

E. E. TURNER.

γ-Pyrrolidino- and γ-pyrrolino-propyl benzoates. L. H. ANDREWS and S. M. McELVAIN (J. Amer. Chem. Soc., 1929, 51, 887—892).—Pure pyrrole, prepared by an improved method, is hydrogenated in presence of Adams' platinum catalyst to pyrrolidine (cf. Willstätter and Hatt, A., 1912, i, 545), which with γ-chloropropyl benzoate at 100° yields γ-1-pyrrolidinopropyl benzoate hydrochloride (I), m. p. 125—126°. Pyrrolone (Knorr and Rabe, A., 1901, i, 163) yields γ-1-pyrrolinopropyl benzoate hydrochloride (II), m. p. 136—138°. Attempts to hydrogenate 2-carbethoxypyrrole and a mixture of 2- and 3-methylpyrroles were unsuccessful. I is a more powerful local anæsthetic than II and, unexpectedly, both are more powerful than γ-piperidinopropyl benzoate hydrochloride (A., 1928, 71).

H. E. F. NORTON.

Alkylated pyrrolones. Synthesis of γ-ketonic and of fatty acids. R. LUKES (J. Czechoslov. Chem. Comm., 1929, 1, 119—136).—The following new pyrrolones have been prepared by the action of the Grignard reagent on the *N*-substituted succinimides (A., 1928, 299): 1-methyl-2-*n*-amyl-5-pyrrolone, b. p. 143—148°/10 mm., and 1-methyl-2-*n*-hexyl-5-pyrrolone, b. p. 148—150°/10 mm. Hydrolysis of the pyrrolones with dilute sulphuric acid afforded the corresponding

γ -ketonic acids, probably through the intermediate formation of a hydrate, whilst electrolytic reduction of the γ -ketonic acids, which need not be isolated in the pure state, with a lead cathode yielded the normal fatty acids. The following keto-acids and normal fatty acids were prepared in this manner: *laevulic acid*, b. p. 150—152°/23 mm., m. p. 33° (oxime, m. p. 96°); *homolaevulic* (β -ketoheptanoic) acid, b. p. 160°/24 mm., m. p. 40° (oxime, m. p. 76°), and *hexoic acid*, b. p. 201°; γ -ketoheptanoic acid, b. p. 167°/19 mm., m. p. 45—46°, and *heptanoic acid*, b. p. 217—218°; γ -keto-octanoic acid, b. p. 160—170°/25 mm. (slight decomp.), m. p. 53°, and *octanoic acid*, b. p. 225—235°; γ -ketononoic acid, m. p. 69—70°, and *nonoic acid*, b. p. 250°; γ -ketodecanoic acid, m. p. 71°, and *decanoic acid*, b. p. 260—265°, m. p. 30°. A. I. VOGEL.

Piperidine derivatives. VII. 1-Alkyl-4-piperidyl benzoates and *p*-aminobenzoates. N. W. BOLYARD and S. M. McELVAIN (J. Amer. Chem. Soc., 1929, 51, 922—928).—3-Carbethoxy-1-alkyl-4-piperidones (A., 1928, 72) have been converted by boiling 20% hydrochloric acid into the following 1-alkyl-4-piperidone hydrochlorides: *methyl*, m. p. 94—95° (corr.); *ethyl*, m. p. 105—106°; *n-propyl*, m. p. 117—118°; *n-butyl*, m. p. 178—180°; *isoamyl*, m. p. 183—185°, and *phenylethyl*, m. p. 182—184°, which are hydrogenated (platinum) and then benzoylated at 160—165° to 1-*methyl*-, m. p. 219—220°; 1-*ethyl*-, m. p. 204—205°; 1-*n-propyl*-, m. p. 210—211°; 1-*n-butyl*-, m. p. 223—224°; 1-*isoamyl*-, m. p. 199—200°, and 1-*phenylethyl*-, m. p. 236—238°, 4-*piperidyl benzoate hydrochlorides*. 1-*Methyl*-, m. p. 197—199°; 1-*ethyl*-, m. p. 204—206°; 1-*n-propyl*-, m. p. 219—220°; 1-*n-butyl*-, m. p. 242—243°; 1-*isoamyl*-, m. p. 243—245°, and 1-*phenylethyl*-, m. p. 242—244°, 4-*piperidyl p-nitrobenzoate hydrochlorides* are hydrogenated (platinum) to 1-*methyl*-, m. p. 231—233°; 1-*ethyl*-, m. p. 183—184°; 1-*n-propyl*-, m. p. 201—203°; 1-*n-butyl*-, m. p. 234—236°; 1-*isoamyl*-, m. p. 233—235°, and 1-*phenylethyl*-, m. p. 238—240°, 4-*piperidyl p-aminobenzoate hydrochlorides*. The benzoates are, in general, more powerful local anaesthetics than the *p*-aminobenzoates and the activity increases with the size of the alkyl group. The results are discussed in relation to previous work (cf. A., 1926, 1044). 1-Phenylethyl-4-piperidyl benzoate hydrochloride is about seven times as powerful as cocaine hydrochloride and is much less toxic.

H. E. F. NOTTON.

Local anaesthetics from 2- β -hydroxyethylpiperidine. C. S. MARVEL and R. S. SHELTON (J. Amer. Chem. Soc., 1929, 51, 915—917).—1-*Methyl*-(a), b. p. 175—178°/35—40 mm., d_4^{20} 0.9840, n_D^{20} 1.4872; 1-*ethyl*-(b), b. p. 136°/27—28 mm., d_4^{20} 0.9730, 1.4885, and 1-*n-propyl*-(c), b. p. 139—141°/27 mm., d_4^{20} 0.9657, n_D^{20} 1.4905, 2- β -hydroxyethylpiperidines (cf. Ladenburg, A., 1898, i, 687; 1910, i, 769) yield *p*-nitrobenzoate hydrochlorides, m. p. (a) 181—182°, (b) 198—199°, (c) 124—126°, which are readily hydrogenated (platinum) to *p*-aminobenzoate hydrochlorides, (a) oily, (b), m. p. 238—239.5°, (c), m. p. 175—176°. These are less active anaesthetics than the corresponding 1-alkyl-3-piperidylmethyl esters (A., 1928, 427).

H. E. F. NOTTON.

Action of aromatic acid chlorides on vinylidiacetoneamine [2 : 2 : 6-trimethyl-4-piperidone]. J. GRAYMORE (J.C.S., 1929, 587—588).—The observation that vinylidiacetoneamine cannot be benzoylated by the Schotten-Baumann method (Kipping and Greasley, A., 1924, i, 144) is confirmed with benzoyl chloride and substituted benzoyl chlorides. The effect is attributed to the existence of the base in the ammonium hydroxide form. Dilute solutions of ammonia and ethylamine are similarly non-reactive. The following derivatives of vinylidiacetoneamine were prepared by interaction of the base (2 mols.) with the appropriate acid chloride: *N*-*m*-nitrobenzoyl-, m. p. 159—160°; *N*-*p*-nitrobenzoyl-, m. p. 170°; *N*-*o*-nitro-*p*-toluoyl-, m. p. 150—151°; *N*-*p*-toluenesulphonyl-, m. p. 184°. R. K. CALLOW.

Bromination of pyridine. S. M. E. ENGLERT and S. M. McELVAIN (J. Amer. Chem. Soc., 1929, 51, 863—866).—Perbromides of pyridine hydrobromide, I, m. p. 132—134° (47% perbromide-Br) and II, m. p. 101—103° (40% perbromide-Br), are conveniently prepared in acetic acid (cf. Trowbridge and Diehl, A., 1898, i, 380). At 230—250° I gives 3 : 5-dibromopyridine (40% of theory), and with pyridine hydrobromide (2 mols.) 3-bromo- (35%) and 3 : 5-dibromo- (10%) -pyridines. II gives 36—38% of the mono- and 30—36% of the di-bromo-derivative, and is the most convenient source of these compounds.

H. E. F. NOTTON.

Nitration of benzylpyridines and oxidation of benzylpiperidines. F. BRYANS and F. L. PYMAN (J.C.S., 1929, 549—553; cf. A., 1927, 255).—Nitration of the three benzylpyridines by the addition of their nitrates to concentrated sulphuric acid gave the following yields of nitration products: from 2-benzylpyridine, 10.4% *m*- and 66.7% *p*-; from 3-benzylpyridine, 63.1% *p*-; from 4-benzylpyridine, 4.8% *o*- and 70.2% *m*-. The 2- and 4-benzylpiperidines and also 2-benzyl-1-methylpiperidine, m. p. 181° (from 2-benzylpiperidine and methyl iodide at 130°), do not simulate the 1-benzyltetrahydroisoquinolines (cf. Pyman, *ibid.*, 1909, 95, 1266, 1738) when oxidised with manganese dioxide and sulphuric acid. The following compounds are new: 1-benzenesulphonyl-2-benzylpiperidine, m. p. 65°; 1-benzoyl-2-benzylpiperidine, m. p. 68°; 1-benzenesulphonyl-4-benzylpiperidine, m. p. 118°; 2-benzylpyridine nitrate, m. p. 116°; 2-*m*-nitrobenzoylpiperidine, m. p. 122°; 3-benzylpyridine nitrate, m. p. 140°; 3-*p*-nitrobenzoylpiperidine, m. p. 88° (*picrate*, m. p. 145—146°; *nitrate*, m. p. 157°); 3-*p*-nitrobenzoylpiperidine, m. p. 185—187°; 4-benzylpyridine nitrate, m. p. 110°; 4-*m*-nitrobenzoylpiperidine, m. p. 129°. 2-*p*-Nitrobenzoylpiperidine hydrochloride has m. p. 187° (lit. 173°).

A. I. VOGEL.

Quinoline derivatives. XI. Synthesis of substituted 2-phenyl-4-ethylquinolines. H. JOHN [and in part M. E. SCHMIED] (J. pr. Chem., 1929, [ii], 121, 177—192).—The following quinolines (prepared by condensation of benzylidene-ethyl methyl ketone with the requisite amine hydrochloride, in yields as indicated) are described: from aniline, 2-phenyl-4-ethylquinoline (14%), m. p. 50° (*picrate*, m. p. 189—190°); from *m*-(1 : 3 : 4)-xylydine, 2-phenyl-6 : 8-dimethyl-4-ethylquinoline (7.5%), m. p. 88° (*picrate*, m. p.

158°); from *o*-anisidine, 8-methoxy-2-phenyl-4-ethylquinoline (13.1%), m. p. 76° (picrate, m. p. 140°); from *m*-toluidine, 2-phenyl-4-ethyl-5-(or -7)methylquinoline (20%), m. p. 112° [picrate, m. p. 185° (decomp. 188°)]; from *m*-aminophenol, 5-(or 7)-hydroxy-2-phenyl-4-ethylquinoline (13.9%), m. p. 219° (picrate, m. p. 211°); from *m*-phenetidine, 5-(or 7)-ethoxy-2-phenyl-4-ethylquinoline (35.7%), m. p. 118° (picrate, m. p. 215—216°); from *p*-toluidine, 2-phenyl-6-methyl-4-ethylquinoline (10.8%), m. p. 109° (picrate, m. p. 188°); from *p*-aminoethylbenzene, 2-phenyl-4:6-diethylquinoline, m. p. 158°; from *p*-chloroaniline, 6-chloro-2-phenyl-4-ethylquinoline (23%), m. p. 65—66° (picrate, m. p. 170°); from *p*-aminophenol, 6-hydroxy-2-phenyl-4-ethylquinoline (3.6%), m. p. 149°, [picrate, m. p. 204° (decomp.)]; potassium salt]; from *p*-anisidine, 6-methoxy-2-phenyl-4-ethylquinoline (14.1%), m. p. 193° (picrate, m. p. 173°); from *p*-phenetidine, 6-ethoxy-2-phenyl-4-ethylquinoline (9.9%), m. p. 122—123° (picrate, m. p. 189°).

The following were prepared by interaction of alkyl halides with the appropriate quinoline (as potassium salt): 5-(or 7)-methoxy-2-phenyl-4-ethylquinoline, m. p. 52°; 6-isobutoxy-2-phenyl-4-ethylquinoline, m. p. 102°; 6-isoamylloxy-2-phenyl-4-ethylquinoline, m. p. 91°; 6-allyloxy-2-phenyl-4-ethylquinoline, m. p. 116°; 6-phenacyloxy-2-phenyl-4-ethylquinoline, m. p. 136°.

The hydrochlorides, sulphates, mercurichlorides, periodides, and (in most cases) nitrates, chromates, and ferrocyanides of the above quinoline derivatives were prepared. R. J. W. LE FEVRE.

Cyclic *N*-hydroxy-compounds and *N*-oxides. G. HELLER (J. pr. Chem., 1929, [ii], 121, 269—272).—Whereas *N*-hydroxyindoles are readily obtained (cf. Reissert, A., 1909, i, 51), attempts to obtain *N*-hydroxyquinolines result in the production of *N*-oxides (cf. Meisenheimer and Stotz, A., 1926, 77; Heller, A., 1910, i, 558; 1928, 302). Thus, reduction of *o*-nitrocinnamoylformic acid with ferrous sulphate and ammonia gives quinoline-*N*-oxide-2-carboxylic acid, whilst *o*-nitrobenzylidenemalonamic acid yields 2-hydroxyquinoline-*N*-oxide-2-carboxylic acid, and not "*N*-hydroxycarbostyrlcarboxylic acid" [1-hydroxy-2-keto-1:2-dihydroquinoline-3-carboxylic acid] (Heller and Wunderlich, A., 1915, i, 301).

H. BURTON.

Synthesis of dehydrogenated isoquinoline derivatives. E. SPATH and N. POLGAR (Monatsh., 1929, 51, 190—204).—Substituted acyl- β -phenylethylamides are dehydrated with phosphoric oxide in boiling toluene into 3:4-dihydroisoquinoline derivatives, which are dehydrogenated with palladium-black at 150—180°. Thus, formhomoveratrylamide, m. p. 40—42°, affords 6:7-dimethoxy-3:4-dihydroisoquinoline [picrate, m. p. 201—203° (lit. 206—208°)], which is dehydrogenated either with palladised asbestos at 205—210° or, better, with palladium-black at 182—185° to 6:7-dimethoxyisoquinoline, m. p. 93—94° (cf. Goldschmidt, A., 1887, 163). Acet-homoveratrylamide, m. p. 94—95°, yields 6:7-dimethoxy-1-methyl-3:4-dihydroisoquinoline [picrate, m. p. 210—212° (lit. 205°)], dehydrogenated to 6:7-dimethoxy-1-methylisoquinoline, m. p. 111—112° [picrate, m. p. (vac.) 247—249° (decomp.)]. Oxid-

ation of this with potassium permanganate gives *m*-hemipinic acid, establishing the constitution. From propion-, m. p. 60—61°, and butyr-homoveratrylamide, m. p. 54—55°, there were obtained 6:7-dimethoxy-1-ethyl- [picrate, m. p. (vac.) 195—196°], and 6:7-dimethoxy-1-propyl-3:4-dihydroisoquinoline [picrate, m. p. (vac.) 180—181°], respectively. These are dehydrogenated to 6:7-dimethoxy-1-ethyl-, m. p. 75—76° (picrate, m. p. 213—214°), and 6:7-dimethoxy-1-propyl-isoquinoline, m. p. 83—84° [picrate, m. p. (vac.) 186—187°]. Similarly, form-, m. p. 62—63°, acet-, m. p. 105—106°, propion-, and butyr-homopiperonylamides give 6:7-methylenedioxy-, m. p. 92—94° [picrate, m. p. (vac.) 230—232°], 6:7-methylenedioxy-1-methyl-, m. p. 89—91° [picrate, m. p. (vac.) 242—244° (decomp.)], 6:7-methylenedioxy-1-ethyl-, m. p. 75—76° [picrate, m. p. (vac.) 205—206° (decomp.)], and 6:7-methylenedioxy-1-propyl-3:4-dihydroisoquinoline, m. p. 78—79° [picrate, m. p. (vac.) 183—184°], respectively. Dehydrogenation of these derivatives gives 6:7-methylenedioxy-, m. p. 127—128° [picrate, m. p. (vac.) 240—241°], 6:7-methylenedioxy-1-methyl-, m. p. 159—160° [picrate, m. p. (vac.) 263—264° (decomp.)], 6:7-methylenedioxy-1-ethyl-, m. p. 96—97° (picrate, m. p. 235—236°), and 6:7-methylenedioxy-1-propyl-isoquinoline, m. p. 88—89° (picrate, m. p. 210—211°), respectively.

H. BURTON.

Doebner reaction. VII. Synthesis with β -aminoanthracene. R. CRUSA and L. MUSAJO (Gazzetta, 1929, 59, 70—74).—The Doebner reaction (cf. A., 1928, 629) with β -aminoanthracene, benzaldehyde, and pyruvic acid gives 3-phenyl- β -anthraquinoline-1-carboxylic acid, m. p. 285° (sodium salt, +5H₂O; methyl ester, m. p. 204°), which when heated above its m. p. yields 3-phenyl- β -anthraquinoline, m. p. 236°. E. W. WIGNALL.

Doebner reaction. VIII. 3-Phenyl- β -anthraquinonequinoline-1-carboxylic acid. L. MUSAJO (Gazzetta, 1929, 59, 74—78).— β -Aminoanthraquinone does not undergo the Doebner reaction as does β -aminoanthracene (preceding abstract). The product which would be expected from the reaction can, however, be obtained by oxidation of the product from 3-aminoquinoline, and is 3-phenyl- β -anthraquinoline-7:12-quinone-1-carboxylic acid, decomp. 250°; potassium (+1.5H₂O), sodium, and silver salts are prepared, and a nitrate, C₂₃H₁₃N₂HNO₃. When the acid is heated, 3-phenyl- β -anthraquinoline-7:12-quinone, m. p. 284°, is formed, which on reduction furnishes blue compounds. E. W. WIGNALL.

Acridine compounds. K. MATSUMURA (J. Amer. Chem. Soc., 1929, 51, 816—820).—The preparation of 2:4:2':4'-tetranitrodiphenylmethane, 2:4:2':4'-tetranitrobenzophenone, and 2:8-diaminoacridone is described. The last is hydrolysed by 40% sulphuric acid at 195° to 2:8-dihydroxyacridone, m. p. above 320°, which cannot, however, be obtained by diazotisation and warming. 2:8-Dimethoxyacridone, m. p. above 320°, is converted by phosphorus pentachloride into 5-chloro-2:8-dimethoxyacridine, m. p. 184° (hydrochloride), which yields with ammonia and copper acetate in absolute alcohol at 140° 5-amino-2:8-dimethoxyacridine, m. p. 268° [hydrochloride, m. p. 315°].

(decomp.); *picrate*, m. p. 285°, decomp. from 273°. 5-Acetamido-2 : 8-dimethoxyacridine, m. p. 277—278°, readily affords 5-acetamido-2 : 8-dimethoxy-10-methylacridinium iodide, m. p. 310° (decomp.), *p*-toluenesulphonate, m. p. 280°, softening from 255°, and chloride, m. p. above 315°. The yields are good throughout.

H. E. F. NOTTON.

5 : 8-Dihydroxy- α -anthrapyridinequinone. H. RAUDNITZ [with G. LAUBE] (Ber., 1929, 62, [B], 509—513).—Addition of phthalic anhydride and quinol to a mixture of sodium and aluminium chlorides at 200° gives the aluminium compound of quinizarin, from which quinizarin, m. p. 198°, is obtained by successive treatment with excess of potassium hydroxide and dilute sulphuric acid. When similarly treated at 200° and finally at 230—240°, phthalic anhydride and 1 : 4-dihydroxynaphthalene afford 1 : 4-dihydroxy-2 : 3-benzanthraquinone, m. p. 349°. Analogously at 180—200°, quinol and quinolinic anhydride yield α -pyrquinizarin,

$C_5H_3N \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C_6H_2(OH)_2$, m. p. 237° (sodium salt), whilst quinolinic anhydride and 1 : 4-dihydroxynaphthalene give 6 : 7-benz- α -pyrquinizarin [5 : 8-dihydroxy-6 : 7-benz- α -anthrapyridinequinone],

$C_5H_3N \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C_{10}H_4(OH)_2$, m. p. 363° (sodium salt).

H. WREN.

Quinazolines. II. Synthesis of 6-ethoxy-3-*p*-ethoxyphenyl-3 : 4-dihydroquinazoline. G. MAFFEI (Gazzetta, 1929, 59, 3—9).—When 2-nitro-*o*-ethoxybenzaldehyde, m. p. 62°, obtained by the action of ethyl iodide and potassium hydroxide on the hydroxy-compound, is heated with *p*-phenetidine, it gives N-(2-nitro-5-ethoxybenzylidene)-*p*-phenetidine, m. p. 92°; this when reduced by sodium sulphide in alcohol gives the 2-amino-compound, m. p. 156°, and, on further reduction by sodium in alcohol, N-(2-amino-*o*-ethoxybenzyl)-*p*-phenetidine, m. p. 81°. This is converted by heating with formic acid into 6-ethoxy-3-*p*-ethoxyphenyl-3 : 4-dihydro-1 : 3-quinazoline (cf. A., 1928, 775), which can be reduced by sodium and amyl alcohol to the 1 : 2 : 3 : 4-tetrahydro-compound, m. p. 144°. 2-Nitro-5-ethoxybenzaldehyde forms an *oxime*, m. p. 125°, which is reduced by ammonium sulphide to 2-amino-*o*-ethoxybenzaldehyde, m. p. 132°, and this by sodium amalgam in alcohol to 2-amino-5-ethoxybenzylamine, forming a dihydrochloride, decomp. from 200°, completely at 235—237°; when this hydrochloride is heated with sodium formate and formic acid, 6-ethoxy-3 : 4-dihydro-1 : 3-quinazoline, m. p. 125—127°, is produced.

The physiological properties of ethoxy-*p*-ethoxyphenyldihydroquinazoline are lost when the C:N double linking is reduced, when either of the ethoxy groups is absent, or is replaced by a methyl group, and when the ethoxyphenyl group is absent. Alkylation of the imine group modifies the anæsthetic property.

E. W. WIGNALL.

Pyrimidines. CIV. isoUracil and derivatives; methods of synthesis. T. B. JOHNSON and W. T. CALDWELL (J. Amer. Chem. Soc., 1929, 51, 873—880).—Further attempts have been made (cf. A., 1907, i, 559) to establish the constitution of orotic

acid by synthesis. Ethyl α -diethoxyacetoacetate and thiocarbamide in alcohol in presence of sodium ethoxide give 6-hydroxy-2-thiol-5-ethoxy-4-ethoxymethylpyrimidine, m. p. 178°, which is desulphurised by chloroacetic acid to 2 : 6-dihydroxy-5-ethoxy-4-ethoxymethylpyrimidine, m. p. 168°, hydrolysed by hydrochloric acid at 120—140° to 2 : 4 : 5 : 6-tetrahydroxypyrimidine, m. p. above 320°. The crude product from ethyl ethoxyacetate and sodium yields with ethyl- ψ -thiocarbamide hydrobromide 6-hydroxy-5-ethoxy-2-ethylthiol-4-ethoxymethylpyrimidine, m. p. 123°, converted by phosphorus pentachloride into 6-chloro-5-ethoxy-2-ethylthiol-4-ethoxymethylpyrimidine, b. p. 165—166°/9—10 mm. This is reduced by zinc dust in aqueous alcohol to 5-ethoxy-2-ethylthiol-4-ethoxymethylpyrimidine, m. p. 167°, hydrolysed by hydrochloric acid to ethyl mercaptan and (?) 2-hydroxy-5-ethoxy-4-ethoxymethylpyrimidine, decomp. 281—284°. The sodio-derivative of ethyl ethoxyoxaloacetate yields with ethyl- ψ -thiocarbamide hydrobromide a little ethyl 6-hydroxy-5-ethoxy-2-ethylthiolpyrimidine-4-carboxylate, m. p. 82—83°, from which are prepared oily ethyl 6-chloro-5-ethoxy-2-ethylthiolpyrimidine-4-carboxylate and ethyl 5-ethoxy-2-ethylthiolpyrimidine-4-carboxylate, m. p. 55—56°. This is hydrolysed at 120° by hydrochloric acid to (?) 2 : 5-dihydroxypyrimidine-4-carboxylic acid (isouracilcarboxylic acid), m. p. 259° (decomp.), which may be identical with orotic acid. Ethyl ethoxyoxaloacetate, ethyl- ψ -thiocarbamide, and aqueous sodium hydroxide give ethyl 2 : 6-dihydroxy-*o*-ethoxypyrimidine-4-carboxylate, m. p. 230°, and the corresponding free acid, m. p. 260°, hydrolysed by hydrochloric acid at 160—165° to 2 : 5 : 6-trihydroxypyrimidine (isobarbituric acid). H. E. F. NOTTON.

Indole derivatives of mixed function. Q. MINGOIA (Gazzetta, 1929, 59, 105—115).—When 3-chloroacetyl-2-methylindole (Salway, J.C.S., 1913, 103, 354) is hydrolysed by alcoholic potassium hydroxide, the keto-alcohol 3-hydroxyacetyl-2-methylindole, m. p. 196° (N-silver derivative; diacetyl derivative, m. p. 101°), is produced. This is oxidised by alkaline potassium permanganate to 2-methylindolyl-3-glyoxylic acid (cf. Oddo and Albanese, A., 1928, 185). Similarly, when the chloro-compound is treated with alcoholic potassium cyanide, 3-cyanoacetyl-2-methylindole, m. p. 249°, is produced, which hydrolyses to 3-acetyl-2-methylindole-*o*-carboxylic acid, m. p. 199—200°, of which mercuric and other salts are prepared.

The chloro-compound reacts with concentrated aqueous ammonia in a sealed tube at 90—95° to form 3-aminoacetyl-2-methylindole, m. p. 240° (decomp.) (*picrate*, m. p. 207—210°; *hydrochloride*), which gives precipitates with various alkaloid reagents. No reaction is observed between the chloro-compound and glycine or alanine in absolute alcoholic solution.

E. W. WIGNALL.

Identification and separation of organic bases with the aid of glyoxalinedicarboxylic acid. H. PAULY and E. LUDWIG (Arch. Pharm., 1929, 267, 143—144).—Polemical. A reply to criticisms by Tamamushi (J. Pharm. Soc. Japan, 1928, 48, 107) of the authors' process (A., 1922, i, 953). S. COFFEY.

Dyes derived from acenaphthenequinone. Acenaphthiminazoles and acenaphthoxazoles.

A. C. SIRCAR and N. C. GUHA-RAY (J. Indian Chem. Soc., 1929, 6, 93—98).—Acenaphthenequinone reacts with aldehydes and ammonia, sometimes yielding the corresponding iminazoles and sometimes the oxazoles (cf. J.C.S., 1923, 123, 1559; A., 1925, i, 980). Thus when acenaphthenequinone and *m*-nitrobenzaldehyde dissolved in boiling amyl alcohol are treated with dry ammonia 2-*m*-nitrophenylacenaphthiminazole, darkens at 220° without melting, is formed. The following substituted acenaphthiminazoles were prepared similarly: 2-phenyl-, not melted at 290°; 2-*o*-hydroxyphenyl-, m. p. 268° (decomp.); 2-*p*-anisyl-, m. p. 268°; 2-4'-hydroxy-3'-methoxyphenyl-, m. p. 263°; 2-*p*-chlorophenyl-, m. p. 264° after shrinking at 242°; 6:7-dinitro-2-5'-bromo-2'-hydroxyphenyl-, not melted at 290°; 6:7-dinitro-2-*p*-anisyl-; 6-nitro-2-*o*-hydroxyphenyl-, and 6-nitro-2-4'-hydroxy-3'-methoxyphenyl-. The following substituted acenaphthoxazoles were obtained from the requisite aldehyde by the above method: 2-*o*-nitrophenyl-, not melted at 290° after shrinking at 263°; 2-*p*-dimethylaminophenyl-; 6:7-dinitro-2-*m*-nitrophenyl-; 6:7-dinitro-2-3':5'-dihydroxyphenyl-; 2-3':5'-dihydroxyphenyl-, and 6-nitro-2-3':5'-dihydroxyphenyl-. The above compounds are coloured, and dye wool with shades varying from orange-yellow to chocolate-brown, from an acid bath. The freshly-precipitated substance (by the addition of water to a solution in concentrated sulphuric acid) is best used for dyeing.

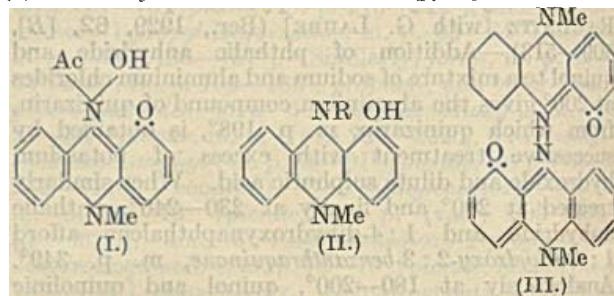
H. BURTON.

Quinoxaline synthesis; derivatives of 2:3-dimethylquinoxaline. S. T. HENDERSON (J.C.S., 1929, 466—468).—The reaction between *o*-phenylenediamine and diacetylmonoxime yields the dimethylquinoxaline derivative of dimethylglyoxime (I) (m. p. 182°, completely liquid at 215°) as an intermediate (cf. Gabriel and Sonn, A., 1908, i, 60), decomposed by acid or alkali to 2:3-dimethylquinoxaline. I is also formed from dimethylglyoxime and dimethylquinoxaline. Bromination of I or of dimethylquinoxaline in alcoholic solution gives 5:6:7:8-tetrabromo-2:3-dimethylquinoxaline, m. p. 234° (decomp.); the latter, together with a substance, $C_6H_8N_2Br_2$, m. p. 150°, is formed by bromination in chloroform. 1:2-Naphthylenediamine and diacetylmonoxime give an intermediate substance, $C_{32}H_{33}O_2N_6$ (m. p. 123°, liquid at 200°), which yielded the base, m. p. 101—102°, with alkali.

A. I. VOGEL.

Pyocyanine, the blue colouring matter of *Bacillus pyocyaneus*. IV. Constitution and synthesis of pyocyanine. F. WREDE and E. STRACK (Z. physiol. Chem., 1929 181, 58—76; cf. A., 1928, 1285).—Analysis of pyocyanine and its crystalline perchlorate and chloroplatinate definitely proves it to have the composition $C_{26}H_{24}O_2N_4$ and to contain two methylimino-groups. Although stable to acids, pyocyanine readily undergoes fission with 2% sodium hydroxide in the presence of oxygen (3 atoms), giving an 80% yield of 1-hydroxyphenazine (acetyl, m. p. 123°, and benzoyl, m. p. 176°, derivatives). With alkali and hydrogen peroxide, formic acid is also produced. Acylation of pyocyanine with acyl chlorides and pyridine yields only 1-hydroxyphenazine derivatives, but acetic anhydride and sulphuric acid yield an acetyl derivative (I) (picrate; chloro-

aurate; chloroplatinate), which is immediately decomposed by alkali, yielding pyocyanine. By catalytic reduction with platinum-black and hydrogen, pyocyanine takes up four atoms of hydrogen, yielding the oily 5-methyl-1-hydroxydihydrophenazine (II; R=H), which is immediately reoxidised by atmospheric oxygen to pyocyanine, and, like the acetyl derivative (I), has only half the mol. wt. of pyocyanine. The



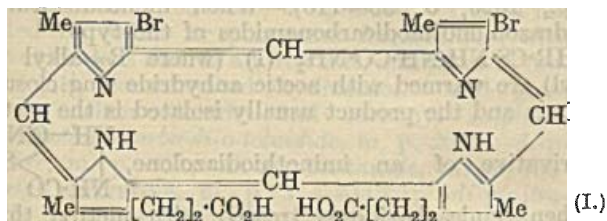
reduction product, unlike the parent pyocyanine, is readily soluble in alkali and is reprecipitated unchanged by acidification of the alkaline solution, and yields a benzoyl derivative, m. p. 150°, and a picrate. Similar reduction of the acetyl derivative, I, yields 1-hydroxy-9-acetyl-4-methyldihydrophenazine (II; R=Ac), m. p. 125—127°, which is soluble in alkali, but yields an alkali-insoluble product when treated with ethereal diazomethane and is converted by the action of concentrated hydrochloric acid and subsequent basification into pyocyanine. These reactions are explained assuming pyocyanine to be III (cf. the structure of methylprasinone; Kehrman and Cherpillod, A., 1925, i, 302), the synthesis of which is effected by the action of sodium hydroxide on the methosulphate of 1-hydroxyphenazine, the latter being obtained by the action of methyl sulphate in a sealed tube at 100°. Benzoylation of dihydrophenazine, obtained by the catalytic reduction of phenazine with platinum and hydrogen in pyridine, yields dibenzoyldihydrophenazine, m. p. 206°. Similarly, 1-methoxydihydrophenazine, obtained by reduction of 1-methoxyphenazine, yields an acetyl derivative, m. p. 175°. The dihydrophenazine derivatives are unstable in the presence of atmospheric oxygen. J. W. BAKER.

Uric acid. T. SHIMODA (J. Biochem. Japan, 1928, 9, 117—185).—Uric acid (20 mg.) dissolved in 0.01N-sodium hydroxide (100 c.c.) is completely destroyed in 14 days at 18—20°; on oxidation, it yielded carbamide and ammonia, but not allantoin. The change is accelerated by oxygen but delayed by nitrogen; it does not take place, even at 37°, in neutral or acid solutions. It is accelerated by rise of temperature, and the velocity is inversely proportional to the uric acid concentration. Uric acid appeared to be protected from destruction by adsorption. The destruction is markedly promoted by liver extracts (optimal p_H 7.3), and slightly stimulated by duodenal contents. Uric acid administered orally is excreted by rabbits chiefly in the urine as urea and ammonia; the destruction of intravenously injected (rabbit) uric acid proceeds in the liver alone.

CHEMICAL ABSTRACTS.

Natural porphyrins. XXIII. Bromoporphyrin I and its conversion into deuteroporphyrin

phyrin. H. FISCHER and G. HUMMEL (Z. physiol. Chem., 1929, 181, 107—129).—The identity of bromoporphyrin I (Fischer and Kotter, A., 1927, 1094) and dibromodeuteroporphyrin (Fischer and Linder, *ibid.*, 262) is rendered highly probable on the basis of the following evidence. By oxidation of bromoporphyrin I it is impossible to isolate with certainty more than 1 mol. of bromocitraconimide (but cf. Fischer and Zeile, this vol., 333). Reduction of bromoporphyrin I by Busch's method (A., 1925, ii, 823) yields deuteroporphyrin (with "chlorin" as a by-product) the identity being established spectroscopically and by direct comparison of the methyl esters. Similarly, debromination of bromoporphyrin I, by fusion with succinic acid, yields deuteroporphyrin and no by-products. Crystallographic data (by STEINMETZ) show that the esters of the bromination product of tetramethylhæmatoporphyrin (A) and dibromodeuteroporphyrin (B) (from deuterohæmin) are identical, but the ester from the product (C) of bromination of hæmatoporphyrin in acetic acid is different from the ester (D) obtained by the removal of iron from the bromination product of the iron salt of tetramethylhæmatoporphyrin. When (D) is seeded with (A), however, crystals identical with those of (B) are obtained. The esters of the tetrabromo-compounds obtained by the action of phosphorus pentabromide on bromoporphyrin I, dibromodeuteroporphyrin, deuteroporphyrin, and deuterohæmin are identical. The phyllin obtained by the action of magnesium methyl bromide on bromoporphyrin I is a ditertiary alcohol, the composition of which agrees better with the dibromodeuteroporphyrin structure (I) (i.e., Br in



place of a $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Br}$ side-chain). Protoporphyrin is converted by methyl-alcoholic potassium hydroxide and pyridine at 200° into mesoporphyrin. By the action of 1% methyl-alcoholic sulphuric acid hæmin is converted into the iron salt of tetramethylhæmatoporphyrin. Fusion of the latter with three parts of resorcinol at 190 — 200° yields deuterohæmin identical with Schumm's pyroporphyrin (A., 1928, 1263). J. W. BAKER.

Formation of hæmin derivatives by pyrogenic reactions. III. Decarboxylation of porphyrins and iron porphyratins; preparation of ætiopyroporphyrin and ætiomesoporphyrin. Preparation of ætioporphyrins from hæmin by the paraffin-phenol-oxalic acid method. Conversion of hæmin into pyroporphyrin. Degradation of Nencki's hæmatoporphyrin, hæmateric acid, uroporphyrin, dimethoxyhæmin dimethyl ester, and hæmatohæmin by resorcinol, and of hæmin by hydroxyquinol. Bacteriochemical production of coproporphyrin. O. SCHUMM (Z. physiol. Chem., 1929, 181, 141—175).—De-

carboxylation of porphyrins is effected by mixing the finely-powdered porphyrin with liquid paraffin and heating at 340 — 360° for several hours. The resulting mixture is diluted with ether, extracted with 5—12% hydrochloric acid or 20% sulphuric acid, the acid extract made alkaline with potassium hydroxide, and the precipitated ætioporphyrin purified by crystallisation from a mixture of chloroform and methyl alcohol. With hæmin and other iron porphyratins the product obtained as above is freed from iron either by treatment with hydrazine hydrate in acetic acid or by heating with a mixture of phenol and oxalic acid. Thus, pyroporphyrin (A., 1928, 1263) affords 5—10% of ætiopyroporphyrin, also obtained from pyratin (pyroporphyrin iron salt) by either of the above methods. When a dilute solution of ætiopyroporphyrin in hydrochloric acid is made alkaline with potassium hydroxide a colloidal solution of the porphyrin is first obtained.

Mesoporphyrin yields about 10% of ætiomesoporphyrin, also formed from mesohæmin after subsequent removal of iron. Hæmateric acid (protoporphyrin) gives a mixture of products one of which is probably ætiopyroporphyrin (spectrum). Uro- and copro-porphyrins afford the corresponding ætioporphyrins, both of which are very similar (spectrum) to ætiomesoporphyrin. When hæmin is heated with liquid paraffin at 350 — 360° and then freed from iron by the phenol-oxalic acid method 4% of ætiomesoporphyrin results, but when the decarboxylation is carried out in boiling paraffin (385°) ætiopyroporphyrin appears to be obtained, showing that the decomposition at the higher temperature follows a different course. Decarboxylation of hæmin by heating with anthracene and subsequent removal of iron by the phenol-oxalic acid method gives a product which appears to be identical (spectrum) with ætiomesoporphyrin. Decomposition of Nencki's hæmatoporphyrin at 340° yields an ætioporphyrin with the same spectrum as ætiomesoporphyrin, but in boiling paraffin a mixture is again obtained. One of the products is probably ætiopyroporphyrin.

When hæmin is dissolved in hot phenol and treated with potassium hydrogen sulphate, and the resulting product precipitated from an alkaline solution with acetic acid and finally purified by Willstätter and Mieg's method (cf. A., 1913, i, 1214), pyroporphyrin results. Subsequent esterification with methyl alcohol affords 20% of the dimethyl ester, m. p. 223° . Degradation of Nencki's hæmatoporphyrin or its iron salt (hæmatohæmin) and hæmateric acid with boiling resorcinol and subsequent esterification of the reaction product with methyl alcohol also yields pyroporphyrin dimethyl ester. When dimethoxyhæmin dimethyl ester is heated with resorcinol at 190 — 195° , the resulting product freed from iron with hydrazine hydrate and acetic acid, and then esterified with methyl alcohol, pyroporphyrin dimethyl ester is also produced. In boiling resorcinol crude pyroporphyrin results. Mesoporphyrin is unaffected by treatment with resorcinol, whilst uroporphyrin affords coproporphyrin dimethyl ester, m. p. 249° . In this last case prolonged heating causes profound decomposition. Hæmin is decomposed by heating with hydroxyquinol to pyratin, which after removal of iron by oxalic

acid and subsequent esterification affords pyroporphyrin dimethyl ester.

Copratoporphyrin iron salt results from the spontaneous putrefaction of blood at 37°. No appreciable amount of any other iron porphyratin is produced at the same time. The copratin, crude or purified, is freed from iron by the hydrazine hydrate-acetic acid method, and purified from the admixed saproporphyrin-*D* by extracting the latter with chloroform in presence of hydrochloric acid. Copratoporphyrin and pyroporphyrin appear to be identical.

H. BURTON.

Derivatives of 4:5-naphth-1:2-thiazole. R. STOLLE and W. BADSTUBNER (J. pr. Chem., 1929, [ii], 121, 266—268).—Treatment of 2:3-diketo-5:6-benzo-2:3-dihydrothionaphthen, m. p. 171° (lit. 168°) [obtained by fission of the corresponding *p*-dimethylamino-2-anil, m. p. 195° (Pummerer, A., 1910, i, 510), with 15% hydrochloric acid], with hydrogen peroxide and aqueous ammonia gives β -naphthisthiazole-2-carboxylamide, m. p. 208°. This is hydrolysed by 2*N*-sodium hydroxide to the corresponding acid, m. p. 197° (decomp.). Similar treatment of 2:3-diketo-4:5-benzo-2:3-dihydrothionaphthen affords as the main product a substance, decomp. 295°, together with small amounts of a compound, decomp. 221°, and β -naphthisthiazole-1-carboxylamide, m. p. 225° with darkening.

H. BURTON.

Aminobenzthiazoles. XI. Synthesis of 5:4'-disubstituted 1-anilinobenzthiazoles from nuclear-substituted thiocarbamilides. G. M. DYSON, R. F. HUNTER, and C. SOYKA (J.C.S., 1929, 458—466).—*s*-Di-*p*-bromophenylthiocarbamide was converted by bromine in chloroform into the *hydropentabromide*, m. p. 170° (decomp.), which yielded 5:4'-dibromo-1-anilinobenzthiazole (I), m. p. 221° [acetyl derivative, m. p. 205—206°; *hydrobromide*, m. p. 250° (decomp.)], with sulphur dioxide; I was also obtained by condensing 1-chloro-5-bromobenzthiazole, m. p. 89° (from *p*-bromophenylthiocarbimide and phosphorus pentachloride at 170—180°), with *p*-bromoaniline and also by decomposing the bromo-additive products from 4'-bromo-1-anilinobenzthiazole, m. p. 214—215° [from phenyl-*p*-bromophenylthiocarbamide through the *hydrotribromide*, m. p. 148° (decomp.)], and from 1-anilinobenzthiazole (*hexabromide*, m. p. 140°) with hydroxylic solvents. Hugershoff's dibromoanilino-benzthiazole (A., 1903, i, 865) consists mainly of 5:4'-dibromo-1-anilinobenzthiazole. Bromination of I in chloroform gave a *hexabromide*, m. p. 254°; the latter yielded an impure *tetrabromo*-substitution derivative when treated with hot alcohol. *s*-Di-*p*-chlorophenylthiocarbamide and bromine yielded a *hydrotribromide*, m. p. 165—167° (decomp.), converted by reduction into 5:4'-dichloro-1-anilinobenzthiazole, m. p. 224° [acetyl derivative, m. p. 186—187°; *hydrobromide*, m. p. 217°; *hexabromide*, m. p. 253° (decomp.)].

s-Phenyl-*p*-chlorophenylthiocarbamide and bromine furnished an additive compound, m. p. 130° (decomp.), converted into 4-chloro-1-anilinobenzthiazole, m. p. 196° (also prepared by condensing 1-chlorobenzthiazole and *p*-chloroaniline). *s*-Di-*p*-iodophenylthiocarbamide similarly yielded additive compounds with

bromine, m. p. 185° and 211°, respectively, both reduced to 5:4'-di-iodo-1-anilinobenzthiazole (also obtained from 1-anilinobenzthiazole and iodine monochloride in acetic acid), m. p. 193° (decomp.). Similarly, *s*-di-*p*-fluorophenylthiocarbamide afforded a *hydrotribromide*, m. p. 150—152° (decomp.), and 5:4'-difluoro-1-anilinobenzthiazole, m. p. 227—228°. 5:4'-Dinitro-1-anilinobenzthiazole, m. p. 280°, obtained from *s*-di-*p*-nitrophenylthiocarbamide, was identical with the compound obtained by the nitration of 1-anilinobenzthiazole. 5:4'-Dicyano-1-anilinobenzthiazole, m. p. 222° [prepared from dicyanodiphenylthiocarbamide through the bromo-additive compound, m. p. 159—160° (decomp.)], when hydrolysed with 25% hydrochloric acid gave 1-anilinobenzthiazole-5:4'-dicarboxylic acid (unmelted at 290°). *s*-Di-*p*-carbethoxyphenylthiocarbamide and bromine yielded a *hydropentabromide*, m. p. 110° (decomp.), converted into ethyl 1-anilinobenzthiazole-5:4'-dicarboxylate, m. p. 190—192°. A dibromo-5:4'-dimethoxy-1-anilinobenzthiazole, m. p. 240°, was obtained from *s*-di-*p*-anisylthiocarbamide through a *bromide*, m. p. 137° (decomp.). Acetyldiphenylthiocarbamide and bromine furnished a *hydrobromide*, m. p. 167° (decomp.), identical with that prepared from bromine, hydrogen bromide, and 1-acetanilidobenzthiazole; the last-named yielded a hexabromo-additive compound, m. p. 163° (decomp.), with bromine. A. I. VOGEL.

Ring closure of hydrazomonothiodicarbonylamides with acetic anhydride. Formation of iminothiodiazolones and iminothiothiazoles. P. C. GUHA and T. K. CHAKRABORTY (J. Indian Chem. Soc., 1929, 6, 99—110).—When monosubstituted hydrazomonothiodicarbonylamides of the type $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ (I) (where R=alkyl or aryl) are warmed with acetic anhydride ring closure occurs and the product usually isolated is the acetyl

derivative of an iminothiodiazolone, $\begin{array}{c} \text{NH}\cdot\text{C}\cdot\text{NR} \\ | \\ \text{NH}\cdot\text{CO} \end{array} > \text{S}$.

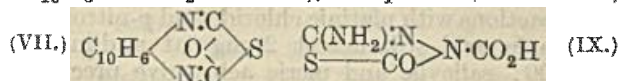
When semicarbazide is treated with methyl thiocarbimide, *hydrazomonothiodicarbonylmethylamide* (I, R=Me), m. p. 212°, results. This is converted by warm acetic anhydride into the 4-acetyl derivative, m. p. 197°, of 2-methylimino-5-keto-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 232°. *Hydrazomonothiodicarbonyllylamide*, m. p. 202°, yields the 3-acetyl derivative, m. p. 171°, of 2-allylimino-5-keto-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 210°, together with a small amount of a substance, m. p. 269°. *Hydrazomonothiodicarbonylphenylamide* gives the 3-acetyl, m. p. 173°, and 3:4-diacyl derivative, m. p. 213°, of 2-anilo-5-keto-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 206°. If the reaction is carried out in presence of sodium acetate at water-bath temperature, only the monoacetyl derivative results. *Hydrazomonothiodicarbonyl-o-tolylamide*, m. p. 201° (decomp.), furnishes the 3-acetyl derivative, m. p. 183°, of 2-o-tolylimino-5-keto-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 210°, whilst *hydrazomonothiodicarbonyl-p-tolylamide*, m. p. 192°, affords a small amount of 2-p-tolylimino-5-thiol-3-acetyl-2:3-dihydro-1:3:4-triazole, m. p. 154°, together with 2-p-tolylimino-5-keto-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 247°. *Hydrazo-*

monothiodicarbonylthylamide, m. p. 200° (decomp.), yields the 3-acetyl derivative, m. p. 218°, of 2-xylylimino- α -keto-2 : 3 : 4 : α -tetrahydro-1 : 3 : 4-thiodiazole, m. p. 232°. Hydrazomonothiodicarbonyl- β -naphthylamide, m. p. 210° (decomp.), is decomposed by warm acetic anhydride into β -naphthylthiocarbimide. When the hydrazomonothiocarbonylphenylamide, $\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, is warmed with acetic anhydride the 3-acetyl, m. p. 275°, and 3 : 4-diacetyl derivatives, m. p. 160°, of 2-imino-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole are obtained in poor yields. When boiling acetic anhydride is used, the products formed are diphenylcarbamide, acetanilide, a small amount of acetimidothiodiazolone (Guha, A., 1923, i, 607), and two substances, m. p. 92–93° and 115°, respectively. The corresponding hydrazomonothiodicarbonyl- α -naphthylamide, m. p. 215°, gives di- α -naphthylcarbamide. *s*-Diphenylhydrazomonothiodicarbonylthylamide affords 2-phenylimino- α -thiol-1-phenyl-2 : 3-dihydro-1 : 3 : 4-triazole, m. p. 208°, by elimination of water; with boiling acetic anhydride the main product is diphenylcarbamide. Hydrazodicarbonylthylamide is unaffected by boiling with acetic anhydride, but at 200° decomposition into carbon dioxide and *s*-diacetylhydrazine occurs.

H. BURTON.

Formation of heterocyclic compounds from diethyl xanthoformate. P. C. GUHA and D. N. DUTTA (J. Indian Chem. Soc., 1929, 6, 65–82).—Diethyl xanthoformate (Holmberg, A., 1905, i, 323) reacts with primary aromatic amines, forming thiomonothiodicarbonylthylamides, $\text{NHR}\cdot\text{CS}\cdot\text{S}\cdot\text{CO}\cdot\text{NHR}$ (I). Thus, with aniline thiomonothiodicarbonylthylamide (I, R=Ph), m. p. 63–64°, is obtained. This is not affected by iodine or potassium ferricyanide, with ferric chloride it affords an iron salt, and when hydrolysed with concentrated hydrochloric acid gives aniline, carbon dioxide, and carbonyl sulphide. Thiomonothiodicarbonylthyl- α -toluidide, m. p. 205°; -di-*p*-toluidide, m. p. 85°; -di-*m*-nitroanilide, m. p. 105° (diacetyl derivative, m. p. 114–115°); -di-*p*-nitroanilide, m. p. 95–96°, and -di- β -naphthylamide, m. p. 90°, are prepared similarly. Phenylhydrazine and diethyl xanthoformate give the compound, $\text{NHPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$ (II), m. p. 73–74°, with evolution of carbon dioxide and hydrogen sulphide, presumably thus: $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CO}_2\text{Et} + \text{NHPh}\cdot\text{NH}_2 \rightarrow \text{SH}\cdot\text{CO}_2\text{Et} + \text{II}$, the intermediate ethyl thiocarbonate being decomposed. When II is heated with concentrated hydrochloric acid the compound $\text{CO}\cdot\text{S}\cdot\text{CO}$ (III), m. p. 135°, results, whilst with 20% potassium hydroxide solution phenylhydrazine and potassium thiocarbonate are produced. With *p*-nitrophenylhydrazine and *as*-phenylethylhydrazine the substances $\text{NH}\cdot\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$ and $\text{NPhEt}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$, m. p. 108–109° and 242°, respectively, are obtained. These are converted by boiling concentrated hydrochloric acid into III. When *o*-phenylenediamine is treated with diethyl xanthoformate in alcoholic solution, *o*-phenylenecarbamide (IV), m. p. 306°, its *N*-monothiocarbonylthyl derivative (V), m. p. 122–123°, and *N*-carbonylthyl-*o*-phenylenethiocarbamide (VI), m. p. 93–94°, are produced. Both V and VI are formed by internal condensation of the intermediate monothio-

diurethane, whilst IV results from V by loss of carbonyl sulphide. Hydrolysis of VI with 20% potassium hydroxide solution gives *o*-phenylenethiocarbamide, m. p. 301–302° (lit. 298° and 292–293°), whilst similar hydrolysis of V yields IV. With 1 : 2-naphthylenediamine hydrogen sulphide is evolved and the compound VII, m. p. 250°, results. When the initial reaction mixture is heated, a substance (VII, with $\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ for S), m. p. 304°, is formed,



presumably by the action of carbethoxynaphthylenediamine on VII. With ethylenediamine in alcoholic solution ethylenethiocarbamide (VIII), m. p. 193–194° (hydrochloride, m. p. 304–305°), and ethylenemonothiodiurethane, m. p. 110–111°, are produced. This last compound is converted by boiling concentrated hydrochloric acid or warm 20% potassium hydroxide solution into VIII.

Diethyl xanthoformate reacts with semicarbazide, yielding ethyl semicarbazidomonothiocarboxylate, m. p. 161°, but with thiosemicarbazide ethyl thiosemicarbazidocarboxylate, m. p. 155–156°, results. This last substance is converted by hot concentrated hydrochloric acid into the compound IX, m. p. 189° after shrinking at 179° (benzylidene derivative, m. p. 158–159°). With 4-phenyl-, 4-*p*-tolyl-, and 4- β -naphthyl-thiosemicarbazides, ethyl 4-phenyl-, m. p. 149–150°, ethyl 4-*p*-tolyl-, m. p. 183–184°, and ethyl 4- β -naphthyl-thiosemicarbazidocarboxylate, m. p. 287–288°, are obtained. Benzidine and tolidine furnish the corresponding monothiodiurethanes, m. p. 211–212° and 125–126°, respectively. H. BURTON.

Polarised light and cocaine decomposition. H. T. DAILEY and H. C. BENEDICT (J. Amer. Chem. Soc., 1929, 51, 808–816).—Repetition of the work of Macht and Anderson (A., 1927, 991) indicates that polarised light, produced by reflexion, or by means of an "Ahrens" prism, is no more effective than ordinary light in causing the decomposition of aqueous cocaine hydrochloride. Reproducible results for the strength of this anaesthetic cannot be obtained by the goldfish method (Adams and others, A., 1926, 834) if each fish is used more than once, or if traces of tin are present in the water. H. E. F. NOTTON.

Copper sulphate-sodium hydroxide test for ephedrine and related compounds. K. K. CHEN (J. Amer. Pharm. Assoc., 1929, 18, 110–116).—The copper sulphate-sodium hydroxide test has been made with six optical isomerides of ephedrine and twenty-one related aromatic amines. Under the conditions described, the three ephedrines can be distinguished from the three ψ -ephedrines and the optical isomerides of ephedrine and ψ -ephedrine from the corresponding racemates. Twenty-two of the amines showed positive results and these all contained a hydroxyl group attached to the carbon atom in the β -position to the nitrogen. No amines with an α -hydroxyl group were examined, but its absence from the side-chain negated the result. Thirteen amines yielded copper complexes soluble in ether and those formed by sixteen amines were insoluble in alkaline solution.

E. H. SHARPLES.

Microchemical reactions of cinchonine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 250—253).—The most sensitive reagent is gentisic acid (2 : 5-dihydroxybenzoic acid), which will detect 1 mg. at a dilution of 1 : 200. The ferrocyanide and ferricyanide tests will detect 5 mg. at a dilution of 1 : 1000.

S. I. LEVY.

Microchemical reactions of cinchonidine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 261—264).—The reactions with platinic chloride and *p*-nitrophenylpropionic acid will detect 2 mg. at a dilution of 1 : 2000; salicylic and picric acids give precipitates with 2 mg. at dilutions of 1 : 1000.

S. I. LEVY.

Microchemical reactions of quinine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 177—182).—The reactions suitable for microchemical examination are described, and directions given for securing the best results. The more sensitive tests will detect 2—5 mg. in a concentration of 1 : 1000.

S. I. LEVY.

Microchemical reactions of quinidine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 197—200).—The reactions suitable for micro-detection of the alkaloid are described. Those with trihydroxybenzoic acid and gold chloride will detect 2 mg. at a concentration of 1 in 2000.

S. I. LEVY.

Reactions of morphine. L. EKKERT (Pharm. Zentr., 1929, 70, 165—167).—About 0.01 g. of the hydrochloride of morphine, ethylmorphine, codeine, heroin, peronin, "paracodeine," apomorphine, narcotine, or "narcophin" is scattered into a porcelain dish and a few drops of an absolute-alcoholic solution of anisaldehyde are added. On the addition of a few drops of concentrated sulphuric acid the liquid immediately develops a colour which changes on careful warming; thirty-nine reactions of the above alkaloids with varying concentrations of reagents are given and also the behaviour with other alkaloids. The reaction enables morphine to be distinguished from ethylmorphine and codeine and all three from other opium alkaloids.

E. H. SHARPLES.

Action of ammonia on halogenated arsines. V. IPATIEV, G. RAZUBAIEV, and W. STROMSKI (Ber., 1929, 62, [B], 598—604).—Halogenated arsines react smoothly with dry ammonia in anhydrous benzene with quantitative precipitation of ammonium chloride and formation of the corresponding amino- or imino-arsine. In these compounds the nitrogen is only feebly attached to the arsenic atom, hydrolysis being readily effected by moisture. The following compounds are described: *aminodiphenylarsine*, m. p. 53°, converted by moist air into diphenylarsenic oxide and oxidised by hydrogen peroxide to diphenylarsinic acid; *iminomethylarsine*, (AsMe.NH)₆, m. p. 205°; *iminophenylarsine*, (AsPh.NH)₄, m. p. about 265°.

H. WREN.

Tryparsamide type. I. Resolution of *N*-phenylalanine-4-arsinic acid and of its amide. C. S. GIBSON, J. D. A. JOHNSON, and B. LEVIN (J.C.S., 1929, 479—488; cf. Fourneau and Nicolitch, this vol., 202).— α -Bromopropionic acid and sodium *p*-aminophenylarsinate give *dl*-*N*-phenylalanine-4-arsinic acid (I), m. p. 207—210° (decomp.) [ethyl ester, m. p. 175—177° (decomp.); methyl ester (II), m. p. 181°

(decomp.)]. *dl*-*N*-Phenylalanineamide-4-arsinic acid when prepared from the methyl ester II and aqueous ammonia (*d* 0.88) has m. p. 233—240° (decomp.) and m. p. 244° (decomp.) from α -bromopropionamide and sodium *p*-aminophenylarsinate. I was resolved, as the sodium salt, with brucine in aqueous solution into the *d*-acid, the *brucine* salt of which crystallises first, m. p. 220—221° (decomp.), [α] of the sodium salt +56.40°, and into the *l*-acid, m. p. 220—221° (decomp.), [α] of the disodium salt -55.94°. Ethyl *d*-acid has m. p. 275—276° (decomp.), [α] +127.9° in ethyl alcohol, ([α] of the sodium salt +103.0°), and the ethyl *N*-phenylalanine-4-arsinic *l*-acid, m. p. 275—276° (decomp.) ([α] -125.8°, in ethyl alcohol; sodium salt [α] -102.8°). The corresponding methyl esters have: *d*-, m. p. 277—278° (decomp.), [sodium salt, [α] +117.6°], *l*-, m. p. 277—278° (decomp.) [sodium salt, [α] -116.3°]; these were separately converted into the optically active amide-acids with aqueous ammonia (*d* 0.88), the amide acid from the *d*-ester (III) had m. p. 242—243° (decomp.) [sodium salt [α] -13.3°]; amide acid from the *l*-methyl ester (IV) had m. p. 242—243° (decomp.) [sodium salt [α] +13.9°]. The rotatory powers of the sodium salts of the acids derived from III and IV were +26.6° and -29.5°, respectively. *dl*-Phenylalanineamide-4-arsinic acid was resolved, as the sodium salt, with quinine into the *l*-amide acid, m. p. 247° (decomp.) [sodium salt, [α] -17.88°], the *quinine* salt of which [α] -123.8°, separated first, and into the *d*-amide acid, m. p. 247° (decomp.) [sodium salt, [α] +16.5°]. I could not be reduced with sodium hyposulphite. All the above rotations are [α]_{D²⁰} in water except where alcohol is stated.

A. I. VOGEL.

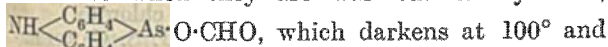
Diphenylaminearsinic acids. I. Derivatives of diphenylamine-4-arsinic acid. H. J. BARBER (J.C.S., 1929, 471—476).—Sodium 4-chloro-3-nitrophenylarsinate condenses in aqueous solution with aromatic amines at 95° to form 2-nitrodiphenylamine-4-arsinic acids. Thus aniline gives 2-nitrodiphenylamine-4-arsinic acid [2-aminodiphenylamine-4-arsinic acid (I), with ferrous hydroxide at 80—90°, m. p. 170—175° (monohydrochloride); 2-acetamidodiphenylamine-4-arsinic acid yielding *N*-phenyl-2-methylbenzimidazole-5(6)-arsinic acid with hydrochloric acid: acetone and I give a substance which is either 2-isopropylideneaminodiphenylamine-4-arsinic acid or *N*-phenyl-2 : 2-dimethyl-2 : 3-dihydrobenzimidazole, whilst nitrous acid and I yield *N*-phenylbenzimidazole-5-arsinic acid]; *p*-aminophenol gives 2-nitro-4'-hydroxydiphenylamine-4-arsinic acid (2-amino-4'-hydroxydiphenylamine-4-arsinic acid; 4'-hydroxy-1-phenyl-1 : 2 : 3-benzimidazole-5-arsinic acid); *p*-aminoacetanilide gives 2-nitro-4'-acetamidodiphenylamine-4-arsinic acid [2-amino-4'-acetamidodiphenylamine-4-arsinic acid; 2 : 4'-diacetamidodiphenylamine-4-arsinic acid; 2 : 4'-diaminodiphenylamine-4-arsinic acid]; 4-amino-2-acetamidophenol gives 2-nitro-3'-acetamido-4'-hydroxydiphenylamine-4-arsinic acid (2-amino-compound), and anthranilic acid gives 2'-carboxy-2-nitrodiphenylamine-4-arsinic acid. Nitration of 2-acetamidodiphenylamine-4-arsinic acid gives a 2' : 4' (?) dinitro-2-acetamidodiphenylamine-4-arsinic acid. 3 : 3'-Diamino-4 : 4'-dianilinoarseno-

benzene and 3 : 3'-diamino-4 : 4'-di-*p*-acetamidoanilino-arsenobenzene were obtained by the reduction of the corresponding arsenic acid with sodium hyposulphite. *o*- and *p*-Nitroanilines do not condense with 4-chloro-3-nitrophenylarsinic acid. A. I. VOGEL.

Behaviour of salvarsan and neosalvarsan towards aldehydes. H. W. VAN URK (Pharm. Weekblad, 1929, 66, 297—298).—Both compounds give colour reactions with aldehydes; the most suitable aldehyde reactions for distinguishing them are those with *o*- and *p*-nitrobenzaldehyde and with furfuraldehyde. S. I. LEVY.

Organic compounds of arsenic. VI. Electrolytic reduction of some arylarsinic acids. K. MATSUYAMA and H. NAKATA (Mem. Coll. Sci. Kyōto, 1929, A, 12, 63—68).—Electrolytic reduction by the method previously described (A., 1927, 785), but using platinum, nickel, or copper cathodes, did not affect the arsenic acid group. 3-Nitro-4-hydroxyphenylarsinic acid yielded 3 : 3'-azoxy-4 : 4'-dihydroxyphenyl-1 : 1'-diarsinic acid, darkening at 210°, decomp. without melting, and 3-amino-4-hydroxyphenylarsinic acid, with only traces of the arsine. 3-Nitro-4-amino-phenylarsinic acid, with a copper cathode, yielded 3 : 4-diaminophenylarsinic acid, darkening at 140°, m. p. 158° (decomp.). Further investigation of the effect of varying concentrations of hydrochloric acid was made (cf. *loc. cit.*). With a mercury cathode, *p*-aminophenylarsinic acid yielded *p*-aminophenylarsine hydrochloride (cf. Fichter and Elkind, A., 1916, i, 444) or 4 : 4'-diaminoarsenobenzene dihydrochloride according as the concentration of acid was below or above 8*N*. *p*-Hydroxyphenylarsinic acid yielded *p*-hydroxyphenylarsine or 4 : 4'-dihydroxy-arsenobenzene at concentrations below or above 4*N*, respectively. R. K. CALLOW.

Meriquinonoid derivatives of 9 : 10-dihydrophenarsazine. I. G. RAZUBATEV (Ber., 1929, 62, [B], 605—616).—10-Chloro (bromo)-9 : 10-dihydrophenarsazine, its oxide, methoxy-derivative, sulphate, and acetate and tridihydrophenarsazineamine give pale yellow solutions in cold formic acid which become intensely red when warmed; the colour disappears rapidly when the solutions are cooled or shaken, but recurs when they are warmed. The formate,

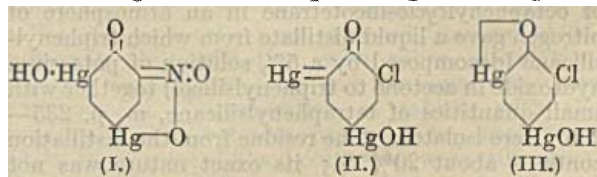


becomes yellow, without melting, at about 150°, does not give a red coloration when heated in acetone or alcohol; if formic acid is added to such solutions the red colour is developed and is accompanied by evolution of carbon dioxide, the liberated hydrogen being used to reduce the arsazine to a coloured derivative. Similar production of the coloured compound is effected by use of spongy platinum, particularly in the presence of hydrogen, stannous chloride, or zinc and acetic acid. With the latter reagents, a colourless solution is ultimately obtained which becomes intensely coloured when exposed to air or treated with a solution of unreduced 10-chloro-9 : 10-dihydrophenarsazine. The observations are compatible with a quinhydrone structure for the coloured compound, but this constitution does not explain the unsaturated nature (addition of oxygen, chlorine,

bromine, iodine, nitric oxide, nitrogen dioxide) or the considerable electrical conductivity of the solutions which indicate the presence of a radical. The meriquinonoid structure of a half-free radical,

$[\text{C}_6\text{H}_4 \begin{array}{c} \text{AsH} \\ \diagdown \text{NH} \end{array} \text{C}_6\text{H}_4] \text{X}$, is preferred to a simpler radical constitution, since the absorption spectrum of the substance exhibits a broad band commencing in the green instead of the lines expected from a radical and the compound behaves as a salt. Coloured solutions are obtained in formic and acetic acids, alcohol, acetone, and phenol from which the colour is not extracted by benzene or other hydrocarbons. Further, the electrical conductivity of 10-chloro-9 : 10-dihydrophenarsazine in formic acid is found to have undergone marked increase after the solution has been warmed. Decolorisation of solutions of the semi-radical by halogen is effected by exactly 1 atom per molecule. The product of the direct addition could not be isolated, theoretical yields of 10-halogeno-9 : 10-dihydrophenarsazine being obtained regardless of the particular acid residue originally united with the nucleus (Cl, Br, O-CHO, HSO₃). In dihydrophenarsazine the hydrogen atom is very loosely united to arsenic, so that it is readily removed by oxygen or sulphur, 0.5 atom of which is required for each molecule of original compound. The regenerated arsazine can again be reduced by warm formic acid and the operation repeated. The action of the oxygen is, however, so vigorous that a part of the formic acid is converted into water and carbon dioxide and a portion of the compound is destroyed, so that ultimately the colour does not recur when the solution is warmed. H. WREN.

Introduction of mercury into benzene derivatives. B. KALINOWSKI (Rocz. Chem., 1929, 9, 132—148).—The following compounds have been prepared : Bromobenzene-2 : 4-dimercuriacetate, m. p. 223°, bromobenzene-2 : 4-dimercurichloride, m. p. 232°, 1 : 4 dibromobenzenedimercuriacetate, *o*-nitrophenol-4 : 6-dimercuriacetate, decomp. 250°, which on hydrolysis yields the anhydride of *o*-nitrophenol-4 : 6-dimercurihydroxide (I), *p*-nitrophenol-2 : 6-dimercuriacetate, decomp. 260°, an anhydride, decomp. 220°, analogous to the preceding, *m*-nitrophenol-



2-mercuriacetate, m. p. 210°, the corresponding anhydride, decomp. 200°, 2 : 4-dinitrophenol-6-mercuriacetate, decomp. 250°, the corresponding anhydride, 2 : 6-dinitrophenol-4-mercuriacetate, decomp. 260°, *o*-chlorophenol-4 : 6-dimercuriacetate, decomp. 250°, the corresponding anhydride (II or III), decomp. 200°, *m*-chlorophenoldimercuriacetate, decomp. 270°, the corresponding anhydride, decomp. 230°, *p*-chlorophenol-2 : 6-dimercuriacetate, decomp. 270°, the corresponding anhydride, the structure of which is analogous to that of the *o*-chlorophenyl derivative (II and III). The introduction of mercury into the benzene ring

follows the same rules as that of other substituents. Mercury is most readily introduced into phenols, and least so into chlorobenzenes. Substituted mercury is readily displaced by halogens, yielding the corresponding halogen derivative. R. TRUSZKOWSKI.

Mercurated halogen compounds of sulphonfluorescein. F. DUNNING and L. H. FARINHOLT (J. Amer. Chem. Soc., 1929, **51**, 804—808).—Sulphonfluorescein yields with chloramine-*T* and acid dichlorosulphonfluorescein. Dibromo- and di-iodosulphonfluoresceins were prepared by Orndorff's method (A., 1924, i, 1190). Tetrahalogeno-*o*-sulphobenzoic anhydrides and resorcinol at 110—120° give dark brown tetrachloro-, tetrabromo-, and tetra-iodo-sulphonfluoresceins, the first two being obtained in poor yield. Mono- and di-hydroxymercuri-derivatives have been prepared from the above seven sulphonfluoresceins by refluxing their disodium salts with mercuric acetate, or their monosodium salts with mercuric oxide, in aqueous solution. A method is given for the determination of mercury in presence of iodine. H. E. F. NOTTON.

Mercuriation of anthraquinonedicarboxylic acids. F. C. WHITMORE and F. L. CARNAHAN (J. Amer. Chem. Soc., 1929, **51**, 856—862).—Mercuric anthraquinone-1:2-dicarboxylate is converted at 235° into anhydro-1-hydroxymercurianthraquinone-2-carboxylic acid, which gives with boiling hydrochloric acid anthraquinone-2-carboxylic acid and with the appropriate halogen 1-iodo- and 1-bromo-, m. p. 267—268°, -anthraquinone-2-carboxylic acids. Its sodium salt gives with hydrochloric acid 1-chloro-mercurianthraquinone-2-carboxylic acid. Mercuric anthraquinone-2:3-dicarboxylate passes at 210—215° into anhydro-2-hydroxymercurianthraquinone-3-carboxylic acid, from which anthraquinone-2-carboxylic acid, 3-bromo-, 3-iodo-, m. p. 289—290°, and 3-chloro-mercuri-anthraquinone-2-carboxylic acids were obtained. H. E. F. NOTTON.

Organic derivatives of silicon. XXXVIII. Formation of tri- and tetra-phenylsilicane and complex synthetical products from octaphenylcyclosilicotetran. F. S. KIPPING and A. G. MURRAY (J.C.S., 1929, 360—367).—Dry distillation of octaphenylcyclosilicotetran in an atmosphere of nitrogen gave a liquid distillate from which triphenylsilicane (decomposed by a 5% solution of potassium hydroxide in acetone to triphenylsilicol) together with small quantities of tetraphenylsilicane, m. p. 235—236°, were isolated. The residue from the distillation contains about 20% Si; its exact nature was not discovered. Ladenburg's triphenylsilicane (A., 1907, i, 668), m. p. 200—203°, is probably impure tetraphenylsilicane. Triphenylsilicane reacts with bromine in chloroform to give hydrogen bromide and triphenylsiliclyl bromide, m. p. 114—118° (decomposed by aqueous acetone to triphenylsilicol). Distillation of octaphenylsilicotetran under conditions similar to the above gave tetraphenylsilicane and an unidentified oil. Attempts to reduce triphenylsiliclyl bromide were unsuccessful. A. I. VOGEL.

Soluble proteins of rabbit muscle. W. S. RITCHIE and A. G. HOGAN (J. Amer. Chem. Soc., 1929, **51**, 880—886).—The proteins extracted from fresh rabbit muscle by 10% sodium chloride (p_H 6) at about 0° have been separated into albumin, globulin, and non-protein fractions. At p_H 6, the globulin precipitated (a) by saturation with sodium chloride, (b) by dialysis, using finally a dialysate of known p_H (4—7), and applying a correction for the globulin precipitable from the filtrate by sodium chloride, (c) by exposure for 6—8 hrs. to ultraviolet light, or (d) by heat-coagulation at 49°, amounts in each case to 50—60% of the total protein. Similar amounts of more gelatinous material are precipitated by methods (a) and (c) at p_H 7—8, but in more acid solutions part of the albumin is also precipitated. Albumin and non-protein nitrogen (about 20% of each) are determined in the filtrates. The globulin/albumin ratio is much higher than that previously reported for muscle tissue (cf. Saxl, A., 1906, ii, 872). The p_H of the extract is increased by the precipitation of the globulin in (b) and (c), but only slightly altered in (a). H. E. F. NOTTON.

Hydrolysis of proteins by ammonia under pressure. W. S. SADIKOV (Biochem. Z., 1929, **205**, 360—368).—Hydrolysis of proteins by ammonium carbonate under pressure at 150—180° gives after 1—6 hrs. principally peptones, and only after 24 hrs. are crystalline products obtainable. Caseinogen gave a peptone suitable for bacteriological purposes and on further hydrolysis a number of products which were crystallisable or separable by precipitation. Leucine was obtained and nine other preparations for which empirical formulae are suggested.

J. H. BIRKINSHAW.

Determination of small amounts of free or organically combined carbon in inorganic substances. D. STROHAL (Arhiv Hemiju, 1929, **3**, 63—72).—The method is essentially that for the determination of carbon in organic elementary analysis, but proportionately larger quantities of material are used and the material is intimately mixed with the copper oxide. The last traces of carbon dioxide are driven from the combustion tube by heating the inlet end, which contains a mixture of manganese dioxide and potassium chlorate.

J. S. CARTER.

Visual conductivity-titration as aid in the determination of phenols. Alkalimetric titration of protocatechualdehyde and its mono-alkyl ethers. O. PFUNDT and C. JUNGE (Ber., 1929, **62**, [B], 515—518).—The usual conductivity apparatus is modified by the substitution of a rectifier and galvanometer for the telephone and the graph is obtained by plotting galvanometer reading against volume of added alkali hydroxide; the end-point is indicated by a sharp inflexion in the graph. Protocatechualdehyde can thus be accurately titrated as a monohydric phenol by sodium hydroxide or, preferably, lithium hydroxide. Accurate results are also recorded for vanillin, isovanillin, bourbonal, and isobourbonal. H. WREN.

Biochemistry.

Respiration of non-medullated nerves. O. MEYERHOF and W. SCHULZ (Biochem. Z., 1929, 206, 158—170).—The respiration and anaerobic lactic acid formation of resting non-medullated nerves of *Maja squinado* is ten times that of the medullated nerves of the frog. Electrical stimulation causes increased oxygen consumption. With 15 min. periods of stimulation and 5—10 min. intervals the increased respiration lasts 1—2 hrs. The oxygen consumption at a stimulation frequency of 10 per sec. is twenty times as great as for frog's ischiadic nerve.

J. H. BIRKINSHAW.

Regulation of respiration. XXV. Lactic acid metabolism of brain. D. A. MCGINTY (Amer. J. Physiol., 1929, 88, 312—325).—With normal oxidations in brain-tissue, lactic acid is absorbed from the arterial blood and utilised by the brain-cells. With impaired oxidations there occurs an excessive production of lactic acid in the brain cells with an outward diffusion into the blood-stream.

B. A. EAGLES.

Regulation of respiration. XXVI. Carbon dioxide content of brain. E. E. KLEINSCHMIDT (Amer. J. Physiol., 1929, 88, 251—258).—A method of preparing brain-tissue for the determination of total carbon dioxide is described. Hæmorrhage or injection of sodium cyanide produced a decrease in the carbon dioxide content of the brain. The buffering capacity of the normal brain is less than that of the normal blood.

B. A. EAGLES.

Alkaline reserve and oxygen capacity of arterial and of venous blood. L. M. HURXTHAL, A. V. BOCK, J. H. TALBOTT, and D. B. DILL (J. Biol. Chem., 1929, 81, 681—685).—In normal individuals at rest and in most pathological cases the carbon dioxide capacity tends to be higher in arterial than in venous blood, the reverse being true during exercise. The differences are, however, small, and are still less marked in the case of the oxygen capacity.

C. R. HARRINGTON.

Benzidine reaction [for blood]. F. SCHWARZ (Deut. Z. ges. gerichtl. Med., 1928, 12, 216—218; Chem. Zentr., 1928, ii, 1701).—Glacial acetic acid (1 c.c.) is added to 50 c.c. of 2% alcoholic benzidine solution, and to 1 c.c. of this solution is then added 1 drop of quinoline or isoquinoline. With this reagent blood can be detected at a dilution of 1 in 4×10^6 .

A. A. ELDRIDGE.

Determination of diffusion constants and calculation of the radius and weight of the hæmoglobin molecule. J. H. NORTHPROP and M. L. ANSON (J. Gen. Physiol., 1929, 12, 543—554).—An apparatus is described for determining the rate of diffusion of a dissolved substance through a thin membrane and the coefficient of diffusion, D , is then known if the constant of the apparatus has been found by standardising it with a simple substance of known diffusion coefficient. The mol. wt. of the substance is then found from Einstein's equation $D = RT/6\pi N r \eta$ (N = Avogadro's constant, viscosity of liquid, r = radius of molecule). Suitable membranes may be prepared from discs of porous

Jena glass and of alundum. The mol. wt. of carbon monoxide-hæmoglobin as determined by this method is $68,000 \pm 1000$.

W. O. KERMACK.

Hæmoglobin concentration of blood of marine fishes. F. G. HALL and I. E. GRAY (J. Biol. Chem., 1929, 81, 589—594).—Figures are given for the hæmoglobin concentration of the blood of fifteen species of teleostean fishes and of two elasmobranchs. The concentration runs parallel with the activity of habit of the various species.

C. R. HARRINGTON.

Pyridine-hæmochromogen. A. E. MIRSKY and M. L. ANSON (J. Gen. Physiol., 1929, 12, 581—586).—It is considered that the conclusion of Hill (A., 1927, 65) that pyridine-hæmochromogen contains two pyridine groups to one reduced hæm group is not justified, as the equilibrium between pyridine and reduced hæm is complicated to an unknown extent by the precipitation of reduced hæm and by the aggregation of pyridine-hæmochromogen.

W. O. KERMACK.

Phosphoaminolipins and sterols of blood-serum and -plasma. A. MACHEBŒUF (Bull. Soc. Chim. biol., 1929, 11, 268—293).—A more detailed account of work already published (this vol., 206).

Specificity and changes of the proteins of blood-plasma. H. BIERRY (Compt. rend., 1929, 188, 740—742).—Intravenous injection of mannose in dogs results in a rise in the protein-sugar of the plasma. Intraperitoneal injection of Witte's peptone in rabbits causes first a fall and then a rise in the free sugar and the protein-sugar of the plasma. It is suggested that in these cases, and indeed generally, the constitution of the proteins is changed under the influence of changes in the metabolism.

G. A. C. GOUGH.

Gravimetric and nephelometric determination of protein fractions of blood. S. RUSZNYAK and J. ERDOS (Biochem. Z., 1929, 206, 482—484).—The results obtained by nephelometric determination of the protein fraction (cf. A., 1923, ii, 891) agree closely with those by the gravimetric method.

C. C. N. VASS.

Blood-constituents. R. KIMURA (Z. Immunitts., 1928, 56, 330—346; Chem. Zentr., 1928, ii, 1787).—Phosphatides were prepared from red blood-corpuscles by extraction with ether, distillation, precipitation with acetone, and fractional extraction with alcohol. Immunisation of rabbits with the residues of the extracts produced no hæmolyisin, whilst the extracted blood-corpuscles were still active. By fractional salting-out with ammonium sulphate were obtained albumin and globulin fractions in which the sulphur, carbon, hydrogen, total nitrogen, amide-, humin-, monoamino-, lysine-, histidine-, and arginine-nitrogen were determined. The chemical differences are reflected serologically, and even among different globulin fractions differences can be observed. The sulphur content of the albumin is generally higher; globulin fractions with more sulphur are more easily salted out.

A. E. ELDRIDGE.

Dialysis of small volumes of serum under sterile conditions. C. I. B. VOGEL (Biochem. J.

1929, 23, 185—187).—The serum is withdrawn by means of a sterile 1 c.c. pipette with a rubber teat. The pipette is then inserted into the dialysing sac and bound to it. The dialysing sac is placed in a vessel through which sterile water flows by gravity.

S. S. ZILVA.

Ammonia content of and ammonia formation in blood. X. Origin of blood-ammonia. W. MOZOLOVSKI (Biochem. Z., 1929, 206, 150—157).—The ammonia formed in blood on keeping is not entirely accounted for by deamination of adenylic acid. The purine base content of the blood of various animals is related to the ammonia production. Adenine is present in blood chiefly as adenylic acid, which on deamination gives inosinic acid; the latter is hydrolysed, phosphoric acid being eliminated. (Cf. A., 1927, 369.) J. H. BIRKINSHAW.

Detection of potassium and sodium in the cytoplasm of red blood-corpuscles by micro-incineration. A. POLICARD and D. PILLET (Compt. rend. Soc. Biol., 1928, 99, 85—86; Chem. Zentr., 1928, ii, 1787).—The potassium and sodium are first converted into sulphates. A. A. ELDRIDGE.

Mineral constituents of blood-platelets and white blood-corpuscles. G. ENDRES and L. HERGET (Z. Biol., 1929, 88, 451—464).—Total solids, total inorganic content, and the concentration of the different cations and anions in the inorganic fraction of the red and white corpuscles, the platelets, and the plasma of horse blood have been studied. The platelets and the white cells appear to be closely related and with respect to their content of cations are generally intermediate between plasma and red cells. With the anions this is true only of the chlorine ion. Like the red cells, they possess a smaller concentration of sodium and calcium but a greater potassium content than the plasma; both the plasma and the red cells possess a hydrogen carbonate concentration greatly in excess of that of the white cells and the platelets and a much smaller inorganic phosphorus content. There is a marked, unbalanced excess of electropositive constituents in the constituents of the ash, 15%, 34%, 35%, and 40% in that from the plasma, white cells, platelets, and red cells, respectively. This is discussed.

F. C. HAPFOLD.

Micro-determination of blood-phosphate. A. E. BRAUNSTEIN (Zhur. exp. Biol. Med., 1928, 9, 277—284).—In the molybdate method a reducing solution containing sodium sulphite and hydrogen sulphite and "eikonogen" (developer) is employed.

CHEMICAL ABSTRACTS.

Blood-sugar regulation in mammals. III. Effect of higher temperatures on blood-sugar. P. WEYL (Biochem. Z., 1929, 206, 485—502).—Rabbits kept at temperatures between 32° and 37° for 5—6 hrs. show a marked increase in blood-sugar usually after 5 min. which begins to decrease after 2—3 hrs. and then attains the initial value. At a subsequent external temperature of 9—12°, the animals show a transient hyperglycemia. When the rabbits are kept for 1 hr. at 35—38° the same phenomena are observed, but the increase in the blood-sugar on the withdrawal of the animal to the lower

temperatures is greater and lasts longer. With dogs only a slight change (+) in the blood-sugar was observed at 35—37° over long or short periods.

C. C. N. VASS.

Variations of capillary blood-sugar in normal young men during the 24 hrs.; effect of sleep and of mild exercise. H. C. TRIMBLE and S. J. MADDOCK (J. Biol. Chem., 1929, 81, 595—611).—The capillary blood-sugar of normal young men varied from about 90—95 mg.-% during sleep at night to 140—150 mg.-% immediately following the midday meal; other normal subjects awake through the night had about 100 mg.-%, so that sleep *per se* has little effect. Mild exercise was also without significant effect on the blood-sugar. C. R. HARRINGTON.

Fermentation residue [of the blood]. Determination of blood-sugar. G. FONTES and L. THIVOLLE (Compt. rend. Soc. Biol., 1928, 98, 1218—1220; Chem. Zentr., 1928, ii, 1700).—Blood (10 c.c.) or oxalate-plasma is treated with 1 g. of yeast, the mixture being shaken for 30—60 min. at 20—40°. It is then deproteinised with tungstic acid and diluted to 50 c.c. The residual reducing substances (which average 0.3% of the carbohydrates originally present) are then determined on 4—5 c.c. of the filtrate by the molybdo-manganometric method.

A. A. ELDRIDGE.

Reducing power [blood-sugar] of filtrates from the blood of the rabbit. E. L. SCOTT [with L. B. DORR] (Arch. Int. Med., 1929, 43, 393—412).—A statistical examination of 1625 observations on 215 rabbits gave a mean reducing power of 123 mg. per 100 c.c. of blood, with a mean deviation of 13 mg. The age, weight, or sex of the animals did not significantly effect their blood-sugar level. Observations made early in the laboratory experience of animals give a lower mean than the normal and a somewhat higher one after the animals have been subjected to many determinations. There is no evidence of seasonal or diurnal variation. A comparison of three series of observations taken from three separate rabbits and a similar number taken from many different animals does not reveal a marked difference in value. Injection of 1 c.c. of saline and subsequent test bleeding at short periods is accompanied by a slight but steady rise in the blood-sugar level. A short period of inanition causes a slight decrease in the reducing power of the rabbit's blood, and the variability in the results is decreased.

F. C. HAPFOLD.

Validity of determinations of "immediately reducing blood-sugars." I. Determination of blood-sugars. II. Total amount of fermentable sugar of the blood. III. Absence of influence of disulphides and thiol compounds on sugar determinations by the phosphomolybdic acid and potassium permanganate method. G. FONTES and L. THIVOLLE (Bull. Soc. Chim. biol., 1929, 11, 146—151, 152—158, 159—167).—I. A discussion of previously published work (A., 1928, 539, 786). The addition of yeast to plasma or to blood, stabilised with oxalic acid, results in complete elimination of the reducing sugars.

II. Deproteinisation of laked blood or of blood-

plasma with tungstic acid affords a filtrate which contains only fermentable sugars; if mercuric nitrate or zinc hydroxide is used, a varying proportion of the sugar is found to be unfermentable. It is suggested that the two last-named reagents displace reducing, unfermentable substances from the proteins.

III. Although in some circumstances large amounts of sulphur compounds interfere in the determinations of sugars by the phosphomolybdic acid and potassium permanganate method (A., 1927, 690), the amounts present in blood exert no detectable influence.

G. A. C. GOUGH.

Fate of acetylcholine in the blood. IV. Dependence of acetylcholine decomposition on hydrogen-ion concentration. F. PLATTNER, O. GALEHR, and Y. KODERA. V. Influence of gum arabic and starch on the fission process. Y. KODERA (Pflüger's Archiv, 1928, 219, 678—693; Chem. Zentr., 1928, ii, 1680).—The fission of acetylcholine decreases with increasing hydrogen-ion concentration or by addition of starch or gum arabic. The catalytic effect of serum and blood-corpuscles is discussed.

A. A. ELDRIDGE.

Specific hæmolysis. I. Specific adsorption of hæmolysin and complement. II. Enzymes of guinea-pig serum. III. Lysinogen of erythrocytes. K. HORINO (J. Biochem. Japan, 1928, 9, 407—421, 423—433, 435—444).—I. Hæmolysin is not adsorbed by kaolin or infusorial earth in a phosphate mixture; at the acidity of a citrate buffer adsorption by kaolin is indicated, whilst it is complete by infusorial earth in a citrate-hydrochloric acid mixture. The adsorption is reversible. The complement is adsorbed by kaolin at slightly alkaline, and by infusorial earth at slightly acid, reaction; adsorption by kaolin is not reversible, and leaching of the infusorial earth adsorbate is incomplete. The complement is considered to consist of three portions, of which one is irreversibly adsorbed.

II. The enzymes of guinea-pig serum (protease, peptase, butyrase, lipase, lecithinase, amylase, and nuclease) are present only in the albumin fraction, but thrombin and the complement middle-piece are mutually replaceable, and both are inactivated when heated at 56° for 30 min.

III. Experiments with the red cells of goat's blood indicate that the erythrocyte fibrinogen-like substance which is precipitated when an aqueous extract of the cells is half-saturated with sodium chloride or treated with carbon dioxide is a lysinogen.

CHEMICAL ABSTRACTS.

Hæmolysis and glycolysis. K. NOSHI (J. Biochem. Japan, 1928, 9, 243—249).—An erythrocyte extract possesses hæmolytic power in a phosphate mixture, but no appreciable glycolytic activity in a citrate medium.

CHEMICAL ABSTRACTS.

Inhibiting action of sucrose on taurocholate, saponin, and oleate hæmolysis. A. C. ROY and K. C. SEN (J. Indian Chem. Soc., 1929, 6, 89—92).—A comparison of the times necessary for hæmolysis of sheep's red blood-corpuscles by sodium taurocholate, saponin, and potassium oleate, in presence of isotonic sodium chloride and sucrose solutions, shows that a considerable inhibition occurs in presence

of the sugar (cf. Ponder and Yeager, A., 1928, 913). The time-dilution curves are normal in both cases. The order of hæmolytic power in both solutions is oleate > saponin > taurocholate. H. BURTON.

Hæmolytic behaviour of mixtures of hæmolysates. K. C. SEN and N. N. MITRA (J. Indian Chem. Soc., 1929, 6, 111—120).—Hæmolysis of sheep's erythrocytes by mixtures of saponin and sodium taurocholate, potassium oleate and sodium taurocholate, and saponin and potassium oleate has been studied. It is found that there is always an accelerating effect of one hæmolysate in presence of another, the total effect probably being additive. In all cases the time-dilution curves are normal. Hydrochloric acid exerts an accelerating effect on the hæmolysis by saponin and sodium taurocholate, but inhibits the action of potassium oleate. This inhibition is due to the liberation of oleic acid, which is a poor hæmolytic agent. The acceleration of potassium oleate hæmolysis by sodium hydroxide (this vol., 340) is probably due to the inhibition of hydrolysis of potassium oleate in low concentration. H. BURTON.

Detection and determination of oxygen in the pulmonary and intestinal gases of cadavers. F. DYRENFURTH (Deut. Z. ges. gerichtl. Med., 1928, 12, 23—29; Chem. Zentr., 1928, ii, 1701).—The tissue is boiled, the gas evolved is collected over concentrated potassium hydroxide solution, and its oxygen content is detected or determined by means of 10—20% pyrogallol solution. A. A. ELDRIDGE.

Fœtus. I. Enzymes in the digestive tract. Trypsinogen in the pancreas. II. A peptone-splitting enzyme in the intestinal canal. III. Lipase in the stomach. T. TACHIBANA (J. Kinki gynæcol. Soc., 1927, 10, Nos. 2, 6; 1928, 11, No. 1; Chem. Zentr., 1928, ii, 1889—1890).—Trypsinogen was observed in the fœtal pancreas in the fourth month, a peptone-splitting enzyme (optimum p_H 7.8) in the intestinal mucous membrane in the third month, and a tributyrin-splitting enzyme in the mucous membrane of the stomach in the fourth month. A. A. ELDRIDGE.

Coagulation of hen's egg-white by biological agents. E. LAGRANGQ (Compt. rend. Soc. Biol., 1928, 98, 1527—1529; Chem. Zentr., 1928, ii, 1574—1575).—When kept for several days, sterile hen's egg-white yields grey masses of coagulated albumin. The egg-white, when diluted with 4 vols. of water and heated at 110—120° does not coagulate, a change in the structure of the molecule taking place. It is then not precipitated by addition of 1% sodium chloride, and only slightly by alcohol. Such egg-white has lost all anaphylactic properties towards similar or unheated egg-white. The heated egg-white is no longer resistant to microbial reactions or to trypsin, pepsin, etc. A. A. ELDRIDGE.

Occurrence of methylguanidine in animal organism. II. Separation of methylguanidine from carnosine and creatinine. I. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1929, 181, 77—82; cf. this vol., 342).—In an attempt to remove from meat extract substances hindering the crystallisation of methylguanidine picrate, the extract

was treated with mercuric chloride and sodium acetate. An alcoholic extract was made from the precipitate and the carnosine and creatinine were removed by mercuric sulphate in sulphuric acid, and by alcoholic zinc chloride, respectively. Methylguanidine was then precipitated as the picrate.

J. H. BIRKINSHAW.

Guaninedeoxypentose from thymus-nucleic acid. P. A. LEVENE and E. S. LONDON (J. Biol. Chem., 1929, **81**, 711—712).—Thymus-nucleic acid was digested with intestinal juice; the solution was treated with 4 vols. of 95% alcohol and the filtrate concentrated. The precipitate which formed on keeping, after purification by the lead process, yielded a substance, $C_{10}H_{13}N_5O_4$, shrinking at 200° but not melting below 290°, $[\alpha]_D^{20} - 37.5^\circ$, which was rapidly hydrolysed by sulphuric acid to give guanine sulphate and a deoxypentose, m. p. 153° after softening at 83°.

C. R. HARRINGTON.

Glutathione and keratin. A. GIROUD and H. BULLIARD (Compt. rend. Soc. Biol., 1928, **98**, 500; Chem. Zentr., 1928, ii, 1783).—Glutathione is the parent of certain sulphur groups of keratin, and is present in significant quantity in the epidermis. It disappears as keratinisation proceeds.

A. A. ELDRIDGE.

Histochemical demonstration of glutathione and its distribution in certain organs. P. DI MATTEI and F. DULZETTO (Atti R. Accad. Lincei, 1928, [vi], **8**, 317—320).—To detect glutathione, the organs, immediately after removal from the animal, are reduced to small fragments, immersed for at least 30 min. in 20% trichloroacetic acid solution, and cut into sections 4—5 μ thick by the freezing method. These are treated, on microscope slides, with fresh 5% sodium nitroprusside solution for 3—4 min., freed from excess of this solution by means of filter-paper, and exposed to ammonia vapour. An amaranth-red coloration, appearing immediately, reveals the location of the glutathione. The sections are rapidly cooled in ice or in a jet of carbon dioxide and examined microscopically at 5°. The distribution of glutathione in various organs is described.

T. H. POPE.

Amino-acids of flesh. III. Diamino-acid content of fish. J. L. ROSEDALE (Biochem. J., 1929, **23**, 161—165).—The diamino-acid content of several tropical fish tissues has been determined by Van Slyke's method and in a few cases by a modification of Kossel's method. This value is higher in the muscles of fish than in similar mammalian tissues. This increase is mainly due to a higher histidine content. Incomplete hydrolysis leads to error in the Van Slyke analysis. Different tissues appear to require different lengths of time to ensure complete hydrolysis with 25% hydrochloric acid. In the separation of histidine and arginine as silver salts unless the mixture is kept slightly acid there is a danger of precipitating some of the arginine together with the histidine.

S. S. ZILVA.

Distribution of arginase in fishes. A. HUNTER (J. Biol. Chem., 1929, **81**, 505—511).—The high content of arginase previously observed for the liver of the dogfish (A., 1925, i, 104) is found also in the

livers of other elasmobranchs; on the other hand, in the *Holocephali* the liver is relatively poor in arginase, the highest concentration of the enzyme being found in the kidney, and a little in the pancreas. The presence of arginase in the cardiac tissue is not a universal characteristic of fishes; in the *Holocephali* the arginase content of the heart is low, and from the hearts of some *Teleostomi* the enzyme is absent.

C. R. HARRINGTON.

Creatine content of tissues of fishes. A. HUNTER (J. Biol. Chem., 1929, **81**, 513—523).—Figures are given for the creatine content of the muscles of fishes of fifteen different species. Considerable differences were found between the various species, and smaller differences between individuals of the same species. In general, fish muscle contains more creatine than mammalian muscle; with fishes as with mammals, white muscle contains more creatine than red, and adult muscle more than fetal.

C. R. HARRINGTON.

Lipins. VI. Lipins of the herring. B. REWALD (Biochem. Z., 1929, **206**, 275—281).—The lipin content (calculated on the basis that the phosphorus content of the pure lipin is 3.9%) of herring flesh, roe, milt, and liver has been found to be 3.561%, 13.883%, 10.295%, and approx. 12.6%, respectively, of the dry weights.

C. C. N. VASS.

Crystalline form of calcium carbonate in otoliths of *Gadus morrhua*. G. LUNDE (Biochem. Z., 1929, **206**, 436—439).—Otoliths of *G. morrhua* contain 76.39% $CaCO_3$, 11.44% CaO , 11.49% H_2O , and organic matter. X-Ray analysis shows that the calcium carbonate is present as aragonite.

C. C. N. VASS.

Digestive enzymes of the oriental fruit moth. H. S. SWINGLE (Ann. Entomol. Soc. Amer., 1928, **21**, 469—475).—The p_H of various parts of the intestine of *Laspeyresia molesta* was determined colorimetrically. Invertase, lipase, trypsin, and erepsin, but not pepsin, cellulase, lactase, maltase, or amylase, were found. The adult moth contains only one digestive enzyme, invertase.

CHEMICAL ABSTRACTS.

Isoelectric point of muscle-protein and buffering power of muscle-juice. L. DE CARO (Atti R. Accad. Lincei, 1929, [vi], **9**, 87—92).—Bottazzi's myoprotein (myogen) (Arch. Sci. Biol., 1926, **8**, 495) has an isoelectric point between p_H 6.0 and 6.9. The values found for the buffering power of the muscle-juice of *Emys*, *Scyllium*, and the electric organ of the torpedo, together with those previously found (Arch. Sci. Biol., 1928, **12**, 578) for the frog, toad, and dog, show that this power, measured by the ratio $\Delta base : \Delta p_H$, exhibits two minima at about p_H 7.7 and 5.7, respectively. This power increases rapidly, from the former value towards the alkaline side, and from the latter value towards the acid side; in the intermediate zone it shows intermediate and varying values.

T. H. POPE.

Phosphocreatine. C. H. FISKE and Y. SUBBAROW (J. Biol. Chem., 1929, **81**, 629—679).—Phosphocreatine (phosphagen of Eggleton and Eggleton, A., 1927, 271, 274, 990; cf. Fiske and Subbarow, A., 1927, 990) can be separated from a protein-free muscle extract by treatment of the latter with

copper acetate at p_H 7.8 followed by extraction of the precipitate with 0.03*N*-sodium hydroxide; the copper is removed with sodium sulphide and the concentrated filtrate treated with barium hydroxide and alcohol; the precipitate is dissolved in water, excess of barium allowed to separate as carbonate, and the filtrate treated with alcohol, when the *barium hydrogen* salt of phosphocreatine crystallises. The yield by this method is not more than 5% of the labile phosphorus of the original extract. Better results are obtained as follows. Muscle is rapidly dissected, frozen in liquid air, pulverised, and extracted with 10 parts of ice-cooled 5% trichloroacetic acid; the filtered extract is neutralised and treated with calcium chloride solution saturated with calcium hydroxide, and to the filtrate are added 3 vols. of alcohol, all operations being conducted at 0°; the partly crystalline precipitate is purified by dissolving in a limited amount of water and reprecipitating with alcohol, the process being repeated four times, yielding the *calcium hydrogen* salt, $C_4H_8O_5N_3PCa_4H_2O$; the yield by this method is 70% of the labile phosphorus, and this is taken as evidence that the whole of the latter is indeed phosphocreatine, the remaining 30% being accounted for by unavoidable losses. Hydrolysis of this salt with boiling water yields the theoretical amount of creatine. On the basis of the analysis of the salt, the structure proposed for phosphocreatine is $H_2PO_3 \cdot NH \cdot C(NH) \cdot NMe \cdot CH_2 \cdot CO_2H$. The titration curve of the calcium hydrogen salt indicates a second acid dissociation constant, pK'_2 4.58. Hydrolysis of phosphocreatine at p_H 5.8, which, according to Rous (J. Exp. Med., 1925, 41, 379 etc.), approximates the intracellular reaction, liberates 0.88 equivalent of base; the possible role of this neutralising power in chemical processes in the muscle is discussed. The determination of the phosphocreatine content of muscle (a) by direct application of the colorimetric method of the authors (A., 1926, 443) to a trichloroacetic acid extract of the tissue and (b), more accurately, after removal of inorganic phosphorus with calcium, is described in detail, and figures are given for normal resting muscle. The phosphocreatine of muscle is hydrolysed when the muscle is stimulated, when the blood supply is cut off, or when lactic acid or potassium chloride is injected intravenously; injection of creatine is without effect.

C. R. HARRINGTON.

Adenylic acids of muscle and yeast. G. EMBDEN and G. SCHMIDT (Z. physiol. Chem., 1929, 181, 130—139; cf. Schmidt, this vol., 346).—Muscle-adenylic acid has m. p. 196—200° (rapid heating), α_D^{20} -47.5° (2% sodium hydroxide), -26.0° (10% hydrochloric acid). Yeast-adenylic acid has m. p. below 195° (mixed m. p. not sharp and lower), α_D^{20} -56.0° (2% sodium hydroxide), -36.5° (10% hydrochloric acid). Inosinic acid is easily isolated from the deaminated muscle product, but not from the yeast product. Acid hydrolysis of muscle-adenylic acid is much slower than that of yeast-adenylic acid.

J. H. BIRKINSHAW.

Influence of the fixation of organs by formaldehyde on the extraction of lipins. M. MLADENOVIC and H. LIEB (Z. physiol. Chem., 1929, 181, 221—226).—Both the ether- and the alcohol-

soluble materials of normal liver are always greater than those from liver after fixation by formaldehyde. The nitrogen, phosphorus, cholesterol, and neutral fat contents of the ethereal extract of fresh liver are considerably greater than those of liver treated with formaldehyde, and since the residue on evaporating the ethereal extract was completely soluble in acetone with the fixed liver, whereas with normal liver 10% of the extract was insoluble, it would appear that the phosphatides are decomposed, some of the products being no longer extracted. P. W. CLUTTERBUCK.

Keratolysis. P. PULEWKA (Arch. exp. Path. Pharm., 1929, 140, 181—193).—The action of alkali sulphides in swelling and dissolving keratin is not to be ascribed to the polysulphide anions, nor is it simply the effect of alkali. Experiments in presence of varying amounts of alkali indicate that the action is dependent on the bivalent sulphide ion and not on the sulphydryl ion or undissociated hydrogen sulphide. The action of the bivalent sulphide ion is not to be ascribed to its lyotropic activity in the sense of the Hofmeister series, but is rather a specific chemical action on the horn protein. The sulphide ions probably act on the cystine group in the protein molecule, and in confirmation of this view it is found that other compounds, e.g., alkali cyanides, which alter the cystine molecule are also active in causing keratolysis.

W. O. KERMAK.

Heavy metals in human liver and their spectrographic detection. H. TURNWALD and F. HAUROWITZ (Z. physiol. Chem., 1929, 181, 176—181).—The liver is incinerated and the residue, dissolved in hydrochloric acid, examined spectrographically. In addition to iron, positive lines for copper, tin, zinc, and manganese were obtained. Phosphorus, calcium, and magnesium are also present. Separation of the liver into enzyme-rich and -poor fractions by extraction with acetone and ether, subsequent extraction of the residue with ammonia, and precipitation of the ammoniacal solution with acetic acid gave four fractions, all of which when incinerated and then examined as above showed the presence of the above heavy metals. There is no relationship between metal and enzyme (esterase, catalase) content.

H. BURTON.

Impregnation [of tissues] with gold. R. ALTSCHUL (Atti R. Accad. Lincei, 1929, [vi], 9, 74—77).—For the impregnation of nervous, connective, muscular, corneal, etc. tissue with gold, the use of mercuric bromide in conjunction with gold chloride yields results differing totally from those furnished by the ordinary methods.

T. H. POPE.

Caseinogen precipitation at the isoelectric point. F. LEBERMANN (Biochem. Z., 1929, 206, 56—59).—The best precipitation of caseinogen from skim milk is attained with 0.1*N*-acetic acid-acetate buffer in the ratio 8:1 at p_H 3.74. The final p_H of the solution, 4.89, differs from the isoelectric point of pure caseinogen, 4.65.

J. H. BIRKINSHAW.

Determination of organic acids in gastric juice by Hehner's method. P. FLEURY and P. AMBERT (Compt. rend. Soc. Biol., 1928, 98, 503—504; Chem. Zentr. 1928, ii, 1918).—Hehner's

method is applicable only in presence of much organic acid and small amounts of other organic substances.

A. A. ELDRIDGE.

Chemical composition of "histamine" gastric juice of man. I and II. L. GRIMBERT and P. FLEURY (J. Pharm. Chim., 1929, [viii], 9, 241—249, 321—331).—"Histamine" gastric juice contains approximately the same amount of protein as the gastric juices of the dog and of man, but is distinctly lower in acidity, total chlorine content, and ratio of total acidity to total chlorine. It has a higher ash content, due mainly to the presence of considerable quantities of phosphorus and calcium.

B. A. EAGLES.

Origin of the alkaline reaction in the intestinal juice. K. OYAMA (J. Biochem. Japan, 1928, 9, 1—16).—Aqueous solutions of neutral salts or sucrose, when introduced into the intestinal canal, cause an increase in alkalinity. The excised intestine adsorbs anions to a greater extent than cations. Injection of aqueous isotonic solutions of neutral salts or dextrose into the intestine causes sodium chloride to pass from the blood into the canal.

CHEMICAL ABSTRACTS.

Colorimetric determination of bile salts. M. CHIRAY and L. CUNY (J. Pharm. Chim., 1929, [viii], 9, 202—215, 250—258).—A method for the determination of bile salts in bile and duodenal juice is described. It is based on the colour reaction of bile salts with furfuraldehyde in the presence of acid.

B. A. EAGLES.

Relation of bile secretion to the velocity of ultrafiltration of blood. F. FALUDI (Magyar Orvosi Arch., 1928, 29, 439—443).—Experiments with the author's apparatus (*ibid.*, 435) indicate that the inhibitive effect of gelatin on the bile secretion is due to its property of decreasing the velocity of ultrafiltration of the serum.

CHEMICAL ABSTRACTS.

Presence of urea in saliva. R. VLADESCO (Compt. rend. Soc. Biol., 1928, 99, 434—436; Chem. Zentr., 1928, ii, 1895).—In man the nitrogen titratable with hypobromite is greater in the saliva than in the blood; the reverse is the case for animals. Moreover, the ammonia-nitrogen of the saliva is much higher in man than in animals. A. A. ELDRIDGE.

Intraocular fluids. II. Magnesium, sodium, and chlorine in the aqueous and vitreous humours and the blood-serum of the ox. III. Inorganic sulphur and phosphorus. E. TRON (Arch. Ophthalmol., 1927, 117, 713—722; 1928, 119, 659—679; Chem. Zentr., 1928, ii, 1894).—The vitreous and aqueous humours of the ox contain Cl 0.44, Na 0.335, Mg 0.001%; these values are compared with those for serum. The serum, aqueous and vitreous humours contain, respectively (mg. per c.c.): inorganic phosphorus 0.047, 0.028, 0.01; sulphur 0.027, 0.012, 0.014. The ocular fluid is regarded as an ultra-filtrate of the serum. A. A. ELDRIDGE.

Chemical nature of the secretion of the corpus luteum. M. TESTA (Arch. exp. Path. Pharm., 1929, 140, 174—180).—Liquor folliculi consists of water 92.49%, solid 7.51%, globulin 2.285%, albumin 3.459%, mucoid 0.907%, dextrose 0.099%, and only

traces of lipins. From histochemical observations it appears that the ovarian deutoplasm, the liquor folliculi, and the secretory vesicles of the granulosa and lutein cells are similar in their chemical nature. The secretion of the corpus luteum and liquor folliculi contain a glycolipoprotein complex, consisting of globulin, albumin, mucoid, and traces of lipid material. W. O. KERMACK.

Colorimetric determination of sulphates in body fluids. E. G. WAKEFIELD (J. Biol. Chem., 1929, 81, 713—721).—The method of Hubbard (*ibid.*, 1927, 74, V) has been developed and is applicable to protein-free blood filtrates, diluted urine, and other body-fluids; the results are usually slightly low. C. R. HARRINGTON.

Distribution of sterols in the faeces of man on a mixed diet. M. BÜRGER and W. WINTERSTEEL (Z. physiol. Chem., 1929, 181, 255—263).—With a man on a mixed diet, the faeces contain besides coprosterol about 50% of other sterols, chiefly cholesterol, and on a diet containing milk and eggs, cholesterol forms the greater part of the total sterols. Administration of large amounts of cholesterol (5 g. in 100 g. of oil) causes only a slight decrease in the percentage amount of coprosterol to total sterol, only a small portion being excreted in the faeces in the first six days. P. W. CLUTTERBUCK.

Adsorption of hydrogen and hydroxyl ions on animal charcoal. II. Measurement of the hydrogen-ion concentration of urine. H. BOHN (Arch. exp. Path. Pharm., 1929, 140, 118—128).—Erroneous results are obtained in the determination of the hydrogen-ion concentration of urine according to the method of Silberstein (A., 1922, ii, 452), since the use of animal charcoal to remove the colouring matter brings about an alteration in the hydrogen-ion concentration. Especially in the case of alkaline urines loss of carbon dioxide must be avoided. In normal individuals the variation of p_H of the urine is found to be comparatively small during the course of a day. W. O. KERMACK.

Urinary elimination of ammonia and nitrogen. II, III, and IV. Some urinary constants. E. RAFFLIN (Bull. Soc. Chim. biol., 1929, 11, 178—188, 189—197, 198—210).—II. Chiefly polemical against Polonovski and Boulanger (Compt. rend. Soc. Biol., 1928, 98, 961). An account of the variation of the constants with a number of pathological conditions is given.

III. The effect of sodium hydrogen carbonate, sodium chloride, calcium chloride, and sulphuric acid on the urinary constants (A., 1928, 1047) is studied. The substances cause a fall, little effect, an increase, and little effect, respectively, in the ratio ammoniacal nitrogen/total nitrogen.

IV. A discussion of the effects of a number of pathological conditions on the urinary constants.

G. A. C. GOUGH.

Mathematical relationships of urinary characteristics. L. LEMATE and E. KAHANE (Bull. Soc. Chim. biol., 1929, 11, 233—241).—A discussion of the constants of Raffin and Hasselbalch (cf. preceding abstract). G. A. C. GOUGH.

Urinary elimination of ammonia in relation to different nitrogenous diets. M. POLONOVSKI and P. BOULANGER (Bull. Soc. Chim. biol., 1929, 11, 211—232).—The ratio of ammoniacal nitrogen to total nitrogen of the urine appears to possess no relation to the nitrogen content of the diet. The constant of Hasselbalch (A., 1916, i, 519) possesses an approximately inverse relation to the p_H of the urine. G. A. C. GOUGH.

Determination of nitrogenous constituents of urine by fractional precipitation with mercuric chloride. B. LUSTIG and B. SPEISER (Biochem. Z., 1929, 206, 340—359).—Urine (50 c.c.) is treated at p_H 5.2 with a saturated aqueous mercuric chloride solution; the resulting precipitate contains the total purines, mucins, the greater proportion of the pigments in pathological urines, and the total proteins except peptones. The filtrate contains creatinine, ammonia, urea, and amino-acids. Treatment of the precipitate with warm 0.3% acetic acid separates the purines; subsequent treatment with 0.5% hydrochloric acid solution removes the uric acid and with highly coloured pathological urines part of the pigment. The colouring matter is then extracted with chloroform and added to the pigment obtained by finally treating the residue with a 1% alcoholic hydrochloric acid solution. The xanthine bases are precipitated quantitatively from the acetic acid solution by sodium hydroxide.

The filtrate is treated with one fourth to one third of its volume of 50% sodium acetate solution, whereby quantitative precipitation of ammonia, creatinine, the remainder of the pigments, allantoin, peptone, and a strongly reducing nitrogenous substance occurs. A deficiency of sodium acetate causes incomplete precipitation; an excess, interference with the determinations of the contents of the filtrate. Separation of the constituents of the precipitate is effected by a 35% sodium acetate solution containing 1% of acetic acid which removes the whole of the ammonia, peptone, and allantoin together with a small amount of creatine which separates out on keeping. An aliquot part of the solution is treated with potassium hydroxide and potassium sulphide and, without filtering, the liberated ammonia is collected in 0.1N hydrochloric acid. Another portion is precipitated with sodium hydroxide and the total nitrogen in the precipitate determined. The residue is treated with warm 1% hydrochloric acid solution, when the whole of the creatinine dissolves together with any remaining pigment which can now be removed by extraction with chloroform. The residue is a strongly reducing nitrogenous substance.

Treatment of the filtrate from the sodium acetate-acetic acid precipitation with 20% sodium hydroxide solution precipitates the whole of the urea, amino-acids, hippuric acid, creatine, and hydroxyproteic acids; each of these was determined in the original solution by standard methods. The filtrate from the sodium hydroxide precipitation contains only traces of a nitrogenous substance.

The method has been adapted to investigate 5 c.c. of urine with an accuracy of $\pm 1-5\%$.

C. C. N. VASS.

Iodometric determination of homogentisic acid in urine. H. LIEB and F. LANYAR (Z. physiol. Chem., 1929, 181, 199—207).—Oxidation of homogentisic acid with iodine (cf. Metz, A., 1928, 195) is quantitative only in presence of an excess of carbonate-free sodium hydrogen carbonate. The end-point of the reaction (starch) can then be determined accurately and the blue colour persists for some time. Provided no other substance which reacts with iodine is present the direct titration with iodine can be used to determine the amount of acid present. When the homogentisic acid-iodine reaction mixture is made slightly acid the liberated iodine is only about half of the theoretical amount (cf. Metz, *loc. cit.*). A large amount of dilute sulphuric acid must be used, and if small quantities of homogentisic acid are present addition of potassium iodide is advisable. The determination is best carried out with 0.05N solutions, when 1 c.c. of thiosulphate = 0.0042016 g. of homogentisic acid. The amount of thiosulphate used in determining the amount of acid in 10 c.c. of urine is about 0.2 c.c. too small, and this factor must be applied to give correct values. The maximal error is then 0.5 mg. of acid in 10 c.c. of urine. H. BURTON.

Preparation of sodium hypobromite reagent [for determination of carbamide]. O. CHARRO (Anal. Fis. Quím., 1928, 26, 446—449).—Sodium hypobromite solution for the determination of carbamide may be prepared conveniently from a stock solution of sodium bromate (6 g.) and sodium bromide (20.5 g.) in water (100 c.c.). If 1 c.c. of concentrated hydrochloric acid is added to 5 c.c. of this solution and then 3.5 c.c. of 30% sodium hydroxide solution, sufficient reagent is obtained for the analysis of 2.5 c.c. of urine. R. K. CALLOW.

Detection of nitrite in urine. L. POPPER and S. WEISS (Wien. klin. Woch., 1928, 41, 1081—1082; Chem. Zentr., 1928, ii, 1802).—The intensity of the colour obtained with the usual benzidine-acetic acid reagent is proportional to the amount of nitrite, but with a constant quantity of nitrite it increases with increasing benzidine concentration. The benzidine reaction is equally as good with urine as the sulph-anilic acid-naphthylamine test.

A. A. ELDRIDGE.

Determination of iodine in urine by the palladous chloride method. H. BERNHARDT (Z. anal. Chem., 1929, 76, 351—354).—The residue obtained by evaporation of the urine is fused with sodium carbonate and peroxide at as low a temperature as possible. The aqueous extract is boiled, acidified, and treated with sodium sulphite to reduce iodate. The palladous chloride solution should contain 1% of alcohol, and sodium chloride must be added to the test solution, if none is already present, to assist in flocculating the precipitated palladous iodide; this is dried at 132° for weighing.

A. R. POWELL.

Renal threshold for chloride in man. R. S. AITKEN (J. Physiol., 1929, 67, 199—210).—The relation between the rate of excretion of chloride by the kidney and the concentration of chloride in the plasma has been observed in two human subjects, over a wide range of plasma-chloride concentration,

under uniform physiological conditions. The nearest approximation to a renal threshold for chloride is in the neighbourhood of 0.555—0.585% of plasma-sodium chloride. It is suggested that the idea of a renal threshold for chloride be abandoned.

B. A. EAGLES.

Rapid determination of acetone and acetoacetic acid in urine. J. A. BEHRE (J. Lab. Clin. Med., 1928, 13, 1155—1159).—The method is based on the colour reaction between acetone and salicylaldehyde, permanent standards being employed.

CHEMICAL ABSTRACTS.

Excretion of ammonia and carbamide by the gills of fish. H. W. SMITH (J. Biol. Chem., 1929, 81, 727—742).—Fresh-water fish were kept in a tank divided by a rubber diaphragm so that the water circulating through the gills could be examined separately from that receiving the urine. The total nitrogen excreted by the gills was 6—10 times as great as that excreted by the kidneys: the branchial excretion consisted almost entirely of ammonia and carbamide, whilst the renal secretion contained the bulk of the creatinine and uric acid.

C. R. HARRINGTON.

Differentiating chemico-biological characteristics in the nasal mucus in healthy subjects and those with nasal abscess. C. A. TORRIGIANI (Rass. int. Clin. Terap., 1927, 8, No. 10, 7 pp.; Chem. Zentr., 1928, ii, 1791).—Nasal mucus normally nearly always contains thiocyanates, which are absent in disease. The amylolytic power of normal mucus is halved in nasal abscess, whilst a proteolytic power is then present, although normally absent (see also Lo Sperimentale, Arch. Biol. norm. pat., 1921, 81, 41—54).

A. A. ELDRIDGE.

Experimental bone-marrow reactions. VI. Adequacy of kidney, pancreas, spleen, and brain for blood regeneration in pigeons with nutritional anaemia. G. L. MULLER and E. SCORPIO (Amer. J. Physiol., 1929, 88, 259—266).—Kidney as an exclusive food is not as effective as pancreas or spleen for blood regeneration in a nutritional anaemia in pigeons caused by starvation. Brain proved to be inadequate as a food.

B. A. EAGLES.

Catalase content of erythrocytes in experimental anaemia. V. S. SUMBAYEV (Zhur. exp. Biol. Med., 1928, 10, 9—17).—When oxalated rabbit's blood is centrifuged, two layers of erythrocytes having different catalase indices separate. Increase in the catalase index of anaemia blood is ascribed to the fact that the blood is younger.

CHEMICAL ABSTRACTS.

Blood-cholesterol in cancer. II. Diagnostic relations. W. L. MATTICK and K. BUCHWALD (J. Cancer Res., 1928, 12, 236—245).—In cancer the cholesterol content of plasma is generally greater than that of whole blood. CHEMICAL ABSTRACTS.

Blood-cholesterol in cancer. III. Relation to non-malignant conditions. W. L. MATTICK and K. BUCHWALD (J. Amer. Med. Assoc., 1928, 91, 1087—1090).—The cholesterol ratio for plasma/whole blood is normally (80% of cases) less than unity, and in cancer (86% of cases) greater than unity. In

non-cancerous disease the ratio was normal in 67% and reversed in 33% of the cases.

CHEMICAL ABSTRACTS.

Pharmacological analysis of carcinoma metabolism. G. HECHT and F. EICHHOLTZ (Biochem. Z., 1929, 206, 282—289).—A number of substances have been shown to exert a specific inhibition of the fermentation processes of tumour cells. Their common characteristic is the power to form complex compounds with the heavy metals, in particular copper, which are said to be the catalysts for the fermentation processes. Lethal doses of copper, in the case of the mouse, are deprived of their toxicity by the injection of these substances.

C. C. N. VASS.

Examination of the gastric contents as an aid to diagnosis of carcinoma of the stomach. D. M. DUNLOP (Edinburgh Med. J., 1928, 35, 497—532).—Carcinoma of the stomach or oesophagus is associated with the absence of free [hydrochloric] acid and the presence of lactic acid in the gastric contents. Gunzberg's test with freshly prepared reagent, but not the Congo-red and "dimethyl" tests, is trustworthy for free hydrochloric acid; MacLean's test, but not Uffelmann's test, is specific for lactic acid.

CHEMICAL ABSTRACTS.

Ammonia content of normal and of pathological human blood. M. LABBE, F. NEPVEUX, and HEJDA (Compt. rend., 1929, 188, 738—740).—The mean value of the ammonia content of normal human blood, determined by the method of Parnas and Heller (A., 1925, i, 323, 454), is 0.47 mg. per litre. In cases of cirrhosis of the liver, diabetes with moderate acidosis, and pulmonary tuberculosis the values are often higher.

G. A. C. GOUGH.

Blood as a physico-chemical system. VIII. Diabetic coma. D. B. DILL, A. V. BOCK, J. S. LAWRENCE, J. H. TALBOTT, and L. J. HENDERSON (J. Biol. Chem., 1929, 81, 551—574).—Nomographic representations are given of the condition of the blood of two patients in diabetic coma.

C. R. HARRINGTON.

Probable significance of the intestinal fermentations in certain morbid conditions. G. GHERARDINI (Folia Clin. Chim. Micros., 1928, 3, 289—344).—Investigation of the volatile fatty acids contained in the faeces of dogs from which the pancreas had been excised showed the presence of these acids in abnormally large amounts, but it was not found possible to determine the intensity of the fermentation producing such excess of acid. An attempt is made to trace a relationship of fermentative processes, considered as the cause of acidification of the intestinal medium, to the absorption and to the chemical composition of the fats eliminated. The fundamental question of the principal seat of the fermentations in question remains unsolved. T. H. POPE.

Chemical changes occurring in the body as the result of certain diseases. III. Composition of the plasma in severe diabetic acidosis and the changes taking place during recovery. A. F. HARTMANN and D. C. DARROW (J. Clin. Invest., 1928, 6, 257—276).—Concentration of the plasma with slight diminution of total base are observed; hydrogen

carbonate and chloride are diminished relatively more than ketonic acid and protein. On administration of water and insulin, with or without carbohydrate, the base released by oxidation of the salts of ketonic acids is at first largely claimed by acids other than carbonic. Later, secretion of chloride, bound to ammonia in the urine, aids in the restoration of plasma-hydrogen carbonate.

CHEMICAL ABSTRACTS.

Determination of hexosephosphoric acid in blood. Its occurrence in the normal and diabetic organism. H. LAWACZECK (Deut. Arch. klin. Med., 1928, 159, 223—234; Chem. Zentr., 1928, ii, 1801).—By precipitation of the lactacidogen with baryta the hexosephosphoric acid is separated from the blood-sugar and other reducing substances, and determined as hexose. For blood, values between 0.63 and 2.14 mg.-% (as dextrose) were obtained. Hence 1% of the dextrose of the blood is united with 1—3% of the organic soluble phosphoric acid of the blood as hexosephosphoric acid. Characteristic differences are not observed in diabetes. There is no connexion between the quantity of blood-sugar and that of hexosephosphoric acid. A. A. ELDRIDGE.

Cholesterol content of blood-plasma in diabetes mellitus. I. M. RABINOVITCH (Arch. Int. Med., 1929, 43, 363—371).—The plasma-cholesterol content affords a trustworthy index to the true progress of the patient. F. C. HAPPOLD.

Cholesterol content of blood-plasma in juvenile diabetes. I. M. RABINOVITCH (Arch. Int. Med., 1929, 43, 372—375).—The plasma-cholesterol content of juvenile diabetics affords the same index of progress in the child as in the adult. F. C. HAPPOLD.

Insulin reaction. J. M. MACGILLIVRAY and R. WAGNER (Biochem. Z., 1929, 206, 136—149).—The effect of insulin injection on diabetic children was studied after a diet rich in carbohydrate and after a low-carbohydrate diet, the calorific value being made up with fat in the latter case. Insulin causes a much steeper fall in the blood-sugar curve after the carbohydrate-rich diet than after the low-carbohydrate diet.

J. H. BIRKINSHAW.

Anomalous fat metabolism in diabetes. I. M. RABINOVITCH and E. S. MILLS (J. Metabol. Res., 1925—1926, 7—8, 87—90).—Administration of insulin caused the blood-fat to fall from the abnormally high value of 18.6 to 2.1. Insulin may cause increased permeability of the tissues to fat.

CHEMICAL ABSTRACTS.

Abnormality in the composition of human fat. S. V. TELFER (Glasgow Med. J., 1928, 110, 137—141).—*Post-mortem* diabetic fat had an iodine value of 59.4 (normal, 71.0); the insoluble fatty acids had m. p. 36—37° (normal, 32—33°), f. p. 35° (30°), iodine value 62.8 (78.6), and contained 38.6% (25.8%) of saturated fatty acids. CHEMICAL ABSTRACTS.

Effect of synthalin on the respiratory quotient of the diabetic patient. W. G. KARR, C. SCHUMANN, and O. H. PETTY (Arch. Int. Med. 1929, 43, 384—392).—Administration of synthalin to the diabetic patient before a meal tends to increase the carbohydrate utilisation by 10—15 g. This is indicated by an increase in the respiratory quotient. Some of the

patients show an increased tolerance for dextrose as measured by the sugar in the blood and urine.

F. C. HAPPOLD.

Arterial carbon dioxide pressure in cardiac dyspnoea. R. R. FRASER, C. F. HARRIS, R. HILTON, and G. C. LINDER (Quart. J. Med., 1928, 22, 1—20).

Cause of death of animals with pancreatic fistula. S. I. PRIKLADOVITZ (Russ. J. Physiol., 1929, 12, 3—28).—The alkali reserve of healthy, adult dogs of different races varies between 40 and 60 c.c. of carbon dioxide under laboratory conditions; the variation was less marked in dogs of the same race. The blood-sugar varies between 50 and 110 mg. per 100 c.c. of blood. There is a marked drop in the alkali reserve of dogs with pancreatic fistula, resulting in the death of the dog with a marked acidosis. There is no change from the normal in the blood-sugar level.

F. C. HAPPOLD.

Cerebroside storing in Gaucher's disease. III. H. LIEB and M. MLADENOVIC (Z. physiol. Chem., 1929, 181, 208—220; cf. A., 1925, i, 189; 1928, 86).—A case of splenohepatomegaly, considered to be a doubtful Gaucher type, is shown to belong to this class owing to the extraction of crude kersin from the spleen and liver. The organs examined had been preserved in formaldehyde; these were first washed free from aldehyde and dried. The phosphorus content of the unpurified extracts of the organs does not represent the true phosphatide content.

The following optical constants for pure kersin are given: $[\alpha]_D^{25}$ —9.18° in chloroform +10% of pyridine, $[\alpha]_D^{25}$ —9.03° in pyridine, $[\alpha]_D^{25}$ —11.59° in chloroform, and $[\alpha]_D^{25}$ —3.89° in alcohol (cf. *loc. cit.*; Walz, A., 1927, 691).

H. BURTON.

Biochemistry and geochemistry of iodine. Etiology and prophylaxis of endemic goitre. G. LUNDE (Northwest. Med., 1928, 27, 412, 479; J. Amer. Med. Assoc., 1928, 91, 1407, 1662).—A discussion of the iodine cycle. CHEMICAL ABSTRACTS.

Iodine metabolism. II. Iodine content of normal and pathological thyroid glands. G. LUNDE, K. CLOSS, and K. WULFERT. **III. Blood-iodide content in primary thyrotoxicosis.** G. LUNDE, K. CLOSS, and O. C. PEDERSEN (Biochem. Z., 1929, 206, 248—260, 261—274).—II. The average weight of a normal Norwegian thyroid gland, in the eight specimens examined, was 24.66 g., with an iodine content of 9.86 mg. Pathological glands showed large fluctuations in iodine content. Treatment with inorganic iodides increased the colloidal iodine in the glands of patients suffering from primary toxic goitre.

III. A review of the previous values obtained for the blood-iodide content is given. The normal blood-iodide content in Oslo was found to vary between 11 and 16 γ -%. A new method is described in which the blood-iodides are separated into alcohol-soluble and -insoluble fractions. In thyrotoxicosis the blood-iodide content increases, especially in the alcohol-insoluble organic fraction. Administration of iodides caused an increase in the alcohol-soluble fraction with a reduction in the insoluble fraction until normal metabolism was reached and the pathological conditions disappeared.

C. C. N. VASS.

Pentosuria in rabbits in experimental stasis icterus and following subcutaneous injection of bile acids. T. KOBAYASHI (*J. Biochem. Japan*, 1928, 9, 251—260).—Bile acids provoke pentosuria, the pentose apparently arising from the body-nucleins.

CHEMICAL ABSTRACTS.

[Excretion of protein in] liver disease. E. ANDREWS, W. A. THOMAS, and K. SCHLEGEL (*Surg., Gynaecol., and Obstet.*, 1928, 47, 178—182).—In certain diseases of the liver protein is excreted in the urine; there is also disturbance of mineral salt (calcium, sodium) balance. CHEMICAL ABSTRACTS.

Porphyryn modalities. A. A. HIJMAN VAN DEN BERGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, 32, 15—19).—A pigment excreted by a subject suffering from congenital porphyrynuria has been found to be identical with coproporphyryn synthesised by H. Fischer from aetioporphyryn III.

F. G. TRYHORN.

Hydrogen-ion concentration and the calcium and phosphorus content of the faeces of rachitic children. T. REDMAN (*Biochem. J.*, 1929, 23, 256—260).—The results suggest a certain degree of correlation between and the percentage of calcium in the faeces of rachitic children. The phosphorus of the faeces has also been determined.

S. S. ZILVA.

Sodium and potassium balances, when used as citrates in acidotic and rachitic conditions in rats. J. H. SPEER, V. V. COLE, and F. W. HEYL (*J. Amer. Pharm. Assoc.*, 1929, 18, 225—228).—The sodium and potassium balances in the previous experiments (cf. this vol., 345) have been determined. The most favourable results require all the bases, but assuming that the potassium, calcium, phosphorus, and magnesium requirements are met, the alkalisation requires a considerable preponderance of sodium, the authors' best results being obtained when Na : K = 5.9 : 1.

E. H. SHARPLES.

Lactic acid in blood during gestation. H. KIENLIN (*Zentr. Gynakol.*, 1926, 2358—2362; 1927, 2271—2273; *Chem. Zentr.*, 1928, ii, 1788).—In pregnancy the lactic acid content of venous blood is approx. 7.5—10 mg.-%, during parturition 20—25 mg.-%; in two cases of eclampsia the values reached 30 mg.-%, although a causal relation is not postulated. High values are, however, associated with convulsions.

A. A. ELDRIDGE.

Composition of the blood and the menstrual cycle. Cholesterol. C. O. GUILLAUMIN and H. VIGNES (*Compt. rend. Soc. Biol.*, 1928, 99, 618—620; *Chem. Zentr.*, 1928, ii, 1679).—During menstruation and between the 17th and 21st day an increase in blood-cholesterol was observed. Values during the period are recorded.

A. A. ELDRIDGE.

Cholesterol metabolism in the incubated egg. K. KUSUI (*Z. physiol. Chem.*, 1929, 181, 101—106).—The amount of free and esterified cholesterol in the various parts of the egg at different stages of incubation was determined. Incubated hens' eggs show a decrease in total cholesterol up to the fourteenth day and then an increase up to the time of hatching. Turtles' eggs show a similar fall and rise.

J. H. BIRKINSHAW.

Fate of diphenylene oxide in intermediary metabolism of the rabbit. A. A. CHRISTOMANOS (*Z. physiol. Chem.*, 1929, 181, 182—184).—Subcutaneous injection of diphenylene oxide results in a considerably increased excretion of hippuric acid in the urine during 12 days, showing that degradation to benzoic acid occurs. No salicylic acid derivative was isolated.

H. BURTON.

Influence of diet on body-fat of white rats. H. C. ECKSTEIN (*J. Biol. Chem.*, 1929, 81, 613—628).—White rats on a fat-free diet deposited body-fat of similar composition regardless of variations in the relative amounts of protein and carbohydrate administered. Addition of myristic acid or of triolein to such a diet caused increased deposition of body-fat, but sodium butyrate was without effect. Marked increase in the proportion of highly unsaturated acids in the body-fat was observed only after administration of triolein. The cholesterol content of the animals was independent of the nature of the diet.

C. R. HARRINGTON.

Behaviour of the combined sugar during alimentary hyperglycaemia. C. TOSCANO (*Folia Clin. Chim. Micros.*, 1928, 3, 344—358).—In dogs alimentary hyperglycaemia is almost always accompanied by diminution of the combined sugar, which may disappear entirely from the blood. Such diminution sometimes corresponds with the greatest intensity of the hyperglycaemia, but often the minimum values of the combined sugar occur when the free sugar has been lowered to about its normal value. The diminution or disappearance of the combined sugar in the blood persists even after injection of insulin. If, during insulin hypoglycaemia, dextrose is rapidly introduced into the circulation, diminution and disappearance of the combined sugar are observed even when the increase in free sugar does not exceed the normal values. Thus, the diminution of combined sugar is not a consequence of the hyperglycaemia, so that it cannot be assumed that diminution of the combined sugar resulting from rapid introduction of dextrose represents a defensive mechanism of the organism against hyperglycaemia. T. H. POPE.

Mechanism of alimentary hyperglycaemia.

I. Influence of ergotamine and atropine on the course of alimentary hyperglycaemia. II. Liberation of insulin by administration of dextrose and its influence on the glycaemic reaction. L. POLLAK (*Arch. exp. Path. Pharm.*, 1929, 140, 1—27, 28—55).—The rise in blood-sugar following administration of dextrose to rabbits is partly inhibited by the administration of ergotamine and of atropine which poison the sympathetic and parasympathetic nervous systems, respectively. When atropine and ergotamine are administered simultaneously inhibition of the rise in blood-sugar is complete. When the dextrose is given intravenously these drugs do not inhibit the blood-sugar rise. The possible causes for these results have been investigated.

II. The rate of secretion of insulin by the pancreas is deduced from the change in the concentration of blood-sugar resulting from the administration of dextrose. When dextrose is given orally or intravenously the consequent secretion of insulin is

inhibited partly by ergotamine or atropine separately but completely when both are given together.

W. O. KERMAK.

Causes of alimentary hyperglycæmia in carbohydrate feeding and deprivation. F. SCHELLONG and H. KRAMER (*Klin. Woch.*, 1928, 7, 1726—1729; *Chem. Zentr.*, 1928, ii, 1893).

Carbohydrate metabolism in fasting. H. M. HINES, J. D. BOYD, and C. E. LEESE (*Amer. J. Physiol.*, 1929, 88, 240—244).—Dextrose was injected intravenously at the rate of 4 g. per kg. body-weight per hr. for a period of 2 hrs. into non-fasting and fasting dogs. Animals in the fasting condition exhibited a greater degree of glycosuria and hyperglycæmia than the non-fasting controls. The difference in response is a quantitative one and not a qualitative one. The effect of fasting on carbohydrate metabolism should be regarded as an impaired function of the organism as a whole. B. A. EAGLES.

Low-carbohydrate feeding. P. GYORGY and H. KELLER (*Biochem. Z.*, 1929, 206, 120—135).—Newly-weaned rats (15—25 days old) fed on a synthetic diet lacking carbohydrate show no inhibition of growth as compared with controls receiving the same diet + carbohydrate, and no hypoglycæmia. It is concluded that the conversion of fat and protein into sugar covers the needs of the growing organism. A diet rich in protein produces a relative kidney hypertrophy. J. H. BIRKINSHAW.

Fate of glycogen injected into the blood circulation of normal and depancreatized dogs. U. LOMBROSO (*Boll. Soc. ital. Biol. sper.*, 1927, 2, 330—332; *Chem. Zentr.*, 1928, ii, 1788).—Intravenous injection of glycogen (1 g. per kg.) into dogs produces considerable glycæmia, and a small increase of the reducing power of the urine; 3 g. per kg. produce intense glycosuria and elimination of polysaccharides in the urine. In depancreatized dogs, 1 g. per kg. causes increased glycosuria and excretion of polysaccharides. Hence in diabetes glycogen placed in the blood stream cannot be utilised. A. A. ELDRIDGE.

Injection of starch into the blood circulation. G. SUNZERI (*Ann. Clin. Med. sper.*, 1928, 17, No. 1, 13 pp.; *Chem. Zentr.*, 1928, ii, 1788—1789).—Soluble starch, injected intravenously into dogs, is chiefly oxidised in the body, only small quantities being eliminated in the urine. Storage of the starch in the organism is never observed. The decomposition of starch in the blood circulation takes place very rapidly. If urinary elimination of starch is prevented, hyperglycæmia is observed. A. A. ELDRIDGE.

Metabolism of lactose. IV. Fate of lactose in the rabbit. R. C. CORLEY (*J. Biol. Chem.*, 1929, 81, 541—544).—After intravenous injection of 1 g. of lactose into rabbits 75% of the sugar was excreted in the urine within 3 hrs., by which time the non-fermentable sugar content of the blood had returned to its normal level. The elimination of lactose was not affected by insulin, but was inhibited by tartrate nephritis accompanied by anuria. Oral administration of lactose had little effect on the non-fermentable reducing substances of the blood. C. R. HARRINGTON.

Significance of respiratory quotients after administration of certain carbohydrates. W. R. CAMPBELL and E. J. MALTBY (*J. Clin. Invest.*, 1928, 6, 303—317).—Dihydroxyacetone, lævulose, and sucrose cause a diminution of the carbon dioxide combining power and an increase in the blood-lactic acid, whilst dextrose, maltose, lactose, galactose, and glycerol do not. CHEMICAL ABSTRACTS.

Gaseous exchange following the administration of dihydroxyacetone. W. R. CAMPBELL and S. SOSKIN (*J. Clin. Invest.*, 1928, 6, 291—302).—Differences in respiratory quotient, oxygen intake, and carbon dioxide elimination for normal and depancreatized animals fed respectively with dihydroxyacetone and dextrose were observed. CHEMICAL ABSTRACTS.

Spleen and carbohydrate metabolism. A. FRANCAVIGLIA (*Folia Clin. Chim. Micros.*, 1928, 3, 359—369).—In rabbits modifications of the blood-sugar are observed from the day succeeding splenectomy, with a tendency to return gradually to normal values. Such modifications consisted in a lowering of the free sugar during fasting with seven out of the ten animals and in increase in the combined sugar with four animals. When dextrose is subsequently introduced by intravenous injection, the free sugar never reaches the high values obtained similarly prior to splenectomy, but the combined sugar at first increases markedly and then decreases to fall into line with the free sugar. The oscillations in blood-sugar normal to healthy animals become wider and more disordered after splenectomy. The modifications in the blood-sugar following splenectomy thus resemble those consequent on administration of insulin, and it appears that the increased external secretion of the pancreas caused by removal of the spleen is accompanied by increase in the internal secretion. T. H. PORE.

Significance of bile acids in carbohydrate metabolism. IV. Antagonistic effect of bile acids against adrenaline. K. MURAKAMI (*J. Biochem. Japan*, 1928, 9, 261—270).—Administration of bile acids to normal or adrenalectomized rabbits lowers fasting blood-sugar, or reduces dextrose hyperglycæmia. It is considered that the diminished adrenaline content of the blood following adrenal extirpation is responsible for the increased bile acid excretion, and that the resulting hyperglycæmia is caused by the increase in bile acid concentration of the blood. CHEMICAL ABSTRACTS.

Significance of bile acids in carbohydrate metabolism. V. Effect of diminished bile acid and of excess of bile acid on the sugar content of the blood. T. OKAMURA (*J. Biochem. Japan*, 1928, 9, 271—283).—Removal of bile causes hyperglycæmia, which can be abolished by administration of bile acids. CHEMICAL ABSTRACTS.

Significance of bile acids in carbohydrate metabolism. VI. Effect of the loss of bile acids and of excessive bile acid administration on the adrenaline content of the suprarenals. T. OKAMURA (*J. Biochem. Japan*, 1928, 9, 445—452).—The adrenaline content of the suprarenal gland of the

rabbit is increased by removal of bile and decreased by oral administration of bile acids or in stasis icterus.

CHEMICAL ABSTRACTS.

Lactic acid excretion in urine and sweat during football. I. SNAPPER and A. GRUNBAUM (Biochem. Z., 1929, 206, 319—333).—Prior to the game only traces of lactic acid were found in the urine of 55 players, after the game only traces of albumin were found in the urine of 74 players. After playing in warm weather (55 players) only six times was urinary lactic acid excretion of more than 60 mg. observed, whereas in cold weather (32 players) this was noticed sixteen times. Clean, salt-free shirts, extracted with water immediately after the game, contained an average of 460 mg. of lactic acid and 846 mg. of chloride; when the amount of sweat excreted was small the lactic acid concentration was higher. The physiological importance of this problem in regard to exercise and the action of the skin is discussed.

C. C. N. VASS.

Lactic acid metabolism of the central nervous system. II. H. JUNGMAHN (Biochem. Z., 1929, 206, 457—467).—In sodium chloride solution, containing 0.1% of dextrose, the total lactic acid content in the surviving spinal cord of the frog increased from 0.113% (average) to 0.133% in the presence of oxygen and from 0.20% to 0.30% in nitrogen. In oxygen the increase occurred solely in the external fluid. Stimulation in oxygen in the presence of dextrose caused a slight increase of lactic acid (cf. this vol., 93). Addition of insulin resulted in a decrease in lactic acid in oxygen and nitrogen. When the medium contained both sugar and insulin a smaller decrease occurred than with insulin alone. A glycolytic enzyme has been detected in the medium surrounding the cord.

C. C. N. VASS.

Specific dynamic action. S. EDERER and J. WALLERSTEIN (Biochem. Z., 1929, 206, 334—339).—With dextrose, either *per os* or intravenously, the specific dynamic action is always obtained at the taking of food, but its duration depends on the amount taken. Subcutaneous injection of ergotamine suspends the action of the sympathetic system; subsequent feeding with sugar reduces the metabolism. The suspension of the specific dynamic action by ergotamine has been found to vary with the individual when meat and bread are absorbed.

C. C. N. VASS.

Protein metabolism and organic evolution. J. NEEDHAM (Sci. Progress, 1929, 92, 633—648).—It is suggested that the main nitrogenous excretory product of an animal depends on the conditions under which its embryos live. Ammonia and urea are associated with aquatic pre-natal life and uric acid with terrestrial pre-natal life. Without a uricotelic metabolism it would have been impossible for terrestrial oviparous animals to survive.

F. C. HAPPOLD.

Increase of hepatic proteins with a diet rich in proteins. C. GAUTIER (Bull. Soc. Chim. biol., 1929, 11, 168—177).—The experiments on frogs (A., 1928, 792) are repeated with the additional determination of the liver-proteins by precipitation with 20% trichloroacetic acid. Whilst the percentage

protein content falls, the total amount of protein increases 2—4 times in the animals receiving cheese.

G. A. C. GOUGH.

Amino-acid catabolism. II. Fate of β -alanine and of ϵ -aminohexanoic acid in the phloridzinised dog. R. C. CORLEY (J. Biol. Chem., 1929, 81, 545—549).—Administration of β -alanine and of ϵ -aminohexanoic acid to phloridzinised dogs caused no significant increase in the excretion of dextrose.

C. R. HARRINGTON.

[Fate of] γ -butyrobetaine, crotonobetaine, and carnitine in animal metabolism. W. LINNEWEEH (Z. physiol. Chem., 1929, 181, 42—53).— γ -Butyrobetaine, crotonobetaine, and carnitine administered subcutaneously to dogs are excreted largely unchanged in the urine. A small amount of the γ -butyrobetaine and less of the crotonobetaine are oxidised to carnitine. γ -Butyrobetaine and crotonobetaine have a weak curare-like action and are lethal in large doses.

J. H. BIRKINSHAW.

Metabolism of tissues growing *in vitro*. III. Cyanic acid as a possible precursor of the ammonia and urea formed by embryo kidney tissue. B. E. HOLMES and E. WATSON (Biochem. J., 1929, 23, 199—205; cf. A., 1927, 479).—Cyanic acid exerts no toxic effect on the tissue of embryo kidney when present in amounts up to 9.0 mg. per 100 c.c. of medium. It is broken down in its presence to ammonia and urea. *L*-Hydantoinacetic acid is also broken down by the embryonic tissue, giving rise to urea and ammonia. In the presence of cyanate, urea disappears from the cultures. This is particularly the case when the tissue is actively growing.

S. S. ZILVA.

Ammonia formation in muscle and its relationship to function and change of condition. VI. Relation of ammonia formation to conversion of adenine nucleotide into inosic acid. J. K. PARNAS (Biochem. Z., 1929, 206, 16—38; cf. A., 1928, 668).—In fresh muscle the purine bases are present chiefly as free nucleotides. The fresh muscle of winter frogs contains 82% of the purine-nitrogen in the adenine nucleus and 18% in the hypoxanthine nucleus, in summer frogs 89% and 11%, respectively. Mechanical injury transforms the greater part of the adenine nucleotide into inosic acid. Grinding for a few mins. gives 23% and 77% purine-nitrogen for adenine and hypoxanthine nuclei, respectively. In winter, the deamination of the adenine nucleotide corresponds quantitatively with the traumatic ammonia formation. Anaerobic stimulation of muscle produces a conversion of adenine into hypoxanthine equivalent to the ammonia production; under aerobic conditions the ammonia produced is greatly in excess. This may be due to deamination of other substances leading to a resynthesis of adenine nucleotide from inosic acid.

J. H. BIRKINSHAW.

Oxygen absorption curve of fatigued muscle as a function of hydrogen-ion concentration. M. COMEL (Atti R. Accad. Lincei, 1928, [vi], 8, 255—257).—The curve of oxygen absorption by fatigued frog's muscle in solutions of varying p_H value shows two points of inflexion and a maximum. Writing where y is the rate of absorption of oxygen,

it is found that $y=0$ when $p_H=5.3$. The complete curve may be represented by $y=ax+bx^2+cx^3+dx^4$, where $x=(p_H-5.3)$. The coefficients a and c are positive, and b and d are negative. On analysis, the curve may be regarded as consisting of three portions divided by the points of inflexion which occur at p_H 7.0 and 6.6, respectively. The first portion, for p_H values near neutrality, corresponds with a high rate of oxygen absorption. Between p_H 6.6 and 6.0 recovery of the muscle is moderately rapid and may be taken to represent physiological conditions. At p_H values below 6.0 the absorption rate falls rapidly, becoming zero at p_H 5.3.

F. G. TRYHORN.

Calcium metabolism in animals. W. DREYFUS (Beitr. path. Anat., 1926, 76, 254—269; Chem. Zentr., 1928, ii, 1584).—The deposition of calcium in acid and alkaline feeding was studied for mice.

A. A. ELDRIDGE.

Factors influencing calcium balance. II. Influence of potential alkalinity on the utilisation of supplementary calcium lactate in young rachitic rats. V. V. COLE, J. H. SPEER, and F. W. HEYL (J. Amer. Pharm. Assoc., 1929, 18, 107—110; cf. this vol., 345).—Previous work has been confirmed and extended, using rachitic rats and studying the effects of various additions to their diet during recuperation. Base-forming or neutral diets are more favourable to calcium retention than an acidotic diet, and base-forming diets favour magnesium, and probably phosphorus, retention. Addition of potential alkalinity more than offsets a less favourable Ca:P ratio, showing better calcium retention than the acidotic controls. At a constant level of phosphorus intake, potassium acts somewhat in antagonism to calcium.

E. H. SHEARPLES.

Phosphorus metabolism. A. V. KHARIT and A. I. LIVSCHITZ (Ark. Biol. Nauk, 1927, 27, 89—99).—In the blood of dogs, inorganic and total phosphorus are highest in the portal, and lowest in the renal vein. The liver retains part of the inorganic and total phosphorus of the serum as well as of the whole blood; similar loss occurs in the kidneys. The constancy of the blood-phosphorus level is maintained not only by food, but also by digestive secretions and the products of tissue catabolism. The following values for inorganic phosphorus and total phosphorus as P_2O_5 (mg.-%) of serum are recorded: portal vein 3.8—7.2, 29.0—35.0; hepatic vein 3.4—6.9, 31.1; renal vein 4.6—6.5, 26.0; femoral artery 3.1—6.8, 27.0—6.8.

CHEMICAL ABSTRACTS.

Phosphorus exchange. II. Rôle of the spleen. III. Effect of adrenaline. A. CHARIT (Arch. Sci. biol. [Moscow], 1928, 28, 145—147, 149—154; Chem. Zentr., 1928, ii, 1897).—The blood leaving the spleen contains more inorganic phosphorus than that entering it. It is supposed that complex organic phosphorus compounds are dissociated in the spleen. Subcutaneous administration of adrenaline reduces the inorganic phosphorus in the blood by 28—30%; no further reduction occurs on administration of dextrose and insulin. It is considered that of the inorganic phosphorus of the blood, only one part can react with carbohydrates.

A. A. ELDRIDGE.

Action of sodium chloride on normal, pregnant, and partly nephrectomised animals. I. Chlorine and water metabolism. H. LUNDIN and R. SCHARF. II. Influence of sodium chloride on the inorganic constituents of the blood. R. SCHARF and H. LUNDIN (J. Metabol. Res., 1925—1926, 7—8, 259—320, 327—355).—Daily administration of large amounts of sodium chloride resulted in a considerable increase in the cation, and a slight increase in the anion, concentration of the blood; the former is apparently compensated by negative radicals of organic acids. The largest increase is shown by potassium; chloride increased by only 9%. After partial nephrectomy different results were obtained. Sodium and chlorine are excreted independently.

CHEMICAL ABSTRACTS.

Physiology of insects; metabolism. P. S. WELCH (Ann. Entomol. Soc. Amer., 1928, 21, 476—488).—A general discussion.

CHEMICAL ABSTRACTS.

Chemical changes during the life cycle of the tent caterpillar (*Malacosoma americana*, Fab.). III. Soluble ash and sulphates. W. RUDOLFS (J. N.Y. Ent. Soc., 1927, 35, 219—229).—Nitrogen is shown to play an important part in the formation of the embryo, the preparation for pupation, and the transformation to the adult. Fats are used and stored for energy; they are not important at any critical stage for tissue-building. The moisture content is directly related to the rate of activity.

CHEMICAL ABSTRACTS.

Permeability of surviving animal membranes. M. JOWETT (Biochem. Z., 1929, 206, 503—504). The large differences between the diffusion coefficients of dextrose in water and in animal membranes (Ammon, A., 1928, 913) are due to the method of calculation.

C. C. N. VASS.

Effect of valency of ions on cellular permeability to water. B. LUCKE and M. McCUTCHEON (J. Gen. Physiol., 1929, 12, 571—580).—Unfertilised eggs of the sea urchin (*Arbacia punctulata*) washed with isotonic dextrose solution to remove ions were suspended in hypotonic dextrose solution containing a complex cobaltammine salt and the rate of swelling of the egg was followed quantitatively by microscopic examination. Of the series of cobaltammine salts of which the cation varied in valency from 1 to 6, the salt with univalent cation was less active than that with the bivalent cation in decreasing the permeability of the cell membrane, but under the above conditions salts with a valency of two and upwards are approximately equal in their activity, the permeability of the membrane being reduced to its permeability in sea-water, which appears to be a minimum for the membrane. If, however, the permeability is increased by adding to the dextrose solution suitable quantities of potassium citrate or potassium sulphate the cobaltammine salts show activities increasing markedly with increase in the valency of the cation. The salts potassium chloride, potassium sulphate, potassium ferri-cyanide, and potassium ferrocyanide increase the permeability of the cell membrane, the order given being that of increasing activity. Similar results were also obtained with another series of salts

containing organic anions, the valencies of which ranged from 1 to 3. W. O. KERMACK.

Biological role of calcium salts. L. AMBARD and F. SCHMID (Compt. rend. Soc. Biol., 1928, 98, 1220—1222; Chem. Zentr., 1928, ii, 1788).—The differences between alkali and calcium chlorides in the behaviour of solutions with protein, and in affecting the solubility of glycine etc. are discussed.

A. A. ELDRIDGE.

Effect of salicylate administration on the acetone substance content of the blood. H. B. MYERS and C. FERGUSON (J. Pharm. Exp. Ther., 1929, 35, 313—319).—Toxic doses of sodium salicylate administered orally or subcutaneously do not produce any marked effect on the acetone, acetoacetic acid, or β -hydroxybutyric acid content of the blood of rabbits.

E. BOYLAND.

Basic titanium salicylate. M. PICHON (J. Pharm. Chim., 1929, [viii], 9, 338—340).—Basic titanium salicylate, $C_6H_5(OH) \cdot CO \cdot OTiO \cdot OH$, was prepared by the action of sodium salicylate on the product obtained from the reaction between titanium chloride and sodium sulphite. The compound is used in skin diseases.

B. A. EAGLES.

Mechanism of synthalin action. G. AHLGREN (Biochem. Z., 1929, 206, 99—108).—Insulin alone delays methylene-blue reduction in presence of minced muscle, insulin+dextrose accelerates it; synthalin has the reverse action in each case. Synthalin+insulin and synthalin+dextrose have a negative or a retarding action, but a mixture of all three strongly accelerates the reduction.

J. H. BIRKINSHAW.

Amount of reducing substance in organs of rabbit with varying blood-sugar content. G. PEYER (Biochem. Z., 1929, 206, 3—15).—The reducing power of the hydrolysed tissue of various organs of the rabbit was determined. The lungs and brain show relatively high values under normal conditions; in hyper- and hypo-glycæmic states increased reducing power of the adrenals is observed. In hyperglycæmia due to stimulation and in synthalin convulsions the brain's content of reducing substances decreases. Lethal doses of synthalin and insulin cause a complete disappearance of the reducing power of muscle but not of the liver. Various groups of muscles show different reducing powers, but symmetrical muscles on each side of the body are substantially the same.

J. H. BIRKINSHAW.

Influence of chemical and other agents on the toxicity and antigenic power of ricin. II. Detoxification of ricin. III. Production of immunity by means of ricin and detoxified ricin. E. B. CARMICHAEL (J. Pharm. Exp. Ther., 1929, 35, 193—221, 223—239).—II. Ricin as prepared by the method of Osborne, Mendel, and Harris (A., 1905, ii, 753) killed animals after subcutaneous injection in doses of 0.02 mg. per kg. body-weight. This toxicity was reduced or completely removed by oxidation with potassium permanganate and to a smaller extent with hydrogen peroxide, ozone, and the halogens, by treatment with Congo-red, but not with basic stains, by boiling, or by exposure to ultra-violet light between wave-lengths 225 and 254 μ .

III. Boiled solutions of ricin still retained part of their antigenic property, but ricin solutions oxidised with large amounts of potassium permanganate lost both antigenic and toxic properties. By careful oxidation with less permanganate it was possible to destroy the toxicity without affecting the antigenic function.

E. BOYLAND.

Effect of hormones, parasympathetic drugs, alkaloids, and various salts on the hypoglycæmic action of bile acids. A. TAKU (J. Biochem. Japan, 1928, 9, 299—319).—The hypoglycæmic action of cholic acid is inhibited by adrenaline, atropine, pilocarpine, morphine, cocaine, caffeine, calcium chloride, or magnesium chloride, and promoted by insulin or potassium chloride; pituitrin is inactive.

CHEMICAL ABSTRACTS.

Effect of cholagogues on the swelling of colloids. F. FALUDI (Magyar Orvosi Arch., 1928, 29, 444—446).—Sodium dehydrocholate and phenylquinolinecarboxylate diminish the swelling of gelatin and agar-agar, but a connexion between this effect and the cholagogue activity is not postulated.

CHEMICAL ABSTRACTS.

Influence of substances of the pilocarpine group on the gaseous exchanges of animals. A. M. PREOBRASCHENSKI (Russ. J. Physiol., 1929, 12, 45—58).—The excretion of carbon dioxide and water and the absorption of oxygen in the rabbit is increased as a result of the injection of pilocarpine in doses from 1 mg. per kg. body-weight. In large doses (10 mg. per kg.), this general increase is maintained, but the oxygen absorption does not increase proportionately to the increased excretion of water and carbon dioxide. Arecoline in doses of 0.1—1 mg. gives results similar to those obtained with pilocarpine, but the general increase of all components with increasing dosage is more proportionately interrelated. With both drugs the excretion of water is the most marked. Physostigmine in doses of 0.1—1 mg. causes an increased excretion of carbon dioxide, but the excretion of water and the absorption of oxygen decrease.

F. C. HAPFOLD.

Role of the tertiary amine group in the dipiperidine nucleus. A. HAZARD and M. POLONOVSKI (Compt. rend., 1929, 188, 822—824).—Intravenous injection of granatoline in dogs causes a peripheral vaso-constriction which is not due to an enhanced excretion of adrenaline, since the same phenomena occur in animals from which the suprarenal glands have been removed. *N*-Methylgranatoline shows a similar action and its effect on the intracardiac endings of the vagus is greater. These properties, however, are not possessed by *N*-methylgranatoline oxide.

G. A. C. GOUGH.

Effect of ergotamine on experimental hyperglycæmia. G. EDA (J. Biochem. Japan, 1928, 9, 285—297).—Experimental hyperglycæmia was reduced, frequently to hypoglycæmia, by subcutaneous injection of ergotamine.

CHEMICAL ABSTRACTS.

Effect of ergotamine on blood-sugar level. L. B. SHPINER (Amer. J. Physiol., 1929, 88, 245—250).—Intramuscular administration of ergotamine prevents the development of an adrenaline hyper-

glycaemia and glycosuria. It lowers the blood-sugar and eliminates the glycosuria in dogs which have been partly depancreatized and given thyroid extract.

B. A. EAGLES.

Poisoning by bittersweet (*Solanum dulcamara*). H. LOWE (Analyst, 1929, 54, 153—154).—Examination of the stomach contents of a dead foal showed the presence of 0.085 g. of a mixture of solanine and solanidine in 250 g. of stomach content, 0.069 g. of mixed solanine and solanidine being found in 100 g. of stomach content of cows poisoned by eating bittersweet. No solanine was found in the dung of the affected cows.

D. G. HEWER.

Locus of action of antipyretics (quinine and similar compounds). O. GERNDT (Arch. exp. Path. Pharm., 1929, 140, 91—117).—When applied directly to the mid-brain in equal doses, quinine is as active as antipyrine in lowering the temperature of an animal in fever as the result of mid-brain puncture or of *B. coli* infection. Eucupin has no antipyretic action. Plasmoquin exerts no antipyretic action when administered intracerebrally and is active when applied subcutaneously in an almost toxic dose.

W. O. KERMACK.

Influence of diuretics on the oxygen consumption of the Starling kidney preparation. H. GREMELS (Arch. exp. Path. Pharm., 1929, 140, 205—219).—The isolated kidney perfused according to Starling's technique consumes oxygen at the rate of 40—100 c.c. per kg. per min. This rate is increased when a diuresis is caused by purine bases, salyrgan, novasurol, strophanthin, and digitoxin, but no significant change takes place during sodium chloride diuresis nor after the administration of thyroxine. The rate of oxygen consumption is decreased by the action of the posterior lobe of the pituitary, and it runs parallel with the excretion of nitrogen.

W. O. KERMACK.

Scilla glucosides. W. GRAF (Arch. exp. Path. Pharm., 1929, 140, 355—379).—A study of the pharmacological action of scillaren-A and -B and of scillaridin-A and -B.

B. A. EAGLES.

Ch'an Su, the dried venom of the Chinese toad. K. K. CHEN and H. JENSEN (J. Amer. Pharm. Assoc., 1929, 18, 224—251).—The history and general characteristics of the dried venom of the Chinese toad are given and the following substances have been isolated: cholesterol containing 0.2% of ergosterol; bufagin, m. p. 217°; a nitrogenous compound, m. p. 200°, which is more toxic than bufagin, and adrenaline, m. p. 212°. The powdered material contains 5.04% of water, 1.09% of volatile matter, and 3.10% of ash and the alcoholic extract is very toxic to animals, causing a marked rise of blood-pressure soon followed by death.

E. H. SHARPLES.

Determination of small amounts of alcohol in the human subject. J. EVANS and A. O. JONES (Analyst, 1929, 54, 134—141).—Southgate's apparatus for determining alcohol in urine is described; the process allows of the use of only 2 c.c. of urine, which are slowly evaporated at 80° in a current of air previously washed in sulphuric acid. The air-alcohol mixture is passed through 15 c.c. of 0.2*N*-potassium dichromate solution, wherein the alcohol is oxidised

to acetic acid. The unreduced dichromate is determined by causing it to liberate iodine from potassium iodide. The alcohol concentration in the urine is at its maximum 1½ hrs. after consumption and falls at the rate of about 12 mg. per hour per 100 g. of blood. If the sample of urine has been excreted at the maximum alcohol point, 96 c.c. of absolute alcohol (235 c.c. of whisky; 1920 c.c. of beer) correspond with 200 mg. of alcohol per 100 c.c. of urine; i.e., mg. of alcohol per 100 c.c. $\times 0.04137$ for whisky gives fluid oz. consumed, or $\times 0.0190$ for beer gives pints. Analytical verification for the method was obtained by checking against a solution of pure alcohol and in urine after different times following the consumption of known quantities of alcohol.

D. G. HEWER.

Effect of anaesthesia and of decerebration on the lactic acid and glycogen of mammalian muscle. J. C. HINSEY and H. A. DAVENPORT (Amer. J. Physiol., 1929, 88, 286—293).—The blood-lactic acid level of decerebrate cats is higher than that of normal cats. In 10 out of 14 experiments the lactic acid content of the tonic gastrocnemius was higher than that of the atonic one. The glycogen contents were essentially the same.

B. A. EAGLES.

Combination of some narcotics with tissues rich and poor in lipins. S. LOEWE and P. MOLYAVKO-VYSSOTSKI (Biochem. Z., 1929, 206, 194—211).—The amount of chloral or bromal hydrate adsorbed by minced tissue (brain and muscle) from the surrounding solution at equilibrium was determined. A correction was applied for swelling. Brain takes up more of the narcotic than muscle, but it is undecided whether the process is one of partition or adsorption.

J. H. BIRKINSHAW.

Muscle poisons causing contraction. I. Novocaine antagonism. K. ZIPF (Arch. exp. Path. Pharm., 1929, 140, 56—90).—The pharmacological actions of caffeine, quinine hydrochloride, Nile-blue sulphate, methylene-blue hydrochloride, and *o*-nitro-aniline in the isolated sartorius muscle of the frog have been investigated both singly and in presence of other organic and inorganic cations. Certain local anaesthetics and atropine exert an antagonistic action, decreasing or abolishing the effects of the above compounds. Base exchange appears to play an important role in producing the observed phenomena.

W. O. KERMACK.

Arsine poisoning. E. MEYER and W. HEUBNER (Biochem. Z., 1929, 206, 212—222).—In a fatal case of arsine poisoning, no methaemoglobin was detected in the blood, but haemoglobin was present in connective tissue. The arsenic content of liver and kidneys was 0.1 g., equally divided between the two organs. The respective percentages on organ weight were 3 mg. and 10 mg.

In a non-fatal case the blood-plasma contained 13 mg.-% of arsenic and the blood-cells none. Haemoglobin and methaemoglobin were present in the urine. The blood was free from methaemoglobin, but after a few minutes in the air methaemoglobin was detected in the haemolytic plasma but not in the corpuscles. In non-fatal cases a portion of the arsenic present in the body is slowly excreted in the urine. The symptoms of arsine poisoning are given. J. H. BIRKINSHAW.

Action of chlorine on men poisoned by toxic smokes. D. C. WALTON and W. A. ELDRIDGE (J. Pharm. Exp. Ther., 1929, 35, 241—256).—The toxic and irritant smokes, diphenylchloroarsine, diphenylcyanoarsine, and diphenylaminechloroarsine lose their irritant property on chlorination. Patients suffering from the irritant effects of these compounds are relieved by inhaling chlorine. E. BOYLAND.

Buffer antiseptics. I. General. II. Phenol-activity, -capacity, and -buffer effect. J. K. GJALDBAEK (Dansk Tidsskr. Farm., 1929, 3, 10—28, 29—75).—I. Buffer antiseptics are substances which contain a supply of an active antiseptic in a more or less inactive form, and can transfer the active substance to water, tissue juices, etc., with which they are brought in contact. The terms A-activity, A-capacity, and A-buffer power are introduced. The A-activity is the concentration of the antiseptic in an aqueous solution which is in equilibrium with the buffer antiseptic, A-capacity is the total amount of removable antiseptic, in g. per 100 g. of buffer antiseptic, and the A-buffer power the ability of the antiseptic to maintain a certain activity. In a buffer antiseptic, the total concentration of the antiseptic (active and inactive form) must be greater than the A-activity, and, when the antiseptic is partly removed, the A-activity must decrease to a smaller extent than does the A-concentration. Sodium silver thiosulphate is an example of a chemically-bound buffer antiseptic. The silver ion is the active antiseptic, and when the silver ions are removed from the solution further liberation of silver ions takes place.

II. Solutions of phenols etc. in glycerol, ethyl alcohol, and certain oils furnish examples of buffer antiseptics in which the buffering is due to the greater solubility of the phenol in the solvent than in water. The author has studied the buffer effect of phenol in oils, ointments, and camphor by measuring the coefficients of distribution of the phenol between the antiseptic solvent and water. The solvents can be divided into two groups; in the first the buffer effect remains constant during the process of phenol discharge, in the second there is an increase in buffer action, since the partition coefficient increases with a decreasing concentration of the phenol in the non-aqueous phase. F. C. HAPFOLD.

Reaction kinetics in the macroheterogeneous medium. S. J. PRZYŁECKI (Biochem. Z., 1929, 206, 60—98).—A theoretical discussion of the factors governing the activation of reactions, with special reference to the effect of structure. J. H. BIRKINSHAW.

Enzyme processes. Action of amylase. Y. SCHAEFFER (Compt. rend. Soc. Biol., 1928, 98, 1491—1494; Chem. Zentr., 1928, ii, 1673).—The maximum yield of sugar was 70%; the speed of its production exhibits several maxima and minima.

A. A. ELDRIDGE.

Changes in the activity of the intestinal juice enzymes depending on the kind of food. I. Amylolytic enzyme. S. V. ANDREYEV and S. I. GEORGIYVSKI (Zhur. exp. Biol. Med., 1928, 10, 169—179).—The amylolytic action of intestinal juice varies according to the starch content of the food.

CHEMICAL ABSTRACTS.

Alleged salt-hydrolysis of starch. N. MALYSCHEV (Biochem. Z., 1929, 206, 401—409).—Takane's results (A., 1926, 1059) were confirmed. Even in non-sterilised solutions hydrolysis occurred only in a few examples. Treatment of the starch solution with air or with pure oxygen did not accelerate hydrolysis, as stated by Biedermann (A., 1923, i, 655).

C. C. N. VASS.

Glycolysis in muscle and other tissues. E. M. CASE (Biochem. J., 1929, 23, 210—218).—Brain, kidney, muscle, and blood-corpuscles activate the production of lactic acid from dextrose by muscle extract (cf. Meyerhof, A., 1927, 590). Grinding, filtering, or any process which destroys or removes intact cells has a corresponding effect in diminishing the activating power of the tissue. In the presence of 0.002*M*-potassium cyanide the activation of glycolysis by brain is not inhibited; kidney glycolysis is, on the other hand, prevented by this concentration of cyanide. The activation of the system muscle+dextrose by yeast, brain, or kidney is unaffected by cyanide. The hydrolysis of phosphoric ester is prevented when muscle-extract is acting on dextrose in the presence of brain or kidney on addition of fluoride. When yeast is employed as activator, fluoride prevents even the synthesis of hexosephosphate from dextrose. Phloridzin, phloroglucinol, amygdalin, and salicin have no effect on the activating action of yeast on glycolysis (cf. Dann and Quastel, A., 1928, 329). Cell-free extracts of Rous chicken sarcoma do not contain this activator. Suspensions of the comparatively uninjured sarcoma tissue possess this power. S. S. ZILVA.

Significance of iron in biological oxidation. I. Role of ferrous salts as aldehydase. II. Role of ferrous salts as oxido-reductases for various organic substances. K. ANDO (J. Biochem. Japan, 1928, 9, 187—199, 201—214).—Similarities in action between Schardinger's enzyme and ferrous salts suggest that the former is an organic iron compound. It is supposed that the enzyme, like ferrous sulphate, attacks a molecule of water, transferring activated hydrogen to the acceptor and oxygen to the donator. Experiments using methylene-blue show that inorganic ferrous salts act as aldehydases. Organic substances which are easily oxidised *in vivo* are good donators for ferrous salts or for the methylene-blue system. Lecithin and the higher fatty acids are powerful accelerators.

CHEMICAL ABSTRACTS.

Occurrence of a citric-dehydrogenase in cucumber seeds and its application to a sensitive biological colour reaction for citric acid. T. THUNBERG (Biochem. Z., 1929, 206, 109—119).—A phosphate extract of cucumber seeds contains an extremely sensitive citric-dehydrogenase which produces the maximum decolorising velocity by the Thunberg methylene-blue technique in presence of less than 0.01 mg. of citric acid. From this a method of testing for small amounts of citric acid, e.g., in milk, is developed. J. H. BIRKINSHAW.

Dehydrogenation of lactic acid. A. HAHN, E. FISCHBACH, and W. HAARMANN (Z. Biol., 1929, 88, 516—522).—The study of the dehydrogenation of

lactic acid (lithium salt) to pyruvic acid by minced muscle preparations is continued (A., 1928, 1281). The reaction can take place with washed muscle preparations without the addition of methylene-blue, but it is greatly enhanced by such addition. Unwashed muscle pulp gives a much greater yield of pyruvic acid, and maximum dehydrogenation takes place when methylene-blue is added to such a system in excess. Dehydrogenation is also observed under anaerobic conditions without the addition of a hydrogen acceptor.

F. C. HAPFOLD.

Influence of structure on the kinetics of desmolases. II. Uricase. Systems uricase-uric acid-liver and kidney pulp. S. J. PRZYŁECKI (Z. physiol. Chem., 1929, 181, 234—254; cf. A., 1928, 1055).—The change in velocity of decomposition of uric acid by the uricase of tissue pulp on disintegration is investigated with and without addition of 1% of propyl alcohol, three sets of experiments being carried out using the whole pulp and the fine and coarse particles thereof, in each case the pulp being used after mincing, and also after grinding with sand, freezing at -12° , and after both these treatments. Both the mechanical disintegration and the presence of alcohol caused considerable acceleration of the reaction. Disintegration caused an increased adsorption of uric acid by the tissue, and addition of alcohol in all cases a considerable elution of uric acid. Most of the uricase is present in the adsorbed condition. Addition of alcohol to the pulp causes elution of about 12.6% of the enzyme. Addition of uric acid also causes a slight elution and addition of both alcohol and uric acid liberates about 30% of the enzyme. Both adsorbed and eluted uricase are active. Alcohol besides eluting uric acid and enzyme also accelerates the penetration of uric acid into the range of action of uricase by increasing cell permeability.

P. W. CLUTTERBUCK.

Mechanism of the action of oxidising catalysts. L. STERN (Compt. rend. Soc. Biol., 1928, 98, 1288—1290; Chem. Zentr., 1928, ii, 1673—1674).—Oxydones are differentiated from oxidases by the fact that they function only in presence of active oxygen, which cannot be replaced by another hydrogen acceptor.

A. A. ELDRIDGE.

Bioluminescence. VII. Solubility of *Cypridina* luciferin in organic solvents. S. KANDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 91—98).—*Cypridina* luciferin after it has been purified by dissolution in methyl alcohol and in ethyl alcohol becomes soluble in benzene, ether, light petroleum, and chloroform, although in the crude state it does not dissolve in these solvents. The insolubility of crude luciferin in benzene is possibly due to association with protein, from which it is separated by the treatment with alcohol. The benzene solution contains active luciferin for about 1 month, whereas the ether solution loses its power to produce light when added to a luciferase solution in a few hours.

W. O. KERMAK.

Specific inhibitions of lipase, especially by fluoride. P. ROTHSCILD (Biochem. Z., 1929, 206, 186—193).—Fluoride produces a marked inhibition of liver-lipase action on various esters which becomes

stronger with increasing acidity. The action is reversible. Arsenite produces strong inhibition which is, however, slightly less at lower p_H values. Certain heavy metals have the same effect independent of but in all these cases the action is irreversible.

J. H. BIRKINSHAW.

Influence of various substances on lipase action. R. F. CORRAN (Biochem. J., 1929, 23, 188—194).—In low concentration lecithin and cholesterol act slightly and to the same extent as augmenters of lipolysis. The values of the augmentations fall with increasing concentration. The influence of sodium and potassium chlorides is only slightly augmentative. Calcium chloride acts as an inhibitor. Ionic lead acts as an augmentor towards lipase in the presence and in the absence of serum. Copper and mercury under the same conditions act as inhibitors. The albumin-pseudoglobulin fraction of blood-serum possesses more than 80% of the co-enzymic activity exhibited by serum. S. S. ZILVA.

Preparation and use of the bone phosphatase. M. MARTLAND and R. ROBISON (Biochem. J., 1929, 23, 237—242).—The enzyme is best prepared from the bones of young growing rachitic rabbits by extraction with chloroform water during 7—10 days, the bones being first split longitudinally and the marrow removed. Evaporation of the filtered extracts in evacuated desiccators over sulphuric acid yields 5—8 mg. of dry solid per c.c., no loss of activity occurring during this process. Purification can be carried out (a) by precipitation with a mixture of alcohol and ether yielding a stable preparation which possesses the original activity; (b) by removal of a protein by precipitation at its isoelectric point (p_H 5.8); (c) by dialysis through a collodion membrane previously immersed for 24 hrs. in 95% alcohol or by ultrafiltration in a Bechhold filter through a collodion disc of similar porosity which yields an inactive filtrate containing the whole of the phosphate. No evidence of the presence of a co-enzyme was obtained. No purification of the enzyme by means of specific adsorption using kaolin, calcium phosphate, or aluminium hydroxide prepared by the method of Willstatter and Kraut was obtained. The application of this method to the hydrolysis of hexosediphosphoric acid and the properties of the hexose so obtained are discussed.

S. S. ZILVA.

Digestion of lecithin by pancreatic enzymes. S. A. PORTIS (J. Amer. Med. Assoc., 1928, 91, 1248—1250).—Normal duodenal contents digest lecithin, whilst gastric contents do not. The action is depressed in cardiac decompensation and untreated gastric ulcer, but not in pregnancy.

CHEMICAL ABSTRACTS.

Enzymic hydrolysis of keratin with the juice of the crop of *Astur palumbarius* (hawk) and *Vultur monachus* (vulture). R. STANKOVIC, V. ARNOVLJEVIC, and P. MATAVULJ (Z. physiol. Chem., 1929, 181, 291—299).—The crop juice of these birds hydrolyses pure keratin, the action being enzymic. The enzyme system is destroyed by heating for 0.5 hr. at 95° . The juice also liberates amino-acids from horny tissue. Keratinolysis proceeds more quickly in the crop of the bird than *in vitro*.

P. W. CLUTTERBUCK.

Specific action of enzyme complexes in fission of polypeptides. E. ABDERHALDEN and F. REICH (Fermentforsch., 1929, 10, 319—329; cf. this vol., 177).—By usual methods are obtained *glycyl-dl-leucyl-β-alanine* (I), m. p. 160° (from *chloroacetyl-dl-leucyl-β-alanine*, m. p. 124—126°), *β-alanyl-dl-leucine* (II), m. p. 245—246° (decomp.), *β-alanylglycyl-dl-leucine* (III), decomp. 125°, and *β-alanyl-dl-leucylglycyl-dl-leucine* (IV), decomp. 125°. With the exception of II, all are hydrolysed by *N*-sodium hydroxide at 37—40°, I more rapidly than the isomeric III. None is hydrolysed by erepsin, but IV is attacked by trypsin-kinase (p_H 8.2) at 37°. *β-Iodopropionylglycyl-dl-leucine*, m. p. 170° (containing a little of the β -chloro-compound), is unattacked by trypsin-kinase.

J. W. BAKER.

Specific action of enzyme complexes in fission of polypeptides. E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1929, 10, 341—364).—In continuation of the investigation of Abderhalden and Schwab (this vol., 176) the hydrolysis of the following polypeptides and their derivatives (prepared by usual methods) with *N*-sodium hydroxide, erepsin (p_H 7.8), and trypsin-kinase (p_H 8.4) at 37° has been studied. No polypeptides containing a free glycine carboxyl group are attacked by trypsin-kinase, although some of their acyl derivatives suffer fission. The following are hydrolysed by trypsin-kinase, but not by erepsin: the *benzoyl*, m. p. 175° (decomp.), *phenylurethane*, m. p. 185° (corr.), and *naphthalene-2-sulphonyl*, m. p. 175° (decomp.), derivatives of *dl-leucylglycylglycine* (I), whilst the reverse is the case with (I), *glycyl-dl-phenylalanine* (II) (naphthalene-2-sulphonyl derivative hydrolysed by trypsin-kinase), *diglycyl-dl-phenylalanine* (III), *dl-phenylalanylglycine* (IV), *dl-phenylalanylglycylglycine* (V), *dl-phenylalanyldiglycylglycine* (VI), m. p. 207° (decomp.) [*phenylurethane*, m. p. 296° (decomp.), which is not attacked by trypsin-kinase] [from *β-phenyl-α-bromopropionylldiglycylglycine*, m. p. 278—279° (decomp.)], and *dl-leucylglycyl-dl-phenylalanine* (VII), m. p. 235° (corr., decomp.; lit. gives 225—228°). The following are hydrolysed by erepsin and somewhat less readily by trypsin-kinase: *diglycylglycyl-dl-phenylalanine* (VIII), m. p. 223° (decomp.) [from *chloroacetyldiglycyl-dl-phenylalanine*, m. p. 184—185° (decomp.), which is not attacked by trypsin-kinase], *dl-phenylalanyltriglycyl-dl-phenylalanine* [from *β-phenyl-α-bromopropionyltriglycyl-dl-phenylalanine*, m. p. 187° (decomp.)], *dl-phenylalanylglycyl-dl-leucine* (IX), m. p. 210° (decomp.) (from *dl-β-phenyl-α-bromopropionylglycyl-dl-leucine*, m. p. 161°, which is hydrolysed by trypsin-kinase), *dl-phenylalanylglycyl-dl-phenylalanine* (X), m. p. 236° (decomp.) (from *dl-β-phenyl-α-bromopropionylglycyl-dl-phenylalanine*, m. p. 174—175°, not hydrolysed by trypsin-kinase). *dl-β-Phenyl-α-bromopropionyl-dl-phenylalanine* is hydrolysed by trypsin-kinase. Of these various derivatives I (and its three derivatives) to X are all hydrolysed by *N*-sodium hydroxide.

J. W. BAKER.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on polypeptides and related compounds. E. ABDERHALDEN and H. BROCKMANN (Fermentforsch., 1929,

10, 330—340).—The conclusions previously reached (this vol., 180) are confirmed by the action of trypsin-kinase and erepsin on the following polypeptides and their derivatives, which are prepared by usual methods. *dl-Leucyltriglycylaniline*, m. p. 202—203° (oily picrate) [from *dl-α-bromoisohexoyltriglycylaniline*, m. p. 229—230° (decomp.)], and *glycyl-dl-α-aminobutyryl-dl-α-aminobutyric acid* are attacked by erepsin (p_H 7.8), but not by trypsin-kinase (p_H 8.4) at 38°. *dl-α-Bromopropionyl-dl-α-aminobutyryl-dl-α-aminobutyric acid*, *dl-α-bromopropionyl-l-leucylglycyl-d-alanine*, *chloroacetyl-d-alanyl-l-leucylglycyl-d-alanine*, and *d-α-bromoisohexoylglycyl-d-alanyl-l-leucylglycyl-d-alanine*, m. p. 206—207°, are all attacked by trypsin-kinase, but not by erepsin, whilst *dl-alanyl-dl-α-aminobutyryl-dl-α-aminobutyric acid* is attacked by both enzymes. The following are not hydrolysed either by erepsin or trypsin-kinase: *chloroacetyl-dl-α-aminobutyryl-dl-α-aminobutyric acid*, *dl-α-bromoisohexoyldi- and -hexaglycylglycine*, *butyryldiglycylglycine*, m. p. 231—232°, and *N-methyl-dl-leucyldiglycylglycine*, m. p. 238° (decomp.). Trypsin-kinase has no action on *chloroacetamidobenzoic acid*. Both *dl-alanyldecarboxyl-dl-leucine* and *dl-alanylcolumine* are hydrolysed by yeast extract (p_H 8.0). *Butyryltriglycylaniline*, m. p. 231—232°, is prepared. All m. p. are corrected.

J. W. BAKER.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on polypeptides and related compounds. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1929, 10, 305—318).—Further information on the reasons for the specific action of enzymes is sought by a study of the action of trypsin-kinase and erepsin on a large number of polypeptides, their acyl and halogenoacyl derivatives. The action of these enzymes has no relation to the length of the chain, since *dl-phenylalanyl-l-tyrosine*, sintering 254°, decomp. 269—270°, and *l-tyrosyl-l-tyrosine* are attacked by trypsin-kinase and not by erepsin, the reverse being the case with the longest known polypeptide (19 amino-acids). The following halogenoacyl derivatives (none of which is attacked by erepsin) are hydrolysed by trypsin-kinase: *chloroacetyl-l-leucylglycine*, *-glycyl-dl-leucine*, *-diglycyl-dl-leucine*, *-d-α-aminobutyric acid*, *-l-α-aminobutyric acid* (slightly), *-dl-valine*, *-l-leucine*, *-d-phenylalanine* (slightly), *-3:5-dibromo-dl-tyrosine*, *dl-α-bromoisohexoyl-triglycyl-dl-leucine*, *-glycyl-dl-leucine*, *-l-bromoisohexoylglycyl-l-leucine*, *di-dl-α-bromopropionyl-l-cystine*, *β-chlorobutyrylglycyl-dl-leucine*, m. p. 139°, *-dl-phenylalanine*, m. p. 130° (slightly), *-glycyl-dl-phenylalanine*, m. p. 174° (slightly), *dl-α-bromopropionyl-dl-phenylalanine*, *-glycyl-dl-phenylalanine*, (cf. also Waldschmidt-Leitz and others, A., 1928, 1401; Abderhalden and Schwab, this vol., 176), whilst the following are unattacked: *chloroacetyl-glycylglycine*, *-d-leucine*, *dl-α-bromoisovaleryl-glycine*, *-glycylglycine*, *dl-α-bromoisohexoylglycine*, *-glycylglycine*, *-dl-α-aminohehoic acid*, *-dl-phenylalanine*, *-l-tyrosine*. The action of trypsin-kinase on the halogenoacyl derivatives of polypeptides containing leucine and glycine diminishes with an increasing number of glycine residues. The following acyl derivatives of amino-acids are attacked by trypsin-kinase; *formyl-l-leucine*, *-l-phenylalanine*,

-*dl*-tyrosine, carbomethoxyformyl-*l*-tyrosine, palmityl-*l*-phenylalanine, and stearyl-*d*-glutamic acid, whilst the following are not attacked: formyl-*dl*-valine, -*d*-leucine, -*dl*-norleucine, -*d*-isoleucine, -*dl*- α -aminoheptonic acid, -*d*-phenylalanine, and carbomethoxy-*l*-tyrosine. It is concluded that the hydroxyl group of tyrosine has no importance in the formation of a complex with trypsin. *dl*-Leucine ethyl ester is attacked by both trypsin-kinase and erepsin, whilst *dl*-tyrosine ethyl ester is hydrolysed only by the former enzyme. On the basis of these results it is concluded that no one specific property is concerned in the action of trypsin and erepsin and it is not improbable that trypsin has a composite character. The authors disagree with the deductions of Waldschmidt-Leitz (*loc. cit.*). It is suggested that the hydrolytic action of the enzyme is indirect. Its specific action is involved only in the formation of the ferment-substrate complex, and in so doing so modifies the whole molecule that a previously inactive hydrogen-ion concentration may then be able to effect fission, the actual hydrolysis thus not being a specific action.

J. W. BAKER.

Specific action of enzymes. Polypeptides containing histidine. E. ABDERHALDEN, R. FLEISCHMANN, and W. IRION (*Fermentforsch.*, 1929, 10, 446—454).—Further evidence (*cf.* preceding abstract) that, contrary to Waldschmidt-Leitz and others (A., 1928, 1401), the electronegative character of the substrate is not important for hydrolysis by trypsin-kinase is found in the fact that erepsin, which readily hydrolyses *l*- and *dl*-leucyl-*l*-histidine (Fischer and Cone, A., 1908, i, 1004), has no action on *d*- and *dl*- α -bromoisohexoyl-*l*-histidine, whilst trypsin hydrolyses the bromo-compounds more slowly than the parent polypeptides, the latter, in turn, however, being less readily hydrolysed by this enzyme than by erepsin. α -Bromoisohexoyl-*l*-histidine is readily hydrolysed by *N*- and even by 0.1*N*-sodium hydroxide, and hence the more dilute alkali must be used to hydrolyse its methyl ester in its preparation. *l*-Leucyl-*l*-histidine is unattacked by *N*-sodium hydroxide at 37° in 72 hrs. Vickery and Leavenworth's method (A., 1928, 1121) for the preparation of histidine is found to be much more costly and uncertain than the older mercuric method.

J. W. BAKER.

Relationship between substrate and enzyme. Influence of erepsin and trypsin-kinase on the decomposition of certain polypeptides. E. ABDERHALDEN and V. VLASSOPOULOS (*Fermentforsch.*, 1929, 10, 365—395).—The action of *N*-sodium hydroxide, erepsin, and trypsin-kinase on various polypeptides derived from α -aminobutyric and α -amino-*n*- and -*iso*-valeric acids and their derivatives has been studied. Erepsin, but not trypsin, effects the hydrolysis of *dl*- α -aminobutyrylglycine (*phenylurethane*, m. p. 188°; *naphthalene-2-sulphonyl* derivative, m. p. 165.5°) and glycyl-*dl*- α -aminobutyric acid (I) (*naphthalene-2-sulphonyl* derivative, m. p. 112—114), whilst neither enzyme attacks *dl*- α -aminobutyrylglycylglycine (II) (*naphthalene-2-sulphonyl* derivative, m. p. 140°) (from *dl*- α -bromobutyrylglycylglycine, m. p. 147°), *dl*- α -aminobutyryldiglycylglycine (*phenylurethane*, m. p. 193°) (from the α -bromo-

compound, m. p. 175°), and *diglycyl-dl*- α -aminobutyric acid (III) (from *chloroacetylglycyl-dl*- α -aminobutyric acid, m. p. 120—121°). The *phenylurethane*, m. p. 195°, of I suffers fission by trypsin-kinase, but not the *phenylurethanes*, m. p. 172° and 208°, respectively, of II and III. In the valine series erepsin hydrolyses *dl*-valyl-*dl*-valine (IV) (*phenylurethane*, m. p. 188—189°; *naphthalene-2-sulphonyl* derivative, m. p. 208°), *d*-valyl-*d*-valine (V), m. p. above 300°, [α]_D²⁰ -54° (water) (*phenylurethane*, m. p. 184°; *naphthalene-2-sulphonyl* derivative, m. p. 213—215°) [obtained in small yield from *d*- α -bromo-*isovaleryl-d*-valine, m. p. 137°, [α]_D²⁰ +13.1° (alcohol), together with *dimethylacrylvaline*, m. p. 137°, the latter not being attacked by extract of pancreas powder or *N*-sodium hydroxide], *glycyl-d*-valyl-*d*-valine (VI), m. p. 220°, [α]_D²⁰ -32° (water) (*naphthalene-2-sulphonyl* derivative), *dl*-norvalyl-*dl*-norvaline (VII), m. p. 270° (decomp.) (*phenylurethane*, m. p. 206°; *naphthalene-2-sulphonyl* derivative, m. p. 177°) (from α -bromo-*n*-valeryl-*dl*-norvaline, m. p. 124—125°, and *glycyl-dl*-norvalyl-*dl*-norvaline (VIII), m. p. 238—240° (*phenylurethane*, m. p. 156°; *naphthalene-2-sulphonyl* derivative, m. p. 195°) (from *chloroacetyl-dl*-norvalyl-*dl*-norvaline, m. p. 147.5°). None of these polypeptides or their derivatives is attacked by trypsin-kinase. All the polypeptides containing *dl*- α -aminobutyric acid in their structure, together with their *phenylurethanes* and *naphthalene-2-sulphonyl* derivatives, are hydrolysed by *N*-sodium hydroxide at 37°, in some cases hydrolysis of the derivatives being more rapid and in others slower than that of the parent polypeptides. In the valine series IV and V are unattacked by *N*-sodium hydroxide, whilst their derivatives, and VI suffer hydrolysis. On the other hand, VII and its derivatives and VIII are slowly hydrolysed.

J. W. BAKER.

Specificity of enzymolytic degradation of polypeptides. Polypeptides containing *dl*-norleucine. E. ABDERHALDEN and H. MAYER (*Fermentforsch.*, 1929, 10, 464—473).—The action of *N*-sodium hydroxide, erepsin, and trypsin-kinase on various polypeptides containing norleucine is investigated. Trypsin-kinase effects the hydrolysis of *chloroacetyl-dl*-norleucine, *dl*- α -bromohexoyl-*dl*-norleucine (I), m. p. 104°, *dl*- α -bromoisohexoyl-*dl*-norleucine (II), m. p. 136°, *dl*- α -bromohexoyl-*dl*-leucine (III), m. p. 158°, *dl*- α -bromoisohexoylglycyl-*dl*-norleucine, *dl*-leucylglycyl-*dl*-norleucine (IV), *dl*- α -bromohexoylglycyl-*dl*-norleucine, m. p. 118°, *dl*-norleucylglycyl-*dl*-norleucine (V), m. p. 240°, *dl*- α -bromohexoylglycyl-*dl*-leucine, m. p. 127°, *dl*-norleucylglycyl-*dl*-leucine (VI), m. p. 245°, and the *phenylurethanes*, m. p. 186° and 202°, respectively, of *dl*-leucyl-*dl*-norleucine (VII), m. p. 256°, and *dl*-norleucyl-*dl*-leucine (VIII), m. p. 253°. Erepsin hydrolyses IV, V, VI, VIII, and *glycyl-dl*-norleucine. *dl*-Norleucyl-*dl*-norleucine, m. p. 259° (*phenylurethane*, m. p. 198°), and IV are too insoluble for investigation. All these polypeptides are hydrolysed by *N*-sodium hydroxide with the exception of I, II, III, VII, and VIII, and the three *phenylurethanes*.

J. W. BAKER.

Behaviour of *N*-sodium hydroxide, erepsin, and trypsin-kinase towards polypeptides containing a 3:5-halogen-substituted tyrosine residue,

glycyl-*d*-tyrosine, glycyl-*dl*-nitrotyrosine, and glycyl-*dl*-*o*-tyrosine. E. ABDERHALDEN and A. SCHMITZ (Fermentforsch., 1929, 10, 428—439).—Investigations of the effect of modifying the carboxyl group of an amino-acid have been made by a study of the action of the above hydrolysing agents on various synthetic polypeptides derived from glycine and substituted tyrosines, all of which are prepared by usual methods. All the undermentioned derivatives are hydrolysed by *N*-sodium hydroxide at 37°, the tripeptides most rapidly and glycyl-*L*-tyrosine most slowly. Erepsin (p_H 7.8) at 37° attacks glycyl-*L*-tyrosine, glycyl-*dl*-3 : 5-dichloro-, m. p. 237°, -3 : 5-dibromo-, m. p. 222—223° (decomp.), and -3 : 5-di-iodo-tyrosine (the first two being obtained, respectively, from chloroacetyl-3 : 5-dichloro-, m. p. 195°, and -3 : 5-dibromo-tyrosine, m. p. 207°), none of which is hydrolysed by trypsin-kinase. Conversely, trypsin-kinase (p_H 8.3), but not erepsin, at 37° effects hydrolysis of chloroacetyl-*dl*-*o*-tyrosine (cf. Ueda, this vol., 75), *dl*-leucylglycyl-*dl*-3 : 5-dichloro-, m. p. 210° (decomp.), -3 : 5-dibromo-, m. p. 220° (decomp.), and -3 : 5-di-iodo-, m. p. 205° (decomp.)-tyrosine (obtained, respectively, from *dl*- α -bromoisohexoylglycyl-*dl*-3 : 5-dichloro-, -dibromo-, and -di-iodo-tyrosine). Neither enzyme attacks glycyl-*dl*-5-nitrotyrosine, m. p. 240° (decomp.) (from chloroacetyl-*dl*-5-nitrotyrosine, m. p. 166°), glycyl-*dl*-*o*-tyrosine, m. p. 150°, or glycyl-*d*-tyrosine, m. p. 160°. Addition of 0.1 or 0.02 mol. of either dichloro- or di-iodo-tyrosine to glycyl-*L*-tyrosine reduces the enzymolytic action of erepsin on this polypeptide. J. W. BAKER.

Homogeneity of trypsin complexes? I, II, and III. E. ABDERHALDEN (Fermentforsch., 1929, 10, 474—477, 478—480, 481—490).—I. Behaviour of various substrates with various trypsin-kinase preparations at various p_H values. [With O. HERMANN.]—From a study of several examples it is found that the activity of trypsin-kinase preparations varies greatly according to the specimen and p_H value used. Thus although some specimens were unable to effect the hydrolysis of *dl*-leucylglycyl-*dl*-leucine at p_H 7.8, hydrolysis occurred at p_H 8.4. In general, halogenoacyl derivatives are more readily attacked at p_H 7.8 than at p_H 8.4, whilst the polypeptides themselves are more readily hydrolysed at the latter value. The significance of these results is discussed.

II. Separation of enzymes with varying activity in the preparation of "trypsin" from pancreas powder. [With E. SCHWAB.]—The enzyme obtained in the usual manner from pig's pancreas is subjected to three adsorptions on alumina at p_H 4.7 to remove erepsin, and the mother-liquor is subsequently adsorbed at p_H 5.6. The eluted enzyme from the latter adsorption does not hydrolyse *dl*-leucylglycine or *dl*-leucylglycyl-*dl*-leucine, but still attacks chloroacetyl-*L*-tyrosine, -*L*-phenylalanine, -*L*-leucine, and glycyl-*d*'-leucine phenylurethane. The final mother-liquor also attacked these halogenoacyl derivatives, but more slowly. By repeated adsorption at p_H 5.6 a mother-liquor is obtained from which is prepared a trypsin preparation which is very unreactive towards these derivatives. Hence the

suggestion that the trypsin complex is not a single individual (Abderhalden and Schwab, this vol., 604) is confirmed.

III. Period of hydrolysis of halogenoacyl-amino-acids and polypeptides by various specimens of trypsin at various p_H values. [With W. ZEISSET.]—The enzymolytic action of the same specimen of trypsin-kinase prepared by the usual methods on a series of halogenoacyl derivatives of polypeptides confirms the previous conclusion (I, above) that hydrolysis is much more rapid at p_H 7.8 than at p_H 8.4. Further, the trypsin preparation obtained by adsorption at p_H 5.6 (II, above) hydrolyses those derivatives which are only slightly attacked by the normal trypsin preparation even more slowly. J. W. BAKER.

Relationship between erepsin and trypsin-kinase and their substrate polypeptides and their derivatives. Attempted isolation of erepsin from intestinal juice and trypsin from pancreas juice. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1929, 10, 440—445).—Erepsin, which by itself does not hydrolyse the halogenoacyl derivatives of α -amino-acids and polypeptides, readily and rapidly hydrolyses a large number of these derivatives when a trace of trypsin is added. This obviously serves as a practical test for the absence of trypsin from erepsin preparations. Hydrolysis of this type of derivatives with trypsin-kinase with addition of a little erepsin proceeds more rapidly for the first hour than with trypsin-kinase alone, but as the hydrolysis proceeds the action of the former mixed enzyme decreases so that the final degree of hydrolysis is the same in each case. Possible explanations of this mutual action are discussed. J. W. BAKER.

Natural activation of proteases of plant latexes. O. AMBROS and A. HARTENECK (Z. physiol. Chem., 1929, 181, 24—41).—Papaw (*Carica papaya*) contains a natural activator which stimulates the hydrolytic activity of the latex towards proteins, protamines, and peptones in the same way as hydrocyanic acid for the commercial papain. This thermolabile activator is termed phytokinase. In half-ripe fruits the latex contains the activator, but in the almost ripe fruits the latex alone is comparatively inactive, the activator is found in the fruit flesh and seeds. Pineapple (*Bromelia sativa*) contains a similar activator. J. H. BIRKINSHAW.

Thermostability and regeneration of inactivated enzymes. V. KULIKOV and M. BOBKON (Zhur. exp. Biol. Med., 1928, 10, 147—152).—If inactivation of enzymes by heat is associated with coagulation of other substances present in the mixture, the enzyme must become adsorbed on the coagulated particles and its regeneration is probably a slow elution process. For proteolytic enzymes the regeneration takes place only when the inactivation is carried out at p_H 7.9.

CHEMICAL ABSTRACTS.

Problems of fermentation. H. VON EULER and K. MYRBACK (Z. physiol. Chem., 1929, 181, 1—14). The role of the hexosephosphoric acids, the question as to whether the Robison ester is the precursor of diphosphate, and the phenomenon of mutation are discussed. J. H. BIRKINSHAW.

Phosphoric esters in alcoholic fermentation. I. Sequence of the formation of phosphoric esters and carbon dioxide in fermentation by dried yeast. E. BOYLAND (Biochem. J., 1929, 23, 219—229).—Up to a limiting concentration of phosphoric esters the basic rate of fermentation varies with the concentration of phosphorus present as phosphoric esters. Up to this same concentration the ratio of diphosphoric ester to monophosphoric ester remains constant, but above the limiting concentration the relative amount of diphosphoric ester increases. The addition of inorganic phosphate to dried yeast fermenting dextrose is followed by esterification and liberation of carbon dioxide, but there is a considerable lag between esterification and the evolution of carbon dioxide. The carbon dioxide liberated by phosphate is somewhat more than equivalent to the added phosphate, but is approximately equivalent to the phosphorus esterified plus the amount of phosphorus as monophosphate formed. In fermentation by dried yeast in presence of phosphate the monophosphoric esters are formed late in the reaction. Under the conditions described in this paper these esters consist mainly of trehalosemonophosphate.

S. S. ZILVA.

Equation of alcoholic fermentation. II. A. HARDEN and F. R. HENLEY (Biochem. J., 1929, 23, 230—236).—In fermentations of dextrose or levulose in presence of phosphate carried out with dried yeast the ratio of extra carbon dioxide evolved to phosphorus esterified tends to be slightly higher than unity. With maceration extract and yeast-juice this ratio tends to be somewhat lower than unity as previously found with zymine. The ratio of hexosediphosphate to hexosemonophosphate formed during the fermentation is usually high for dried yeast, but is very variable for maceration extract and yeast-juice, the product in extreme cases consisting almost entirely of either the diphosphate or monophosphate. The most constant ratio which was observed is that of extra carbon dioxide to total phosphorus esterified, which varies only about $\pm 10\%$, although the proportions of diphosphate and monophosphate may vary from 96% of diphosphate to 86% of monophosphate. The equation of Harden and Young cannot be applied to those cases in which a large proportion of hexosemonophosphate is produced, whilst the ratio carbon dioxide/total phosphorus esterified remains at about 0.9.

S. S. ZILVA.

Alcoholic fermentation. XVIII. Behaviour of yeast to glyceraldehyde and glyceric acid. S. KOSTYTSHEV and K. JEGOROVA (Z. physiol. Chem., 1929, 181, 264—280).—Glyceric acid and glyceraldehyde are not fermented by yeast to any significant extent and cannot therefore be intermediate products of alcoholic fermentation.

P. W. CLUTTERBUCK.

Mechanism of fluoride inhibition and the dissociation curve of fluor-methæmoglobin. F. LIPMANN (Biochem. Z., 1929, 206, 171—185).—The inhibition of fermentation by fluoride is completely reversible and in accordance with the mass action law. It increases with acidity; this is consistent with complex formation between enzyme and fluoride.

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The dissociation constant of fluor-methæmoglobin was determined. The dissociation is a unimolecular reaction. The oxidation of oxalic acid by permanganate and hydrogen peroxide decomposition by tervalent iron are inhibited by fluoride.

J. H. BIRKINSHAW.

Top yeast. H. VON EULER and H. NILSSON (Z. physiol. Chem., 1929, 181, 281—290).—The fermenting power and oxygen utilisation of fresh yeast and of washed and unwashed dried yeast with and without addition of boiled juice are greatly decreased by treating the yeast with hydrogen sulphide. With fresh yeast both the fermenting power and the oxygen utilisation are decreased to one quarter, whilst with unwashed dried yeast the fermenting power is decreased to one eighth and the oxygen utilisation to one fourteenth of the control values. The co-enzyme of dried yeast obtained by treating fresh yeast for 24 hrs. with hydrogen sulphide and drying may be washed out with water.

P. W. CLUTTERBUCK.

Ergosterol content of yeast. A. HEIDUSCHKA and H. LINDNER (Z. physiol. Chem., 1929, 181, 15—23).—Ergosterol was prepared from yeast by heating with alcoholic potassium hydroxide. On evaporation of the alcohol crystals separated, the ether extract of which yielded ergosterol. Colorimetric determinations showed that the ergosterol content of yeast and moulds is subject to wide variations according to the method of cultivation.

J. H. BIRKINSHAW.

Formation of fumaric acid in sugar cultures of *Rhizopus nigricans* and its behaviour with pyruvic acid. W. S. BUTKEWITSCH and M. W. FEDEROFF (Biochem. Z., 1929, 206, 440—456).—The results confirm the findings of Ehrlich and Bender (A., 1928, 95). In the presence of calcium carbonate the pyruvic acid underwent a change which bore no relationship to the activity of the mould. The empirical formula of the isolated monobasic acid is $C_7H_6O_4$.

C. C. N. VASS.

Metabolism of amino-acids by *Paramoecium caudatum*. F. E. EMERY (J. Morph. Physiol., 1928, 45, 555—577).—The rate of metabolism of the amino-acids was: phenylalanine 7.7, tryptophan 9.6, glycine 9.6, leucine 12.0, glutamic acid 13.2, alanine 15.5, arginine 15.9, tyrosine 17.7, aspartic acid 25.1, cysteine hydrochloride 26.3, glutamic acid hydrochloride 45.6, mixture of all except arginine 48.3%. Cystine was not utilised or converted into cysteine. The values for histidine and lysine were 10—15% and about 5%.

CHEMICAL ABSTRACTS.

Steric relationships in the dismutation of phenylglyoxal hydrate by various bacteria. S. HAYASHI (Biochem. Z., 1929, 206, 223—227).—*B. proteus*, *B. fluorescens*, *B. pyocyaneus*, and *B. prodigiosus* all convert phenylglyoxal hydrate into *d*(-)-mandelic acid. The optimum p_H is 7. *B. coli* produces the same change best at p_H 8.1; the acid consists of 65—75% *d*(-)-form; in the analogous dismutation of methylglyoxal hydrate this organism produces inactive lactic acid.

J. H. BIRKINSHAW.

Decomposition of fats by bacteria. F. E. HAAG (Arch. Hyg., 1928, 100, 271—308; Chem. Zentr., 1928, ii, 1891—1892).—The ease of decom-

position of fatty acids by bacteria depends on the chemical, and not on the physical, properties of the fats. A bactericidal action by the higher fatty acids was not observed; a solvent action on the bacteria by the alkali soaps is concerned. A. A. ELDRIDGE.

Reduction of sulphates by micro-organisms in presence of fats. G. SELIBER (Compt. rend. Soc. Biol., 1928, 99, 544—546; Chem. Zentr., 1928, ii, 1781—1782).—Reducing micro-organisms decompose sulphates with production of hydrogen sulphide if fat or its products of decomposition are present, the fat being anaerobically decomposed. Both processes can proceed at the sea-bottom. A. A. ELDRIDGE.

Proteolytic bacteria of milk. IV. Action of proteolytic milk bacteria on amino-acids and other simple nitrogenous compounds. W. C. FRAZIER and P. RUFF (J. Bact., 1928, 16, 231—245).—Some of the organisms which can use carbamide as sole source of nitrogen liberate ammonia, whilst others produce an acid reaction. Organisms which can use ammonia as sole source of nitrogen appear to use any of the simpler amino-acids if a fermentable sugar is present. Differentiation of organisms may probably be based on differences in utilisation of amino-acids as sources of both nitrogen and carbon.

CHEMICAL ABSTRACTS.

Rennin action. I. Rennin production by *Bacillus prodigiosus*. II. Effect of rennin on sodium caseinogenate. J. G. WAHLIN (J. Bact., 1928, 16, 355—373, 375—386).—The production of rennin by *B. prodigiosus* in a medium containing complex proteins, amino-acids, and ammonia is more active at 37° than at 20°; raw cultures are more active than filtrates. The rennin is more thermostable, and less susceptible to oxalates and to the caseinogen concentration than is calf rennin. It coagulates heated milk more readily than calf rennin. Rennin renders the protein of sodium caseinogenate or milk more readily precipitable by salts. Certain types of proteolytic bacteria similarly affect sodium caseinogenate.

CHEMICAL ABSTRACTS.

Nitrogen exchange in *Bacillus mycoides*. I. Influence of medium on growth and nitrogen exchange. II. Proteolytic enzymes. H. GLINKA-TSCHERNORUTZKY (Biochem. Z., 1929, 206, 301—307, 308—313).—I. Cultures of *B. mycoides* in 1% peptone decomposed the protein with ammonia production. Addition of dextrose (1%) reduced the decomposition. In caseinogen-peptone medium an increased ammonia content with a decreased amino-acid content was observed. Medium containing only monoamino-acids yielded light and delayed growths.

II. A trypsin-like enzyme has been extracted from *B. mycoides*. Results obtained from a dextrose medium support the views of Waksman, that dextrose forms a high energy source for the bacteria and so diminishes the decomposition of the proteins.

C. C. N. VASS.

Carnitine, crotonobetaine, and γ -butyrobetaine in putrefaction. W. LINNEWER (Z. physiol. Chem., 1929, 181, 54—57).—Both carnitine and crotonobetaine are reduced to β -butyrobetaine by putrefactive organisms.

J. H. BIRKINSHAW.

Genesis and character of bacterial poisons. M. EISLER (Z. Immunitats., 1928, 56, 209—233; Chem. Zentr., 1928, ii, 1781).—Bacterial poisons are regarded as extractive materials of dead bacteria rather than as secretory products of living bacteria.

A. A. ELDRIDGE.

Absorption of tuberculin. A. BOQUET, L. NEGRE, and J. VALTIS (Compt. rend. Soc. Biol., 1928, 99, 9—12; Chem. Zentr., 1928, ii, 1892).—If tuberculin is treated with a sufficient quantity of finely-divided carbon, it is freed from all active (antigenic and toxic) substances. The adsorption complex so formed is irreversible and indissoluble *in vivo*.

A. A. ELDRIDGE.

Carbohydrate content of the alcohol-soluble antigen of tubercle bacilli. K. KNOWLTON and M. PINNER (Amer. Rev. Tuberculosis, 1928, 18, 502—504).—The antigen is almost certainly of lipoid nature.

CHEMICAL ABSTRACTS.

Bacteria. XXIII. Comparative yields of water-soluble protein carbohydrate from tubercle bacilli from various sources. T. B. JOHNSON and A. G. RENFREW (Amer. Rev. Tuberculosis, 1928, 18, 505—512).—A technique is described. The yield of carbohydrate is reduced, and that of the active protein is very low, when autoclaved cells are used.

CHEMICAL ABSTRACTS.

Physico-chemical conditions of the thermostability of diphtheria antitoxin. V. KULIKOV, P. SMIRNOV, and M. BOBKOVA (Compt. rend. Soc. Biol., 1928, 98, 1503—1504; Chem. Zentr., 1928, ii, 1579).—On addition of alkali to the antitoxin gradual precipitation takes place in the p_H range 4.8—7.0; at maximal precipitation (p_H 6.1—6.5) all the antitoxin is present in the precipitate. Heating and treatment with acid also lead to concentration of the antitoxin or removal of attendant substances.

A. A. ELDRIDGE.

Nature of the bactericidal agents (bactericidins) in duodenal juice. W. LOWENBERG (Z. ges. exp. Med., 1928, 62, 184—216; Chem. Zentr., 1928, ii, 1585).—The substances are resistant to heat, and in their behaviour on dialysis and ultrafiltration are between proteins and crystalloids; they are not readily absorbed. They are not identical with the bactericidal substances of serum, with pancreas enzymes, or with bacteriophages.

A. A. ELDRIDGE.

Chemical constitution and germicidal activity of amines, ketones, and aldehydes. F. W. TILLEY and J. M. SCHAFER (J. Bact., 1928, 16, 279—285).—For primary alkylamines and *Bacillus typhosus* the average ratio between successive molecular phenol coefficients was 2.0, and with *Staphylococcus aureus* 3.3. For alkyl ketones and *B. typhosus* the average ratio was 3.25; unsatisfactory experiments with aldehydes indicated values of 2.5 or more.

CHEMICAL ABSTRACTS.

Commercial bacteriological peptones. J. G. McALPINE and G. D. BRIGHAM (J. Bact., 1928, 16, 251—256).—A study of the nitrogen distribution in Difco-Bacto, Difco-Proteose, Fairchild, and Witte peptones.

CHEMICAL ABSTRACTS.

Factors affecting the growth of surface colonies of bacteria. P. K. BATES (Abst. Thesis Mass. Inst.

Tech., No. 3, Jan., 1929, 39—40).—The area of a bacterial colony on an agar surface increases at a rate characteristic of each species. Growth is greater in a humid than in a dry atmosphere, and in a neutral than in an acid medium, and is inhibited by lack of oxygen. The character of the colonies varies with the concentration of the agar gel, and with the temperature; at 25°, growth is slower than at 37°, but much larger colonies are formed. E. W. WIGNALL.

Behaviour of calcium in administration of adrenaline. H. LAWACZECK (Deut. Arch. klin. Med., 1928, 160, 309—322; Chem. Zentr., 1928, ii, 1893).—Administration of adrenaline does not change the total blood-calcium, but a greater proportion of the calcium is ultrafilterable. A. A. ELDRIDGE.

Effect of insulin and adrenaline on the distribution of dextrose in the blood. S. I. VINKOV (Zhur. exp. Biol. Med., 1928, 9, 394—407).—Large doses of insulin remove the difference between the red cells and plasma of pigeon's blood as regards uneven distribution of dextrose and residual reduction. The effect of adrenaline is to accentuate the difference in the concentration of dextrose between cells and plasma, the cells suffering loss of dextrose.

CHEMICAL ABSTRACTS.

Carbohydrate balance of fasting rats after insulin and adrenaline injections. C. F. CORI and G. T. CORI (Biochem. Z., 1929, 206, 39—55).—Between the 24th and 48th hr. the total glycogen of fasting rats decreases by about 15%. The respiratory quotient is not changed by adrenaline injection, but the oxygen consumption increases. After moderate doses of insulin the respiratory quotient rises slightly, but the oxygen uptake is constant. Three hrs. after adrenaline injection muscle-glycogen is 57 mg. lower and liver-glycogen 36 mg. higher per 100 g. of animal. Muscle-glycogen is transformed into liver-glycogen by way of lactic acid. After insulin, muscle-glycogen is 34 mg. lower and furnishes part of the carbohydrate burnt. The already low liver-glycogen scarcely changes. Insulin increases the combustion of blood-sugar in the peripheral tissue. The mechanism of insulin and adrenaline action is discussed.

J. H. BIRKINSHAW.

Insulin and gluconeogenesis. M. W. GOLDBLATT (Biochem. J., 1929, 23, 243—255).—Experiments on rats, rabbits, and man show that insulin can stimulate the new formation of glycogen from endogenous sources. The theory that insulin inhibits gluconeogenesis is untenable. S. S. ZILVA.

Biological characteristic of bound sugar. Fasting dogs. C. TOSCANO (Polichinico, 1927, 11 pp.; Chem. Zentr., 1928, ii, 1583).—By the action of insulin a general diminution of free and bound sugar first takes place. Long fasting does not increase the normal bound blood-sugar value. A state of high bound sugar regularly follows a diminution, the free sugar being lowered. Considerable increase of bound sugar does not cause a decrease of free sugar. Administration of adrenaline causes rapid increase of the free sugar with simultaneous decrease of the bound sugar. It is supposed that adrenaline causes the degradation of the former to the latter.

A. A. ELDRIDGE.

Mechanism of the reduction of blood-sugar values by the action of insulin. B. MATSUOKA (Compt. rend. Soc. Biol., 1928, 98, 1178—1179; Chem. Zentr., 1928, ii, 1786).—The hypoglycæmic action of insulin depends on the formation of lactacidogen in the liver and probably in the muscles, and on the conversion of lactacidogen into glycogen.

A. A. ELDRIDGE.

Insulin and excretion of urine. R. AGNOLI (Arch. biol., 1926, 10 pp.; Chem. Zentr., 1928, ii, 1786).—Insulin decreases urinary excretion; the effect is not conditioned by hypoglycæmia, and is abolished by oral administration of urea.

A. A. ELDRIDGE.

Beta-hormone. B. P. WIESNER and J. S. PATEL (Nature, 1929, 123, 449).—The corpus luteum (cattle) contains an extractable substance which causes some of the effects ascribed to the hypothetical beta-hormone, e.g., it prevents the atrophy of the uterus in ovariectomised mature mice. It is concluded that the substance is a factor responsible for pseudopregnancy in diphasic animals and for the premenstruum in monophasic animals. A. A. ELDRIDGE.

Ovarian hormone. Influence of the corpus luteum on the sexual cycle. G. COTTE and G. PALLOT (Compt. rend. Soc. Biol., 1928, 99, 69—72; Chem. Zentr., 1928, ii, 1892).—There exist in the ovary two hormones of opposing action; one, belonging to the corpus luteum, hinders ovulation.

A. A. ELDRIDGE.

Physiology of glands. CXIV. L. ASHER. Activation of adrenal glands by thyroxine. F. ZIMMERMANN (Biochem. Z., 1929, 206, 369—400).—The modification of Hagedorn and Jensen's method introduced by Issekutz and Both (cf. A., 1927, 600) was used to determine the glycogen content of the bilateral muscles, taken separately, of the hind-leg of a rat. Normal muscles showed an average glycogen content of 0.79% with a maximum absolute variation between the values obtained from the separate portions of the muscle of 2.94%. After injection of adrenaline (1:10,000) the glycogen content decreased by 21.8%, with 1:1000 by 25.28%, and in the case of adrenaline (1:10,000)+2% of novocaine by 28.85%. The glycogen content of the liver after injection of adrenaline (1:10,000) was 1.79%, after 1:1000 0.90%. When adrenaline (1:1000) was injected approximately 6 hrs. after an injection of thyroxine (1:1000) the glycogen content in muscle fell by 37.06% and the glycogen content of the liver was 0.257%. Thyroxine increased the action of adrenaline on the carbohydrate metabolism. C. C. N. VASS.

Chemical nature of vitamin-A. J. C. DRUMMOND and L. C. BAKER (Biochem. J., 1929, 23, 274—291; cf. Drummond, Channon, and Coward, A., 1926, 206).—The unsaponifiable fraction of cod-liver oil after removal of the greater part of the cholesterol tends to decompose on fractionation (0.01—2 mm. pressure) with serious loss of the vitamin. The constituents of this unsaponifiable fraction are not readily reduced by hydrogen in the presence of platinum or palladium catalysts. The unsaponifiable fraction from sheep-liver fat also decomposes considerably on distillation in a high vacuum. This is due to

the presence of the highly-unsaturated hydrocarbons resembling squalene (cf. Channon and Marrian, A., 1926, 638). The sheep-liver fractions are also resistant to hydrogenation. The distillation of the unsaponifiable fractions from Greenland shark-liver oil and Japanese shark-liver oil which consists mainly of selachyl, batyl, chimyl, and oleyl alcohols is accompanied by comparatively little destruction of the vitamin. "Biosterin" of Takahashi and his colleagues consists to a very large extent of substances other than vitamin-A. The structure for chimyl alcohol suggested by Heilbron and Owens (A., 1928, 616) is confirmed. S. S. ZILVA.

Limitations of the antimony trichloride test for determination of vitamin-A. W. S. JONES, A. E. BRIOD, S. ARZOMANIAN, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1929, 18, 253—256).—Of 13 samples of cod-liver oil only 5 yielded colorimetric assays within 15% of the biological assays, and of the remaining 8, all except 2 gave colorimetric values which exceeded the biological by 20—600%.

E. H. SHARPLES.

Biochemistry of carotin-like substances. B. VON EULER, H. VON EULER, and P. KARRER (Helv. Chem. Acta, 1929, 12, 278—285).—Contrary to the results of Drummond, Channon, and Coward (A., 1920, i, 908; 1926, 206), it is found that the addition of daily doses of 0.10—0.03 mg. of purified carotin to the basic diet of rats causes an increase in growth similar to that obtained with vitamin-A. Moreover, the colorimetric determination of carotin in the liver by the antimony chloride reaction gives results in rats which had been given carotin (19 and 29 Lovibond units) comparable to those obtained with rats fed on a normal diet (25—35 Lovibond units). The growth increase is not a general effect of all carotin-like substances, since negative results are obtained with the isomeric lycopin (and its carboxylic acid, cf. this vol., 569), xanthophyll, α -crocetin, bixin, and capsanthin (all of which, however, give a positive antimony trichloride reaction), but positive results are obtained with dihydro- α -crocetin if vitamin-D (in the form of irradiated arachis oil) is included in the diet. No growth increase occurs if the latter vitamin is absent, and this absence probably explains the contrary results of the earlier investigators. J. W. BAKER.

Relation of vitamin-A to greenness of plant tissue. II. Vitamin-A content of asparagus. J. W. CRIST and M. DYE (J. Biol. Chem., 1929, 81, 525—532).—Green asparagus is much more active in promoting the growth of rats on a diet deficient in vitamin-A than is bleached asparagus; this confirms the previously suggested relationship of vitamin-A to greenness in plant tissue (A., 1927, 904).

C. R. HARRINGTON.

Vitamin content of tomatoes ripened artificially and naturally. M. C. HOUSE, P. M. NELSON, and E. S. HABER (J. Biol. Chem., 1929, 81, 495—504).—The amount of vitamin-A and -B in tomatoes increases during ripening to an equal degree whether the process takes place naturally on the plants or whether the fruit is picked green and ripened by exposure to the air or to ethylene. The maximum

development of vitamin-C is obtained only in fruit allowed to ripen naturally on the plant.

C. R. HARRINGTON.

Vitamin-A content of the subcutaneous fat of the dolphin (*Delphinus delphis*). S. N. NATZKO (Zhur. exp. Biol. Med., 1928, 10, 163—166).—In experiments with rats, dolphin fat and cod-liver oil gave equally good results. CHEMICAL ABSTRACTS.

Metabolism and vitamin-A. C. M. McCAY and V. E. NELSON (J. Metabol. Res., 1925—1926, 7—8, 199—204).—Albumin is a normal constituent of rat's urine. In vitamin-A deficiency the volume, density, acidity, and nitrogen partition of the urine are unaffected. CHEMICAL ABSTRACTS.

Vitamin-D from sterols of mummified Egyptian brain. H. KING, O. ROSENHEIM, and T. A. WEBSTER (Biochem. J., 1929, 23, 166—167).—Cholesteryl esters were prepared from a mummified brain of Coptic origin dating from about 500 A.D. by warming the tissue in 2% potassium hydroxide and extraction with ether. On recrystallisation from ethyl acetate and from acetone a white product, m. p. 78—80°, $[\alpha]_{540}^{20}$ —29°, was obtained. The crude esters after the removal of "oxycholesterol" gave colour reactions for ergosterol and showed the absorption spectrum of ergosterol in the region 280—290 μ . The irradiated esters in daily doses of 2 and 4 mg. showed the same antirachitic action as 0.05 γ of irradiated ergosterol. The ergosterol content of cholesterol isolated from the mummified brain is of the same order as that from fresh brain.

S. S. ZILVA.

Activity of irradiated ergosterol. R. FABRE and H. SIMONNET (J. Pharm. Chim., 1929, [viii], 9, 331—338).—A discussion of the current methods used in testing antirachitic activity. B. A. EAGLES.

Photochemical action of sterols of diverse origin. L. HUGOUNENQ and E. COUTURE (Compt. rend., 1929, 188, 742—743).—Sterols derived from silk-worm moths and brewer's yeast show the action on the photographic plate already described (this vol., 359), whilst sterols obtained from ox-blood or snails show no action after 15 days' exposure.

G. A. C. GOUGH.

Effect of excessive doses of irradiated ergosterol on the calcium and phosphorus content of the blood. L. J. HARRIS and C. P. STEWART (Biochem. J., 1929, 23, 206—209).—The administration of a complete synthetic diet containing 0.1% of irradiated ergosterol produces in the rat a 50% increase of blood inorganic phosphate and a 25% increase of serum-calcium. In adult rabbits receiving a normal mixed diet the administration of 10 mg. *per diem* of irradiated ergosterol per animal is followed, after upwards of a fortnight at the normal level, by a 50% increase in the blood inorganic phosphate. On the other hand, after 6 weeks there is no significant rise in serum-calcium, although abnormal deposits of calcium are already to be observed in the body.

S. S. ZILVA.

Hypervitaminosis and vitamin balance. II. Specificity of vitamin-D in irradiated ergosterol poisoning. III. Pathology of hypervitaminosis-D. L. J. HARRIS and T. MOORE

(Biochem J., 1929, 23, 261—273; cf. Harris and Moore, this vol., 105).—A diet containing 0.1% of ergosterol in which vitamin-D has been destroyed by prolonged over-irradiation does not produce the condition of hypervitaminosis. Ergosterol irradiated in oil or in alcohol when fed at the same vitamin-D levels (0.025%) produced hypervitaminosis of the same degree of severity. Ergosterol irradiated in absence of any solvent also produces specific ill effects. This evidence supports the theory that excessive doses of vitamin-D are toxic *per se*. Besides the features already described in the literature, rats and rabbits suffering from hypervitaminosis show a remarkably high blood-phosphate, a tendency towards diminished p_{H} of faeces, diminished heart rate, and at death atrophy of the thymus. S. S. ZILVA.

Changes in rat's organs due to large overdoses of "vigantol." F. HOLTZ and T. VON BRAND (Z. physiol. Chem., 1929, 181, 227—233).—Tables give the weight changes of normal rats and of rats to which were administered excessive amounts of "vigantol" (vitamin-D preparation) in olive oil (100,000 times the therapeutic dose) and the kidney, lung, heart, aorta, liver, spleen, and blood vessels were examined for metabolic changes, particularly in respect to calcium, similar to those observed by Kreitmair and Moll (A., 1928, 1406). These effects were often obtained, but it seemed possible that they were due not to hypervitaminosis but to some impurity in the "vigantol." P. W. CLUTTERBUCK.

Coloration of living vegetable cells by neutral-red. GUILLIERMOND (Compt. rend., 1929, 188, 813—815).—Concentrated solutions of neutral-red cause a flocculation of the colloids of the vacuoles of yeast cells and coloration of the vacuole without death of the cell. G. A. C. GOUGH.

Fixation of chondriosomes of the vegetable cell. M. MASCRÉ (Compt. rend., 1929, 188, 811—813).—Whilst the chondriosomes of *Elodea canadensis* are dissolved by treatment with acetic acid, a sufficient preliminary treatment with formaldehyde inhibits the destruction. G. A. C. GOUGH.

Fluorescence of vegetable juices in filtered ultra-violet rays. G. T. DRAGONE (Atti R. Accad. Lincei, 1928, [vi], 8, 602—605).—Under the influence of rays of wave-length 3650 Å., the resins of a number of *Coniferae* and the essential oils of the pericarp of various *Citrus* species exhibit fluorescence, which is generally blue but sometimes green or brown. These substances evidently protect the parts of the plants producing them from harmful radiations by converting these into innocuous rays of greater wavelength. T. H. POPE.

Periodic determinations of soil respiration and the bacterial activity of forest soils. D. FEHER (Biochem. Z., 1929, 206, 418—435).—Determinations of the carbon dioxide content of forest air, soil respiration, the numbers of bacteria, protozoa, and fungi, air temperature, ground temperature, humus content, and the intensity of the light in the open and in the wood have been made throughout a year. When the results are presented graphically, a remarkable correlation is observed between the bacterial

content of the ground and the carbon dioxide production, which is evidenced in the parallelism of the number of aerobic bacteria and the soil respiration. Agreement is also shown in the seasonal variation of the carbon dioxide content of the forest air, the soil respiration, and the assimilation of carbon dioxide by the trees. The activities of the various groups of soil bacteria have been examined throughout the year.

C. C. N. VASS.

Kinetics of photosynthesis in plants. Theoretical interpretation of Harder's results on the assimilation of carbon dioxide by *Fontinalis*. J. C. GHOSH (Jahrb. wiss. Bot., 1928, 69, 572—586).—On the basis of the theory of Willstätter and Stoll, the following formula is deduced for the rate of assimilation of carbon dioxide by the plant under the action of light: $1/V = 1/nK_1C + 1/nK_2I + K_2/nK_3K_4IC + 1/nK_4$, where V is the velocity of assimilation, I is the intensity of light, C is concentration of carbon dioxide. K_1 , K_2 , K_3 and K_4 are constants, and n is the original number of chlorophyll molecules per unit chloroplastid surface. The formula fits well the figures obtained by Harder (Jahrb. wiss. Bot., 1921, 60, 568) for the velocity of assimilation under constant light intensity and varying carbon dioxide concentrations and with constant carbon dioxide concentrations with varying light intensity. Figures obtained by Warburg from experiments on *Chlorella* are also in harmony with the theory. W. O. KERMACK.

Photo-synthesis in absence of oxygen. E. N. HARVEY (Plant Physiol., 1928, 3, 85—89).—Certain marine algae can produce oxygen (detected by luminous bacteria) from carbon dioxide when illuminated in absence of oxygen. CHEMICAL ABSTRACTS.

Retardation of the ripening of pears by exclusion of oxygen. F. KIDD and C. WEST (Nature, 1929, 123, 315—316).—When pears are preserved in an atmosphere of nitrogen the macroscopic changes of "ripening" are almost completely inhibited. With shorter time of exposure, however, ripening subsequently takes place in air, the rate of ripening being a function of the concentration of oxygen and of that of carbon dioxide over a considerable range. A. A. ELDRIDGE.

Variation in the composition of the cell-wall in oats during growth. F. ROGOZINSKI and M. STARZEWSKA (Bull. Acad. Polonaise, 1928, B, 127—132).—The ash content of the cell-walls in oats diminishes gradually during the growth of the plant. Cellulose, pentosan, and lignin contents increase rapidly during the development of the plant, reaching maxima 12—14 weeks after germination.

E. A. LUNT.

Influence of hydrogen-ion concentration on the development of *Coffea arabica*. T. DE CAMARGO, R. BOLLIGER, and P. C. DE MELLO (Compt. rend., 1929, 188, 878—880).—Specimens of this plant have been grown in sand moistened with a solution of the requisite salts adjusted to different p_{H} values (4.2—7.2) with sulphuric acid. The ash, the dry weight, and the weight of the roots of the plant increase with decreasing p_{H} , whilst the potassium content and the weight of the stems show an opposite effect. The

nitrogen, magnesium, sodium, and calcium contents remain almost unchanged. G. A. C. GOUGH.

Effect of hydrogen-ion concentration on the growth of *Agaricus campestris*. D. FREAR, J. F. STYER, and D. E. HALEY (Plant Physiol., 1928, 3, 91—94).—The optimal p_H of the synthetic culture media was 6.0; the value decreased by 2.0 during growth. CHEMICAL ABSTRACTS.

Influence of the absolute reaction of the soil on the formation and composition of tarragon essence. H. DEEL and (MME.) H. DEEL (Bull. Soc. chim., 1929, [iv], 45, 175—177).—The effect of five artificial manures on the growth and yield of essence of *Artemisia dracunculus* has been determined. The optimum p_H value of the soil at the time of harvest is about 6.2. With greater p_H values the yield of plant and of essence diminishes, but when the yield of essence is expressed as the percentage weight of the plant the influence of the p_H value of the soil is negligible. Analyses of the essences from various crops shows that the optimum p_H value also corresponds with the maximum (66.28%) phenol content. F. G. TRYHORN.

Relation of nitrogen metabolism to plant succulence. W. H. PEARSALL and J. EWING (Ann. Bot., 1929, 43, 27—34).—In the case of the radish and turnip an abundant supply of nitrates produces amino-acid accumulation with consequent reduction of the p_H of the cell-sap in the plant. It is suggested that these conditions are the cause of the increased water content and reduced transpiration of such plants. E. A. LUNT.

Nitrogen metabolism in the soya bean. J. E. WEBSTER (Plant Physiol., 1928, 3, 31—43).—Analyses of high-nitrogen and low-nitrogen series of soya-bean cultures showed that, in general, the variations of the various types of nitrogen compounds in the roots, leaves, and stems of any particular series are similar. Leaves, stems, or seeds do not appear to draw on the nitrogen reserve of the roots. Amino-acids having amide-groupings are no more important than other amino-acids in protein metabolism, although amide-nitrogen may be one of the most soluble storage forms. Ammonia is the first and last product of plant metabolism. The various forms of nitrogen fluctuate daily. CHEMICAL ABSTRACTS.

Nitrogen metabolism in *Polyanthus narcissus*. G. T. NIGHTINGALE and W. R. ROBBINS (N. J. Agric. Exp. Sta. Bull., 1928, No. 472, 1—32).—Within the roots, nitrates are reduced to nitrites and ammonia, reducing sugars are oxidised, and (also in the storage tissues) the percentage and amount of higher carbohydrates are reduced. In bulbs in darkness, as a result of assimilation of nitrate, the amounts of organic protein, proteose, basic-, amide-, and amino-nitrogen increased. The active centres and tops are relatively high in the simpler carbohydrates and the less complex forms of organic nitrogen, whilst the storage tissue contains a relatively large amount of nitrogen as protein, and carbohydrates as starch and dextrin. CHEMICAL ABSTRACTS.

Loss of nitrogen on drying plants. N. N. IVANOV and M. J. LISCHKEVITSCH (Biochem. Z., 1929, 205, 329—348).—Plant materials dried at 75° to

constant weight show a further loss at 105°. This consists in part of nitrogen which is lost as ammonia. The ammonia varies from almost zero in wheat and lupin flour, where the nitrogen is chiefly in the form of proteins, to nearly 20% in certain fungi, where it is present as carbamide. The ether-soluble material is increased threefold and the nitrogen extracted by alcohol and water diminishes to about half. J. H. BIRKINSHAW.

Root-forming substance. F. W. WENT (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 35—39).—A hormone which is able to promote root formation and is non-specific and resistant to heating at 100° may be extracted from leaves of *Acalypha* and from germinating barley. That the action is non-specific was shown by the fact that the root-forming substance produced from leaves of *Carica papaya* promoted root formation in *Acalypha*. This substance seems to be transported by the phloem and is formed in leaves and sprouting buds and in considerable quantities in the branches. F. G. TRYHORN.

Nectar in relation to honey production. O. W. PARK (J. Econ. Entomol., 1928, 21, 789—790).—Most of the samples of nectar examined contained 40—55% of sugar, the proportion varying considerably for a given source. The sugar concentration was inversely proportional to the relative humidity of the air; light was less important.

Composition of sugar obtained by complete saccharification of pine wood. I. E. HAGG-LUND (Biochem. Z., 1929, 206, 245—247).—Sugar from pine wood contains 0.41% OMe. The methoxyl compound is soluble in water, undergoes fermentation with yeast, and, unlike lignin, is hydrolysed by 4% hydrochloric acid at 120° in 1 hr. or by 42% hydrochloric acid in the cold in 24 hrs. C. C. N. VASS.

Plant colloids. XXII. Potato amylopectin prepared by different methods. M. SAMEC (Biochem. Z., 1929, 205, 104—110).—A variety of methods is shown to yield identical products. P. W. CLUTTERBUCK.

Iodine liberator from *Laminaria*. H. D. KAY (Nature, 1929, 123, 317).—The liberation of iodine from potassium iodide by an acidified extract of *Laminaria* fronds (Dillon, this vol., 360) might be due to the presence of iodate. A. A. ELDRIDGE.

Behaviour of plants after treatment of the seed with mercury. W. HEUBNER (Z. physikal. Chem., 1928, 139, 198—210).—Growth of wheat seeds which have been treated with solutions of various mercury salts has been compared with that from untreated seeds. The number of treated seeds germinating is much the greater, but the total weight of a single shoot is not increased. The length of the stalk appears to be smaller at first but eventually becomes greater than that obtained from the untreated seed. No definite support is obtained for the view that such mercury compounds have a stimulating action on the growth of the plant; the beneficial action is confined to destruction of harmful fungi on the seed.

Samples of wheat grown from treated seed have been examined for mercury and in certain cases

evidence of the presence of small quantities even in the ears has been obtained. R. N. KERR.

Physiological function of magnesium in plants. E. CANALS (Bull. Soc. Chim. biol., 1929, 11, 14—45).—Crude preparations of invertase from brewers' yeast show a rough proportionality between their activity and their magnesium content. Invertase precipitated from aqueous solution with alcohol shows a low activity which is increased to a value below that of the original material by the addition of magnesium sulphate. Activity is lower in the same sample at higher p_H values. Electrolysis of aqueous solutions of invertase, whether containing sucrose or not, results in a partial migration of the magnesium to the cathode; dialysed invertase shows little variation in magnesium content when subjected to electrolysis. From these results it is concluded that the invertase molecule contains magnesium in a non-ionic form.

When pea seeds are allowed to germinate and grow in solutions of appropriate salts, much less growth is observed if magnesium is absent. If calcium ions are absent or if solutions of magnesium sulphate alone are used, magnesium salts exert a toxic action. In these experiments and also in the growth of maize and lupins, magnesium solutions show an appreciable effect at 0.001%, an optimum effect at 0.05%, and a toxic effect at 0.1%. Magnesium salts also possess a marked influence on the growth of *Saccharomyces Kephir* and *Bacillus caucasicus*. G. A. C. GOUGH.

Presence of monotropitin in *Gaultheria procumbens*, L., after drying. M. BRIDEL and (MLLE.) S. GRILLON (J. Pharm. Chim., 1929, [viii], 9, 193—202; cf. A., 1928, 1224).—Monotropitin was determined, with the aid of rhamnodiastase, in various parts of the plant, *G. procumbens*, before and after drying. The dried plant contains the glucoside, but a large proportion is destroyed on drying.

E. H. SHARPLES.

Glucosides of *Digitalis purpurea*. RAYMOND-HAMET (Compt. rend., 1929, 188, 461—463).—Digitatin prepared according to the method of Nativelle possesses the same toxicity for dogs as digitoxin prepared by Cloetta (A., 1921, i, 39).

G. A. C. GOUGH.

Constituents of *Ginkgo biloba* leaves. I. S. FURUKAWA (Bull. Inst. Phys. Chem. Res., Tokyo, 1929, 8, 5—7).—The alcoholic extract from the dried leaves was evaporated and from the resinous residue, by use of various solvents, were separated the following: a substance, $C_{11}H_{12}O_4 \cdot 2H_2O$, m. p. 325°, which contains a lactone ring (diacetyl derivative, m. p. 290—292°); a homologue of flavone (?), $C_{16}H_{12}O_6 \cdot 0.5H_2O$, m. p. 240° (triacetyl derivative, m. p. 170—171°; dimethyl derivative, m. p. 224—226°); a secondary alcohol, $C_{27}H_{56}O$, m. p. 80—80.5°, probably identical with ginnol (Kawamura, A., 1928, 1291); a phytosterol (?), m. p. 240—241°; and a substance, $C_{23}H_{40}O_4$, m. p. 296° (decomp.) (diacetyl derivative, m. p. 169—170°). B. W. ANDERSON.

Constituents of corn-silk. T. NOGUCHI (Bull. Inst. Phys. Chem. Res., Tokyo, 1929, 8, 143—151).—Corn-silk, the style and stigma of the pistil of maize, is used as a diuretic. The ether extract yielded an alcohol, $C_{33}H_{66}O$, m. p. 74—75°, which gave a mono-

acetyl derivative. Phytosterol was separated from the oil after hydrolysis. Colour reactions indicated the presence of flavones, and of ketose, aldose, and pentose sugars. A phenylhydrazone, m. p. 180—181°, was isolated. Vitamins-A, -B, and possibly -E were present. R. K. CALLOW.

Ergosterol isolated from the Japanese edible fungus *Cortinellus Shiitake*. M. SUMI (Biochem. Z., 1929, 204, 397—411).—The ergosterol has physiological properties very similar to those of that derived from other sources. In its absorption spectrum a band at 250 μ has been discovered.

W. MCCARTNEY.

[Determination of] nitrate content of tobacco. T. ANDREADIS (Biochem. Z., 1929, 204, 484—492).—Wagner's modification of Schlosing's method for the determination of the nitrate content of tobacco (cf. Kissling, "Handbuch der Tabakkunde," 1925) gives accurate results only provided the gas to be measured is treated with potassium hydroxide after collection over water; otherwise the presence of carbon dioxide causes error. The modified method may be used for the determination of nitrate in other plants and plant preparations. W. MCCARTNEY.

Isolation of protocatechuic acid from pigmented onion scales; significance in relation to resistance to disease. K. P. LINK, H. R. ANGELL, and J. C. WALKER (J. Biol. Chem., 1929, 81, 369—375).—Onion scales were extracted with water, the extract was treated with basic lead acetate, and the precipitate decomposed with hydrogen sulphide; the lead-free filtrate was evaporated under diminished pressure and the residue extracted with alcohol. The alcoholic solution, after clearing with charcoal, concentrating, and treating with light petroleum, yielded protocatechuic acid in a yield of 0.1% of the starting material. The presence of this compound is responsible, at least in part, for the resistance of onions to fungoid diseases. C. H. HARRINGTON.

Infection of the wheat plant by *Ophiobolus graminis*. H. FELLOWS (J. Agric. Res., 1928, 37, 647—661).—Microchemical analyses made on the roots of wheat plants attacked by *O. graminis* indicate a reduction in the amount of cellulose present and an increase in the amounts of lignin and suberin. Other cell constituents appeared unmodified.

E. A. LUNT.

Hexylresorcinol and phenylethylresorcinol as remedies against pathogenic plant fungi. J. HOUBEN and H. W. WOLLENWEBER (Biochem. Z., 1929, 204, 448—455).—Very small amounts of these substances prevent the growth of organisms, such as *Graphium ulmi*, *Penicillium glaucum*, *Nectria galligena*, *Fusarium*, *Calonectria graminicola*. The quantities required, which differ according to the organism, vary from less than 0.0025 to 0.04% (hexyl derivative) and from 0.0164% to more than 0.0328% (phenylethyl derivative). Cultures on gelatin treated with small amounts of the substances and exposed for months in the open show neither turbidity nor growth of mould. W. MCCARTNEY.

Apparatus for filtration and precipitation with subsequent filtration in an atmosphere of

nitrogen. V. GRABE and K. FREUND (Biochem. Z., 1929, 205, 259—263).—An apparatus used in the preparation of phosphatides is described which enables the filtration, precipitation of dialysate, and filtration of the precipitate to be accomplished in an atmosphere of nitrogen, thus avoiding oxidative changes.

P. W. CLUTTERBUCK.

Micro-determination of carbon dioxide in air. A. KROGH and P. B. REHBERG (Biochem. Z., 1929, 205, 265—272; cf. A., 1925, i, 852).—About 100 c.c. of air are aspirated through standard barium hydroxide solution, which is then titrated with hydrochloric acid from a micro-burette. Lead tubes are to be avoided, since they absorb carbon dioxide.

J. H. BIRKINSHAW.

Determination of the respiration of bacteria, tissue cultures, and surviving cells. F. SILBERSTEIN and F. RAPPAPORT (Biochem. Z., 1929, 204, 439—447).—The respiratory exchanges of these cells can be measured with Van Slyke's apparatus for analysis of blood-gases provided that the materials are brought into a medium consisting of suitably purified hæmoglobin solution. Within certain limits the amounts of oxygen consumed and carbon dioxide produced are independent of the amount of hæmoglobin present, of the number of cells used, and of the duration of the experiment.

W. MCCARTNEY.

Micro-determination of oxalic acid. A. LEULIER, L. VELLUZ, and H. GRIFFON (Bull. Soc. Chim. biol., 1929, 11, 46—57).—Details are given for an approximate micro-determination of oxalic acid in solutions containing simple organic constituents. Lime water is used as a source of calcium; phosphates do not affect the reducing power of the precipitate towards potassium permanganate. It is an advantage to add an excess of potassium permanganate in the oxidation of the calcium oxalate and to determine the excess by iodometry.

G. A. C. GOUGH.

Sources of error in the determination of tyrosine, phenol, and uric acid by phosphotungstic acid. E. SCHEINER (Biochem. Z., 1929, 205, 245—255).—The reagents of Folin and Denis used for the colorimetric determination of uric acid, tyrosine, and phenols consist essentially of a labile complex polyphosphotungstic acid which readily parts with oxygen to reducing substrates with the formation of the blue oxide. This property is unspecific and leads to misleading results. All inorganic reducing agents (except nitrous acid) and hydrogen peroxide give the blue colour. Bivalent iron reduces the reagent in very small concentration (0.01 mg. of iron gives a blue colour). Unsaturated aldehydes, fatty acids, and aromatic amines give the blue colour, the intensity of reduction in the latter case being proportional to the number of amino-groups. The leuco-base of triphenylmethane dyes, hæmoglobin, chlorophyll, and urinary pigments all reduce, giving a blue solution.

P. W. CLUTTERBUCK.

Purine substances and uric acid. L. DAMAS (Bull. Sci. pharmacol., 1928, 35, 111—123; Chem. Zentr., 1928, ii, 1468—1469).—A discussion of analytical methods.

A. A. ELDRIDGE.

Detection of cantharidin [in urine etc.]. R. FISCHER (Arch. Pharm., 1929, 267, 31—35).—The specimen is distilled in steam in presence of phosphoric acid, the distillate extracted with chloroform, and the dried solution evaporated in a current of air. The residue is dissolved in ether and the solution evaporated at 60° in a special micro-sublimation apparatus. The cantharidin is subsequently sublimed at 120—130° on to a cover glass. The latter is washed in light petroleum and viewed under the microscope, when characteristic crystals of cantharidin are observed, which are identified by conversion into barium cantharidate (cf. van Zijp, Pharm. Weekblad, 1917, 54, 295). The reactions described by Klein (B., 1910, 1225) and David (B., 1927, 124) are not characteristic. Better results may be obtained by sublimation in a vacuum. The cantharidin in 20—30 c.c. of urine at a dilution of 1 : 150,000 can be detected and with larger volumes the dilution may be as high as 1 : 500,000. The cantharidin may be dissolved in lanolin and tested for vesicant action, the minimum dose being 0.02—0.015 mg.

S. COFFEY.

Determination of copper in biological material. C. A. ELVEHJEM and C. W. LINDOW (J. Biol. Chem., 1929, 81, 435—443).—The material is incinerated and the ash dissolved in dilute hydrochloric acid; the solution is made alkaline with sodium hydroxide, re-acidified with acetic acid, and treated with potassium thiocyanate and pyridine; it is then shaken with chloroform, which extracts the green colour (cf. Biazzo, B., 1926, 382), and the latter is compared with that given by a known amount of copper. In presence of large amounts of iron or of calcium phosphate the copper must be precipitated as the sulphide (in the former case after preliminary reduction of the iron to the ferrous condition); 0.02 mg. of copper can be determined.

C. R. HARRINGTON.

Determination of small amounts of iodine by the Dupre-Winkler method. J. A. HOJER (Biochem. Z., 1929, 205, 273—296).—The sources of error in the Fellenberg method (*ibid.*, 1923, 139, 391; A., 1925, i, 329) for the volumetric determination of iodine are critically examined. It is proposed to replace the chlorine water used for oxidising the iodide by bromine water when bromine is not determined.

J. H. BIRKINSHAW.

Micro-determination of mercury. J. BODNAR and E. SZEP (Biochem. Z., 1929, 205, 219—229).—A method is described for the determination of very small amounts of mercury (0.04—10 γ). The mercury in presence of a trace of copper is separated on a pure iron wire, distilled off, and collected as a droplet, the diameter of which is measured, and the weight is thus calculable.

P. W. CLUTTERBUCK.

Micro-determination of sodium in biological liquids and tissues. P. GRABAR (Bull. Soc. Chim. biol., 1929, 11, 58—64).—After oxidation of the organic matter by treatment with hot nitric acid in a silica flask, phosphates are removed from the residue as ferric phosphate and the sodium is determined by a modification of the uranium method of Blanchetiere (A., 1923, ii, 579). The average error is within 1%.

G. A. C. GOUGH.

BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

JUNE, 1929.

General, Physical, and Inorganic Chemistry.

Hartmann formula for calibration of spectral apparatus. F. HOFFMANN (Physikal. Z., 1929, 30, 238—239).—The Hartmann formula, $p = p_0 + C/(\lambda - \lambda_0)^a$ ($\lambda_0 = 0.2$, $a = 1$, roughly), can be expressed differently with advantage, e.g., $p\lambda = a + b\lambda + cp$; $p(\lambda - c) = a + b\lambda$ and $\lambda(p - b) = a + cp$ ($a = C - p_0\lambda$, $b = p_0$, $c = \lambda_0$). Similar equations can be obtained using ν instead of λ . The use of linear expressions as above is preferable for convenience and accuracy to the expression $\nu = \nu_0 + ap + bp^2$ used by Russell and Shenstone (J. Opt. Soc. Amer., 1928, 16, 298).

R. A. MORTON.

Electrified spherical films and the Stark effect. L. DÉCOMBE (Compt. rend., 1929, 188, 1094—1096).

Intensity and polarisation of forbidden lines. A. RUBINOWICZ (Z. Physik, 1929, 53, 267—273).—Expressions are deduced for determining the intensity and polarisation of radiation due to forbidden transitions in a one-electron system with central symmetry.

E. B. ROBERTSON.

Breadth of resonance lines and possibility of their displacement towards the red by repeated scattering. W. ORTHMANN and P. FRINGSHEIM (Z. Physik, 1929, 53, 367—379).—A theoretical discussion of the effect of absorption and multiple scattering in vapours on the form of resonance lines.

E. B. ROBERTSON.

Spectrum emitted by a carbon plate under bombardment. A. A. NEWBOLD (Phil. Mag., 1929, [vii], 7, 706—719).—The electrostatic method developed by Richardson and Bazzoni (A., 1917, ii, 521) for the examination of radiations from gases and vapours and adopted by Lukirsky (A., 1924, ii, 215, 368) for the detection of soft X-rays is shown to be capable of use in precision measurements of the latter. It has been employed for the examination of the spectrum emitted by a carbon plate by electrons with energy up to 600 volts. Over the frequency range 5700—26,000 the spectrum obtained resembled closely that determined by Millikan and Bowen for gaseous carbon.

A. E. MITCHELL.

Spectra of alkali metals excited by active nitrogen. J. OKUBO and H. HAMADA (Phil. Mag., 1929, [vii], 7, 729—736).—Previous work (A., 1928, 10) has been extended to a study of the effects of the density of the vapours of sodium, potassium, and caesium on their spectra excited by active nitrogen. With sodium it is found that as the temperature of the metal is raised the initial yellow glow becomes

filled with a greenish-yellow core which with further rise in temperature becomes definitely green. In this core the first subordinate series is more enhanced than the principal series, whilst in the yellow glow this effect is reversed; also the intensities of the lines in the former series are greater than those of corresponding energy in the latter series. In the core the intensity maximum is displaced towards the higher member, whilst in the yellow glow the reverse is the case. The core exhibits the green band spectrum, due to sodium molecules, in the position between the $2p-4d$ and $2p-6d$ lines. Analogous effects were obtained with the other metals.

A. E. MITCHELL.

Selective absorption by excited mercury vapour. E. P. METCALFE and B. VENKATESACHAR (Nature, 1929, 123, 761).—A statement of priority (cf. Ponte, A., 1928, 808).

A. A. ELDRIDGE.

Broadening of spectral lines. B. TRUMPY (Z. Physik, 53, 57—60).—Anomalies discovered in earlier work (A., 1927, 179, 997) on the broadening of the mercury line 2537 Å. at high partial pressures of foreign gases are discussed, and a theory of the interaction of impact and radiation as a cause of broadening is put forward as an explanation.

E. B. ROBERTSON.

Patterns and Paschen-Back analogue in the Stark effect for neon. J. S. FOSTER and W. ROWLES (Proc. Roy. Soc., 1929, A, 123, 80—103).—An extension of Nyquist's work on neon (Physical Rev., 1917, 10, 226). Using the modified Lo Surdo discharge tube and high-potential apparatus previously described (Foster, A., 1927, 179), an examination has been made of the Stark effect for 150 lines in the neon spectrum in high fields. The observed patterns for the individual arc lines are in no case more complex than, and in the majority of cases appear to be identical with, those reported in parhelium for lines associated with the same n , l values for the outer electron in initial and final states. A considerable number of diffuse and combination lines exhibit a simpler pattern, consisting apparently of but one parallel and one perpendicular component, and the displacement may be as great as that of the standard (0,1) component. In low fields, especially, the displacements are relatively large. The intensities, however, are somewhat different in that the perpendicular component is much the stronger. The displacements in fields above 100,000 volts/cm. are in fairly good agreement with the results of quantum mechanics. The displacements for the different members of a complex line are

such that the structure tends to fuse and form the normal Stark effect characteristic of the corresponding singlet line, in a manner analogous to the appearance of the Paschen-Back effect in high magnetic fields. This effect is not symmetrical with respect to the normal line group, and is partial in the sense that only the initial terms are appreciably affected. The interpretations of the Stark effect in neon recently given by Stark ("Handbuch der Physik," 1926, 23, 146) and by Ishida (A., 1928, 1066) are discussed.

L. L. BIRCUMSHAW.

Helium band spectrum. S. IMANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 193—209).—Continuing with improved methods the work of Dicke, Takamine, and Suga (A., 1928, 1295), the region 3000—7000 Å. was investigated and the results were tabulated. Two new parhelium bands $2S_0-7P_0$ and $2S_0-8P_0$ at 3366 and 3307 Å., and a new orthohelium band $2s_0-5p_1$ at 3181 Å. were found. Bands $2s_1-5p_1$ and $2s_1-5p_0$ of orthohelium (cf. Weizel and Fuchtbauer, A., 1927, 909) are completed up to the first line in every branch. Extended observations on Curtis' band (cf. A., 1923, ii, 351) $2s_0-5p_0$ are made.

N. M. BLIGH.

Excitation of helium lines. R. VON HIRSCH and R. DOPEL (Ann. Physik, 1929, [v], 1, 963—976).—The fading constant ("Abklingkonstante") of the stronger, photographically active helium lines has been obtained. The apparatus and method of calculation are described. There is considerable difference in the constant for the different lines examined. The experiments were carried out with four cathodes of different forms in order to make allowances for distortion due to pressure. The constants for both the strongest lines (λ 4472 and λ 3889 Å.) are independent of the method of excitation.

A. J. MEE.

Energy of the helium atom in the ground state. E. A. HYLLERAAS (Physikal. Z., 1929, 30, 249—250).—The older quantum theory failed to account for the ionisation potential of helium, Bohr's first model leading to 28.15 volts, a second model studied by Bohr and Kramers leading to 20.63 volts, whilst Lyman's spectroscopic data required 24.46 volts. The new quantum theory yields the value 24.35 volts (A., 1927, 808; 1928, 698) and the reality of the remaining small discrepancy has now been studied. Lyman's ground term can be expressed as $\lambda = -1.45175$, the author's earlier work led to $\lambda = -1.4496$, whereas considerations now shown in outline lead only to $\lambda = -1.45162$.

R. A. MORTON.

Calculation of the energy of helium in the fundamental state and the lowest terms of orthohelium. E. A. HYLLERAAS (Z. Physik, 1929, 54, 347—366).—Mathematical.

J. W. SMITH.

Properties of the terms of the helium molecule. G. H. DIEKE (Nature, 1929, 113, 716—717).

Spectrum of H_2 . Bands analogous to the parhelium line spectrum. I. O. W. RICHARDSON and P. M. DAVIDSON (Proc. Roy. Soc., 1929, A, 123, 54—80; cf. A., 1928, 345, 812).—A re-examination of the series of band systems previously described (*loc. cit.*) with the help of Gale, Monk, and Lee's tables has shown that the bands already published are only

a small fragment of a much larger number of related bands. Instead of 6 progressions with a maximum of 4 members each there are now more than 50 progressions, several of them extending to 9 members, including most of the strength of the secondary spectrum from 3394 to 8902 Å. The irregular doublets previously described have now disappeared, the lines of all the bands being single. The final states of all these progressions belong to the electronic state 2^1S . There are no combinations between any of the lines of these bands and those of the α , β , γ , etc. bands, but, on the other hand, they seem to have the same final states as the B states of Dicke and Hopfield, and so will presumably combine with the lines of the Lyman bands. A detailed account is given of the properties of the system $3^1B \rightarrow 2^1S$ (the strong Q band system, in which each band consists solely of one single Q form branch); and of the system $3^1C \rightarrow 2^1S$ (the system with R very strong, P weak). The two systems are similar in that they have upper states with practically the same moment of inertia for large m , and the intensity distribution in corresponding bands of the system is very similar. Whilst no lines of the Q system show the Zeeman effect, every strong line of the system with R strong, P weak shows it.

L. L. BIRCUMSHAW.

Stark effect in a violet region of the secondary spectrum of hydrogen. J. K. L. MACDONALD (Proc. Roy. Soc., 1929, A, 123, 103—107).—Observations have been made on the Stark effect for 20 lines in the violet region 3980—4080 Å. The lines on the violet side of the region investigated are displaced towards the violet, and those on the red side towards the red; there is a slight overlapping of the two groups. No close agreement is observed with previous investigations. Five of the normal lines examined have a very close structure which has not been reported before.

L. L. BIRCUMSHAW.

Relative intensities of Stark components in hydrogen. J. S. FOSTER and L. CHALK (Proc. Roy. Soc., 1929, A, 123, 108—118; cf. A., 1926, i, 1070; 1927, 179).—Three modifications of the Lo Surdo discharge tube are described, suitable for measuring the relative intensities of Stark components and their relative advantages are discussed. Using a neutral glass wedge, direct and indirect determinations have been made of the intensities of the stronger components of H_α , H_β , H_γ , and H_δ . The results for H_α , H_β , and H_γ are found to agree, within the limits of experimental error, with Schrödinger's calculations. The measurements on H_δ are uncertain and the results for the p components of H_γ are not satisfactory. It is considered probable that the variation from Schrödinger is principally due to experimental difficulties.

L. L. BIRCUMSHAW.

Continuous spectrum of the hydrogen tube. D. CHALONGE and M. LAMBREY (Compt. rend., 1929, 188, 1104—1106).—The intensity of the continuous spectrum obtained from the authors' hydrogen discharge tube (A., 1927, 489) increases very slowly with pressure (1.5—4 mm.) and passes through a maximum at 2—3 mm. It also increases slowly with decrease of wave-length (from 4400 Å.) and attains a maximum at 2200 Å. Since the distribution of energy in the

spectrum undergoes no appreciable modification with changing conditions of discharge and with different tubes it is suggested that such tubes might be useful as standards of intensity in the ultra-violet region.

J. GRANT.

Fulcher bands of hydrogen. I. SANDEMAN (Proc. Roy. Soc. Edin., 1929, 49, [i], 48—64).—A co-ordination and extension of Richardson's arrangement (cf. A., 1926, 873; 1927, 1) and the measurements of Gale, Monk, and Lee (A., 1928, 1166). A number of combination relations are given for the lines of the Fulcher bands. These indicate three main branches in each band, R' , Q , and P' branches, the Q branch being identical with that of Richardson. The R' and P' branches have a common initial level differing from that of the Q branch, whilst all three have a common final level. The arrangement yields term differences consistent throughout the bands, and in agreement with the new quantum mechanics.

N. M. BLIGH.

Photometry of hydrogen and calcium lines in stellar spectra. (Miss) C. H. PAYNE and (Miss) E. T. R. WILLIAMS (Month. Not. Roy. Astron. Soc., 1929, 89, 526—538).

Hydrogen chromosphere. W. H. MCCREA (Month. Not. Roy. Astron. Soc., 1929, 89, 483—497).—The pressure, density law, and means of support of hydrogen in the chromosphere are of a nature quite different from those of calcium. From the absolute measurement of H_γ the normal atoms are estimated to be present at the base of the chromosphere to the extent of 10^{12} atoms per c.c.; from observations on the continuous spectrum at the head of the Balmer series the ionised atoms in the same region are thought to be present at the rate of 2×10^{10} atoms per c.c. Ionisation in the chromosphere is discussed. It is shown that Ca^+ under the conditions usually assumed would probably be ionised to Ca^{++} , but that the excess of ionised hydrogen prevents this. The usual factors supposed to be effective in chromospheric equilibrium are not so in the case of hydrogen, and the possibility that they are effective in other stars is discussed (cf. this vol., 117).

R. A. MORTON.

$3d$ trajectory in the ionised atoms P II, S II, S III, and Cl III. Cl III quadruplets. J. GILLES (Compt. rend., 1929, 188, 1158—1160).—The $3d$ trajectory falls between the $4s$ and $4p$ trajectories for the elements in the order phosphorus, sulphur, and chlorine. For Cl III the quadruplets ($a3d^4P - a4p^4S$), ($a3d^4P - a4p^4P$), and ($a3d^4P - a4p^4D$) were established (cf. Bloch, A., 1927, 396), the term $3d^4P$ being inverted as in the cases of O II and S II. The term $3dD$ has a value of approximately 144,300.

J. GRANT.

Separation of the various spark spectra of antimony. R. SOULILLOU (Compt. rend., 1929, 188, 1103—1104).—The spark spectrum of pure antimony, comprising 300 lines between 3800 and 1900 Å., may be grouped into three classes due to Sb II, Sb III, and Sb IV corresponding with increasing intensities of excitation. The first group is made up of two sub-groups, but the two last are perfectly homogeneous (cf. Kimura and Nakamura, A., 1924, ii, 799). The spectra are accompanied by an independent, feeble continuous emission localised in the

annular region near the bend of the tube. A number of lines, including some not previously observed, are tabulated with their intensities.

J. GRANT.

Arc spectrum of samarium. Measurements made at normal pressure between λ 2750 and 2200 Å. S. PINA DE RUBIES (Compt. rend., 1929, 188, 1101—1102).—An extension of earlier work (this vol., 479).

J. GRANT.

Spectral relations between certain iso-electronic systems and sequences. I. Ca I, Sc II, Ti III, V IV, and Cr V. H. E. WHITE (Physical Rev., 1929, [ii], 33, 538—546).—The spectra of V IV and Cr V should resemble closely the spectra of Ca I, Sc II, and Ti III, and extrapolations from known data for these have led to the identification of about 30 energy levels in both triply-ionised vanadium and quadruply-ionised chromium. The strongest lines in these spectra arise from combinations between 3P , 3D , 3F , 1P , $^1D'$, $^1F(3d4p)$ and 3D , $^1D(3d4s)$ and 1S , $^3P'$, 1D , $^3F'$, $^1G(3d^2)$. The Moseley diagram and the irregular doublet law are used to determine the approximate positions of the various singlet and triplet levels and the location of the radiated frequencies. Lande's interval rule and, with one exception, Hund's rule are obeyed. The ionisation potentials of the $3d$ electrons of V IV and Cr V are determined, respectively, as 48.3 and 72.8 volts.

N. M. BLIGH.

Spark spectrum of nickel (Ni II). R. J. LANG (Physical Rev., 1929, [ii], 33, 547—548; cf. A., 1928, 679).—Twenty-six lines resulting from intercombinations between the lowest terms $d^9 2D_{3,3}$ and eleven more terms of the d^8p configuration b^4S' , b^4P , b^4D' ; c^2S' , c^2P , c^2D' ; b^2P , b^2D' , b^2F ; c^2F ; b^2G' are tabulated and classified. These lines lie between 1537 and 1250 Å. (cf. Menzies, this vol., 226).

N. M. BLIGH.

Variation in the intensities of mercury spectrum lines with pressure of the vapour. J. G. FRAYNE and C. G. MONTGOMERY (Physical Rev., 1929, [ii], 33, 549—552).—The relative intensities of lines in the mercury spectrum in the direct-current arc and in the high-frequency discharge at low pressure were measured and tabulated for the wave-length range 7000—3000 Å. In the low-pressure discharge, there is an increase in intensity, relative to the triplet line 5460, of the singlet members, the sharp series showing the greatest increases; the relative intensity increases rapidly with ascending members of the series; combination singlets appear strong in the red. Five new lines in the sharp singlet series were observed.

N. M. BLIGH.

Spark spectra of iodine. L. BLOCH and E. BLOCH (Ann. Physique, 1929, [x], 11, 141—166).—The iodine spectrum produced in the electrodeless oscillatory discharge has been studied from 7350 to 2220 Å. A large number of new lines, especially in the extreme red, have been measured for the first time. Four successive degrees of excitation are apparent, as compared with three for chlorine and bromine. The oscillatory discharge through iodine at low pressures is accompanied by a violet fluorescence resembling that exhibited by chlorine and bromine.

H. F. GILLBE.

Arc spectrum of phosphorus. D. G. DHAVALÉ (Nature, 1929, 123, 799).—The presence of phosphorus in the sun is held to be established.

A. A. ELDRIDGE.

Transition probabilities in the lithium atom. III. B. TRUMPY (Z. Physik, 1929, 54, 372—384; cf. A., 1927, 998; 1928, 1067).—Mathematical.

J. W. SMITH.

Duplicity of the *D*-terms of sodium and potassium. A. FERCHMIN and S. FRISCH (Z. Physik, 1929, 53, 326—330).—The potassium lines $2^2P_{3/2}$ — 5^2D , 5832 Å., and $2^2P_{3/2}$ — 6^2D , 5360 Å., have been examined with a Michelson echelon grating, and each has been found to possess a weaker satellite. The arrangement of the 2D -terms is "inverted" (i.e., the larger term has the smaller *j*-value); $\Delta 5^2D_{3/2,5/2} = 0.52$ cm.⁻¹; $\Delta 6^2D_{3/2,5/2} = 0.24$ cm.⁻¹. The sodium line $2^2P_{3/2}$ — 4^2D , 5688 Å., has been examined with the echelon grating and a large Lummer plate and found to be single; $\Delta 4^2D_{3/2,5/2} = 0.1 > 0$ cm.⁻¹. E. B. ROBERTSON.

Electrons that are "pulled out" from metals. E. H. HALL (Proc. Nat. Acad. Sci., 1929, 15, 241—251).—Theoretical. In connexion with his theory of two classes of conduction electrons, the author investigates the minimum number of thermions, compared with the valency electrons or with the atoms, necessary to accord with his energy data and with the results of Millikan and Eyring (A., 1926, 219). The data of these and other authors are used, with the help of Oppenheimer's applications of wave mechanics to the phenomena. The values obtained for the number of thermions per c.c. range from 1.8×10^{15} to 8×10^{17} .

N. M. BLIGH.

Mechanism of spark discharge. L. J. NEUMAN (Proc. Nat. Acad. Sci., 1929, 15, 259—265).—The methods of distinguishing the possible mechanisms of a source of electrons at or near a cathode surface in a gas were made the basis of a critical experiment to decide which mechanism was the essential one in the spark discharge. A tube containing nickel electrodes and a sodium cathode in argon at various pressures was used, and voltage-pressure curves are given. The main conclusions reached are: in argon at low pressures the cathode material plays an important part, and the principal mechanism by which positive ions liberate electrons from the cathode depends on the velocity or impact energy of the positive ions with the cathode; as the pressure increases the predominating mechanisms of electron production change from those in which electrons are liberated from the cathode by the bombardment of swiftly-moving positive ions to those in which electrons are generated in the gas by collisions between swiftly-moving positive ions and neutral molecules.

N. M. BLIGH.

Experiments with the electrolytic generator. V. M. SCHULGIN (Physikal. Z., 1929, 30, 235—237).—Improvements in the electrolytic generator (*ibid.*, 1928, 29, 724—726) are described. The high-frequency oscillations (of the Tesla type) which are generated arise apparently from hydrogen liberated at the platinum electrode.

R. A. MORTON.

Thermionic emission through double layers. W. GEORGESON (Proc. Camb. Phil. Soc., 1929, 25, 175—185).—Theoretical.

Measurement of excitation and ionisation potentials by the diffusion method. W. GLIWITZKY (Ann. Physik, 1929, [v], 1, 701—720; cf. Bartels and Gliwitzky, A., 1928, 452).—The measurements on argon have been confirmed and extended and a helium-neon mixture has been studied. Full details of the new technique are given.

R. A. MORTON.

Regularity of the total photo-electric emission. R. SUHRMANN (Z. Physik, 1929, 54, 99—107).—The total photo-electric emission observed when platinum foil is irradiated with black-body radiation from a source at different temperatures has been found to be in good agreement with theoretically deduced values.

J. W. SMITH.

High values of *e/m* obtained with a Thomson vacuum tube. S. RAY (Z. Elektrochem., 1929, 35, 209—210).—A discussion of variable values of the charge on an electron obtained from measurements with the Thomson tube.

H. T. S. BRITTON.

Exponential yield of positive ions in argon. (Miss) K. B. BLODGETT (Proc. Nat. Acad. Sci., 1929, 15, 230—234).—An electric discharge was passed through an argon-filled tube and the current carried by electrons and by positive ions was measured. Graphs are given of the current-voltage for various temperatures, the arc current, electron current against voltage for three pressures, and for three temperatures. A mechanism to account for the observed relationships is suggested.

N. M. BLIGH.

Mobility distribution and rate of formation of negative ions in air. J. L. HAMSHERE (Proc. Camb. Phil. Soc., 1929, 25, 205—218).—A modification of the alternating-field method of measuring ionic mobility in a gas gives an experimental curve showing upper and lower limits for the mobility. From this a distribution curve is derived which has a calculable resolving power. The mobility of negative ions in dry air shows a continuous distribution between the limits 2.15 and 1.45, with a peak value about 1.8. At low pressures the current is resolved into ions and free electrons. From the relative numbers reaching the electrometer it is found that the electron makes an average of 9.4×10^4 collisions before capture, independent of field strength and pressure, and therefore independent of the electron speed over a velocity range 2×10^5 to 7×10^5 cm./sec.

N. M. BLIGH.

Secondary electron emission from solid metal surfaces. C. F. SHARMAN (Proc. Camb. Phil. Soc., 1929, 25, 237—254; cf. A., 1927, 287).—The mechanism of electron reflexion and the calculation of the total secondary effect are considered theoretically, and secondary emission is shown to be a complicated phenomenon involving many monatomic layers. The experimental study of slow δ -ray or true secondary emission from copper is described, and energy-distribution curves are given. An inverse square distribution law is applied, and tested experimentally by a retarding-potential method. The energy distribution of the total electronic emission can be represented by two curves, one for the electrons originally in the metal, and falling considerably below the inverse square distribution at high energies,

and the other for the primary electrons reflected from the surface. N. M. BLIGH.

Motion of ions in constant fields. L. PAGE (Physical Rev., 1929, [ii], 33, 553—558).—Theoretical. It is shown that the effect of a constant electrical or gravitational force on ions passing through a constant magnetic field is to cause the circular or helical ion paths to advance in a direction at right angles to both the force and the field with a constant velocity. Ion paths relative to a rotating earth are discussed on the assumption that the earth's field is purely magnetic relative to the inertial system of the centre of the earth. N. M. BLIGH.

Angular scattering of electrons in helium, neon, hydrogen, and nitrogen. G. P. HARNWELL (Physical Rev., 1929, [ii], 33, 559—571; cf. A., 1928, 1169).—The angular distribution of electrons of various energies scattered by the gases was investigated qualitatively. It was found that those electrons which were scattered elastically were in general deflected through only a few degrees. Those which had sustained an exciting collision were scattered through slightly larger angles. Evidence of electrons which had undergone two inelastic collisions was obtained, and these were distributed through still larger angles. A general tendency for slower electrons to be scattered through larger angles was observed. N. M. BLIGH.

Dependence of electron emission from metals on field strengths and temperatures. R. A. MILLIKAN and C. C. LAURITSEN (Physical Rev., 1929, [ii], 33, 598—604).—A combined field-current and thermionic equation has been deduced, and field currents have been shown to be independent of temperature up to about 1100° Abs., when the energy of thermal agitation begins to assist the fields appreciably in causing the escape of electrons from metals. These results have been questioned by de Bruyne (cf. this vol., 3; also Fowler and Nordheim, A., 1928, 681). Further support for the original views is given. N. M. BLIGH.

Rate of formation of negative ions by electron attachment. A. M. CRAVATH (Physical Rev., 1929, [ii], 33, 605—613).—A new method is described by which the fraction of the collisions between electrons and molecules which result in the attachment of the electron to form a negative ion has been measured in air and oxygen as a function of the average electron energy, the gas pressure, and the moisture content. In oxygen this fraction increased with either increase or decrease of average electron energy about a minimum of 0.9 volt, and in air increased for energies below this value. It increased rapidly with pressure at low constant energy, and was of the same order of magnitude in moisture as in oxygen, but in mixtures of these two was much larger than in either alone. Evidence of the detachment of electrons from negative ions in oxygen at very high fields was found. N. M. BLIGH.

Test of the theoretical explanation of secondary electron emissions. H. DAENE and G. SCHNEBERWITZ (Z. Physik, 1929, 53, 404—421).—Klemperer and Joffé have given an explanation of the Wehnelt phenomenon of secondary electron emission which

cannot be confirmed by the authors. A new one, based on the assumption of a potential layer arising from the striking of primary electrons, is deduced. Distribution curves for secondary electrons emitted from glass and platinum are given.

G. E. WENTWORTH.

Reactions in ionised gases from the point of view of Faraday's law. S. S. JOSHI (Trans. Faraday Soc., 1929, 25, 143—147).—If univalent electrolytes are considered to be electrochemical analogues of ionised gases, then Faraday's ratio M/F may be obtained from the data for the decomposition of nitrous oxide by a silent electric discharge (cf. this vol., 521). The large values of M/F are explained in terms of the theory of the kinetics of a chemical change in the silent discharge previously advanced (Elliott, Joshi, and Lunt, A., 1927, 630). Assuming collisions between nitrous oxide molecules and electrons only (i.e., in the initial stages of the decomposition), it is calculated that 1.9×10^3 mols. are decomposed per electron. J. GRANT.

Refraction of light waves by electrons. S. K. MITRA and H. RAKSHIT (Nature, 1929, 123, 796—797).

Electron deflexion by metallic films. E. RUPF (Ann. Physik, 1929, [v], 1, 773—800).—Electrical measuring arrangements have been devised for studying the deflexion phenomena which occur when electrons pass through thin sheets of foil, in this case of metals possessing cubic lattices. From the refractive indices for electron waves the inner lattice potentials of silver and nickel are found to be near 12 and 17 volts, respectively. The spatial and localised velocity distribution of the deflected electrons reveals a selective effect in certain directions, which leads to a definition of deflected electrons as those electrons which, after traversing the metallic foil, undergo deflexion in a selective angular range without suffering appreciable loss in velocity. All other electrons are regarded as scattered. The application of the refractive index for electron waves to the problem is discussed and it is pointed out that the foil is a conglomerate of small crystals and not a strictly plane parallel plate. Data are recorded for nickel, aluminium, silver, and chromium. R. A. MORTON.

Electron reflexion and deflexion at uniaxial crystalline surfaces. E. RUPF (Ann. Physik, 1929, [v], 1, 801—814).—When fairly slow electrons pass through metal foil deviations occur from the de Broglie relation $\lambda = h/mv$ which are accounted for by the introduction of a refractive index $\mu > 1$. The physical basis for this term is the existence of a positive inner lattice potential E_0 corresponding with the relation $\mu = (V + E_0/V)^{1/2}$, V being the electron velocity in volts. The reflexion of electrons from uniaxial crystalline nickel, copper, silver, gold, aluminium, and lead (metals with cubic face-centred lattices) has been studied. Volatilisation from tungsten enabled most of the crystals to be oriented with the 111 plane parallel to the surface under investigation. It is found that the refractive index for electron waves is greater than 1 for all metals, that it decreases towards unity with increasing velocity, and that for a given velocity it is constant for a given metallic lattice.

E_0 varies between 11 and 17 volts. The values obtained by this and other methods are compared, and correlated with Sommerfeld's theory of metallic conduction.
R. A. MORTON.

Application of electron diffraction to the investigation of gas adsorption. L. H. GERMER (*Z. Physik*, 1929, **54**, 408—421).—Under suitable experimental conditions diffraction diagrams of four very different types can be obtained from the electron diffraction from a single crystal of nickel. Of these, one records the space lattice of the metal, the second the structure of the surface layer of the metal, a third that of a monatomic adsorbed gas film, and the fourth that of a thicker gas film. Hence it is claimed that this method affords a rapid new method of studying gas adsorption and crystal structure.

J. W. SMITH.

Electron reflexion from cobalt, and electron waves. M. N. DAVIS (*Nature*, 1929, **123**, 680—681).—The secondary emission on bombardment of the metal by electrons of known velocity has been resolved into its velocity components.

A. A. ELDRIDGE.

Temperatures of positive ions in a uniformly ionised gas. J. M. DEWEY (*Nature*, 1929, **123**, 681).—By the use of data on the width of lines emitted from the negative glow of the helium arc, and assuming that the positive ions acquire energy solely from the energy of random motion of the electrons whilst they lose energy by collision with the molecules of neutral helium at a rate which may be calculated from kinetic theory, the temperature of positive helium ions is calculated from the electron temperature and the pressure of the gas in a field-free space.

A. A. ELDRIDGE.

Selenium and cathode rays. C. E. S. PHILLIPS (*Nature*, 1929, **123**, 681—682).—When a cell, prepared by condensing the vapour of heated selenium on a gold grid, was exposed to cathode rays, a rapid diminution of resistance, which could be widely varied by deviating the rays with a magnet, occurred. The effect is not attributed to the production of X-rays in the selenium.

A. A. ELDRIDGE.

Elastic collisions of electrons with helium. N. F. MOTT (*Nature*, 1929, **113**, 717).—The scattering predicted by the wave mechanics has been worked out by a method involving two separate approximations.

A. A. ELDRIDGE.

Mass-spectrum of lead from broggerite. C. N. FENNER and C. S. PIGGOT (*Nature*, 1929, **123**, 793).—The composition and age of the broggerite from which Aston's sample of lead tetramethyl (this vol., 370) was prepared are discussed. The proportion of Pb^{208} is computed to be 2.64%. The uranium-thorium equivalence factor (0.38) may require correction.

A. A. ELDRIDGE.

Groupings of radioactive atoms. H. JEDRZEJOVSKI (*Compt. rend.*, 1929, **188**, 1043—1045).—Chamié's method (*A.*, 1928, 810) has been used for the study of the distribution of radioactive matter in activated sources. Direct activation in radon and activation in a vacuum by the α -recoil of radium-*B* (from radium-*A*) or by the β -recoil of radium-*C* (from radium-*B*) gave characteristic groupings analogous to

those obtained by Chamié. Images from sources prepared by distillation of radium-*B*+*C* in a vacuum or at atmospheric pressure, however, were quite different, and indicate that the destruction of the groupings by distillation is due to the removal in succession of the outer atoms. These groupings are unchanged after 15 min. at 350°, but once they are destroyed they do not tend to form again rapidly.

J. GRANT.

Grouping of the atoms of radioactive elements. (Mlle.) C. CHAMIÉ (*J. Phys. Radium*, 1929, [vi], **10**, 44—48; cf. *A.*, 1928, 810).—The radioactive mixture is put into close contact with a photographic plate, so that the α -particles have their whole path in the gelatin. A number of "star" effects is then obtained, each of which indicates the position of a radioactive group. If the plate is covered with mercury which has absorbed a little radioactive material, the same grouping effect is always found on development, no matter what method has been employed to activate the mercury. From this it is concluded that these radioactive groups existed in the original mixture and had been absorbed unchanged by the mercury. The groups will remain unchanged for weeks in mercury. To investigate the presence of these groups in radioactive gas mixtures, the gas was streamed against a photographic plate and the same effect was obtained, showing the presence of complexes. In a similar way the presence of groups in liquids has been demonstrated. It is concluded that these groups contain many atoms, and their origin and properties are discussed.

J. L. BUCHAN.

Conditions of formation of groups of radioactive atoms. H. HERSZFINKIEL and H. JEDRZEJOVSKI (*Compt. rend.*, 1929, **188**, 1167—1169; cf. *A.*, 1928, 215).—Radioactive deposits produced by distillation on to a thin mica surface show groupings only in the presence of impurities, the smallest trace of which suffices to act as a nucleus for their formation. Thus, the groupings were more sharply defined when a drop of hydrochloric acid was placed on the mica before distillation, or was used to wash it after distillation, than when distilled water was used. It was shown that solutions free from groupings will activate filter-paper by direct adsorption and that groups present on a mica surface do not penetrate it under the influence of radioactive recoil.

J. GRANT.

[β -Particle] recoil. L. WERTENSTEIN (*Compt. rend.*, 1929, **188**, 1045—1047).—Radioactive sources prepared by direct activation in radon or by means of the α -recoil of radium-*B* (from radium-*A*) give recoil products containing radium-*B* and -*C*, whilst a source prepared by distillation in a vacuum from a platinum surface of the collected deposit gives pure radium-*C* (cf. preceding abstract). The yield of recoil product is not influenced by the method of preparation, but decreases rapidly with time and as a result of pre-heating the source at 250°. It is dependent on the emitting and receiving surfaces, a maximum yield of 20% being obtained with a clean aluminium source and bismuth receiver after a few minutes' exposure; it is unchanged if the receiver is cooled in liquid air.

J. GRANT.

Mode of action of the electron counter of Geiger and Müller. H. KNIPEKAMP (Physikal. Z., 1929, 30, 237—238).—Experiments with treated and untreated wire (cf. Geiger and Müller, this vol., 114) show that under the correct electrical conditions plain wire is effective. The condition of the surface of the anode wire cannot be more than a secondary factor in the operation of the counter. R. A. MORTON.

Energy relations in artificial disintegration. (SIR) E. RUTHERFORD and J. CHADWICK (Proc. Camb. Phil. Soc., 1929, 25, 186—192).—When certain elements are disintegrated by α -particle bombardment rotons are liberated and the α -particle is assumed to be captured by the nucleus. The energy changes of this type of reaction are investigated theoretically with the help of data for the maximum ranges of the protons obtained by experiments on aluminium. Support is obtained for the view that nuclei of the same element do not have identical masses.

N. M. BLIGH.

Distribution of range of the α -particles from radium-C' and thorium-C'. N. FEATHER and R. R. NIMMO (Proc. Camb. Phil. Soc., 1929, 25, 198—204; cf. this vol., 371).—The particles of abnormally short range were investigated from measurements of tracks formed in an expansion chamber for 2134 and 729 α -particles from thorium-C' and radium-C', respectively, and range-distribution curves were obtained. The origin of marked differences in the proportion of short-range particles in each is discussed. Estimates of the linear straggling coefficients relative to the absorption of the two groups of particles in air are made.

N. M. BLIGH.

Number of high-velocity β -rays. H. M. CAVE (Proc. Camb. Phil. Soc., 1929, 25, 222—224; cf. Yovanovitch and D'Espine, A., 1927, 915).—A simple determination was made of the average number of high-velocity β -particles per disintegration from radium-B+C, and it is concluded that the number of such particles is certainly less than 1 per 500 and probably less than 1 per 1000 disintegrations.

N. M. BLIGH.

Evaluation of the α -radiation of the active deposit of actinium by measurement of its β -radiation. NAHMAS (Compt. rend., 1929, 188, 1165—1167).—The absolute value of the α -radiation from actinium-C may be determined from the ratio of the ionisation current produced by the β -radiation to that due to the α -radiation remaining after the former has become feeble. Ionisation from the effect of β -rays during the measurement of the α -radiation amounts to 0.013 of the current due to the latter, and is determined by the use of an aluminium screen 0.06 mm. thick to cut off all the α -radiation.

J. GRANT.

Determination of radium content from the γ -radiation. W. A. SOKOLOV (Z. Physik, 1929, 54, 385—398).—For determination of radium content the method of γ -radiation measurement is much more accurate than that of the α -radiation and moreover for this purpose the material requires no chemical treatment such as is necessary for emanation measurement. A new form of γ -ray electroscope is described, using the same principle as that of Dorsay (J. Opt.

Soc. Amer., 1922, 6, 633), the chief improvements made being in making the space for the material to be investigated much larger and the substitution of a forked electrode for the cylinder used by Dorsay. By this means it has been found possible to measure radium contents as low as 2 parts in 10^{10} of radium-containing minerals. J. W. SMITH.

Atomic disintegration. W. BOTHE and H. FRANZ (Z. Physik, 53, 1929, 313—316).—The essential differences between results obtained by these authors and Kirsch and Pettersson (this vol., 234) are stated. No correlation seems possible.

G. E. WENTWORTH.

Cosmic radiation and radioactive disintegration. N. DOBRONRAVOV, P. LUKIRSKY, and V. PAVLOV (Nature, 1929, 123, 760).—Experiments with two nearly equal quantities of radon, the exact ratio of the activities of which had been determined, did not reveal any action of cosmic rays on the speed of disintegration, although the possibility of such action, e.g., in causing the disintegration of the first member of the radioactive family, is not thereby excluded.

A. A. ELDRIDGE.

Nature of penetrating radiation. W. BOTHE and W. KOLHORSTER (Nature, 1929, 123, 638, and Naturwiss., 1929, 17, 271—273).—It is concluded from experimental evidence that the penetrating radiation is not of γ - but of corpuscular type.

A. A. ELDRIDGE.

Theory of quantum jumps. J. ULLMO (J. Phys. Radium, 1929, [vi], 10, 15—31).—Mathematical.

Foundation of Nernst's hypothesis of formation of radioactive elements on the basis of wave-mechanics. J. KUDAR (Z. Physik, 1929, 53, 166—167).—Mathematical note.

Diagram of quantum states and the formation of the elements in the periodic system. O. M. CORBINO (Nuovo Cim., 1928, 5, lvii—lxiv; Chem. Zentr., 1929, i, 185).— n -Values from 1 to 7 ($K-Q$) are plotted as abscissæ against the corresponding states $k=0$ to $k=3$ (s, p, d, f) as ordinates; the states are divided into groups corresponding with different k -values.

A. A. ELDRIDGE.

Distribution of charge and current in an atom consisting of many electrons obeying Dirac's equations. D. R. HARTREE (Proc. Camb. Phil. Soc., 1929, 25, 225—236).—An approximation for the many-electron atom is applied to electrons obeying Schrodinger's wave equation and also to those obeying Dirac's equation, in order to divide the electron groups into half groups for which the distribution of charge is spherically symmetrical. An investigation is made as to whether the direction of the spin axis of the electron can ever be specified, and it is concluded that this can be done only for states for which the magnetic quantum number m has its extreme value $\pm j$.

N. M. BLIGH.

Theory of columnar ionisation. II. G. JAFFÉ (Ann. Physik, 1929, [v], 1, 977—1008; cf. A., 1913, ii, 658).—Mainly mathematical. The theory of ionisation in columns advanced in the earlier paper is extended and developed and a formula is derived for

the increase in ionisation density. A comparison is made with experimental results. A. J. MEE.

Theoretical expression for the life of the atom in the metastable state. M. SAHA and D. S. KOTHARI (Naturwiss., 1929, 17, 271).—Classical theories lead to the expression $T = 3mc^3/8\pi e^2\nu^2$ for the life of the excited atom in the metastable state, (Abklingungszeit), and for $\nu = 10^4c$ the value is of the order 10^{-8} sec. A rough expression for the life of the atom in the metastable state is given by $T = 3c^5m^2/\pi^2e^2h\nu^3$, and taking $\nu = 10^4c$, T is 1.5×10^{-1} sec., in agreement with experimental values found by Kannenstine and Hertz. R. A. MORTON.

Estimates of the ages of the Whin Sill and the Cleveland Dyke by the helium method. V. S. DUBEY and A. HOLMES (Nature, 1929, 123, 794—795).—Values, respectively, of 182 and 26×10^6 years are obtained. A. A. ELDRIDGE.

Quantum mechanics of many-electron systems. P. A. M. DIRAC (Proc. Roy. Soc., 1929, A, 123, 714—733).—The methods and results of group theory are translated into the language of quantum mechanics so as to obtain a treatment of the "exchange" (Austausch) phenomena of electrons. The general theory is given of systems containing a number of similar particles, showing the existence of sets of states such that a transition can never take place from a state in one set to a state in another. The theory is then applied to the case when the particles are electrons, taking into consideration the spin of the electrons and Pauli's exclusion principle, and a proof is obtained of the fundamental theorem of multiplet structure, that for each stationary state of the atom there is one definite numerical value for s , the magnitude of the total spin vector. The perturbation theory is applied to an approximate calculation of the energy level of the states, the result being expressible by a simple formula, showing that, in the first approximation, the exchange interaction due to the equivalence of the electrons may be replaced by a coupling between their spins, the energy of this coupling for each pair of electrons being equal to the scalar product of their spin vectors multiplied by a numerical coefficient given by the exchange energy. In this way a justification is obtained for the assumptions of the old orbit theory.

L. L. BIRCUMSHAW.

Discussion on the structure of atomic nuclei. (Proc. Roy. Soc., 1929, A, 123, 373—390).—(SIR) E. RUTHERFORD. The progress which has been made in the last fifteen years is reviewed. Three methods of attacking the problem are discussed: (1) the proof of the isotopic constitution of the ordinary elements and the accurate determination of the masses of the individual isotopes; (2) the artificial disintegration of the elements by bombardment with α -particles, and (3) the study of the wave-lengths of the penetrating γ -rays which have their origin in the disintegration of the radioactive nucleus. Earlier work on isotopes showed that the masses of the elements are approximately expressed by whole numbers (oxygen=16), but the main interest now lies in the departures from the whole-number rule. The second method of attack shows definitely that the actual

structure of the nucleus can be altered by the application of external agencies, whilst the third gives evidence of the modes of vibration of the particles constituting the nucleus. In a study of the scattering effects of α -particles of elements from copper (at. no. 29) to uranium (at. no. 92) it is found that the scattering is normal—i.e., assuming the inverse square law the number of α -particles scattered through an angle of about 135° varies as $1/E^2$, where E is the energy of the α -particles. From this it is concluded that the radius of the copper nucleus is less than the closest distance of approach (about 10^{-12} cm.), whilst for uranium this distance is about 3×10^{-12} cm. The scattering of the lighter elements is quite abnormal and a detailed study of these deviations leads to the conclusion that the close approach of an α -particle to the nucleus causes a polarisation of the charged constituents of the latter. This gives rise to an attractive force which varies as the 5th power of the distance from the centre of the nucleus. Calculations on this basis agree fairly well with the experimental observations on aluminium. The nuclei cannot be regarded as point forces, but have a certain structure and volume, and the latter may in some cases be flat ellipsoid rather than spherical. Scattering experiments show that a swift α -particle cannot penetrate deeply into the nucleus of uranium, whilst other considerations indicate that this should occur. An explanation of this difference can be obtained by applying the ideas of wave mechanics, but this makes the radius of the uranium nucleus very small (about 7×10^{-13} cm.), and in this small nuclear volume 238 protons and 146 electrons must be accommodated. A picture is presented of the gradual building up of atomic nuclei in which the latter are composed of α -particles, protons, and electrons which, owing to the distortional forces, attract each other strongly. A highly concentrated and firmly bound nucleus results, accompanied by the emission of energy and this binding is closest for atomic mass 120, where the loss of mass due to packing is a maximum. The nucleus consists, therefore, of a very tightly-packed structure at the centre, becoming less dense as the outside is approached, and is a system surrounded by a potential barrier which normally prevents α -particles from escaping. This view explains why atoms heavier than uranium cannot exist permanently.

F. W. ASTON. The packing fractions of the elements are discussed, and the essential differences between the light atoms of odd atomic number (hydrogen, lithium, beryllium) and those of even atomic number (helium, carbon, oxygen) are emphasised.

J. CHADWICK. Experiments on artificial disintegration by α -particles reveal the fact that protons liberated from the odd-numbered elements have greater maximum energies than those from even-numbered, and if the disintegration consists of the capture of an α -particle and the emission of a proton, then an element of odd number will be changed into one of even number, and *vice versa*. This suggests, in agreement with other evidence, that the even elements are more stable than the odd.

C. D. ELLIS. The nature and origin of the γ -rays occurring in radioactive disintegrations are discussed.

These rays are more frequently associated with the β -ray type of disintegration and appear to be homogeneous to at least 1 part in 1000 parts. Experiments in progress on the intensities of the photo-electric groups emitted from lead when exposed to γ -radiation from a radioactive source provide some evidence of a curious coupling between the nucleus and the electronic system.

G. GAMOW. A theory is suggested which treats an assembly of α -particles—*e.g.*, the α -particles constituting a nucleus—with attractive forces between them, which vary rapidly with the distance, as a small drop of water with the particles held together by surface tension. From the equation connecting the energy of the α -particles with the surface tension of the imaginary water drop and the quantum condition of ordinary quantum mechanics, a relation is obtained between the "drop energy" and the number of α -particles contained in the drop (*i.e.*, the at. wt. of the nucleus). The shape of the curve for this relation agrees well with Aston's curve showing the defect of mass. On the basis of wave mechanics this model can be treated by Hartree's method of self-consistent field.

R. H. FOWLER. The nucleus is pictured as a tiny enclosure surrounded by a potential hill and enclosing an α -particle (represented by a standing wave), of which the energy is less than the potential energy at the top of the barrier. On the classical theory it will stay inside for ever, but on the quantum theory there is a finite chance that the wave can leak out through the thin wall. Its chance of doing this will be greater, the greater is the energy of the α -particle, the thinner the barrier it has to go through, and the smaller the height of this barrier. A virtue of this theory is that it gives the Geiger-Nuttall law of α -ray disintegration independently of the details of nuclear structure.

O. W. RICHARDSON. Spectroscopic evidence is submitted in favour of the rotation of the nuclei.

L. L. BIRCUMSHAW.

Synthesis of elements. G. I. POKROVSKI (Z. Physik, 1929, 54, 123—132).—Mathematical. The energy and frequency of the radiation which would be produced by combination of a single proton with an atomic nucleus are calculated. The period of vibration of this radiation is shown to be equal to a whole number of chronons. The frequencies calculated for particular cases agree with the observations of Millikan and Cameron (A., 1928, 1303) on high-frequency radiation.

J. W. SMITH.

Ordinary matter and radiant energy as different phases of one and the same fundamental state. W. ANDERSON (Z. Physik, 1929, 54, 433—444).—Mathematical.

J. W. SMITH.

Quantum theory of the atomic nucleus. T. SEXL (Z. Physik, 1929, 54, 445—448).—Mathematical.

J. W. SMITH.

Chromium echelette gratings on optical flats for infra-red investigations. R. W. WOOD (Phil. Mag., 1929, [vii], 7, 742—744).—The preparation of chromium echelette gratings is described. The method of ruling is as described previously (*ibid.*, 1910, [vi], 20, 886), except that a suitably-cut diamond

replaces the carborundum crystal. The grating is ruled on optically flat copper and after the ruling the surface is electroplated with chromium, the deposition of which is without effect on the distribution of the light. Gratings of this description up to 4 in. diameter have been made and can be supplied to laboratories requiring them. They can be ruled for concentration at any desired wave-length and with any desired spacing. Concave gratings of this type of 1 and 2 m. radius have been made. A. E. MITCHELL.

σ -Type doubling and electron spin in the spectra of diatomic molecules. J. H. VAN VLECK (Physical Rev., 1929, [ii], 33, 467—506).—The two rotational effects considered together with their inter-relation are the distortion and the σ -type doubling of spectral lines due to removal of the degeneracy associated with the energy equality of left- and right-handed axial rotations in stationary molecules. The methods of matrix and wave mechanics are used. A summary and comparison with Mulliken's experimental data (*cf.* following abstract) are given.

N. M. BLIGH.

Electronic states and band spectrum structure in diatomic molecules. VIII. Some empirical relations in σ -type doubling. R. S. MULLIKEN (Physical Rev., 1929, [ii], 33, 507—511; *cf.* A., 1928, 1166).—Some empirical relations are summarised, and the magnitudes of the doublet intervals are considered. The observed relations agree with the work of Van Vleck (*cf.* preceding abstract), which shows definitely that the 3P levels involved in the second positive nitrogen bands are both normal and not inverted.

N. M. BLIGH.

Structure of multiplet *S*-states in diatomic molecules. I. H. A. KRAMERS (Z. Physik, 1929, 53, 422—428).—A theoretical explanation of the characteristic multiplicity of normal 3S -states in the O_2 molecule.

E. B. ROBERTSON.

Structure of multiplet *S*-terms in diatomic molecules. II. H. A. KRAMERS (Z. Physik, 1929, 53, 429—438).—Mathematical. E. B. ROBERTSON.

Two-quantum excited states of the hydrogen molecule. E. C. KEMBLE and C. ZENER (Physical Rev., 1929, [ii], 33, 512—537).—An extension of the work of Heitler and London and of Sugiura (*cf.* A., 1927, 923; 1928, 345) on the interactions of normal hydrogen atoms by the method of wave mechanics, to cases of certain excited states of the H_2 molecule which dissociate adiabatically into a normal H atom and a two-quantum excited H atom. The application of the results to the qualitative prediction of the nature of the different excited states of the molecule and to London's theory of non-polar valency is considered. The principles of selection for transitions between the various types of electronic state are formulated and compared with the rules of Kronig (*cf.* A., 1928, 456). A first-order perturbation theory computation of the potential energy curves for the *P* states shows that two of them have the form requisite for the formation of stable molecules, and may be identified respectively with the *C*-state upper level for Werner bands, and the 2^3P -state reported by Richardson (*cf.* A., 1927, 495).

N. M. BLIGH.

Band systems of the hydrogen molecule. R. MECKE and W. FINKELNBURG (*Naturwiss.*, 1929, 17, 255—256).—Analysis of the many-lined spectrum of hydrogen discloses the predominance of singlet and triplet systems. In addition to 550 lines already classified, 725 lines are now shown to belong to 60 bands with 179 branches of a new triplet system ascribed to the hydrogen molecule. The bands consist of three intense *Q*-like branches ($\Delta m = 0$) and two weaker branches ($\Delta m = \pm 2$). The 2^3S end term is common to all the new bands. Relevant terms and molecular constants are given. Since the more intense lines of the spectrum have now been rigidly classified, the role of H_2^+ and H_3 in the many-lined spectrum must be subordinate compared with that of H_2 molecules. R. A. MORTON.

Absorption band spectrum of chlorine. A. ELLIOTT (*Proc. Roy. Soc.*, 1929, A, 123, 629—644).—An analysis has been made of the rotation structure of the three chlorine bands $2 \rightarrow 17$, $2 \rightarrow 18$, and $2 \rightarrow 19$, using an absorption tube 1.6 m. long containing chlorine at 1 atm. A feature of the bands is the close similarity of the *P* and *R* branches and the remarkable way in which they run side by side. No *Q* branches are found. The values obtained for the molecular constants indicate that the normal chlorine molecule expands considerably on the absorption of a quantum of radiation. Taking Kuhn's assignment of quantum numbers for the initial state (in absorption) with the addition of one half unit (cf. A., 1926, 1192), the quantum numbers for the excited state are calculated from the magnitude of the isotopic separation of the band origins. These are found to be rather high, as the first band observed in the progression in which $n'' - 1$ has the value $n' = 12$. The lines comprising the bands due to the molecule $Cl^{35}Cl^{35}$ show an alternation in intensity, the ratio of strong to weak lines being about 1.42 : 1. This effect is not, however, present in the non-symmetrical molecule $Cl^{35}Cl^{37}$. This is in accordance with the theory of Hund (A., 1927, 495), which states that alternation in intensity of band lines is to be expected only when the nuclear masses are equal. The molecules $Cl^{35}Cl^{35}$ and $Cl^{35}Cl^{37}$ have different moments of inertia but equal internuclear distances, and must be identical except in respect of nuclear mass. The mean intensity of the lines in each band is approximately proportional to the number of molecules present of the kind required to produce the band.

L. L. BIRCUMSHAW.

Constitution of oxygen. H. D. BABCOCK (*Nature*, 1929, 123, 761).—The *A'* band of oxygen has been augmented from 26 to 73 lines, of which about half belong to the alternate system of doublets which are to be expected from the molecule $O^{16}O^{18}$. The relative abundance of the molecules $O^{16}O^{16}$ and $O^{16}O^{18}$ is approx. 1250 : 1 (cf. Giaque and Johnston, this vol., 369; Aston, this vol., 484).

A. A. ELDRIDGE.

Absorption of ultra-violet radiation by ozone. A. LAUCHLI (*Z. Physik*, 1929, 53, 92—94).—The absorption coefficients of ozone for light of wavelengths between 2378 and 3341 Å. have been measured. The ozone was determined by a differential method

similar to Warburg's, and the intensity of the light determined by means of a photo-electric cell with thermionic valve amplification. The effect of scattered light on the absorption coefficient was investigated, and found to be greatest for the lines 2482 and 2652 Å. and negligible for the resonance line 2537 Å. For the wave-length range 2800—3350 Å., which is of importance in atmospheric absorption, the absorption coefficient is given by an empirical formula.

E. B. ROBERTSON.

Ozone absorption during the long Arctic night. S. ROSSELAND (*Nature*, 1929, 123, 761).

Active nitrogen. P. K. KICHLU and S. BASU (*Nature*, 1929, 113, 715—716).—Active nitrogen is molecular nitrogen in a metastable condition; its life can be varied by the regulation of pressure, increasing continuously and regularly with decrease of pressure. Infra-red lines of nitrogen belonging to the electronic configurations $2L_2M_1 \leftarrow 2L_2M_2$ have been produced by exciting nitrogen and active nitrogen with an uncondensed discharge under identical conditions; no change in the relative intensity of lines was observed, whence no appreciable density of atoms is present.

A. A. ELDRIDGE.

Active nitrogen. (LORD) RAYLEIGH (*Nature*, 1929, 113, 716).—A reply to Kichlu and Basu (preceding abstract).

A. A. ELDRIDGE.

Infra-red radiations of active nitrogen. P. K. KICHLU and D. P. ACHARYA (*Proc. Roy. Soc.*, 1929, A, 123, 168—171).—The band spectrum of active nitrogen has been photographed in the infra-red, and it is shown that the bands extending from 7500 to 8900 Å. consist of an extension of the first positive group of nitrogen occurring in the yellow, green, and red regions. The fact that no trace is found of the group of lines of atomic nitrogen at 8200 Å. indicates that the analogy between active nitrogen and active hydrogen is not complete (cf. Sponer, A., 1926, 8).

L. L. BIRCUMSHAW.

Active nitrogen. II. Influence of surface on the afterglows in nitrogen and oxygen. III. Mutual effect of nitrogen and oxygen on their respective afterglows. B. LEWIS (*J. Amer. Chem. Soc.*, 1929, 51, 654—665, 665—674).—II. The introduction of oxygen into nitrogen immediately after the latter has been subjected to high-tension discharge does not produce an afterglow. The nature of the surface of the containing vessel seems to be a determining factor governing the visibility of the afterglow in nitrogen and in oxygen. Thus nitrogen, pure or containing a trace of oxygen, at very low pressure shows prolonged afterglow when treated in an ordinary vessel, but with continued baking of the vessel the glow progressively disappears. Similar results were found for pure oxygen. Afterglow which has been removed in this manner may be restored by adding sufficient water vapour to cover the surface of the vessel. The phenomena are the same in a paraffin-covered vessel as in an ordinary glass vessel. Heat decreases the duration and intensity of the afterglow in an uncleaned vessel, and *vice-versa* (reversed temperature effect). The oxygen afterglow, which decays abruptly, appears to be quenched at liquid air temperatures, whereas the nitrogen afterglow is intensified.

III. Curves are given representing the duration of the afterglow as a function of pressure for a series of nitrogen and oxygen mixtures. Normal oxygen molecules have a marked quenching action on the nitrogen afterglow, but normal nitrogen molecules do not affect the oxygen afterglow. The kinetic aspect of the phenomena is discussed. S. K. TWEEDY.

Spectral absorption of lithium hydride and the molecular constants of LiH. G. NAKAMURA (Z. physikal. Chem., 1929, B, 3, 80—82).—An analysis of the absorption spectrum of lithium hydride is given. The band system consists of a number of bands fading towards the red. Each band is made up of a simple *P*- and a simple *R*-line, and is similar to the ultra-violet bands of BeH^+ . The moments of inertia of the lithium hydride molecule in the normal state are calculated. A. J. MEE.

Titanium oxide bands in the orange, red, and infra-red region. F. LOWATER (Nature, 1929, 123, 644).—Bands in the region 5600—8000 Å. have been analysed into a singlet system in the orange, due to the electronic transition $^1P \rightarrow ^1S$, and a triplet system in the red and infra-red due to the transition $^3S \rightarrow ^3P$.

A. A. ELDRIDGE.

Effect of adsorbed ions on the light absorption of heavy metal halides. K. FAJANS and G. KARAGUNIS (Naturwiss., 1929, 17, 274).—When Ag^+ and Tl^+ ions are adsorbed by colloidal silver bromide or Pb^{++} ions by lead iodide, the strongly anion-deforming cations bring about an increased extinction detectable on the long-wave descending portion of the absorption curve. Silver iodide, so highly dispersed that scattered radiation plays a minor part, permits the measurement of intensities on both sides of the absorption maximum at 420 μ . Adsorption of Ag^+ in this case causes the intensity of the whole band to be increased markedly without appreciable shift of the wave-length of maximum absorption. The adsorption of Ag^+ on the silver iodide lattice increases either the number of atoms in the particular state or the number of quantum transitions, of which the band forms a measure. The transition is probably involved in the photo-electric conductivity and the photo-decomposition of the silver halide. The sequence: $\text{Ag}_n\text{I}_n \rightarrow [\text{Ag}_n\text{I}_n]\text{Ag}^+ \rightarrow \text{Ag}_2\text{I}^+$ is in accord with observation since Ag_2I^+ shows negligible absorption in the visible and there is no ultra-violet maximum until 245.5 μ is reached. R. A. MORTON.

Absorption spectrum of liquid benzene. J. W. ELLIS (Physical Rev., 1929, [ii], 33, 625—626).—A criticism of the work of Barnes and Fulweiler (cf. A., 1928, 1306). N. M. BLIGH.

Absorption spectrum of liquid benzene. J. BARNES (Physical Rev., 1929, [ii], 33, 627).—A reply to Ellis (cf. preceding abstract). N. M. BLIGH.

Structure and activation of the molecules of aliphatic aldehydes. III. Absorption spectra of solutions. S. A. SCHOU (J. Chim. phys., 1929, 26, 69—90; cf. this vol., 236).—Measurements have been made of the absorption spectra of formaldehyde vapour and of solutions in hexane. The maxima for these two states are at 2935 and 2940 Å., respectively, showing that formaldehyde in the unimolecular state

absorbs in the same region as acetaldehyde and propaldehyde. In aqueous formaldehyde solution there is less than 1 mol. of $\text{H}\cdot\text{CHO}$ for 1200 mols. of the hydrated or polymerised form. The absorption spectra of acetaldehyde in aqueous and in hexane solution indicate that the enolic form can exist under conditions where the aldehyde is polymerised, e.g., in alkaline solution or when the polymerisation is catalysed by an acid. Measurements have also been made of the absorption of propaldehyde and of chloral in aqueous and in hexane solution.

O. J. WALKER.

Intensity of the *K*-lines of the X-ray spectrum in relation to atomic number. H. T. MEYER (Wiss. Veroff. Siemens-Konzern, 1929, 7, [2], 108—162).—Methods for determining the intensities of X-ray lines recorded photographically are described, together with refinements and corrections. The relative intensities of the *K*-lines in the spectra of the elements from indium (49) to titanium (22), with the exceptions of masurium and krypton, have been determined. Taking $K\alpha_1$ as 100, α_2 varies from 46.0 to 54.9, β_1 from 15.8 to 26.1, and β_2 from 0.15 to 4.22. On the whole, the ratio α_2 agrees very well with the theoretical value 2 : 1, whilst $\alpha_1 : \beta_1 = 4 : 1$, a result without known theoretical basis. The relatively small deviations from the 2 : 1 and 4 : 1 ratios are to a great extent smoothed out by plotting $\alpha_2 Z / \alpha_1 A$ against atomic number, *A* being the atomic weight, and *Z* the atomic number. No such effect is observed for the ratio $\beta_2 : \alpha_1$. From gadolinium onwards the ratio β_2 / α_1 increases with increasing atomic number, indium being anomalous. When $(\alpha_2 - \beta_1) / \alpha_1$ and $(\alpha_2 - \beta_1) Z / \alpha_1 A$ are plotted against atomic number, a gradual decrease is recorded from vanadium to bromine, whilst from rubidium to indium practically constant values are obtained. The ratio β' / β_1 has been determined for manganese and the ratio α_3 / α_1 for manganese, chromium, and vanadium.

R. A. MORTON.

Intensity of scattered light, and its dependence on temperature. C. LANDSBERG and M. LEONOWITSCH (Z. Physik, 1929, 53, 439—448).—The intensities of the lines in the spectrum of light scattered by quartz have been investigated by means of a photographic photometer, and the intensity of the strongest red satellite is found to be about 40% of that of the principal line. On raising the temperature, the intensity of the red satellites remains practically constant, that of the principal line increases as the absolute temperature, and that of the violet satellites increases even more quickly. E. B. ROBERTSON.

Theory of sensitised fluorescence. A. CARELLI (Z. Physik, 1929, 53, 210—215).—On Schrodinger's theory, an explanation is given of the preference for the resonance state in the conversion of energy of excitation in collisions of the second kind, as observed in the sensitised fluorescence of metal vapour mixtures.

E. B. ROBERTSON.

X-Ray luminescence of mercury vapour. S. MROZOVSKI (Z. Physik, 1929, 54, 422—426).—Careful spectroscopic investigation of the X-ray luminescence of mercury vapour leads to the conclusion that it is not the direct X-ray fluorescence which plays the

major rôle in this case, but that the visible and ultra-violet spectrum is excited by the slow-moving photo-electrons.

J. W. SMITH.

Phosphorescence and photochemical activity of some organic and inorganic substances after ultra-violet irradiation. F. KIRCHHOF (Physikal. Z., 1929, 30, 240—241).—A faintly green paper after ultra-violet irradiation was found to darken a photographic plate. The effect is not purely chemical (*i.e.*, the irradiation is essential), nor is it due to the slight phosphorescence which arises when the ash is tested separately. Photoactivity is observed with fluorene and zinc salts of organic sulphonic acids, but there is no necessary connexion between photoactivity and visible phosphorescence (using an ultra-violet analysis cabinet).

R. A. MORTON.

Phosphorescence of beryllium sulphide and a luminescent-analytical arrangement particularly for feebly phosphorescent preparations. E. TIEDE and F. GOLDSCHMIDT (Ber., 1929, 62, [B], 758—762).—Beryllium oxide is converted by ignition with sugar charcoal in a current of chlorine or hydrogen chloride into beryllium chloride, which, after repeated sublimation, is heated in a stream of hydrogen sulphide. The pale grey, apparently amorphous beryllium sulphide thus prepared, which contains traces of chloride, is non-phosphorescent but yields weak phosphors after suitable treatment with bismuth or antimony. Beryllium sulphide, prepared from the pure metal and sulphur vapour in a current of hydrogen at 1000—1300°, without addition of excitant or flux, exhibits a feeble but distinct blue phosphorescence. The effect may be enhanced by addition of sodium chloride. It is attributed to the presence of iron in minute amount, but the effect is not increased by known addition of further amounts of the metal.

The analytical arrangement consists of a metal arc (iron, copper, or nickel) as source of the light which is passed through a black glass filter and uviolet glass lens. The range of the light is 400—300 μ . Intense illumination of very small surfaces is thus achieved and the arrangement is particularly suitable for minute objects.

H. WREN.

Cause of the phosphorescence of calcium tungstate. A. SCHLEEDÉ and T. TSAO (Ber., 1929, 62, [B], 763—768).—Technical tungstic acid or ammonium tungstate is purified by alternate treatment with concentrated hydrochloric acid (or aqua regia) and sodium hydroxide or ammonia and converted by calcium chloride into calcium tungstate which is ignited at 1000°. The Röntgen-fluorescence of the preparation is about equal to that of the best technical specimens, whilst phosphorescence is sometimes present, sometimes absent. The latter property is inhibited by addition of calcium molybdate, but the fluorescence is sensibly diminished. Similar preparations are obtained from ammonium tungstate and calcium chloride in very dilute solution. Calcium tungstate, prepared from repeatedly crystallised sodium tungstate and calcium chloride, still exhibited phosphorescence but a non-phosphorescent material resulted when re-crystallised ammonium tungstate was used as initial material. Röntgenographic

examination of the residues obtained from the mother-liquors from the ammonium tungstate disclosed the presence of arsenic and molybdenum. The addition of ammonium arsenate to ammonium tungstate previous to precipitation with calcium chloride leads to preparations with good fluorescence but marked phosphorescence; similar results are induced by ammonium antimonate. Ammonium molybdate does not induce phosphorescence.

H. WREN.

Optical relationship between alkali halide phosphors and complex salt solutions. H. FROMHERZ and W. MENSCHICK (Z. physikal. Chem., 1929, B, 3, 1—40, and Naturwiss., 1929, 17, 274—275).—Recent work on forces in crystals and in solutions of electrolytes leads to the supposition that the phosphors obtained by the addition of a trace of a heavy metal salt to an alkali halide, and the solutions of heavy metal salts in concentrated solutions of alkali halides, owe their origin to the same cause, *viz.*, the formation of complex ions. The crystalline phosphors have sharp absorption bands in the ultra-violet. It was hoped to show that the solutions of heavy metal salts in alkali halide solutions have similar absorption bands. For this purpose the crystalline phosphors described by Smakula (A., 1927, 1125) were investigated, *viz.*, alkali halide and silver halide, and alkali halide and copper halide. The extinction curves of the following pure solutions were obtained: sodium chloride, sodium bromide, potassium chloride, potassium bromide, potassium iodide, sodium perchlorate, silver perchlorate, cupric perchlorate, cupric chloride, and cupric bromide. The spectral absorption of the following complex solutions were also investigated: sodium chloride+silver chloride, potassium chloride+silver chloride, sodium bromide+silver bromide, potassium bromide+silver bromide, potassium iodide+silver iodide, silver perchlorate+silver iodide, potassium chloride+cupric chloride, potassium bromide+cupric bromide, potassium chloride+cuprous chloride, potassium bromide+cuprous bromide. By graphically subtracting the extinction curves, those of the pure complexes were obtained, and the curves for the crystals and the solutions were compared. The absorption bands of the pure alkali halide solutions are displaced towards the red by about 30 $m\mu$ in comparison with those of the crystalline compounds. The bands obtained with complex alkali halide solutions of silver and cupric salts agree in form, position, and sharpness with those of the corresponding crystals. The bands are displaced by only 6—10 $m\mu$ towards the red. From the ratio of the size of the absorption bands in the crystals and in the complex solutions it is shown that only 0.2—2% of the heavy metal salt is in the crystal lattice itself in an optically active form. The results show that association of atomic ions to form complex ions is the cause of the characteristic absorption bands and optical excitability of crystalline phosphors.

A. J. MEE.

Theory of Raman effect. L. FERNANDES (Atti R. Accad. Lincei, 1929, [vi], 9, 407—409).

Raman effect and negative absorption. B. ROSSI (Atti R. Accad. Lincei, 1929, [vi], 9, 319—324).—Mathematical.

Raman effect in atomic hydrogen. B. PODOLSKY (Nature, 1929, 123, 761).—A theoretical note.

A. A. ELDRIDGE.

Raman effect in diatomic gases. F. RASETTI (Proc. Nat. Acad. Sci., 1929, 15, 234—237; cf. Ramdas, A., 1928, 1307).—With the object of testing certain deductions on the Raman effect (A., 1928, 685, 1075) made from the new quantum mechanics, experiments were conducted on the effect for oxygen, nitrogen, and carbon monoxide. The results were found to be in accordance with the quantum theory of dispersion.

N. M. BLIGH.

Raman effect in gases. I. Hydrogen chloride and ammonia. R. W. WOOD (Phil. Mag., 1929, [vii], 7, 744—749).—Apparatus has been developed for the examination of the spectra of scattered light in gases and has been employed to measure the effects in hydrogen chloride. The mercury line 4046 Å. excites a modified line at 4581.8 Å. The frequency difference between the exciting line and the modified line corresponds with a wave-length of 3.466 μ in the infra-red. This is almost exactly the wave-length of the centre of the gap between the branches of the absorption band found by Imes. It is therefore identified as a *Q* branch not observed in absorption. A number of nearly equidistant bands close to the mercury line 4358 Å. are found to correspond fairly closely with alternate bands in rotation bands observed by Czerny. For ammonia the band at 3 μ was identified, but no trace of the strong NH_3 bands at 6.1 or 10.5 μ .

A. E. MITCHELL.

Selection rules in the Raman effect. F. RASETTI (Nature, 1929, 123, 757—759).—Experimental support is afforded for the selection rule whereby in order that a shift corresponding with the transition $i \rightarrow k$ may be observed, it is necessary that both states i and k combine at least with a third state l . The Raman scattering becomes intense when the energy, $h\nu$, of the impinging quantum is near to $E_i - E_l$; if $E_i - E_l = h\nu$, fluorescence is observed. Using the mercury line 2536 Å., in oxygen and nitrogen there appear on both sides of the line a number of equally spaced lines, evidently due to rotational transitions. The spacing is considered theoretically, and for nitrogen the observed and calculated values are tabulated. The moment of inertia of the N_2 molecule is computed to be $13.8 \pm 0.1 \times 10^{40}$ g. cm.² It appears that in the normal state of N_2 , only even rotational states are present, or these have a higher statistical weight than the odd ones. An explanation of the fact that the Raman lines corresponding with vibrational transitions in nitrogen and oxygen show no rotational structure is offered. The Raman spectrum of gaseous hydrogen has also been observed. Data for carbon dioxide support Eucken's model.

A. A. ELDRIDGE.

Raman effect in quartz. M. CZERNY (Z. Physik, 1929, 53, 317—325).—The infra-red absorption of quartz, for wave-lengths greater than 30 μ , has been investigated with a grating spectrometer. Of the absorption maxima expected from the Raman effect, those occurring at 38 and 78 μ have been found, but the one expected to occur at 48 μ appears to be absent. The result is discussed with reference

to the great differences between the relative intensities of Raman lines and of the corresponding infra-red absorption bands.

E. B. ROBERTSON.

Secondary radiations in light diffused by calc spar. J. CABANNES (Compt. rend., 1929, 188, 1041—1043; cf. Daure, this vol., 240).—The depolarisations of the two principal secondary lines of calcite have been studied. Each line may be considered to be emitted by a number of "virtual oscillators," the mean square of the electric displacement of which may then be calculated with respect to three axes at right angles. Contrary to Raman's theory, the radiation 280 cm.⁻¹ appears to be derived from oscillators which vibrate in an incoherent manner, the amplitude being the same whatever their orientation with respect to the exciting vibration. The displacement of the oscillators of the line 1083 cm.⁻¹ (which may be derived from vibrations of the carbon atoms of the carbonate ions) is always parallel to the incident vibration whether this is parallel or perpendicular to the ternary axis.

J. GRANT.

Photo-electric emission from phototropic mercury compounds. S. V. R. RAO and H. E. WATSON (J. Indian Inst. Sci., 1929, 12A, 17—29).—The photo-electric emission from twelve phototropic mercury compounds (cf. this vol., 660) has been measured by a thermionic valve method (Toy and others, A., 1927, 293). In the dark the emission is zero or negligible. On exposure to the light of a mercury-vapour lamp the emission increases to a maximum after 250—300 sec. and then remains steady without signs of photo-electric fatigue even after exposures up to 80 min. duration. At 2 mm. pressure a maximum current of 82×10^{-11} amp. was recorded for the substance $\text{HgI}_2 \cdot 2\text{HgS}$. The photosensitiveness falls on heating or on keeping in the dark almost to that of the freshly-prepared compounds. The emission of darkened compounds is constant, whether the darkening was caused by visible or ultra-violet light. Some indication was found that for related compounds the photo-electric and phototropic properties run parallel.

F. G. TRYHORN.

Electric moments of molecules and methods of determining them. G. B. BONINO and P. CELLA (Gazzetta, 1929, 59, 79—105).—A discussion of the importance of electrical molecular moments and a critical review of methods which have been used in determining them from measurements of specific inductive capacity. An oscillating valve circuit which has been found by the authors to be satisfactory is described and results are given of measurements of the dielectric constants of carbon tetrachloride and tetrachloroethylene at various temperatures, using benzene as a reference liquid in each case. The values of the constants for the internal molecular fields of these molecules calculated from the above measurements by the authors differ considerably from the classical values. These discrepancies are discussed in relation to Debye's theory.

F. G. TRYHORN.

Molecular structure and dipole moment. W. HÜCKEL (Z. physikal. Chem., 1929, B, 2, 451—457).—In order to explain the dipole moment possessed by symmetrical organic compounds of the type C_xY_x it has been assumed that the carbon atom has a pyramidal

structure instead of a tetrahedral one. This structure is discussed, and it is shown that the occurrence of dipole moments in these compounds is not in contradiction with classical stereochemistry.

A. J. MEE.

Non-polar combination and atomic refraction. II. R. SAMUEL (*Z. Physik*, 1929, 53, 380—403).—In the calculation of molecular refraction of an organic molecule two different refractive equivalents are chosen, instead of the usual value, as the radical functions positively or negatively in the molecule. Many unexplained anomalies disappear. Among these are exaltation, depression, or the necessity of different values for the atomic refraction of the nitrogen atom in amines and other compounds. By this method some conclusions on the function of the radical in non-polar molecules are reached.

G. E. WENTWORTH.

Measurement of the dielectric constants of liquids, with a determination of the dielectric constant of benzene. L. HARTSHORN and D. A. OLIVER (*Proc. Roy. Soc.*, 1929, A, 123, 664—685).—In view of the large discrepancies in the values obtained by different observers for the dielectric constant of any one liquid, the various methods of measurement have been studied and all are found to involve errors. A highly accurate method has been worked out, by means of which the dielectric constant of a given liquid can be determined with a probable error of 1 part in 10,000 parts. It is shown that the test condenser must possess a capacity of at least $100\ \mu\mu\ F$, must be as rigid as possible, and must be completely enclosed in a conducting screen; the air gap between the plates must have a minimum value of 1 mm., the plate systems must be insulated from the screen, and it must be possible to disconnect the plate systems from the leads at points inside the screen without appreciably changing the position of the leads. Data are given for the absolute determination of the dielectric constant of a sample of commercial benzene (A.R. grade) with such a condenser, which needs about 500 c.c. of liquid to fill it. Measurements were then made to show that if one liquid is standardised absolutely, and comparisons are made between it and a second liquid by a method requiring only a small quantity of the second liquid, the value so obtained is identical with that found by the direct use of the absolute method. Finally, the dielectric constant of highly purified benzene was found by the comparison method to be $2.282_{\pm 5}$ at 20° (vacuum = 1). Moisture appears to be the only impurity of importance in dielectric constant measurements.

L. L. BIRCUMSHAW.

Measurement of weakly elliptically polarised light in the ultra-violet. G. SZIVESSY and C. MUNSTER (*Z. Physik*, 1929, 53, 13—51).—A method is described for determining the constants of the vibration path of weakly elliptically polarised ultra-violet light. The azimuth of the path can be estimated to within the fraction of a minute, and an eccentricity of 0.005 to an accuracy of about 1%.

E. B. ROBERTSON.

Paramagnetism and the structure of combined atoms. B. CABRERA (*Anal. Fis. Quím.*, 1929, 27, 73—107).—The mechanics of the atom, as modified

by combination with other atoms, is discussed from the point of view of magnetic behaviour. Langevin's formula leads to values of the magnetic moment which confirm the existence of the magneton of Weiss, a conception which leads to a new hypothesis governing the configuration of combined atoms and responsible also for chemical valency. Sidgwick's theory of the formation of new electronic shells in the nuclear atom of a complex molecule has many difficulties from the magnetic point of view.

H. F. GILLBE.

Diamagnetic anomaly (observed) of gases. A. GLASER (*Ann. Physik*, 1929, [v], 1, 814—820).—Certain diamagnetic molecular gases exhibit an anomaly in the pressure-susceptibility curve. Oxygen, which is paramagnetic, does not show the effect. Investigation of the behaviour of argon and neon discloses that under conditions favourable to the observation of the diamagnetic anomaly (*e.g.*, in carbon dioxide or nitrogen) neither of the rare gases shows any departure from the linear relationship. This result is ascribed to the atomic character of the gases. Control experiments provide no support for the view that traces of moisture are responsible for the anomaly.

R. A. MORTON.

Atomic dynamics of ferromagnetic substances. R. SWINNE (*Wiss. Veroff. Siemens-Konzern*, 1929, 7, [2], 85—99).—Ferromagnetism occurs only in crystals with a non-polar lattice. The idea of a "bound outer electron," distinct from the electron of the valency linking, is discussed in relation to the electronic structure of metals in the transition series of the periodic table. The work of Heitler, London, and Heisenberg is considered in relation to ferromagnetism (*cf.* A., 1928, 344, 589, 1077, 1300).

R. A. MORTON.

Diamagnetism of some binary halogen compounds. R. HOCART (*Compt. rend.*, 1929, 188, 1151—1153).—Determinations of the magnetisation coefficients of hydrogen chloride and of a number of metallic chlorides in the solid state and in solution have been carried out by the ascension and translation pendulum methods with accuracies of at least 0.1 and 0.3%, respectively. The diamagnetism of the ions in solution is not strictly additive.

J. GRANT.

Diamagnetism of the azoxyanisole crystal and Larmor's precession. G. FOX (*Compt. rend.*, 1929, 188, 1154—1156).—The mean coefficient of magnetisation of monoclinic *p*-azoxyanisole is -5.69×10^{-7} . The value found for δ (0.283) indicates that Larmor's theorem of the precession of an electron around the field does not apply, but is compatible with the existence of partial precession. The orientation of the orbits in fixed circuits, however, is in agreement with Pascal's laws of additivity, and if the molecules are completely oriented the values of the principal coefficients are a measure of the molecular disymmetry. Molecular orientation is more complete in the crystal than in the nematic substance in an intense field.

J. GRANT.

Magnetic moment of the lithium atom. D. A. JACKSON (*Z. Physik*, 1929, 53, 458).—Polemical against Taylor (*this vol.*, 491).

Magnetic moment of the lithium atom. O. STERN (Z. Physik, 1929, 54, 158).—Polemical; cf. Taylor (this vol., 491); Jackson (preceding).

J. W. SMITH.

Spectroscopic confirmation of the quantum-mechanical theory of homopolar linking. W. HEITLER and G. HERZBERG (Z. Physik, 1929, 53, 52–56).—Evidence from band spectra is discussed which indicates that certain atoms, such as carbon, become capable, on excitation, of entering into firmer chemical combination. This is in accordance with the quantum-mechanical theory of homopolar chemical linking, according to which, in many cases, an atom must be excited in order to exert its full valency. Thus, the quadrivalent carbon atom arises out of the normal bivalent atom by excitation of about 1.6 volts (5S state).

E. B. ROBERTSON.

Configuration of quadrivalent atoms. T. M. LOWRY (Proc. Camb. Phil. Soc., 1929, 25, 219–221).—The problem of the configuration of *cis*- and *trans*-forms of radicals or molecules of the type MA_4 has been solved by the X-ray analysis of crystals of both types and the results are supported by the change in the crystallographic system of the two series.

N. M. BLIGH.

Constitution of the boron hydrides. E. WIBERG (Z. anorg. Chem., 1929, 179, 309–320).—Polemical against Muller (this vol., 13).

H. F. GILLBE.

Structure of the CH_4 molecule. G. W. BRINDLEY (Nature, 1929, 123, 760–761).—The results of Hogness and Kvalnes (this vol., 242) accord with the view that the four chemical linkings in methane consist of pairs of shared electrons, each pair being formed by an *L*-electron of the carbon atom and a hydrogen electron. Since there are two 2_1 and two 2_2 electrons in the carbon atom, two of the linkings will differ from the other two (Lonsdale, A., 1928, 1079). Models of the methane molecule having either a C^{4-} or a C^{4+} central ion are unacceptable.

A. A. ELDRIDGE.

Rectilinear diameter of ethylene. E. MATHIAS, C. A. CROMMELIN, and H. G. WATTS (Ann. Physique, 1929, [x], 11, 343–353).—The densities of liquid ethylene and of the saturated vapour were determined over a wide range of temperature and tabulated together with the calculated diameters. The observed and calculated vapour tensions and latent heat of vaporisation are similarly tabulated and good general agreement between the two sets of values is obtained.

N. M. BLIGH.

Absolute velocity of a water molecule emitted on the dehydration of a crystalline hydrate. A. S. PREDVODITELEV (Z. Physik, 1929, 54, 159–160).—A correction of earlier calculations (cf. this vol., 21).

J. W. SMITH.

Scattering of X-rays by graphite. W. EHRENBERG (Z. Physik, 1929, 53, 234–236).—Spectroscopic examination of X-ray scattering of graphite cannot confirm the results of Davis and Mitchell (A., 1928, 1168). No deviated lines are observed except the Compton line.

G. E. WENTWORTH.

Evaluation of Debye-Scherrer spectrograms. G. KETTMANN (Z. Physik, 1929, 53, 198–209).—A

graphical method is given for the evaluation of the grating constants in the Debye-Scherrer spectrograms. With substances giving only small interference the accuracy of the evaluation is increased by using radiations of several frequencies.

G. E. WENTWORTH.

Occurrence of structure lines at the *K*-absorption band edge of bromine. H. T. MEYER (Wiss. Veröff. Siemens-Konzern, 1929, 7, [2], 101–107).—At the *K*-absorption band edge of bromine obtained by absorption with sodium or potassium bromate in the solid state or in solution, structure lines have been recorded which do not appear when sodium or potassium bromide is used as the absorbing material. This is considered to be a striking example of the effect of chemical linking on the *K*-absorption, since the atomic number (35) is so high. The wave-length differences of the lines correspond with 39.6, 119.6, and 241.4 volts.

R. A. MORTON.

Superposed X-radiations. *J*-Phenomenon. IX. C. G. BARKLA and M. M. SEN GUPTA (Phil. Mag., 1929, [vii], 7, 737–742).—Previous results of Barkla and Mackenzie on the *J*-discontinuities produced by the superposition of X-ray beams from separate sources have been confirmed by superimposing X-ray beams scattered from paper or paraffin wax. Precautions were taken to ensure that the two scattered beams did not become superimposed until in close proximity to the aluminium absorbers employed to detect the displacement of the *J*-discontinuities.

A. E. MITCHELL.

X-Ray diffraction haloes in aqueous solutions of electrolytes. H. SHIBA and T. WATANABE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 187–192; cf. Krishnamurti, A., 1928, 1079).—Results were tabulated for solutions of various concentrations of sulphuric acid, the hydroxides of lithium, sodium, potassium, and ammonium, the chlorides and nitrates of lithium, sodium, potassium, beryllium, and aluminium, and the chlorides of ammonium and magnesium. The electrolytes could be classified into three groups having, respectively, a halo approximately the same size as that of water, a halo which expands with concentration, and a halo which contracts as concentration increases. The halo contraction seemed to be closely related to the formation of a complex of the cation with water. In general, the diffraction at small angles becomes weak as the concentration is increased.

N. M. BLIGH.

Total reflexion of X-rays from nickel films. II. H. W. EDWARDS (Physical Rev., 1929, [ii], 33, 463–466; cf. A., 1927, 921; this vol., 123).—The critical angle for thin nickel films sputtered on platinum which was sputtered on a glass support was found to decrease logarithmically with increasing thickness of nickel film except for an increase with the thinnest films. Results indicate that total reflexion is not purely a surface phenomenon.

N. M. BLIGH.

Diffraction of X-rays in liquids and liquid mixtures. H. F. HERTLEIN (Z. Physik, 1929, 54, 341–346).—The X-ray diffraction in mixtures of methyl, ethyl, and propyl alcohols with water has been investigated. The results indicate that the effect is of an intermolecular nature, as supposed by

Stewart, Morrow, and Skinner (A., 1927, 1015; 1928, 224).
J. W. SMITH.

Spectral analytical determination of readily fusible and liquid substances by means of Lenard tubes. O. EISENHUT and E. KAUPP (Z. Physik, 1929, 54, 427—432).—Details are given of a convenient method of excitation of characteristic X-rays by means of cathode rays from a Lenard tube, schemes for eliminating the usual experimental errors being fully described. This method has been tested with iron, selenium, and gallium, the wave-lengths of the *K* series of the last-named element, hitherto uncertain, having been measured carefully. The extreme sensitivity of the method is illustrated by measurements on iron with a very small admixture of mercuric oxide.
J. W. SMITH.

Fine structure of the normal scattered molybdenum $K\alpha$ -radiation from graphite. D. COSTER, I. NITTA, and W. J. THIJSEN (Nature, 1929, 123, 642).—The experiments of Davis and Mitchell (A., 1928, 1168) have been repeated, using the photographic method, but no difference between the structure of the primary radiation and that of the "undisplaced" scattered line was detected. If there should exist in the X-ray spectrum something analogous to the Raman effect in the optical region, it would be expected to give rise, not to lines, but to a continuous spectrum.
A. A. ELDRIDGE.

Violation of the selection principle for the principal quantum number. S. IDEI (Nature, 1929, 123, 643).—New measurements in the *L*-series for tantalum, tungsten, platinum, and gold give values of ν/R more accurate than those recorded by Thibaud and Soltan (A., 1927, 1000; 1928, 339). It appears that the doublets found by these authors may be due to transitions $N_{IV} N_{VI}$ and $N_V N_{VII}$.
A. A. ELDRIDGE.

Measurement of the $K\alpha$ line of carbon. C. E. HOWE (Proc. Nat. Acad. Sci., 1929, 15, 251—253).—In view of previous divergent values the wave-length of the $K\alpha$ line of carbon was determined accurately by an improved method. An unweighted mean value of 44.60 correct to 0.04 Å. was obtained.
N. M. Blich.

Densitometric measurements of the $K\alpha$ line of carbon. C. B. BAZZONI, FAUST, and WEATHERBY (Nature, 1929, 113, 717).—Separation of components has been accomplished for the $K\alpha$ lines of carbon (four principal components, 44.2, 42.0, 45.4, 46.15 Å.) and boron.
A. A. ELDRIDGE.

Crystal structure of some binary compounds of the platinum metals. L. THOMASSEN (Z. physikal. Chem., 1929, B, 2, 349—379).—A number of binary compounds of the platinum metals and antimony, tellurium, selenium, and sulphur were prepared and their crystalline structure was investigated by the powder method. The compounds were classified into three groups according to their structure. The pyrites group contains five new compounds: osmium ditelluride, OsTe_2 ($a=6.369\pm0.003$ Å.), osmium diselenide, OsSe_2 ($a=5.933\pm0.002$ Å.), ruthenium ditelluride, RuTe_2 ($a=6.360\pm0.002$ Å.), ruthenium diselenide, RuSe_2 ($a=5.921\pm0.002$ Å.), and platinum

diantimonide, PtSb_2 ($a=6.428\pm0.003$ Å.). Systems with the compositions OsTe , OsSe , RuTe , and RuSe are shown to be mixtures of the corresponding di-compounds with the metal. The second group, cadmium iodide type, contains palladium ditelluride, PdTe_2 ($a=4.028\pm0.003$ Å.; $c=5.118\pm0.004$ Å.), platinum ditelluride, PtTe_2 ($a=4.010\pm0.004$ Å.; $c=5.201\pm0.005$ Å.), platinum diselenide, PtSe_2 ($a=3.724\pm0.004$ Å.; $c=5.062\pm0.004$ Å.), platinum disulphide, PtS_2 ($a=3.537\pm0.004$ Å.; $c=5.019\pm0.005$ Å.). It was possible to prepare only one member of the series containing palladium, viz., palladium ditelluride, PdTe_2 . The third group, nickel arsenide type, contains palladium monotelluride, PdTe ($a=4.127\pm0.004$ Å.; $c=5.663\pm0.005$ Å.). Since there is a certain analogy between the structure of these compounds and that of the ferrous metals, it might be expected that they would possess ferromagnetic properties. On testing with a bar magnet, and with an electromagnet at liquid air temperature, no positive results could be obtained. Further compounds, similar to the above, have also been tested, and whilst weak para- or dia-magnetism was found there was no indication of ferromagnetism.
A. J. MEE.

X-Ray diagram of native cellulose. K. R. ANDRESS (Z. physikal. Chem., 1929, B, 2, 380—394).—The intensities of points on the X-ray diagram of native cellulose are examined. The intensities calculated from the position of the atoms in Meyer and Mark's model of the cellulose molecule are in satisfactory agreement with those actually observed.
A. J. MEE.

Ionic arrangement. H. J. KIST (Rec. trav. chim., 1929, 48, 310—311).—Calculations are made of the positions assumed by ions arranged around a positive nucleus. With three negative ions, the positions will be at the apices of an equilateral triangle in a great circle, with four, at the corners of a sphenoid of tetrahedral type. An octahedral arrangement is found in the case of six ions, and with eight ions positions are occupied at the corners of a tetragonal trapezohedron which is so truncated that eight corners are produced.
F. G. TRYHORN.

Imperfections of crystals. F. ZWICKY (Proc. Nat. Acad. Sci., 1929, 15, 253—259).—Theoretical. It is shown that the discrepancy between the theoretical and experimental values for the breaking strength of dry crystals can be satisfactorily accounted for by the presence of microscopic cracks in the surface of the crystals and occurring between the blocks or "mosaics" of the crystal, in accordance with Smekal's views (cf. A., 1927, 192). This cracking is shown to be connected with the surface energy, and the shape and dimensions of the cracks can be deduced approximately. The theory explains the fact that the theoretical value of the breaking strength can be approached under suitable circumstances and surface conditions, and its bearing on crystal growth, chemical imperfections, and the absorption of gases by metals is considered.
N. M. Blich.

X-Ray study of surface or interfacial orientations by the tangential drop method. J. J. TRILLAT (J. Phys. Radium, 1929, [vi], 10, 32—43).—

The basis of the method is that a pencil of X-rays suffers diffraction at the surface of a drop. As this surface is curved, the same effect is obtained as when the rays are diffracted by a crystal which is turned slowly about an axis, except that all the diffraction rays are obtained simultaneously. This method can be applied to solid or liquid drops, surrounded either by air or by another liquid. With a layer of fatty acid on a drop of mercury it is found that the film of attack, composed of the mercury salt, consists first of a layer of molecules with their $\cdot\text{CO}_2\text{Hg}$ groups anchored to the mercury and the rest of the chain standing up. The next layer has its methyl groups adjacent to the methyl groups of the first layer and its $\cdot\text{CO}_2\text{Hg}$ adjacent to the $\cdot\text{CO}_2\text{Hg}$ of the third layer, and so on. It is also concluded that the carbon atoms in the fatty acid chain have a zig-zag formation and that the chains themselves are slightly inclined to the normal to the surface of the drop. The solid-air interfaces of some long-chain compounds have been examined by allowing a drop of the melted substance to solidify by slow cooling. It is found that the surface layer of the drop consists of perfectly oriented molecules, similar to the surface of contact with glass but probably with the methyl groups outermost. The modifications which lead oleate undergoes with change of temperature have been investigated.

J. L. BUCHAN.

Possible dissymmetry of corrosion figures obtained by an active isotropic liquid. L. ROYER (Compt. rend., 1929, 188, 1176—1178).—The etching effects of malic, aspartic, gluconic, camphoric, glyceric, pyruvic, and mucic acids on a cleavage plane of calcite parallel to the reticular plane $p(100)$ were examined. When the acids were optically active the corrosion figures were dissymmetrical with respect to the plane of symmetry P normal to the face under observation; when the liquids were inactive the figures were perfectly symmetrical (cf. Herzfeld and Hettich, A., 1926, 889).

J. GRANT.

Single crystals of silver. E. W. R. STEACIE and F. J. TOOLE (J. Amer. Chem. Soc., 1929, 51, 1134—1135).—Very pure silver which has been fused and kept just below the m. p. for several days and then cooled very slowly dissolves non-uniformly in dilute nitric acid, gradually assuming the shape of an octagonal prism. The silver must not come into contact with oxygen during the operations. The crystal form of the prism is briefly described.

S. K. TWEEDY.

X-Ray investigation of the internal stress in carbon steels. S. SEKITO (Sci. Rep. Tohoku Imp. Univ., 1928, 17, 1227—1236).—Lattice distortion in carbon steels containing 0.1, 0.3, and 0.5% C as the result of cold-drawing from 3.0 to 0.67 mm. diameter was determined from the broadening of the spectral lines. The maximum variation in the lattice parameter was 0.4%, corresponding with an internal stress of 84 kg./mm.², which is slightly less than the tensile strength of these steels.

C. J. SMITHELLS.

Crystal structure of strontium and barium. F. EBERT and H. HARTMANN (Z. anorg. Chem., 1929, 179, 418—420).—Strontium crystallises in the cubic system, with a face-centred lattice having a 6.05 Å.

Barium also crystallises in the cubic system, but the lattice is space-centred, with a 5.01 Å.; the atomic radii are: strontium, 2.135 Å., barium, 2.17 Å.

H. F. GILLBE.

Crystal structure of tetraethylammonium iodide. R. W. G. WYCKOFF (Z. Krist., 1928, 67, 550—554; Chem. Zentr., 1928, ii, 2221).—Tetraethylammonium iodide has a 8.87, c 6.95 Å.; the unit cell contains two molecules of NET_4I .

A. A. ELDRIDGE.

Crystal structure of titanium monoxide. H. BRAKKEN (Z. Krist., 1928, 67, 547—549; Chem. Zentr., 1928, ii, 2220).—The atomic lattice is face-centred cubic, a 4.235±0.005 Å.

A. A. ELDRIDGE.

Crystal structure of some rhombic compounds MX_2 . H. BRAKKEN and L. HARANG (Z. Krist., 1928, 68, 123—138; Chem. Zentr., 1928, ii, 2219).—Lead chloride has a 4.49, b 7.66, c 9.15 Å.; axial ratio $a:b:c=0.586:1:1.194$. Lead bromide has a 4.70, b 7.98, c 9.47 Å.; $a:b:c=0.589:1:1.186$. In both cases the unit cell contains four molecules of PbX_2 ; space-group V^{10} . The structure is discussed. Mercuric chloride has a 4.30, b 5.93, c 12.66 Å.; $a:b:c=0.7255:1:2.1336$. The unit cell contains four molecules of HgCl_2 ; space-group V^{10} . The structure is considered to resemble that of the lead halides.

A. A. ELDRIDGE.

Distribution of foreign substances in single crystals of zinc. M. STRAUMANIS (Z. anorg. Chem., 1929, 180, 1—10).—Single crystals of zinc deposited from molten zinc containing cadmium possess a banded structure owing to the simultaneous separation of cadmium in layers parallel to the basal faces of the crystals. There is also a slight separation in a perpendicular direction, showing that the cadmium forms a network. With as little as 0.2% Cd this structure can still be detected, so that, contrary to the findings of Rosbaud and Schmid (A., 1925, ii, 488), it must be concluded that even this small amount of cadmium does not form a mixed crystal. The cleavage of the crystals indicates that the cadmium assumes the same orientation as the zinc, and forms an integral part of the lattice. Aluminium, bismuth, magnesium, and tin behave in the same way as cadmium.

R. CUTHILL.

Crystal structure of thin metallic films. (Mlle.) S. DEMBINSKA (Z. Physik, 1929, 54, 46—52).—Employing Bragg's method, the crystal structure of thin films (7—18 μ thickness) of platinum, copper, and nickel crystals formed by cathodic or thermal sputtering have been investigated. The films show definite orientation, but there is a dispersion of the reflexion line of the (111) plane, the magnitude of which depends on the nature of the plate supporting the metallic film.

J. W. SMITH.

Recrystallisation of single crystals of aluminium. II. Orientation of the crystals formed by recrystallisation under strong deformation. W. G. BURGERS and J. C. M. BASART (Z. Physik, 1929, 54, 74—91; cf. this vol., 384).—If single aluminium crystals are stretched until they are one fourth their original thickness and then heated for a short time at 600°, the orientation of the crystals then formed

shows a statistical anisotropy. The variation of this orientation with the treatment given to the crystals has been studied by stereoscopic X-ray spectrograms.

J. W. SMITH.

Anomalous after-effect with quartz. H. SÆGUSA and S. SHIMIZU (*Nature*, 1929, 113, 713—714).—An anomalous after-effect in the apparent resistivity of quartz is ascribed to some property of the atomic lattice.

A. A. ELDRIDGE.

Change of electrical conductivity in strong magnetic fields. I. Experimental results. II. Analysis and interpretation of the experimental results. P. KAPITZA (*Proc. Roy. Soc.*, 1929, A, 123, 292—341, 342—372).—I. By means of an improved form of the apparatus previously employed for measuring the change of resistance of bismuth crystals in magnetic fields up to 300 kilogauss (A., 1928, 825), a study has been made of the change of resistance in a transverse field at the ordinary temperature, at the temperature of solid carbon dioxide and ether, and at the temperature of liquid nitrogen for the following metals: lithium, sodium, copper, silver, gold, beryllium, magnesium, zinc, cadmium, mercury, aluminium, gallium, indium, thallium, graphite, germanium, tin, lead, titanium, zirconium, thorium, arsenic, antimony, bismuth, vanadium, tantalum, chromium, molybdenum, tungsten, tellurium, manganese, iron, nickel, palladium, platinum; and for a gold-silver alloy and a copper-arsenic alloy (Cu-As). Measurements were also made in a parallel field with copper, cadmium, aluminium, gallium, and molybdenum. The metals were very highly purified. The influence of impurities on the phenomena studied was found to be very marked, particularly in the lighter elements, and invariably reduced the change of resistance. All the curves showing change of resistance with magnetic field, except those for iron and nickel (the latter being the only metal studied in which a decrease of resistance was observed instead of an increase), are exactly similar in character. The increase of the resistance at the beginning is proportional to the square of the magnetic field, but later is directly proportional to the field. This change from the square to the linear law takes place gradually after a critical field H_k which for different substances ranges from 5 to 250 kilogauss. The linear part of the curve appears to be independent of the crystalline state of the metal, and to be related to the position of the element in the periodic table. The results are compared with those of previous investigators. The suggestion that the strongly diamagnetic substances give a larger change of resistance (de Haas, *Proc. Roy. Acad. Amsterdam*, 1914, 16, 1110) is not confirmed.

II. A general theory is developed of the phenomenon of change of resistance in a magnetic field. It is assumed that the change of resistance follows a linear law which is fully established only when the field is well above the critical value (H_k), and is masked below H_k by an initial disturbance, already existing in the metal, equivalent to that produced by a magnetic field distributed at random in the conductor. When the outside field is applied, the disturbance causing the increase of resistance is now the vectorial sum of these two disturbances and the increase of resistance is pro-

portional to this sum. Expressions are derived which represent the experimental facts within the limits of error, and by means of which the "ideal" resistance

may be separated from the "additional" resistance ΔR_0 produced by internal disturbances. R_i is found to be a constant for a given temperature, independent of the physical and chemical state of the metal, but diminishes rapidly with fall of temperature, whilst ΔR_0 is independent of the temperature but is affected by the physical state of the conductor, having a higher value in a hard-drawn wire than in an annealed wire. ΔR_0 is identified with the "residual" resistance (Kamerlingh Onnes) which is observed near the absolute zero. A comparison of ΔR_0 for the superconductors mercury, thallium, tin, lead, and indium with the resistance near the threshold of superconductivity shows that the values lie within the limits of the variation of the resistance at the threshold observed by Kamerlingh Onnes for different specimens of the same superconductor. This indicates that the phenomenon of superconductivity consists in the disappearance of the additional resistance, the resistance of the conductor then being equal to R_i . It is concluded that superconductivity is a general phenomenon in all metals, but is masked by the additional resistance which disappears at very low temperatures in certain metals.

L. L. BIRCHMASHAW.

Susceptibility and change in resistivity of metals in a magnetic field. F. BLOCK (*Z. Physik*, 1929, 53, 216—227).—The paramagnetic behaviour of metals is investigated from the point of view of the conception that the so-called "free electrons," responsible for the electrical conductivity, are not free but move in a periodic field of force. It is shown also that the change of resistance in a magnetic field can be formulated to the correct order of magnitude if the spin orientation is considered with the Sommerfeld formula for the periodic field of force.

G. E. WENTWORTH.

Influence of grain-size on the magnetic properties of iron. O. VON AUWERS (*Wiss. Veroff. Siemens-Konzern*, 1929, 7, [2], 197—209).—The fall in watt/kg. for electrolytic iron decreases as the cube root of the grain-size, but this relationship is strongly influenced by heat-treatment. Grain-size also affects coercivity forces, remanence, and permeability curves, but saturation value and specific resistance are uninfluenced. The role of grain-size is less important after heating in hydrogen, and is further reduced by heating in a moderately good vacuum (oxygen). Chemical effects between oxygen and carbon are important. The influence of grain-size on magnetic properties is essentially secondary in nature, depending on surface contamination by oxides and carbides.

R. A. MORTON.

Method of measuring the electrical resistances of alloys. A. L. NORBURY (*Phil. Mag.*, 1929, [vii], 7, 662—669).—The method consists in determining the electrical resistance between the equator of a ball or the shoulder of a 90° cone of a metal, such as steel or copper, and the plane surface of the metal under test into which it is pressed by loading, and measuring the diameter of the impression so made. Calibration curves are made by measuring these

quantities with combinations of metals of known resistance, and these are employed to give the results for other metals. Contact resistances are eliminated by the etching of the surfaces to be brought into contact. The method has the advantage that it can be used in the determination of the resistances of materials of which only small pieces are available. The plane surface required need not exceed an area of 5 by 0.5 mm.

A. E. MITCHELL.

Preparation, optical and magneto-optical properties of very thin iron layers. M. CAU (Ann. Physique, 1929, [x], 11, 354—449).—The transparency, reflecting power, optical and geometric thickness, and Faraday and Kerr effects were studied for thin iron films prepared by distillation in a vacuum and by cathodic deposition. The optical effects were calculated theoretically and plotted as functions of film thickness. Comparison of calculated and experimental results shows, in the case of deposited iron, a general agreement, the constants being the same as for iron in bulk. In the case of the distilled films the results, as well as those for the magneto-optical effects, are somewhat discordant, and the classical optical theory of metals is apparently not applicable. The reflexion effects can be calculated from the transmission effects on simple theoretical grounds and show good agreement with experimental results. It is concluded that the deposited films, in spite of discrepancies due to differences of crystal structure, are more regular than the distilled films and approximate more closely to iron in bulk. Classical optical theory is applicable to a close approximation. Distilled films, which are more allied to the amorphous state, and of complex structure, give different results.

N. M. BUGH.

Fundamental law of paramagnetic magnetisation of a crystal, and the law of paramagnetic rotatory dispersion. J. BECQUEREL and W. J. DE HAAS (Compt. rend., 1929, 188, 1156—1158).—Ladenburg's formula expressing the rotation in terms of the wave-lengths of the activated absorption bands (A., 1927, 493) is confirmed in the case of tysonite (A., 1928, 823) between 4.21° and 1.95° Abs. to within 0.1%, and also for parisite. It is concluded that the high paramagnetic rotation of tysonite compared with its diamagnetic rotation is due to the Ce^{+++} ion, the hyperbolic tangent law established in this case (*loc. cit.*) being an indication of the reversal of the sense of the magnetic moment.

J. GRANT.

Magnetisation of single crystals of cobalt. S. KAYA (Sci. Rep. Tohoku Imp. Univ., 1928, 17, 1157—1177).—Large single crystals of cobalt were prepared by slow cooling through the transformation point at 470° , and two discs 4.5 mm. in diameter were cut so as to present (0001) and (1010) planes, respectively. In the (1010) plane magnetisation was easy in the [0001] direction but difficult in the [1010] direction, the maximum permeabilities being 380 and 4, respectively. The parallel and perpendicular components of magnetisation vary with a period of 180° in this plane. In the (0001) plane magnetisation was difficult in the directions of both the principal axes [1010] and [1120]. The saturation value for a single crystal rod having its axis parallel to direction of easy magnetisation [0001] was 1422 at 26° . The results

are in agreement with the theory of Honda and Okubo (*ibid.*, 1926, 15, 449).

C. J. SMITHELLS.

Connexion between size of crystal nucleus and magnetic properties of pure nickel. G. J. SIZOO (Z. Physik, 1929, 53, 449—457).—The conditions of recrystallisation of nickel are studied. The manganese content must be below 0.2% before recrystallisation phenomena may be produced by mechanical and thermal processes. Twin crystals then form easily. A study of the magnetic properties in connexion with the size of the crystal nucleus gives the same results as were obtained with iron.

G. E. WENTWORTH.

Influence of pressure from all sides on metallic conductivity of low temperature. H. J. SEEMANN (Physikal. Z., 1929, 30, 256—258).—The pressure coefficient γ , where $\gamma = \Delta w/w \cdot p$, Δw being the change of the resistance w under a pressure p , has been given by Onnes and Beckmann (Comm. Leiden, 1912, 312) as $\gamma = -17 \times 10^{-16}$ at -252.7° and -22.5×10^{-6} at -183° , whilst Lisell found $\gamma = -14.4 \times 10^{-6}$ at 0° , the metal being lead. In the present work, the pressure coefficient for copper has been determined over the range 50—150 kg./cm.² and at 0° $\gamma = -2.14 (\pm 0.013) \times 10^{-6}$, whilst at -195° $\gamma = -5.17 \times 10^{-6}$, the extreme determinations being 20% from the mean. It is probable that reduction of temperature will, in general, increase the pressure coefficient of the resistance of a metal.

R. A. MORTON.

Crystal structure and ferromagnetism. W. SCHMIDT (Physikal. Z., 1929, 30, 259—261).—Temperature discontinuities in various physical properties of iron conform with considerable accuracy with the relation $T = nT_s/m$, T_s being the m. p. of iron (ca. 1803° Abs.), $m = 14$, n being an integer less than 14, and T corresponding with an experimental discontinuity. The temperature 901.6° Abs., for instance, corresponds with 883° Abs., at which point the line expressing the variation between atomic distance and temperature for α - and δ -iron is intersected by the extrapolated similar line for γ -iron. There do not appear to be experimental data corresponding with $n = 1, 5$, or 6 . The expression may be of more general significance to critical temperatures of metals; e.g., tin melts at 504.9° Abs., and discontinuities at 434° and 291° are consistent with $m = 14$.

R. A. MORTON.

Coercive power. I. Coercive power and mechanical hardness. A. KUSSMANN and B. SCHARNOW (Z. Physik, 1929, 54, 1—15).—The dependence of the coercive power (magnetic hardness) on the mechanical hardness and on the structure of alloys has been investigated. It has been established that in solid solution (mixed crystals) in which mechanical hardness, electrical resistance, etc. are considerably higher than with the pure metals, the coercive power is only slightly changed, and that no direct relation with the mechanical hardness of the alloy exists. In heterogeneous mixtures the coercive power is always much higher, independently of the mechanical hardness. This is attributed to the tension set up by contraction of the ferromagnetic material in the mixture.

J. W. SMITH.

Piezo-electric effect of diamond. W. A. WOOSTER (Min. Mag., 1929, 22, 65—59).—An even

pressure of about 300 g. was applied by means of an electro-magnet on an octahedral face of diamond. The results show that, within the limits of error of the experiment, diamond is not piezo-electric, the electrical charge developed being less than 0.005 of that obtained when a plate of quartz cut perpendicular to an electric axis was used.

L. J. SPENCER.

Optical activity of quartz perpendicular to the optic axis. G. SZIVESSY and C. SCHWEERS (Ann. Physik, 1929, [v], 1, 891—947).—First, the results of the crystal lattice theory as applied to the problem are given. The optical behaviour of any non-absorbing, active crystal is known if the position of the symmetry-axis system, the principal refractive indices, and the components of the gyration tensors along the optical symmetry axes are known. The laws relating to the propagation of light in non-absorbing, active crystals are collected. The components of the gyration tensors for trigonal enantiomorphic crystals are worked out. For a crystal of this class the gyration surface is an ellipsoid or a hyperboloid with the optic axis as axis of rotation. The numerical values for the components of the gyration tensors are obtained for α -quartz. The results do not agree with those of Voigt or of Wever, for the methods used by these workers are in error. The experimental method and apparatus are described. The component of the gyration tensor perpendicular to the optic axis for α -quartz is very small. The gyration surface is a very elongated ellipsoid with a vanishingly small equatorial diameter. A critical examination of the methods of Voigt and Wever is given, and the sources of inaccuracy are pointed out.

A. J. MEE.

Behaviour of a single crystal of zinc subjected to alternating torsional stresses. H. J. GOUGH and H. L. COX (Proc. Roy. Soc., 1929, A, 123, 143—167).—A single zinc crystal was subjected to alternating torsional stressing. The principal slip plane was the basal (0001) plane, the direction of slip being that of the most highly stressed (shear stress) primitive direction contained by the basal plane. The specimen showed a clearly defined "visible slip limit" at a range of stress between ± 0.87 and ± 0.98 ton/inch², and a limiting range of resolved shear stress between ± 1.0 and ± 1.3 tons/inch². The twinning plane was identified as first order pyramidal (0112 type), producing a twinned basal plane making an angle of $94^\circ 5'$ with the original basal plane. The observed twin formation occurs as a result of the previous basal plane slip, and is not due to slip on the twinning plane. The particular twinning planes (of the six available sets) operative are determined principally by the direction of slip on the basal plane and probably by normal stress considerations. It is shown that twinning can be accomplished by small atomic translations confined to a plane normal to the twinning plane. Fracture consisted of one main crack which followed three directions. It is shown clearly that the prismatic planes are neither slip nor cleavage planes, and it is considered probable that what have been interpreted in the past as cleavages on prismatic planes have been fractures along the twinned basal planes.

L. L. BIRCUMSHAW.

Influence of finely-divided particles on the coercive force. W. KOSTER (Z. anorg. Chem., 1929, 179, 297—308).—The size and arrangement of finely-divided particles in a ferromagnetic alloy have considerable influence on its magnetic properties. Experiments with iron-carbon and iron-nitrogen mixtures are described.

H. F. GILLBE.

Stretching of cadmium crystals. W. BOAS and E. SCHMID (Z. Physik, 1929, 54, 16—45).—The solidification of metallic crystals is discussed from the point of view of the critical limiting tension of plastic deformation. X-Ray investigations on stretched cadmium crystals show that the velocity of crystallisation exerts a very important influence on the readiness of slip along the basic translational plane. The diminution of the critical tension by tempering, the energy change on slipping, and mechanical twin formation were also investigated and the change in the space lattice of cadmium and zinc crystals on stretching was deduced.

J. W. SMITH.

Crystallographic slip on stretching zinc and cadmium. G. MASING (Wiss. Veroff. Siemens-Konzern, 1929, 7, [2], 210—216).—Twin formation occurs to a considerable extent when zinc and cadmium are stretched. The effect can be followed in relation to the longitudinal extension.

R. A. MORTON.

Electrical conductivity of vapours of salts. H. QUERENGASSER (Z. Elektrochem., 1929, 35, 199—206).—Various forms of apparatus are described for the measurement of the conductivity of vapours of salts, e.g., mercuric, ammonium, lithium, and ferric chlorides, cadmium iodide, and carbon tetrachloride. Curves are given showing the relationship between current and the *P.D.* applied, and also the diminution with time of current which can be passed through mercuric chloride vapour when subjected to a constant *P.D.* The surface of the glass vessel in which the vapour was enclosed, and also the conductivity of the glass used, had an important influence on the conductivity of the vapours.

H. T. S. BRITTON.

Change of conductivity of cuprous oxide. H. KOSTER (Z. Physik, 1929, 54, 367—371).—The difference in conductivity of a cuprous oxide film with polarity has been investigated by using the oxidised copper strip as one electrode and another pure copper strip as the other. The non-symmetrical conductivity of the cuprous oxide film does not appear when the latter is produced by heating the copper strip, excepting to a slight extent at the mid-point of the copper strip, the most strongly heated part. It is concluded that the cuprous oxide crystals orient themselves as they grow out of the mother copper and that these crystals conduct more freely in one direction than in the other. The variation in the resistance of such films with temperature has also been investigated over the range -20° to $+100^\circ$.

J. W. SMITH.

Variation of density and refractive index [of liquids] with the temperature. W. HERZ (Z. anorg. Chem., 1929, 180, 159—160).—The expansion coefficient, α , and the temperature coefficient of the refractive index, β , of 23 liquids have been calculated at two temperatures, t and t_1 , which are $8/12$ and $7/12$, respectively, of the corresponding critical temperature,

by means of the relationships $\alpha = [1/(t_1 - t)] [(d - d_1)/d_1]$ and $\beta = [1/(t_1 - t)] [(n - n_1)/n_1]$ where d is the density and n the refractive index. The ratio $\alpha : \beta$ has a value in the neighbourhood of 3 for most of the liquids.

O. J. WALKER.

Measurement of refractive index of water between wave-lengths of 23 and 73 cm. E. FRANKENBERGER (Ann. Physik, 1929, [v], 1, 948—962).—An apparatus is described for measuring the refractive index of water for electric waves in the wave-length range 23—73 cm. The accuracy of the method is discussed, and it is shown that the use of Drude's second method is attended with a systematic error, which in the case of water amounts to 3—3.5 parts per thousand. The results with distilled water show that the index is practically constant over the range examined. In order to verify earlier work on the anomalous dispersion of sodium silicate solutions (A., 1927, 295), experiments were made with a colloidal solution of silicic acid, a solution of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 2\text{H}_2\text{O}$), a solution of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$), and dilute sodium hydroxide solution. These solutions were examined only in the range 50—60 cm. No bands of anomalous dispersion were found.

A. J. MEE.

Refractive index of sodium vapour and width of D_1 in absorption. S. A. KORFF (Physical Rev., 1929, [ii], 33, 584—588).—A continuation of the work of Stewart and Korff (cf. A., 1928, 1310). The variation of refractive index and the relation of dispersion to the width of the D lines in absorption are found to agree approximately with the classical formulæ. These optical methods give a value of the order 10^{-13} cm. for the radius of the electron.

N. M. BLIGH.

Specific heats of acetone, methyl, ethyl, and n -propyl alcohols at low temperatures. S. MITSUKURI and K. HARA (Bull. Chem. Soc. Japan, 1929, 4, 77—80; cf. this vol., 386).—The specific heats are recorded of the above substances at temperatures between 160° and 270° Abs., over which range an approximately linear relationship holds.

A description is given of the calorimeter system employed in which a Dewar vessel, containing light petroleum, cooled by the circulation of liquid air through a copper spiral, serves as a jacket to the calorimeter proper, a metal cylinder suspended in a brass tube, and heated by a manganin spiral. The cooling stream is cut off at the beginning of the experiment, and the true heating curve for the system is derived from the observed by making the assumption that the temperature of the Dewar jacket remains constant during the heating period.

F. G. TRYHORN.

Specific heat of superheated steam for pressures between 30 and 120 atm. and at saturation temperatures to 450°. O. KNOBLAUCH and W. KOCH (Naturwiss., 1929, 17, 269—270).—The c_p isobars in the c_p - t diagram have been determined at 30, 40, 60, 80, and 120 atm. over the range 225—450°.

R. A. MORTON.

Specific heats of some condensed gases between 10° Abs. and their triple points. K. CLUSIUS (Z. physikal. Chem., 1929, B, 3, 41—79).—

An apparatus for the measurement of the specific heats of condensed gases below 10° Abs. is described. The specific heats of nitrogen, oxygen, carbon monoxide, methane, and hydrogen chloride were determined from 10° Abs. down to their triple points. The results of other workers are in general agreement, but those of Giauque and Wiebe (A., 1928, 228) on hydrogen chloride show a systematic deviation lying outside the limits of experimental error, which must be ascribed to an error in their temperature scale. The heats of fusion of the gases were determined afresh. For methane a new transition point was found at 20.4° Abs. The lead resistance thermometer is described, and a table of its resistance ratios down to 9° Abs. is given.

A. J. MEE.

Heat capacities of ethyl and hexyl alcohols from 16° to 298° Abs. and the corresponding entropies and free energies. K. K. KELLEY (J. Amer. Chem. Soc., 1929, 51, 779—786).—The specific heats of ethyl alcohol (including the glacial form) and of hexyl alcohol are recorded. The m. p., molal heats of fusion (g.-cal.), molal entropies (g.-cal./1° at 25°), and molal free energies (g.-cal. at 25°) are, respectively, for ethyl alcohol: 158.5° Abs., 1200, 38.4, and —43,300, and for hexyl alcohol: 225.8° Abs., 3676, 68.6, and —41,700. Parks' conclusions on the entropy relations between members of a homologous series of saturated aliphatic compounds (A., 1926, 784) are qualitatively confirmed.

S. K. TWEEDY.

Heat capacities of isopropyl alcohol and acetone from 16° to 298° Abs. and the corresponding entropies and free energies. K. K. KELLEY (J. Amer. Chem. Soc., 1929, 51, 1145—1150).—The specific heat curve for acetone exhibits an irregularity at 126° Abs., indicating that a transition occurs in the crystals. The specific heat of liquid acetone passes through a minimum just above the m. p. The following molar quantities were determined for isopropyl alcohol and acetone, respectively: m. p., 184.67°, 176.62° Abs.; heat of fusion at m. p. (g.-cal.), 1284, 1366; entropy (g.-cal./1°) at 298.1° Abs., 43.0, 47.9; free energy (g.-cal.) at 298.1° Abs., —48100, —36700. The free energy and entropy for the thermal decomposition of isopropyl alcohol vapour are calculated (cf. A., 1928, 709).

S. K. TWEEDY.

Apparent influence of an electric field on the b. p. of benzene. J. W. SMITH (J.C.S., 1929, 788—791, cf. Baker, *ibid.*, 1928, 1051).—When an electric field is applied to benzene in a tube heated in an oil-bath, a thermometer in the liquid indicates an apparent rise of b. p., the vapour temperature remaining normal. This experiment is repeated and extended. The effect is considerably reduced by stirring, and is not observed when the tube is heated directly with a small flame (cf. Smits, A., 1928, 1189). The abnormality is attributed to superheating induced by the removal of charged nuclei from the system. No change in vapour pressure occurs when benzene is subjected to an electric field.

N. M. BLIGH.

Ebullioscopic paradox. A. BERTHOUD, E. BRINER, and A. SCHIDLOF (J. Chim. phys., 1929, 26, 149—151; cf. A., 1927, 1029).—A reply to Mazzuchelli (A., 1928, 128) and to Verschaffelt (Wis. en nat. Tijds., 1928, 4, 1).

C. W. GIBBY.

Solid helium at high temperatures. F. SIMON (Naturwiss., 1929, 17, 256).—The m. p./pressure curve of helium has been studied further (cf. this vol., 386, 497). The m. p. at 1800 kg./cm.² is 20° Abs., and at 36·90 kg./cm.², 32° Abs. Unless a critical transition region is approached, the theoretical reasoning which is valid up to 32° indicates that at 80° Abs. and the ordinary temperature, pressures of 15,000 and 100,000 kg./cm.², respectively, should effect solidification of helium.

R. A. MORTON.

Volatilisation at the cathode of the mercury arc light. E. KOBEL (Physikal. Z., 1929, 30, 233—235; cf. von Issendorf, this vol., 227).—The mercury lost from the cathode of a rectifier is accounted for by volatilisation distributed over the entire surface and not localised at the focal spot. If the movement of the focus is arrested the vaporisation decreases, since the change in the loss from the cathode is greater than can be ascribed to the cessation of sputtering. In order to test the hypothesis that the mean stationary surface temperature of the cathode is greater for a moving focus than for a steady focus, an experiment was carried out on the effect of a motionless jet of flame as compared with the same flame sweeping over a surface of water at a constant height. It was found that the rise in temperature and the loss of weight from a definite initial volume were both less for the stationary than for the moving jet. This experiment indicates that the mean surface temperature of the mercury cathode is the controlling factor. The rate of evaporation in the mercury surface at different temperatures apart from the focal spot has been compared with the loss at the focal spot as calculated by Gunther-Schulze. By means of efficient cooling, the volatilisation can be reduced to a small fraction of the amount calculated on the Gunther-Schulze basis, without materially affecting the electrical properties of the arc.

R. A. MORTON.

Upper limit of energy density and the degradation of gas at high temperatures. S. SUZUKI (Proc. Imp. Acad. Tokyo, 1929, 5, 64—67).—Mathematical. The equation of state of a gas in the state of degradation at high temperatures is derived, assuming the existence of an upper limit of energy density.

O. J. WALKER.

Statistics of Bose and Einstein and of Fermi and Dirac and the upper limit of energy density. S. SUZUKI (Proc. Imp. Acad. Tokyo, 1929, 5, 68—71).—Mathematical.

O. J. WALKER.

Thermal expansions of mercury and vitreous silica. F. J. HARLOW (Phil. Mag., 1929, [vii], 7, 674—685).—Various results of different observers for the coefficients of expansion of mercury and vitreous silica have been examined and the most probable values deduced. The most probable value of the linear coefficient of thermal expansion of vitreous silica is given by the expression $S_0' = \{66.3 - 3879/(t + 103)\} \times 10^{-8}$ or for the range 0—300° $V_t/V_0 = 1 + 10^{-8}\{93.6t + 0.7776t^2 - 0.003315t^3 + 0.000005244t^4\}$, where V_t is the volume of 1 c.c. at 0° measured at t° . Over the same temperature range the values for mercury fit two different curves. For the range 0—100°, $V_t/V_0 = 1 + 10^{-8}\{18153.8t + 0.7548t^2 + 0.001533t^3 + 0.00000536t^4\}$ and for the range 100—300° $V_t/V_0 = 1 + 10^{-8}\{17559.1$

$+ 369555/(634.7 - t)\}$. A table of values of V_t/V_0 for mercury is given.

A. E. MITCHELL.

Determination of vapour densities at the ordinary temperature. E. F. LINHORST (J. Amer. Chem. Soc., 1929, 51, 1165—1167).— w g. of liquid, mol. wt. M , are evaporated at the ordinary temperature in a vessel, volume v , connected by means of an oil manometer with another, similar, vessel, the pressures in the two vessels being equal and well below one atmosphere. If p is the pressure registered by the manometer, than $pvM = wRT$.

S. K. TWEEDY.

Vapour pressure at high temperatures. C. ZWIKKER (Physica, 1928, 8, 241—250; Chem. Zentr., 1928, ii, 2108).—In the vapour-pressure equation for high temperatures, $\log p = -A/T + B$, B has practically the same value for all metals. The relation $B = -\frac{1}{2} \log T + 3 \log \theta - 1/2.303 + 1.29 + 3/2 \log M$, where M is the mol. wt., $\theta = 136.1 \sqrt{m. p. \times (MV^{2/3})}$, and $\log T$ is a mean value for the temperature range concerned, gives for fifteen metals almost constant values for B (approx. 9.33). The mean value of B for 20 metals is 9.7.

A. A. ELDRIDGE.

Vapour pressure and vapour density of intensively dried ammonium chloride. W. H. RODEBUSH and J. C. MICHALEK (J. Amer. Chem. Soc., 1929, 51, 748—789; cf. A., 1928, 469).—The vapour pressure of ammonium chloride was measured at varying degrees of dryness over the temperature range 470—560° Abs. Intensive drying seems not to affect the vapour pressure, and the results are all reproduced to within 1% by the equation $\log p (\text{mm.}) = 10.1070 - 4402.1/T$. The vapour is probably completely dissociated under all conditions. The vapour density was measured by the Knudsen method, but the slowness of evaporation of the salt in a vacuum vitiated the results. The vapour densities measured by Stock's buoyancy method (A., 1924, ii, 405) indicated complete dissociation. A high-capacity mercury-vapour pump is described in which volatile matter is removed from the condensed mercury before it reaches the reservoir. An improved glass diaphragm manometer is also described.

S. K. TWEEDY.

Vapour pressures of ethyl selenide, tin tetramethyl, and lead tetramethyl. Y. TANAKA and Y. NAGAI (Proc. Imp. Acad. Tokyo, 1929, 5, 78—79).—The vapour pressures of these compounds have been measured by a statical method at 25° and 35°. The values of L/T coincide closely with those calculated from the revised rule of Trouton, showing that these liquids are all normal. Equations are given showing the relations between vapour pressure and temperature.

O. J. WALKER.

Hydrated aluminium silicates. II. Dehydration vapour pressure of kaolin. C. J. VAN NIEUWENBURG and H. A. J. PIETERS (Rec. trav. chim., 1929, 48, 406—416; cf. this vol., 280).—The vapour pressure of kaolin was determined at different temperatures and for different water content of the surrounding atmosphere. The dissociation pressure was found to be a function of the water content over the whole range. Temperature-pressure-water content diagrams were determined by three different methods.

A. FREEMAN.

One-component system silica. III. Stability regions of quartz, tridymite, and cristobalite. C. J. VAN NIEUWENBURG (Rec. trav. chim., 1929, 48, 402—405; cf. A., 1928, 709).—The stability regions of the different solid phases in the system silica were re-investigated by a new method using only 1% of lithium carbonate as a catalyst. The presence of tridymite and cristobalite was investigated by constructing thermal dilation diagrams. The stability regions of quartz, tridymite, and cristobalite as described by Fenner (A., 1913, ii, 133) were confirmed.

A. FREIMAN.

Isotonic liquids. F. A. H. SCHREINEMAKERS (Rec. trav. chim., 1929, 48, 393—401).—Theoretical. A generalised definition of isotonic liquids is given. Introducing a conception of osmotic water attraction the influence of temperature and pressure on this property is considered and the relation between f. p., vapour pressure, and osmotic pressure and isotonic liquids is deduced as well as the influence of temperature and pressure on isotonic liquids. A. FREIMAN.

Physical properties of liquids. I. Sonic interferometer. Velocity of sound in some organic liquids and their compressibilities. E. B. FREYER [with J. C. HUBBARD and D. H. ANDREWS] (J. Amer. Chem. Soc., 1929, 51, 759—770).—The velocity of sound in some organic liquids was measured at 10° intervals up to 50° by the method of Hubbard and Loomis. The sonic interferometer previously described (A., 1928, 828) was further developed with particular reference to temperature control, and to prevention of evaporation of the liquid and of contamination of the liquid with water vapour from the air. The velocity of sound is a linear function of temperature for each liquid; in the case of benzene, aniline, and α -bromonaphthalene slight divergences from linearity occur just before the m. p., indicating that orientation of some kind occurs before freezing. The adiabatic compressibilities are calculated from the results.

S. K. TWEEDY.

Propagation of sound in gases. D. G. BOURGIN (Phil. Mag., 1929, [vii], 7, 821—841).—Theoretical.

Internal resistance in instantaneous processes in relation to the entropy changes taking place in them. N. V. TANCOP (J. Russ. Phys. Chem. Soc., 1929, 61, 41—52).—The crystallisation of super-cooled liquids and of supersaturated solutions, the condensation of supersaturated vapours, and spontaneous chemical processes are considered from the point of view of the author's law of minimum change of entropy (cf. A., 1917, ii, 367; 1925, ii, 868) and are found to accord with it.

A. FREIMAN.

Atomic volume relations in certain isomorphous series. III. A. F. HALLIMOND (Min. Mag., 1929, 22, 70—76).—From the atomic volumes previously deduced (A., 1928, 107, 942) and the observed compressibilities of the metals, compressibilities for the alkali halides which are in agreement with observed values are calculated.

L. J. SPENCER.

Viscosity of liquids above their b. p. V. T. TITANI (Bull. Chem. Soc. Japan, 1929, 4, 68—75; cf. A., 1927, 1019).—The formula relating molecular fluidity to molecular volume and temperature, previ-

ously derived, has been tested further by its application to recent data for the viscosity of ethyl ether and acetone with satisfactory results.

F. G. TRYHORN.

Molecular dimensions of organic compounds. I. General considerations. T. M. LOWRY and A. G. NASINI (Proc. Roy. Soc., 1929, A, 123, 686—691).—With the object of determining if the persistent similarity of b. p. observed by Victor Meyer for benzene and thiophen and their derivatives extends also to their other properties, a comparative examination has been made of the physical properties of benzene and thiophen, toluene and 2-methylthiophen, and benzene and cyclohexane (the b. p. and f. p. of the last pair differing by less than 1°). In particular, a comparison has been made of the collision areas (A) of the molecules, as deduced from the viscosities of the vapours. Some striking regularities are observed. Thus a decrease in A of about 2 Å.² occurs on passing from benzene to thiophen and from toluene to 2-methylthiophen, whilst the replacement of H by Me is accompanied by a constant increment of 3 Å.² Also on passing from benzene to pyridine an increase of about 1 Å.² is found. A result of these small successive changes is to produce an almost complete identity in the values of A for pyridine and 2-methylthiophen. A marked similarity is also observed between other physical properties (*e. g.*, b. p. and f. p.) of these two compounds. In no case is the marked similarity of properties which Langmuir found in the case of "isosteric" substances observed; the vapours show regular increments rather than identity of properties, and the physical properties of the liquids and solids show even wider differences.

L. L. BIRCUMSHAW.

Molecular dimensions of organic compounds. II. Viscosity of vapours: benzene, toluene, and cyclohexane. III. Viscosity of vapours: thiophen and 2-methylthiophen, pyridine, and thiazole. A. G. NASINI (Proc. Roy. Soc., 1929, A, 123, 692—704, 704—713; cf. preceding abstract).—II. Details are given of a modified form of Rankine's apparatus for measuring the viscosity of vapours, by means of which the viscosities of benzene, toluene, and cyclohexane have been determined from 15° to 251°, 61° to 252°, and 46° to 205°, respectively. The values are found to be independent of the pressure over a fairly wide range. On plotting against the temperature, straight lines are obtained passing through the origin. The following values are deduced for Sutherland's constant S and the mean collision area A : benzene, $S=380$, $A=19.0$ Å.²; toluene, $S=370$, $A=21.8$ Å.²; cyclohexane, $S=330$, $A=22.3$ Å.² The values of A for benzene and toluene are compared with those deduced from Bragg's crystal models (cf. Mack, A., 1925, ii, 1124). Although the absolute values differ by about 50%, the differences are of similar magnitude.

III. The viscosity apparatus is further modified for use with substances available only in small quantities. By reducing the "condensation pressure" to zero, the viscosity of a vapour can be determined without also determining the vapour-pressure curves. It is shown both theoretically and experimentally that this method leads to trustworthy results. The viscosities

of thiophen, methylthiophen, and pyridine are recorded over the temperature ranges 20—245.5°, 50—250°, and 96—268°, respectively, and some provisional values are given for thiazole. When plotted against the temperature, the viscosity data fall on a straight line passing through the origin, with the exception of the thiazole values. The following values are deduced for S and A ; thiophen, $S=407$, $A=16.7 \text{ Å}^2$; methylthiophen, $S=400$, $A=19.9 \text{ Å}^2$; pyridine, $S=320$, $A=20.0 \text{ Å}^2$. The following new data are also recorded for 2-methylthiophen: $d_4^{20} 1.016$, b. p. 112.1°, m. p. -51°, $t_c 321^\circ$, $\eta_{25} 0.00667$ (of liquid), $\gamma_{24.5} 30.8 \text{ dynes/cm}^2$.

L. L. BIRCUMSHAW.

Gaseous mixtures. N. CARRARA (Nuovo Cim., 1928, 5, 224—233; Chem. Zentr., 1928, ii, 2217).—For mixtures of non-reacting gases the conditions of equilibrium are calculated from the original state of the individual gases and the conditions of preparation of the mixture.

A. A. ELDRIDGE.

Densities of butyric acid-water mixtures. J. GRINDLEY and C. R. BURY (J.C.S., 1929, 679—684).—The densities of butyric acid-water mixtures at 0°, 12°, 18°, 25°, and 34.94° have been determined. If the contraction due to mixing is plotted against the composition of the mixture, the resulting curve undergoes an abrupt change in slope at a point corresponding with a concentration of about 15% of acid. This is attributed to the presence of micelles in the mixtures, a conclusion which receives further support from a calculation of the partial specific volumes of the components.

R. CUTHILL.

Surface tension of mixtures of associated and non-associated liquids. K. M. STACHORSKY (Z. Elektrochem., 1929, 35, 185—186).—Equations are derived which permit the calculation of (1) the surface tension of a binary mixture, composed of an associated and a non-associated liquid, from the surface tensions of the components and the molecular proportions in which they are present, and (2) the degree of association of an associated liquid, from the surface tension for a mixture containing this and a non-associated liquid.

H. T. S. BRITTON.

Determination of parachors of substances in solution. D. L. HAMMICK and L. W. ANDREW (J.C.S., 1929, 754—759).—The parachors of binary mixtures of organic liquids are additively constituted of the parachors of the constituents, provided that these have surface tensions not differing by more than about 5—6 dynes/cm. If the difference is greater, there may be a slight divergence from the mixture rule, but the value for the pure solute can then be obtained by linear extrapolation.

R. CUTHILL.

Raoult's law. W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1929, 33, 361—370).—When Raoult's equation is applied to concentrated solutions, the mol. wts. are theoretically those of the two components in the condition of vapour. In the equation actually used by Raoult the mol. wt. of one of the components in the liquid phase is introduced, a fact which has not been recognised, since, in ideal solutions, the mol. wt. of liquid and vapour are supposed to be identical. In view of this, most of the experimental work dealing with variations from the law needs

revision. Consideration of the data of previous investigators for the systems methyl alcohol-water, methyl alcohol-acetone, water-acetone, and acetone-ether shows that the equation $(G_1/G_2)^n = K(p_2/p_1)^n$ where G_1 and G_2 are the weights of the components in the solution, and p_2 and p_1 are the vapour pressure and partial pressure of the pure solvent and solvent in the solution, respectively, holds over a wide range of concentration even for associated liquids. When $n=1$, and $K=M_1/M_2$, this equation reduces to Raoult's law. In the new equation n is a measure of the relative polymerisation and is independent of the units, whilst K depends mainly on the units used, the mol. wt. in the vapour phase, and the solubility. Dobson's data for ethyl alcohol and water (J.C.S., 1925, 127, 2866) have been calculated up to a mol. fraction of alcohol equal to 0.6 without recourse to variations from the gas laws or to the activity concept, and the distribution of acetone between water and methyl alcohol separated by a rubber membrane (Morton, this vol., 502) has also been calculated. Finally, it is pointed out that Henry's law and Nernst's distribution law should be expressed in mass and not volume concentrations as is usually the case.

L. S. THEOBALD.

Systems *n*-butyl alcohol-water and *n*-butyl alcohol-acetone-water. D. C. JONES (J.C.S., 1929, 799—813).—Investigation of the miscibility of *n*-butyl alcohol and water from the critical solution temperature (124.75°) to about -15° by the synthetic method shows that the solubility of the alcohol in water is minimal at about 52°, whereas the solubility of water in the alcohol decreases with falling temperature throughout; there is no indication of the existence of a lower critical solution temperature. By means of similar experiments with water and mixtures of the alcohol with acetone, the binodal surface for the ternary system between the same temperatures has been obtained, and here also no tendency for the formation of closed solubility rings is observed. The ternary critical solution temperatures for water, *n*-butyl alcohol, and hydrogen chloride are much more sensitive to traces of impurities than is the binary critical solution temperature for water and *n*-butyl alcohol. The factors determining the miscibility of liquids are discussed.

R. CUTHILL.

Diffusion velocity of silver in silver telluride, antimonide, and stannide. G. VON HEVESY and W. SEITH (Z. anorg. Chem., 1929, 180, 150—158).—The diffusion velocities of silver in the above compounds have been derived from measurements of the diffusion coefficients of the latter in the corresponding compounds of copper. The diffusion constant, D , of silver telluride in copper telluride varies with the temperature, T , according to $D=A \cdot e^{-B/T}$, where $A=2.027 \times 10^5$ and $B=10430$. At 581° $D=1 \text{ cm}^2/\text{day}$. At temperatures which are the same fraction of their m. p. the diffusion velocities of silver antimonide and silver stannide are of the order of 10^{-2} and $10^{-4} \text{ cm}^2/\text{day}$, respectively. In heteropolar compounds and in metals the diffusion velocities of the atoms are exceedingly small, whereas in substances which are intermediate between these two types they are large.

O. J. WALKER.

Solid solutions, isomorphism, and symmorphisms among the oxides of bivalent metals. I. The systems CaO-CdO , CaO-MnO , CaO-CoO , CaO-NiO , and CaO-MgO . G. NATTA and L. PASSERINI. II. The systems CoO-NiO , CoO-MgO , CoO-MnO , CoO-CdO , NiO-MgO , NiO-MnO , and NiO-CdO . L. PASSERINI (*Gazzetta*, 1929, 59, 129—143, 144—154).—I. An examination has been made by the X-ray powder method of a number of binary systems of bivalent metallic oxides. In general a mixture of the precipitated hydroxides was heated at a temperature somewhat above that at which complete dehydration occurred. The photographs given by these calcined products were compared with those given by the oxides separately and by mechanical mixtures of the pairs of oxides.

Complete miscibility in the solid state occurs in the system CaO-CdO and, within the limits of experimental error, the deformation of the lattice is proportional to the composition of the solid solution. By keeping a mechanical mixture of these two oxides at a temperature above 600° a solid solution is formed by diffusion identical with that formed from the mixed precipitated hydroxides.

Partial miscibility, little dependent on temperature, occurs in the system CaO-MnO . No evidence of the formation of solid solutions was found with the systems CaO-NiO , CaO-CdO , and CaO-MgO . In the last-named system a temperature of 1500° did not bring about dissolution.

II. Complete miscibility, with deformation of the lattice proportionate to the composition, occurs in the systems CoO-NiO , CoO-MgO , CoO-MnO , and NiO-MgO . Miscibility is partial in the system NiO-MnO , and is absent from the systems CoO-CdO and NiO-CdO .

A comparison of the results shows that in these systems of oxides possessing similar lattices the solubility in the solid state decreases rapidly with increase in the diameter of the metal ions.

F. G. TRYHORN.

Partition law. III. Application of van Laar's partition law to a condensed system derived from molten metals. R. LORENZ and G. SCHULZ [with F. ERBE] (*Z. anorg. Chem.*, 1929, 179, 339—344).—Van Laar's partition law yields a satisfactory constant for the partition of silver between molten aluminium and molten lead over a range of 0.9—30 at.-% Ag in aluminium. H. F. GILLBE.

Solubility of antimony in water. J. GRANT (*Analyst*, 1929, 54, 227—228).—Finely-divided antimony is soluble in distilled water in the presence of oxygen, and this property is regarded as a possible source of error in the Clarke method (this vol., 417) and in any analytical procedure where deposits of antimony (e.g., those produced electrolytically) have to be washed. D. G. HEWER.

Sorption of hydrogen by the platinum metals. E. MÜLLER and K. SCHWABE (*Z. Elektrochem.*, 1929, 35, 165—184).—The authors have measured the amounts of hydrogen sorbed by the metals of the platinum group immediately after their formation by the reduction of the oxides by hydrogen at different temperatures. The apparatus used was similar to that of Mond, Ramsay, and Shields (*A.*, 1895, ii, 492).

The methods used in the preparation of ruthenium dioxide, the hydrated dioxides of osmium, iridium, and platinum, hydrated palladous oxide, and rhodium sesquioxide are described. These oxides were subjected to the action of hydrogen under various conditions and the volumes of gas occluded by the metals so formed were ascertained by subtracting the volumes of hydrogen required for reduction from the respective total volumes of hydrogen taken up. The data indicate that the quantity of occluded hydrogen depends on the temperature at which the oxide is reduced and on the time taken, on the method of preparing the oxide, and on the rate at which the metals are treated with hydrogen. Moreover, the platinum metals were found to be capable of sorbing greater quantities of hydrogen immediately after their formation than after they have been kept for some time. The previously published figures relating to the capacities which these metals have for occluding hydrogen are without real meaning, for as with charcoal, much depends on the surface area per unit mass. Thus with osmium the amounts of hydrogen taken up by 1 volume of the metal varied from 660 to 2000 volumes. H. T. S. BRITTON.

Adsorption of hydrogen on the surface of an electrodeless discharge tube. M. C. JOHNSON (*Proc. Roy. Soc.*, 1929, A, 123, 603—613).—Measurements have been made of the progressive decrease in the rate at which hydrogen disappears (the fatigue) under the action of the electrodeless discharge (cf. Thomson, A., 1928, 3). The hydrogen, contained in a glass bulb which could be evacuated to the cathode-ray stage and baked during evacuation up to 300° , was excited and dissociated by the high-frequency currents induced from a surrounding solenoid, and the fatigue was followed by means of a continuous reading micro-manometer. The resulting sequences of curves indicate that the fatigue is a two-fold phenomenon. There is (a) a saturation observable in any one curve and almost completed in about 4 min., and (b) a decrease in the depth reached by this saturation curve on repetition of the experiment after re-baking. The capacity of the glass surface is obviously never greater than when newly made and first gassed out, and the surface is saturated when the hydrogen layer is unimolecular but not closely packed. The average separation of atomic centres in the adsorbed layer on two specimens at saturation is calculated to be 1.3 and 1.8×10^{-8} cm., respectively. Closest packing of Bohr orbits would give 1.06×10^{-8} cm., whilst attachment to the solid atom by atom, assuming all spaces occupied, would give a probable minimum value of 1.9×10^{-8} cm. The structure of the adsorbed layer is discussed. The heat of adsorption of hydrogen on glass, calculated by means of Frenkel's formula (*A.*, 1925, ii, 194), is found to be 1.115 and 1.06×10^4 g.-cal. g.-mol., respectively, for the two specimens.

L. L. BIRCHM-HAW.

Adsorption of gases by glass surfaces. M. CRESPI (*Anal. Fis. Quím.*, 1929, 27, 108—119).—The apparatus used previously has been modified by replacing the system of small tubes by small bulbs equal in total volume to the large comparison bulb; measurements may thus be made with gases exhibiting

a high degree of adsorption. The adsorption of carbon dioxide at 13° is given by $0.93 \times 10^{-8} \cdot p^{0.44}$ from 1 to 0.25 atm.; the number of moles of carbon dioxide adsorbed per cm.² at 760 mm. and the ordinary temperature is 2.7×10^{-15} , as compared with 2.4×10^{-15} for chloroform. H. F. GILLBE.

Behaviour of outgassed activated charcoal with electrolytes. R. BURSTEIN and A. FRUMKIN (Z. physikal. Chem., 1929, 141, 219—220).—Sugar charcoal was heated to 1000° in a vacuum, and was then placed in contact with a solution of an electrolyte also in a vacuum. There was no hydrolytic adsorption. When, however, the charcoal was exposed to air it at once began to adsorb acids. A. J. MEE.

Relationship between gas content and adsorption of electrolytes by activated charcoal. I. B. BRUNS and A. FRUMKIN (Z. physikal. Chem., 1929, 141, 141—157).—Activated sugar charcoal was prepared, and part of it was platinised. The adsorbing power of this charcoal for acids and bases was then determined. It was found that the adsorption of acids by unplatinised charcoal in a hydrogen atmosphere is different from that in an air atmosphere, but that the difference is not very great. If platinised charcoal is used the difference is very much increased; indeed, with a sufficiently high concentration of platinum the adsorption of hydrochloric acid in the presence of hydrogen is reduced to zero. These conclusions were supported by observations on the adsorption of other acids (viz., sulphuric and phosphoric acids), when similar results were obtained. The amount of acid adsorbed by platinised charcoal in an atmosphere of air is much greater than that adsorbed by platinum-free charcoal under the same conditions. These phenomena must be ionic in nature because the adsorption of benzoic acid is unaffected by the atmosphere or type of charcoal used. In the case of bases (sodium hydroxide was used) there was no adsorption by charcoal, platinised or platinum-free, in the presence of air, but in the presence of hydrogen the amount adsorbed increased with increasing platinum content. An attempt is made to explain these facts on electrochemical theory. The activated charcoal behaves in aqueous solutions as a gas electrode, the adsorption of strong electrolytes being due to the formation of an electrical double layer at the carbon-solution interface. In the presence of air the activated charcoal sends out hydroxyl ions into the solution, becomes positively charged, and attracts anions. Hence acids will be adsorbed. Charcoal containing a certain quantity of platinum will discharge hydrogen ions into the solution if it is in an atmosphere of hydrogen. It will thereby become charged negatively and will attract cations. The formation of the double layer will, in this case, be bound up with adsorption of alkali. A. J. MEE.

Relationship between gas content and adsorption of electrolytes by activated charcoal. II. R. BURSTEIN and A. FRUMKIN (Z. physikal. Chem., 1929, 141, 158—166).—Activated charcoal was heated to about 1000° in an atmosphere of hydrogen and was then introduced into an oxygen-free solution in complete exclusion of air. There was a complete inversion of the adsorptive properties of the charcoal.

Whereas previously acid was adsorbed, no acid was now taken up. A neutral solution in contact with the charcoal became acid. On exposing the charcoal to air it took up oxygen and developed its original adsorbing powers. It was found that the presence of sulphur dioxide in the charcoal, adsorbed from the laboratory atmosphere, lowered the power of the charcoal to adsorb acids. This capacity was, however, restored on heating in a stream of hydrogen. It was also observed that adsorbed hydrochloric acid is more readily liberated when the charcoal is heated in a current of hydrogen than it is when the hydrogen is replaced by nitrogen. A. J. MEE.

Adsorption of hydroxybenzenes and other aromatic compounds and their replacing action on each other at the interface water-charcoal. I. M. KOLTHOFF and E. VAN DER GOOT (Rec. trav. chim., 1929, 48, 265—287).—A study of the adsorption of various aromatic compounds by charcoal from aqueous solution has been made to determine whether the number of polar groups in a molecule and the configuration of phenolic compounds bear any relation to the form of their adsorption isotherms, and whether the number of molecules adsorbed at an interface represents any real measure of the adsorption affinity. The adsorption of the following substances was investigated: phenol, aniline, methylaniline, dimethylaniline, o-cresol, resorcinol, quinol, pyrocatechol, pyrogallol, phloroglucinol, *p*- and *m*-nitrophenol, gallic acid, pyridine, antipyrine, picric acid, benzoic acid, salicylic acid, sulphosalicylic acid, and benzenesulphonic acid. In addition a series of measurements was made with solutions containing two solutes.

In almost all cases the Freundlich adsorption equation could be satisfactorily applied to the results. The index $1/n$ in this equation was found to be related to the number of polar groups in the adsorbed molecule. The values of the index for molecules containing one, two, or three polar groups were respectively in the ratios 3 : 2 : 1. The index falls to very small values as the number of polar groups is increased, indicating that the affinity between the charcoal and the adsorptive increases under such conditions. This behaviour at a water-charcoal surface is converse to that at a water-air interface for the same substances. The polar groups of the benzene derivatives are directed, not to the bulk of the solution, but to the charcoal face, probably as a result of the presence of a layer of adsorbed water molecules on the latter. No real measure of the adsorbability of a substance is obtained by expressing the amount adsorbed as millimols. per g. of charcoal. When milliequivalents are used as units for this purpose, the equivalent number for benzene derivatives of non-electrolyte character is proportional to the number of polar groups in the molecule. Di- and tri-hydroxybenzenes are almost without influence on the surface tension of a phenol solution, but at a charcoal surface phenol is replaced by di- and tri-hydroxybenzene derivatives.

Usually, but not without exception, the influence of sodium chloride is to increase the adsorption of aromatic compounds by charcoal.

F. G. TRYHORN.

Adsorption of phenols at the interfaces water-air, water-charcoal, and water-mercury. A. FRUMKIN (Rec. trav. chim., 1929, 48, 288—290).—Data for the adsorption of hydroxybenzene derivatives at the interfaces water-air and water-mercury are compared with the unexpected results obtained by Kolthoff and van der Goot (cf. preceding abstract) for the adsorption of the same compounds at the interface water-charcoal. F. G. TRYHORN.

Dependence of adsorption of a dissolved substance on the properties of the solution and the solvent. W. HERZ and L. LORENZ (Kolloid-Z., 1929, 47, 331—334).—Solutions of iodine in benzene and in carbon tetrachloride were prepared and measurements were made of the densities and viscosities of the solutions and their mixtures. The solubility of iodine in these solvents was determined and also the densities and viscosities of the saturated solutions. Measurements were made of the adsorption of iodine from these solutions by finely-divided charcoal and the adsorption values were compared with the physical properties of the solutions mentioned above. Since both the solvents are non-polar, similar experiments were conducted with mixtures of heptane and dipropyl ether, where one constituent is a dipole, and further experiments were carried out in ethyl alcohol and absolute acetic acid as polar solvents. Similar results were obtained in all these cases, and it is concluded that constant relations exist between the adsorbability of a substance from organic solvents and their mixtures on the one hand and the solubility of the substance and the density and viscosity of the saturated solution and of the solvent on the other hand. E. S. HEDGES.

Soap. VIII. Adsorption of soap at the contact surface of two liquid phases. M. NONAKA (J. Soc. Chem. Ind. Japan, 1928, 31, 297—300).—The adsorption of soap at the contact surface between benzene or toluene and an aqueous solution of sodium oleate or palmitate is much greater than would be expected on the assumption of the formation of a unimolecular layer, and it is suggested that a unimicellar layer is formed. The adsorbed layer consists of neutral soap, whilst the free fatty acids are dissolved in the adsorbents. When air is used as adsorbent instead of benzene or toluene, the adsorbed layer consists of neutral soap together with free fatty acids. It is concluded that the aqueous soap solution consists of aggregates of hydrated soap molecules in admixture with an emulsion of the free fatty acids formed by the hydrolysis of the soap. From such solutions the fatty acid is first adsorbed, and when this has passed into the adsorbent, or is insufficient to cover the contact surface, then the aggregates are adsorbed. The adsorption phenomena are not the same when the adsorbent is changed. Therefore the washing properties of the soap, which are dependent on adsorption, will vary according to the nature of the washed material. Y. NAGAI.

Soap solutions. VI. Composition of the substances adsorbed by various adsorbents. J. MIKUMO (J. Soc. Chem. Ind. Japan, 1928, 31, 410—416).—Solutions of sodium oleate were shaken with various adsorbents, allowed to settle, and then filtered.

The filtrate was analysed for oleic acid and total alkali, and the composition of the adsorbed matter was calculated from these data. Carbon, fibres of filter paper, silk, artificial silk, wool, hide powder, kaolin, and Japanese acid clay were used as the adsorbents. All these adsorbents react with soap, the reaction being partly chemical, and the adsorption hydrolytic. The adsorbed matter is a mixture of sodium oleate, oleic acid, sodium hydroxide, and their dissociation products; its composition varies with the conditions of the experiment. Carbon has very large adsorbing capacity, and absorbs always only acidic soap, even from alkaline solution, whilst the others absorb basic substances. Potassium oleate behaves similarly to the sodium salt. The mechanism of the washing action of soap solution is considered to involve two main factors, wetting and peptising. The cleaning action is mainly due to the simple soap molecules, simple soap ions, and acid soap sol. Y. NAGAI.

Dependence of surface tension and of heat of evaporation on density and temperature up to the critical temperature. J. J. VAN LAAR (Z. anorg. Chem., 1929, 180, 193—214).—Mathematical, giving a more detailed and extended presentation of earlier work. The relation between surface tension (γ) and density is given by $\gamma = 0.1100fd_1(d_1 - d_2)^3 \times p_c \sqrt{v_c/N}$, where f is a correction factor and the other quantities have the usual significance. The available data for benzene and ether are used to verify the formula, which is valid up to the critical temperature. The variation of γ with temperature is discussed and the expression $\gamma_c = p_c v_c^{1/3} / 10.9$ is obtained for the surface tension at the b. p.; this is the same as the experimentally obtained Dutoit-Friderich expression. The internal (λ) and total (L) heats of evaporation for benzene are calculated. These give constant values for the expressions $\lambda/\gamma^{\frac{1}{2}}$ and $L/\gamma^{\frac{1}{2}}$, which are derived theoretically. A theoretical derivation is also given for the Ramsay and Shields molecular surface energy equation. O. J. WALKER.

Deposition and surface tension. J. WULFF (Nature, 1929, 123, 682).—A preliminary report of experiments on the influence of curvature and surface tension on the nature of adsorption and deposition of iodine (cf. Luce, this vol., 658).

A. A. ELDRIDGE.

Interfacial tension between mineral oils and aqueous solutions. Influence of degree of refining and degree of alteration of oils. H. WEISS and E. VELLINGER (Compt. rend., 1929, 188, 1099—1101; cf. this vol., 503).—The p_H -interfacial tension curves of the system, mineral oil-aqueous solution of an electrolyte, vary with the degree of refinement of the oil. J. GRANT.

Floating mercury on water. C. A. C. BURTON (Nature, 1929, 123, 759).—In Adam's conclusion (this vol., 391) that the mercury-air tension must have been reduced by the order of 100—200 dynes, the part played by curvature of the surfaces in determining conditions for equilibrium or spreading was neglected; this consideration is examined. A. A. ELDRIDGE.

[Floating mercury on water.] H. H. DIXON (Nature, 1929, 123, 759).—Mercury drops on water

may be supported by flotation, and not by surface tension.

A. A. ELDRIDGE.

Effect of proteins in diminishing surface tension. F. BOTTAZZI (Arch. Sci. biol., 1927, 10, 456—506; Chem. Zentr., 1928, ii, 1988).—Solutions of proteins which remain dissolved at the isoelectric point show at that point minimal surface tension. The increase of surface tension on each side of the isoelectric point depends on the dissociation of the protein salt, the protein (or other substance) in the form of undissociated molecules diminishing the surface tension to the greatest extent.

A. A. ELDRIDGE.

Invisible oxide films on metals. H. C. H. CARPENTER (Nature, 1929, 123, 682).—The formation of invisible oxide films on copper, lead, and iron has been demonstrated by Vernon (A., 1926, 1108; B., 1927, 301; cf. Constable, this vol., 503).

A. A. ELDRIDGE.

Formation of thin films of organic colloids on mercury surfaces. R. L. KEENAN (Kolloid-Z., 1929, 47, 289—294).—A method for the preparation of thin films of substances on a surface of mercury is described. Experiments have been carried out with several kinds of cellulose acetate of varying viscosity and in different solvents. In the case of nitrobenzene as solvent, the thickness of the film varies inversely as the viscosity of the solution. Further experiments were conducted with crepe rubber and with isoelectric gelatin. The films of cellulose acetate and of gelatin were hard, whilst the rubber film was elastic. The limiting value of the thickness of the film increases with the number of different kinds of atoms in the molecule; thus, the thicknesses for rubber, cellulose acetate, and gelatin are, respectively, 1.5, 2.5—5.0, and 7.0 Å. The conclusion is reached that the molecules in the films are arranged in long chains or in the form of a network.

E. S. HEDGES.

Osmosis of liquids. II. F. A. H. SCHREINEMAKERS (J. Gen. Physiol., 1929, 12, 555—569).—Two solutions separated by a membrane are allowed to diffuse under osmotic forces and the resulting changes are followed by analysing small quantities withdrawn from each solution (cf. A., 1928, 233). The type of curve obtained is dependent on the membrane used, two different samples of pig's bladder giving different types of curves with the same solutions.

W. O. KERMAK.

Ultrafiltration dialysis and osmometry by means of collodion sacs. M. SIGAUD (Ann. Inst. Pasteur, 1929, 43, 190—217).—A detailed description is given of the technique required in the preparation of collodion cells of convenient form for ultrafiltration, dialysis, and osmometry, especially when sterility and freedom from chemical contamination are required.

H. F. GILLBE.

Suspension of sand in water. H. E. HURST (Proc. Roy. Soc., 1929, A, 124, 196—201).—By means of an apparatus, somewhat similar to the paddle-wheel apparatus used by Joule to determine J , and designed to give, as far as possible, uniformly distributed turbulent motion without any steady flow, a study has been made of the laws governing the suspension in

water of samples of rounded desert-sand. Three kinds of sand, of diameter 0.9, 0.4, and 0.2 mm., respectively, and many different speeds of the propeller were used. The results show that for a given sample of sand and propeller speed, the concentration of sand n at height h is given by $n = n_0 e^{-\alpha h}$, where α is a function of the speed of the propeller and varies with the kind of sand. Curves are plotted showing the relation between the mean square velocity of agitation of the particles and the square of the revolutions of the propeller. The investigation indicates that the particles in suspension due to uniformly distributed turbulent motion in a liquid behave like the molecules in a gas.

L. L. BIRCUMSHAW.

Equilibria between acids and bases in a gaseous phase. Volatility product of salts. Applications. A. TIAN (J. Chim. phys., 1929, 26, 91—116).—A theoretical study has been made of the formation of smokes by the interaction of volatile acids and bases. Such a reaction is always reversible, and the precipitation of the salt forming the smoke must obey a law of the mass action type. The expression $[\text{acid}] \times [\text{base}] = P$ is derived, where P is the "volatility product" of the salt formed, and is analogous to the solubility product in solutions. This expression is verified experimentally from a study of the interaction of acetic acid and pyridine in the vapour state. The dissociation in the vapour phase of salts formed from volatile constituents is considered. The strengths of the acidic and basic constituents are the important factors which determine precipitation of the salt. If a mixture of two salt vapours can give rise to a salt with strong constituents, then this salt tends to be precipitated as a smoke. The validity of this statement, which forms a general law, is verified experimentally.

The conditions favourable for the formation of smokes are investigated, and a method is developed for the determination of small amounts of acidic and basic constituents of a gaseous mixture. Investigation has also been made of the effect of water vapour, which for strong acids and bases increases the sensitivity of the method.

O. J. WALKER.

Chemical composition and dispersity of crystalline particles. W. OSTWALD and A. VON BUZÁGH (Kolloid-Z., 1929, 47, 314—323).—The composition of the elementary cell of a crystal as disclosed by X-ray examination differs from the stoichiometric composition of large crystals, the two merging into one another as the size of the crystal increases. This progression with increasing size of crystal has been investigated and is illustrated by means of curves for some typical forms of space lattice (rock salt, fluorspar, caesium chloride, cuprite, and rutile). The convergence of the two compositions occurs in crystals having a length of about 10^{-6} to 10^{-5} cm., i.e., typical colloidal dimensions. It follows that the composition of the colloidal particles in sols and highly disperse precipitates can vary with the size of the particles, e.g., a highly disperse calcium fluoride sol prepared by a condensation method may be richer in calcium ions than a similar sol of lower dispersity. The difficulties inherent in an experimental verification

of these views are discussed. It is suggested that the "lattice blocks" of Smekal's theory of crystal structure are identical with crystallites which have reached a stoichiometric composition, the progression from the fine-structure composition to the stoichiometric composition being marked by a stabilisation of the crystallites. E. S. HEDGES.

Preparation of many-coloured silver sols by means of hydrogen peroxide. E. WIEGEL (Kolloid-Z., 1929, 47, 323—325).—Silver sols which appear yellow, red, violet, or blue in transmitted light may be prepared without the aid of gelatin as a protective colloid. The method consists of adding hydrogen peroxide to a highly disperse Carey Lea's silver sol containing a small quantity of dextrin. The colour produced after the catalytic decomposition of the hydrogen peroxide depends on the amount of hydrogen peroxide used and on the rate of addition. The colour of the sols in reflected light is complementary to that in transmitted light.

E. S. HEDGES.

Spontaneous formation of nuclei in dilute, highly supersaturated gold solutions. P. A. THIESSEN (Z. anorg. Chem., 1929, 180, 57—64).—When a dilute aqueous solution of chloroauric acid is being reduced with hydrogen peroxide, carbon monoxide, potassium thiocyanate, or ultra-violet light, the number of gold nuclei present at any particular moment may be determined by adding hydroxylamine hydrochloride, or hydrazine sulphate, which cause existing nuclei to grow so large that they can be counted under the ultramicroscope, yet do not themselves give rise to an appreciable number of new nuclei. The rate of formation of nuclei increases for a short time after reduction has started, then becomes fairly steady, and ultimately diminishes. In explanation of the period of induction, it is suggested that the rate of formation of nuclei increases with increase in the degree of supersaturation, which initially rises steadily owing to the progress of the reduction. Soon, however, the products of reaction reach such a concentration as would bring the reaction to a standstill if they were not removed as nuclei, the rate of formation of which therefore becomes constant. Finally, the concentration of chloroauric acid becomes so small that this degree of supersaturation cannot be maintained, and the rate therefore starts to diminish. With ultra-violet light, the number of nuclei ultimately starts to decrease again, apparently owing to coagulation. From the foregoing it becomes possible to prepare gold hydrosols with particles of any desired size without the aid of nuclei by starting with a suitable concentration of gold, and developing the nuclei at the appropriate point. R. CUTHILL.

Smallest crystal nuclei in highly supersaturated gold solutions. P. A. THIESSEN (Z. anorg. Chem., 1929, 180, 110—114).—When auric chloride is reduced with potassium thiocyanate, the smallest gold particles which will serve as nuclei for the formation of a gold sol (cf. preceding abstract) are of approximately the same dimensions as the smallest gold crystals capable of growth. R. CUTHILL.

Colloidal behaviour of the sulphides and hydroxides of cadmium and zinc. (Miss) W.

DAUS and O. F. TOWER (J. Physical Chem., 1929, 33, 605—612; cf. Hausmann, A., 1904, ii, 547).—Liesegang's rings of cadmium and zinc sulphides are formed in 1% agar-agar and in 5% gelatin, but not in silica gel. The sulphide ion must be in the gel and the metallic ion above in order to obtain good banding, which occurs at an optimum concentration in each case. The results can be explained by Bradford's theory of ring formation (A., 1922, ii, 358) with the proviso that sulphide ions are adsorbed more strongly than the metallic ions by the precipitated sulphides. Colloidal solutions of cadmium and zinc hydroxides have been prepared by a method analogous to that used for nickel hydroxide (Tower, A., 1924, ii, 237). The cadmium hydroxide is stable and positively charged, whilst the zinc hydroxide is somewhat unstable. Gels of these two hydroxides in glycerol have also been obtained by the method used for nickel hydroxide gel (Tower and Cooke, A., 1922, ii, 853).

L. S. THEOBALD.

Electrolyte-free colloidal ferric oxide. P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1929, 180, 115—119).—Electrolyte-free ferric oxide sols prepared by hydrolysis of ferric ethoxide are markedly lyophobic, being extremely sensitive to electrolytes; the disperse particles are negatively charged. Acids and ferric chloride alter the sign of the charge, and impart to the sol the characteristics of ordinary ferric oxide sols prepared by hydrolysis of ferric compounds and dialysis, so that the lyophilic nature of such sols is to be attributed to the traces of electrolytes present. Small amounts of alkali have a stabilising effect without influencing the charge, but larger amounts cause coagulation. R. CUTHILL.

Equilibrium in the system colloidal ferric hydroxide-hydrochloric acid-water. E. HEYMANN (Kolloid-Z., 1929, 47, 325—330; cf. this vol., 260).—An experimental investigation has been made of the equilibrium between colloidal ferric hydroxide and hydrochloric acid, and the results show that for a given concentration of hydrochloric acid the amount of ferric chloride formed increases with the concentration of ferric hydroxide used. The expression $[HCl]^3/[FeCl_3]=K$ is therefore only approximate. The active mass of the colloidal hydrolysis product of ferric chloride is not regarded as constant, but increases with the concentration of the colloid. The reaction between colloidal ferric hydroxide and hydrochloric acid takes place, not only on the surface of the particles, but also within the surface. The equilibrium is also influenced by the degree of dispersion of the ferric hydroxide: thus, coarsely disperse ferric hydroxide is in equilibrium with a smaller concentration of ferric chloride than the highly disperse colloid. The dispersity varies with age, and by altering this condition micelles of different chemical composition can be produced. The micelles richest in chlorine are obtained by the ageing of ferric chloride solutions and those poorest in chlorine by mixing ferric hydroxide sol (prepared from iron pentacarbonyl by the method of Freundlich) with hydrochloric acid.

E. S. HEDGES.

Colloidal platinum. V. Coagulation by electrolytes in acid solution. VI. Behaviour

of platinum sols in basic solution. S. W. PENNYCUICK (J.C.S., 1929, 618—623, 623—633; cf. A., 1928, 1090).—V. Conductivity measurements show that when salts are added to acid platinum sols the salt cation partly replaces the hydrogen ion in the surface hexahydroxy-acid. With increase in the salt concentration the activity of the colloid ion is reduced to such a point that coagulation can occur, the relation between the coagulative power of an ion and its valency being explicable in terms of its attraction for the colloid ion. The amount of a particular salt required to effect coagulation decreases with increase in the acidity of the sol, probably due to the acid as well as the salt playing a part in such coagulations. With ferric chloride and aluminium sulphate at very low concentrations, it is apparently the free acid reduced by hydrolysis which is the coagulant; the hydroxide plays no part.

VI. When platinum sols are titrated with barium hydroxide, the amount of alkali taken up is much greater than corresponds with the hexahydroxy-acid on the surface of the colloid particles. This excess of alkali is apparently fixed on the surface by lower oxides of platinum which are too weak to form acids with water, yet are able to form salts with bases. If salts bring about coagulation by repressing the ionisation of the salt of the hexahydroxy-acid, their effect will be opposed by alkalis, which will render the lower oxides ionogenic, and so tend to maintain the charge on the colloid particles. The coagulative powers of salts prove, in fact, to be much reduced by addition of alkalis, which will also frequently peptise the coagula produced by salts. Sometimes peptisation can be achieved by washing with water only.

R. CUTHILL.

Peptisation of ignited ferric oxides and formation of a ferric oxide mirror. A. KRAUSE (Z. anorg. Chem., 1929, 180, 120—126).—Ferric ferrite, obtained by the interaction of ortho- and meta-ferric hydroxides, is, after being ignited, readily peptised by dilute acids. The resulting "c-ferric oxide" sol contains positively-charged particles, and its hydrophobic nature is evident from the readiness with which it deposits a ferric oxide mirror on the walls of the containing vessel. Ortho-ferric hydroxide partly converted into ferric ferrite by ageing under water or sodium hydroxide solution yields the same sol after ignition. Ortho- and meta-ferric oxides are not peptised by acids after ignition, but the meta-oxide, unlike ferric ferrite and the ortho-oxide, is peptised by dilute ammonia solution after ignition. The meta-ferric acetate hydrosol has only a slight tendency to produce a mirror, and the ortho-acetate hydrosol has none, and even exerts a stabilising influence on the meta- and c-sols. It may therefore be concluded that there are three series of ferric oxides and hydroxides.

R. CUTHILL.

Lyophilic colloids. I. Osmotic experiments and viscosity measurements with caoutchouc solutions. H. KROEPELIN (Kolloid-Z., 1929, 47, 294—304).—Measurements of the osmotic pressure of caoutchouc solutions have been made at 11° and 40° and from the results the vapour pressure and its temperature coefficient and also the heat of dilution have been calculated. The material used was a

cold ethereal extract of the substance extracted by acetone from crêpe. The micellar weight of caoutchouc has been calculated from a simplified van der Waals equation and leads to the value 200,000. Viscosity measurements were conducted, using capillaries of various diameters, and the results show that the apparent viscosity is a definite function of the middle velocity gradients: measurements with different capillaries give the same value so long as the middle velocity gradients are chosen. In all the caoutchouc solutions examined, the apparent viscosity is a linear function of the logarithm of the velocity gradient. No simple relation has been found between viscosity and osmotic pressure in these solutions.

E. S. HEDGES.

[Effect of ethyl alcohol on] silver sols. S. KLOSZY (J. Physical Chem., 1929, 33, 621—626).—The composition and physical properties of silver sols prepared by the method of Carmody (Thesis, Catholic University, U.S.A.) and containing various percentages of ethyl alcohol have been investigated. The densities are almost identical with those of the dispersion media, but contrary to Woudstra (A., 1908, ii, 818), the viscosities are slightly less. The migration velocities decrease with an increase in the alcohol content up to 20% by weight and then remain constant up to 40%. Alcohol also sensitises the sols towards coagulation by potassium, calcium, and aluminium ions. The calculated values of the boundary potential rise after the addition of 25% of alcohol.

L. S. THEOBALD.

Dispersoidological investigations. XXIV. Dispersoidology of gold. P. P. VON WEIMARN (Repts. Imp. Ind. Inst. Osaka, 1929, 9, No. 7, 9—79).—The relation between the size of crystals and the concentrations of the reacting solutions is discussed and the views of Zsigmondy are shown to be opposed to those of the author. It is shown that the increase in the mean size of crystals with increase of concentration of the reacting solutions observed in some cases is an indication of the existence of some anomaly in the course of the precipitation process. An account is given of the preparation of colloidal solutions of "gold iodide," "gold thiocyanate," and "gold citrate" and of their transformation into gold sols. The chemical composition of these substances is not constant. It is suggested that colloidal gold iodide may find an application in medicine. The existing simple view of the mechanism of the formation of gold sols as a spontaneous crystallisation from super-saturated solutions of gold is considered to be insufficient, in particular because it cannot account for the different results obtained by using equal concentrations of different salts and gold compounds. The question is considered whether it is possible to obtain colloidal solutions of gold without the preliminary formation of colloidal solutions of sparingly soluble gold compounds. Methods are given for the preparation of gold sols of orange-red and pure orange colour. The orange sols retain their orange colour only for a few hours, but the orange-red sols retain their colour for some months, ultimately becoming pure red. The particles producing the orange coloration are smaller than those present in red gold sols. The ammonia test (a blue ring produced at the boundary of contact

of concentrated ammonia solutions and a red gold sol containing small quantities of gold compounds) is criticised. The gold compounds concerned are divided into three groups: (a) those which give a blue ring after a short time, (b) those giving no ring at all, (c) those giving a coloured ring slowly and with the colour changing from purplish-red to blue. It is pointed out that gold is far from being one of the simplest subjects for dispersoidological investigations; it is inclined to the formation of complex compounds and these are not characterised by stability and they undergo rapid changes in their chemical composition.

E. S. HEDGES.

Coagulation and particle size. P. A. THIESSEN, K. L. THATER, and B. KANDELAHY (*Z. anorg. Chem.*, 1929, 180, 11—18).—By determining the minimum amounts of a particular electrolyte necessary to coagulate gold sols of various degrees of dispersity, and also comparing the rates of coagulation by a particular concentration of electrolyte, it has been found that with decrease in the size of the colloid particles the stability in respect of coagulation by electrolytes increases. Since the electrokinetic potential of the particles varies with the composition of the intermicellar liquid, it must be concluded that the critical potential for coagulation depends on the degree of dispersity.

R. CUTHILL.

Conductivity-diffusion method for studying the coagulation of colloidal ferric oxide. C. H. SORUM (*J. Amer. Chem. Soc.*, 1929, 51, 1154—1162).—Attempts were made to determine the critical electrolyte concentration necessary to coagulate ferric hydroxide sols by increasing the electrolyte concentration very gradually and determining the effect on the conductivity of the sol. Since coagulation is considered to be accompanied or preceded by the adsorption of the coagulating ion, the conductivity should fall abruptly at the critical point. The graphs of resistance against time for experiments in which the gradual addition of the electrolyte was effected by a diffusion process do indeed show discontinuities, but although these may be attributable to the cause mentioned, they may also be due to the sudden localised coagulation preventing uniform distribution of the electrolyte. Gradual concentration of the electrolyte by evaporation was found to be unsatisfactory.

S. K. TWEEDY.

Morphology of chemical reactions in colloidal media. M. S. DUNIN and F. M. SCHEMJAKIN (*Kolloid-Z.*, 1929, 47, 335—341).—A study has been made of the interaction of solutions of potassium ferrocyanide and silver nitrate at various concentrations in 5% gelatin. The experiments were carried out by placing a drop of a saturated solution of one of the reagents on a thin layer of gelatin containing a dilute solution of the other reagent and observing the nature of the field of diffusion. It is concluded that reactions of this type in gels fall into one of three classes: (a) the diffusion field consists of periodic rings (typified by silver nitrate and potassium dichromate), (b) the diffusion field is in the form of a rosette and rings form inside the drop (silver nitrate and potassium ferrocyanide), (c) the diffusion field is homogeneous (silver nitrate and potassium chloride).

In the reaction between silver nitrate and potassium ferrocyanide the conditions for the formation of rosettes are most favourable when potassium ferrocyanide is the inner electrolyte and at a concentration of 0.05—0.01*N*. Rosettes are not formed when silver nitrate is the inner electrolyte, but are formed when a saturated solution of copper sulphate is used in place of silver nitrate. The morphology of the structures also depends on the quality of the gelatin.

E. S. HEDGES.

Method of investigating coagulation and peptisation phenomena. A. VON BUZAGH (*Kolloid-Z.*, 1929, 47, 370—372).—A preliminary communication of a method for following the process of coagulation and peptisation by direct observation.

E. S. HEDGES.

Influence of dimensions of the capillary on the streaming anomalies of colloidal liquids in the capillary viscosimeter. W. HALLER and V. TRAKAS (*Kolloid-Z.*, 1929, 47, 304—310).—In the streaming of colloidal liquids a critical value is derived, which is characteristic for the appearance of structure viscosity, resembling Reynolds' value for turbulence. An explanation of some viscosity anomalies of colloidal solutions is offered. The equation of de Waele and Wo. Ostwald has been reduced, so that the two constants involved are no longer dependent on the dimensions of the apparatus, but only on the substances.

E. S. HEDGES.

Capillarity. X. Further formulation of capillary structures. K. SCHULTZE (*Kolloid-Z.*, 1929, 47, 310—313; cf. A., 1928, 232).—A theoretical consideration of different types of capillaries.

E. S. HEDGES.

Diffusibility and dispersity of dyes and their relation to colour at various hydrogen-ion concentrations. A. PISCHINGER (*Z. Zellforsch. Mikros. Anat.*, 1927, 5, 347—385; *Chem. Zentr.*, 1928, ii, 1865—1866).—The speed of diffusion of methylene-blue in gelatin gels diminishes, and that of crystal-ponceau increases from the acid side towards neutrality; that of methylene-blue in water is constant between p_H 2.5 and 7.8. Hence the variations depend on the change of adsorptive power of the gelatin with change in p_H . The relation between the charge of the dye and the colloid protein determines the flocculating effect; methylene-blue displaces the optimum for denatured serum-albumin slightly towards the alkaline side, and crystal-ponceau slightly towards the acid side. Colour changes due to the formation of adsorption compounds, e.g., of nucleic acid and methylene-blue, are discussed.

A. A. ELDRIDGE.

Rennin action in relation to electrokinetic phenomena. G. A. RICHARDSON and L. S. PALMER (*J. Physical Chem.*, 1928, 33, 557—576).—The isoelectric point of rennin determined by a cataphoretic method lies at p_H 6.9—7.0. The addition of rennin to sols of calcium caseinogenate having p_H 6.1—6.9 reduces the rate of migration of the caseinogenate micelles, indicating that rennin lowers the electrical charge on negatively-charged, semilyophilic micelles. At p_H 7.0—7.25 the rate of migration increases, but at p_H 7.5—7.69 no change occurs. The addition of rennin to calcium caseinate solutions with p_H

6.45 also has no effect on migration. Heating neutral and slightly acid caseinogenate sols increases the rate of migration, indicating an increase in charge of the protein micelles, and the action of rennin on such heated sols is to decrease the rate of migration, but not to the extent which is observed with unheated sols.

L. S. THEOBALD.

Action of caffeine on absorption of water by colloids. J. SZELOCZEY (Biochem. Z., 1929, 206, 290—300).—The gelation temperature of a gelatin solution is depressed by the addition of caffeine. The caffeine raises the proportion of "free" water and this action depends not only on the concentration of the caffeine and on the p_H of the solution, but also on the nature of the colloid. C. C. N. VASS.

Influence of a second liquid on the formation of soap gels. H. N. HOLMES and R. N. MAXSON (5th Coll. Symp. Mon., 1928, 287—300).—Traces of water assist the dispersion of potassium stearate in turpentine and the formation of a gel on cooling. Addition of a small quantity of water increases the ability of sodium stearate, but decreases that of sodium oleate, to hold turpentine. Potassium oleate does not readily disperse in turpentine. Oleic acid assists sodium oleate or stearate to hold turpentine; oleic or stearic acid depresses gel formation with sodium stearate, and assists it with calcium stearate, in paraffin oil. With sodium stearate and benzene, oleic acid aids dispersion; with stearic acid there is a critical zone above which no gels are formed, although gels are not formed without stearic acid.

CHEMICAL ABSTRACTS.

Structure of solutions of gelatin. MARINESCO (Compt. rend., 1929, 188, 1163—1165; cf. A., 1928, 1321).—The dielectric constant at 20° of solutions of commercial gelatin (ash 0.4%) for λ 6.50 m. increases rapidly and linearly with concentration and reaches a sharp maximum for a 0.75% solution ($\epsilon=108$). It then falls rapidly. This maximum corresponds with the transformation of the gelatin from one to the other of the two forms in which according to Smith (A., 1919, i, 179) it may exist. It is shown that in concentrations of 2—3%, one gram of solid gelatin fixes approximately 9 c.c. of water. J. GRANT.

Setting of gelatin sols. A. LOTTERMOSER and W. MATTHAES (Z. physikal. Chem., 1929, 141, 129—136).—The cooling curves of gelatin solutions of varying concentrations (10, 20, 30, and 60%) were compared with those for corresponding quantities of water, and the temperature differences as indicated by the curves were then plotted against temperature. In all cases there are inflexions in these difference curves. In the case of the 10%, 20%, and 30% solutions the initial rise in temperature occurred at 31°, 36°, and 38°, respectively; the most rapid rises were between 26° and 27°, 30.5° and 32°, and between 32° and 33.5°, respectively; and the total rises were 1.4°, 1.55°, and 1.8°, respectively. The more concentrated the solution the less sudden was the rise. This may be due to viscosity or hysteresis phenomena. Similar experiments were carried out with potassium palmitate solutions with analogous results. It is probable that this phenomenon occurs with all temperature-reversible colloids. A. J. MEE.

Swelling of gelatin and the volume of surrounding solution. J. H. NORTHROP and M. KUNITZ (J. Gen. Physiol., 1929, 12, 537—542).—When various quantities of acid of different concentrations are added to purified isoelectric gelatin the degree of swelling of the gelatin is dependent solely on the final p_H of the supernatant acid, a result in accordance with the theories of Procter, Wilson, and Loeb. If, however, the gelatin contains salts, the final concentration of these salts will depend on the amount of acid used and so the degree of swelling will be determined, not only by the final p_H of the supernatant fluid, but also by the quantity of acid added. This conclusion is confirmed by experiment.

W. O. KERMAK.

Influence of size, shape, and conductivity of microscopically visible particles on cataphoretic mobility. H. A. ABRAMSON and L. MICHAELIS (J. Gen. Physiol., 1929, 12, 587—598).—The cataphoretic mobilities of globules of nujol, benzyl alcohol, paraffin oil, cacao butter, or castor oil suspended in a solution of sucrose of approximately the same density containing a small quantity of an electrolyte have been determined by a microscopical method. In each case the mobility is independent of the size of the particles. Needle-shaped particles of asbestos likewise move with a speed independent of their length and during cataphoresis do not orient themselves in any particular direction relatively to the potential gradient. In presence of gelatin, which ensures that the electrokinetic potential is independent of the substance composing the particle, spherical globules of paraffin oil or mastic and needles of asbestos or *m*-aminobenzoic acid migrate with equal mobilities, thus demonstrating that under the same electrokinetic potential the velocities of cylinders and of spheres are equal, a conclusion which is opposed to that reached theoretically by Debye and Huckel. Paraffin droplets, quartz particles, droplets of benzyl alcohol, carbon particles, and particles of agar, in spite of their different conductivities, possess equal mobilities when suspended in a medium containing gelatin.

W. O. KERMAK.

Hydrolysis of gelatin by means of acid and alkali. I. S. YAITSCHNIKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 109—118).—Gelatin was hydrolysed by means of either *N*- or 0.2*N*-sulphuric acid or sodium hydroxide solution at 37° or 100° and for periods up to 16 hrs. The action is more vigorous at higher concentrations and higher temperatures, and alkali has been found to be the more efficient hydrolysing agent. A graphic method is described which permits the progress of hydrolysis to be determined.

A. FREIMAN.

Chemical and physical changes in gelatin solutions during hydrolysis. J. H. NORTHROP (J. Gen. Physiol., 1929, 12, 529—535).—The physical and chemical changes occurring in gelatin as the result of hydrolysis by pepsin have been followed by determining the viscosity at various hydrogen-ion concentrations and also the "formol" titration values. A slight increase in formol titration value corresponds with a large decrease in viscosity. The greatest degree of physical change relative to chemical change occurs in 1% gelatin at a low when the initial

viscosity is high. These results are in conformity with the theory of Loeb and Kunitz (A., 1927, 726) relative to the structure of gelatin solutions.

W. O. KERMAK.

Combination of gelatin with hydrochloric acid.

II. New determinations of the isoelectric point and combining capacity of a purified gelatin. D. I. HITCHCOCK (J. Gen. Physiol., 1929, 12, 495—509).—The isoelectric point of a purified sample of Cooper's gelatin was determined by ascertaining the points of minimum osmotic pressure and of maximum turbidity. These methods both show the isoelectric point to be at p_H 5.05. Fairly concentrated solutions of gelatin were used to determine the hydrogen ions and chlorine ions combined with this protein at a p_H between 1 and 2. Over this range the quantity of combined hydrogen ion is constant and equal to 9.4×10^{-4} equiv. of hydrogen per gram of gelatin, whilst in 0.1M-hydrochloric acid 1 g. of gelatin combines with 1.7×10^{-4} equiv. of chlorine.

W. O. KERMAK.

Chemical antagonism of ions. III. Effect of salt mixtures on gelatin activity.

H. S. SIMMS (J. Gen. Physiol., 1929, 12, 511—528).—To a 1.25% solution of sodium (or potassium) gelatinate (p_H 7.37) various quantities of sodium chloride, potassium chloride, and magnesium chloride were added either separately, in pairs, or all three together, and the p_H of the resulting solutions was determined. Sodium chloride at all the concentrations used (up to M) lowers the p_H of the sodium gelatinate solution and potassium chloride lowers the p_H up to 0.01M, but more concentrated solutions raise it. The results obtained with mixtures show that the effect is not the sum of the effects of the separate salts, but that the action of one salt may antagonise that of the other, even when both salts have univalent cations.

W. O. KERMAK.

Properties of fibres of coagulated gelatin. R. COLLIN (Compt. rend. Soc. Biol., 1928, 98, 1353—1355; Chem. Zentr., 1928, ii, 1963).—Fibres obtained by dropping glass beads from a 10% gelatin solution into absolute alcohol exhibit double refraction. The colour reactions of the coagulated gelatin are the same as those of collagen fibrils; a close physico-chemical relation is indicated.

A. A. ELDRIDGE.

Colloidal chemical reactions between sols of proteins and polymeric carbohydrates. II. Wo. OSTWALD and R. H. HERTEL (Kolloid-Z., 1929, 47, 357—370; cf. this vol., 507).—Experiments have been conducted on the influence of acids, alkalis, neutral salts, and salts at various hydrogen-ion concentrations on the separation of a mixture of sols of gelatin and starch. The volume of the new phase produced is related to the hydrogen-ion concentration in a similar way to other colloid chemical properties, e.g., swelling. A minimum is observed in approximately neutral and weakly alkaline regions, whilst a maximum appears in acid and also in strongly alkaline regions. The influence of salts, particularly with regard to the anions, is in conformity with their place in the Hofmeister series. The phenomenon is considered to be due to flocculation as a result of the mutual dehydration of two sols and this idea is discussed in connexion with other mutual precipitations

such as serological precipitation reactions. The kind of starch used affects the results considerably: the starches used appear in the following order of degree of hydration: potato-, rice-, maize-, wheat-starch.

E. S. HEDGES.

Thermodynamic activities of the proteins.

G. S. ADAIR (J. Amer. Chem. Soc., 1929, 51, 696—707; cf. A., 1928, 1326).—Formulae are derived correlating the thermodynamic activities of protein salts with their observed osmotic pressures. Provisional values for the activity coefficients of a salt of haemoglobin (Hb) designated by the formula $Hb(Na+K)_{8.5}$ have been determined.

S. K. TWEEDY.

Physico-chemical properties of antitoxic and normal sera. S. KASARNOVSKY (Kolloid-Z., 1929, 47, 351—357).—In regard to the antagonistic effects of normal and immune sera on hydrophobic colloids, the coagulating and peptising influences of diphtheria immune sera are stronger than those of normal sera. The diphtheria sera are also more readily gelatinised.

E. S. HEDGES.

Calculation of molecular polarisation of dissolved substances at infinite dilution.

G. HEDESTRAND (Z. physikal. Chem., 1929, B, 2, 428—444).—A formula is derived from which the molecular polarisation and dipole moments of substances at infinite dilution can be calculated from a knowledge of the dielectric constant and density of the solution as a function of concentration. The formula is applied to the calculation of the dipole moments of a number of organic substances in different solvents.

A. J. MEE.

B. p. of aqueous solutions. W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1929, 33, 591—604).—The Washburn-Read modification of the Cottrell b.-p. apparatus is shown not to inhibit the superheating of water—a test for which is described—but a new modification is described which permits the accurate determination of the b. p. of dilute aqueous solutions. Dilute solutions of potassium nitrate and the potassium halides are now found to be completely dissociated at infinite dilution. An apparatus for the determination of the b. p. of aqueous solutions under pressures from 10 to 20 atm. is described, together with some preliminary results for boric acid and potassium chloride; the latter appears to be as abnormal at higher temperatures as it is at 0° or 100°. The divergences from commonly accepted theories revealed by a study of b.-p. data (cf. Kahlenberg, A., 1901, ii, 540) are discussed.

L. S. THEOBALD.

Relation between specific rotatory power and refractive index of a solution.

A. P. PERSCHKE (J. Russ. Phys. Chem. Soc., 1929, 61, 119—122).—It is shown that the specific rotatory power and the refractive index are connected by the same logarithmic expression $\log [\alpha] = a + b \log n$ which applies to a pure liquid.

A. FREEMAN.

Natural rotation of polarised light by optically active bases. II. Rotation of *d*- α -phenylethylamine and its hydrochloride in solution: rotation of active tetrahydro-2-methylquinoline. W. LEITHE (Monatsh., 1929, 51, 381—385).—Solvents which produce little change in the optical rotation of

d- α -pipecoline (A., 1928, 1022), such as ether, cyclohexane, *n*-heptane, and benzene, cause a slight increase in the specific rotation of *d*- α -phenylethylamine ($[\alpha]_D^{25}$ 0.9561; $[\alpha]_D^{25}$ +40.67° in the liquid state); carbon tetrachloride, chloroform, ethyl acetate, and pyridine cause a slight decrease, whilst solvents of the alcohol-water type cause a decrease of 10–15°. Solvents which affect the rotation of *d*- α -pipecoline have less influence on *d*- α -phenylethylamine. The specific rotation of the hydrochloride, which is also dextrorotatory ($[\alpha]_D^{25}$ +7.4° in 24.93 wt.-% aqueous solution), also varies slightly with the concentration of the solution and the solvent used. The phenyl group thus has an appreciable effect on the rotation and on the solvent effect. With the exception of ether and water, variation in the specific volume of the solutions runs parallel with the change in rotation, especially in the case of the hydrochloride. The opposite effects of different solvents, salt formation, and benzylation on the rotations of *l*- α -methylindoline and *l*-tetrahydro-2-methylquinoline (Pope and others, J.C.S., 1899, 75, 1116; 1904, 85, 1330) are discussed and it is suggested that levorotatory tetrahydro-2-methylquinoline has really a *d*-configuration, the levorotation being due to secondary influences such as the solvent. J. W. BAKER.

Van der Waals' equation and thermodynamics. J. E. VERSCHAFFELT (Compt. rend., 1929, 188, 1037–1039).—Polemical against Karpen (this vol., 387), and an amplification of the author's original deductions. J. GRANT.

Calculation of van der Waals' *a* constants from Dühring's specific factors derived from van Laar's formula for the vapour-pressure curve. R. LORENZ (Z. anorg. Chem., 1929, 179, 293–296).—Mathematical. The quantity *A* in the simple vapour-pressure equation $\log p = -A/T + C$ may be calculated for any substance from the value *A'* for another similar substance by means of the equation $q = A/A'$, where *q* is the "specific factor." H. F. GILLBE.

Thermodynamics of gases which show degeneracy. G. N. LEWIS and J. E. MAYER (Proc. Nat. Acad. Sci., 1929, 15, 208–218; cf. A., 1928, 1096).—Theoretical. An extension, based on previous simple statistical assumptions, to all types of molecules, of the work of Bose on photons and of Einstein on monatomic molecules. Boltzmann's equation for distribution with respect to energy is shown to be not generally valid, and from an investigation on molecules possessing internal energy a generalised form of this equation is deduced. The case of an arbitrarily quantised system, an ideal monatomic gas, is considered and the equation $S = 5E/3T - kN \log A$ is derived for the entropy; in this *A* may be regarded as a measure of the degeneracy. A simple generalised equation is also obtained for the total entropy of a gas in terms of the total number of molecules, the total translational energy, and the total internal energy. N. M. BLIGH.

Electrolytic solution tension and the ionic states. VI. K. FREDENHAGEN (Z. physikal. Chem., 1929, 141, 195–216; cf. this vol., 513).—By comparing the theories of interionic force and solution force, it is shown that whilst they originate

from different assumptions, they lead ultimately to the same result, viz., that in the region of dilute solutions the solution force must increase with increasing concentration. Objections are raised against the underlying assumption of the theory of interionic force, viz., that ions in a solution are solvated gas ions, and that the interaction between solvent and solute is independent of the concentration. The deviations from the dilution law are examined on the basis of a solution force changing with concentration. It is shown that the conception of the existence of ionic states can explain the characteristics of the absorption spectra of strong and weak electrolytes. A. J. MEE.

Dissociation and the colour of free radicals. C. B. WOOSTER (J. Amer. Chem. Soc., 1929, 51, 1163–1165).—The degrees of dissociation derived from cryoscopic measurements do not warrant the conclusion that the equilibrium constant of a tautomeric process varies with dilution. The conclusions reached by Gomberg and Sullivan (A., 1922, i, 929) from their experimental results, therefore, are incompatible with the evidence on which they are based. Calculation shows that the measurements of these experimenters are not sufficiently accurate to test thoroughly the relation between colour and dissociation. S. K. TWEEDY.

Equilibrium in aqueous solution between ammonium acetate, acetamide, and water. E. E. LINEKEN and G. H. BURROWS (J. Amer. Chem. Soc., 1929, 51, 1106–1112).—The components were heated at 172°, 184°, or 193° in a sealed glass tube, the equilibrium concentration being determined by conductivity measurements. The results indicate that the amide is formed through the ions of the ammonium acetate (cf. Walker and Hambley, J.C.S., 1895, 67, 753). The effect of heating at 184° and 193° in a pyrex vessel on the conductivity of water is recorded. S. K. TWEEDY.

Cryoscopic determination of the molecular equilibria of resorcinol in aqueous solutions of potassium chloride. F. BOURION and C. TUTTLE (Compt. rend., 1929, 188, 1110–1111; cf. A., 1927, 515).—Measurements by Raoult's method, slightly modified, suggest that resorcinol in 0.5 and 1.225*M*-potassium chloride solution forms simple, double, and triple molecules, whilst in pure water the last two only are observed. The fact that the cryoscopic constant is higher than in water and increases with the chloride concentration may be attributed to the adsorption of water by the salt. J. GRANT.

Combination of proteins and amino-acids with acids and alkalis. II. Titration curves of amino-acids in presence of formaldehyde. L. J. HARRIS (Proc. Roy. Soc., 1929, B, 104, 412–439).—The titration curves of various amino-acids determined in presence of 16% formaldehyde are consistent with the view that the apparent acid dissociation constant of the ampholyte is about a thousand times as great as that of the amino-acid in the absence of formaldehyde. With smaller concentrations of formaldehyde the apparent dissociation constant depends on the concentration of formaldehyde present, and up to about 8%, gradually increases with increase

in the formaldehyde. The results are best explained on the zwitterion theory of amino-acids, according to which the apparent acid dissociation constant is really dependent on the amino-group, whilst the apparent basic dissociation constant is dependent on the acidic group. In presence of formaldehyde, which combines with the amino-group, the apparent basic dissociation constant remains practically unchanged, whilst the apparent acid dissociation constant is increased. The conditions most favourable for carrying out the Sørensen formol titration are detailed.

W. O. KERMAK.

Equilibrium in the liquid state between potassium, sodium, and their bromides. E. RINCK (Compt. rend., 1929, 188, 1108—1109).—The law of mass action holds for the reaction $\text{KBr} + \text{Na} = \text{K} + \text{NaBr}$, the value $c=28.8$ being obtained between 800° and 1000° (maximum variation 20%). The thermal value of the direct reaction is -9.5 g.-cal. at the ordinary temperature and zero at 800—1000°.

J. GRANT.

Activity coefficients of ions in very dilute methyl alcohol solutions. J. W. WILLIAMS (J. Amer. Chem. Soc., 1929, 51, 1112—1119).—The activity coefficients in methyl alcohol at 20° of sparingly soluble cobaltammine salts of two valency types were determined by the solubility method. In sufficiently dilute solutions the limiting law of Debye and Hückel is approximately obeyed. The range of applicability of the theory seems to depend on the nature of the solute. As the dielectric constant of the solvent decreases, the highest concentration at which the simple activity theory is obeyed probably decreases also.

S. K. TWEEDY.

Activity coefficients of diacetone alcohol in aqueous salt solutions. G. ÅKERLÖF (J. Amer. Chem. Soc., 1929, 51, 984—997).—The activity coefficients, γ , of diacetone alcohol in solutions of alkali metal, magnesium, and aluminium salts were measured at 24° by the distribution method, the concentration changes being determined interferometrically. The values of γ are independent of the concentration of the alcohol in the salt solution. The quotient $(\log \gamma)/N$ is constant for a given salt, N being the concentration of the salt solution (cf. Randall and Failey, Chem. Rev., 1927, 4, 291). The activity coefficients are of the same order of magnitude as those obtained for ethyl acetate and for some gases in the same salt solutions. No satisfactory explanation can be offered for the changes of the decomposition velocity of diacetone alcohol in various solutions of strong electrolytes (cf. A., 1928, 716).

S. K. TWEEDY.

Osmotic and activity coefficients. R. C. CANTELO (J. Physical Chem., 1929, 33, 627—632).—Mathematical. Alternative derivations of the Debye-Hückel equations for activity and osmotic coefficients are presented.

L. S. THEOBALD.

Significance of internal diffusion in the regulation of chemical equilibria. G. TAMMANN (Nachr. Ges. Wiss. Göttingen, 1927, 394—406; Chem. Zentr., 1928, ii, 1853—1854).—A discussion.

A. A. ELDRIDGE.

Transformation of supercooled liquids into glasses. G. TAMMANN (Nachr. Ges. Wiss. Göttingen,

1927, 457—464; Chem. Zentr., 1928, ii, 1855—1856).—In the transitions between viscous liquids and glasses there is a lower limiting temperature, t_f , recognisable for the former, and an upper limiting temperature, t_g , for the latter. Between t_f and t_g individual properties of the substance change to an abnormally great extent. This is ascribed, not to molecular changes, but to a great increase of the internal pressure.

A. A. ELDRIDGE.

Alkalinity of soap solutions as measured by indicators. J. W. MCBAIN and (Miss) K. HAY (J.C.S., 1929, 589—601).—Very few indicators can be used to measure the p_n of soap solutions, but by means of alizarin-yellow *G* and phenolphthalein, which are the most satisfactory, the hydroxyl-ion concentrations in solutions of sodium and potassium soaps at 20° and 90° over a wide range of concentrations have been determined. The results agree with the view that the alkalinity is due to the formation of acid soap, whereby an excess of free hydroxyl ions results in the solution. In sufficiently dilute solution, the soap is crystalloidal, and the degree of hydrolysis depends simply on the mol. wt. With increase in concentration the hydroxyl-ion concentration rises to a flat maximum and ultimately falls again, presumably owing to replacement of the simple fatty ions by micelles, which are hydrolysed to a smaller extent.

R. CUTHILL.

Amphoteric character of lead oxide and peroxide. H. TOPELMANN (J. pr. Chem., 1929, [ii], 121, 320—363).—Measurements of the solubilities in water and in sodium hydroxide solutions (1×10^{-4} — $1N$) have been made at 25° and the conductivities of the solutions determined. Sources of error, arising from the disintegration of the particles by rotation of the vessel, the slowness with which the equilibrium is established, the dissolution of alkali from the glass (greatest in aqueous solutions), and the resulting silicification of the particles have been studied. From these observations a technique involving a shortened reaction period with very slow rotation in waxed glass vessels (with control in platinum vessels) is evolved, and the solubility and conductivity data are compared with those in the literature. The olive, red, and white (hydrated) forms of lead oxide (PbO) were each investigated, their solubilities in N - and $0.01N$ -sodium hydroxide and water at 25° being, respectively, 5.82×10^{-2} , 7.05×10^{-4} , 3.35×10^{-4} (olive); 3.71×10^{-2} , $> 4.5 \times 10^{-4}$, 2.14×10^{-4} (red); and 7.29×10^{-2} , 9.49×10^{-4} , 5.72×10^{-4} mol./litre, and the specific conductances 30—35, —, and 38.2×10^{-6} ohm $^{-1}$, respectively. The solubility in very dilute alkali is less than that in water, the lead cation concentration diminishing with increasing hydroxyl-ion concentration, but above a $0.01N$ -concentration of sodium hydroxide the solubility rapidly increases owing to chemical interaction between the hydroxyl ions and the lead anions, indicating the amphoteric nature of this oxide. The dissolution of lead peroxide in alkali occurs much more slowly, the solubilities at 25° in 5.01 , 1.0 , and $0.1N$ -sodium hydroxide being, respectively, 8.1×10^{-3} , 9×10^{-5} , and 1×10^{-6} mol./litre. On the basis of these results the dissociation constant of white, hydrated lead oxide as a monobasic acid (k_a) is

8.1×10^{-12} , and as a mono-acid base (k_b) 9.6×10^{-4} , whence the measurement of its amphoteric character, obtained by the ratio k_a/k_b , is 8.4×10^{-9} , the basic character being much more strongly pronounced. The solubility products, $C_{\text{PbO}_2\text{H}} \times C_{\text{H}^+}$, and $C_{\text{PbOH}^+} \times C_{\text{OH}^-}$, for the white, hydrated oxide are, respectively, 10.1×10^{-16} and 2.56×10^{-8} , whilst the value of the former for the olive form is 7.9×10^{-16} . The relations between the chemical properties and amphoteric character of the two lead oxides are discussed with reference to their atomic structure, and it would seem that the peroxide is the more acidic, the value of k_a/k_b being greater than unity, although the actual dissociation constants cannot be compared, since the quantity of dissolved, undissociated peroxide is unknown. The activity product of lead peroxide as a dibasic acid, $[A_{\text{H}}]^2 \times A_{\text{PbO}_2\text{H}_2}$, has the value 4.4×10^{-33} .

J. W. BAKER.

Dissociation pressure of vanadium pentoxide. E. F. MILAN (J. Physical Chem., 1929, 33, 498—508).—The oxygen pressures of initially pure vanadium pentoxide have been measured over the range 25—1125°, together with the pressures of different mixtures of vanadium pentoxide and tetroxide over the range 700—1125°. The pentoxide is unstable above its m. p. The dissociation pressure at a given temperature depends on the composition of the mass. The pressure for fused masses containing practically 100% V_2O_5 is much greater than for those containing 10% V_2O_4 or more. The variations of oxygen pressure are not in accord with Raoult's law. Curves showing the relation between pressure, composition, and temperature are given.

L. S. THEOBALD.

Phase diagram of calcium-sodium. R. LORENZ and R. WINZER (Z. anorg. Chem., 1929, 179, 281—286).—The m. p. of calcium (98.76%) is 809°. With sodium a eutectic mixture is formed containing 86 at.-% Ca and having m. p. 700°.

H. F. GILLBE.

Ceramics of highly refractory substances. II. System ZrO_2 -CaO. O. RUFF, F. EBERT, and E. STEPHAN (Z. anorg. Chem., 1929, 180, 215—224; cf. B., 1929, 474).—The m.-p. diagram of the system ZrO_2 -CaO has been determined by means of a special oven with an oxy-acetylene burner. The existence of a compound CaZrO_3 is indicated and confirmed by means of Debye-Scherrer X-ray measurements. Calcium oxide forms mixed crystals with zirconium oxide from 0 to 40 mol.-% CaO. The compound has a monoclinic structure and $d \ 4.78 \pm 0.05$ ($d_{\text{calc.}} \ 4.74 \pm 0.05$). The systems ZrO_2 -MgO and ZrO_2 -CaO are compared.

O. J. WALKER.

Solubilities of lead phosphates. H. MILLET and M. JOWETT (J. Amer. Chem. Soc., 1929, 51, 997—1004).—The solubility products (in terms of activity) of lead orthophosphate, s_3 , and of lead hydrogen orthophosphate, PbHPO_4 , s_2 , have been determined by measuring the *E.M.F.* of cells of the type $\text{Pb}|\text{Pb salt soln.}|\text{satd. KCl}|\text{N-calomel electrode}$, and ascertaining the hydrogen-ion activity of the lead solution by means of the quinhydrone electrode. The values found were: $\log s_3 = -42.1$ at 25° and -42.0 at 37.5°; $\log s_2 = -9.9$ at 25° and -9.62 at 37.5°. The logarithm of the second ionisation con-

stant of orthophosphoric acid is -7.17 at 25°, and -7.058 at 37.5°. The calculated heat of dissolution of the hydrogen salt is $-10,000$ g.-cal. at infinite dilution. Calculation shows that the normal orthophosphate is the stable lead phosphate under the conditions prevailing in the human body, and that a slight shift to the acid side does not convert this salt into the hydrogen phosphate.

S. K. TWEEDY.

Ionisation constants of orthophosphoric acid. M. JOWETT and H. MILLER (J. Amer. Chem. Soc., 1929, 51, 1004—1010).—The logarithm of the first ionisation constant is -2.10 at 25° and -2.16 at 37.5°. From previously published data the logarithm of the third ionisation constant is calculated to be -12.1 at 20° (cf. preceding abstract). The calculated heats (evolved) of the following reactions: $\text{H}_3\text{PO}_4 \rightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$ and $\text{H}_2\text{PO}_4^- \rightarrow \text{H}^+ + \text{HPO}_4^{2-}$ are $+2000$ and -2300 g.-cal., respectively.

S. K. TWEEDY.

Heterogeneous equilibria at 97° in systems containing water, sodium sulphate, and sulphates of the vitriol type. A. BENRATH and H. BENRATH (Z. anorg. Chem., 1929, 179, 369—378).—Isotherms for ternary systems containing water and sodium sulphate, together with zinc, cadmium, ferrous, manganous, cobaltous, nickelous, or copper sulphate have been determined from 0° to 100°. At 97° all these sulphates, except those of copper and nickel, exist as monohydrates. Double sulphates are formed in all cases: $\text{ZnSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ are of the astrakanite type; $\text{FeSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ of the loweite type, whilst $\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4$ is of the glauberite type. Double salts of the vanthoffite composition are formed from those components which give rise to salts of the glauberite and loweite types.

H. F. GILLBE.

Ternary system potassium perchlorate-sodium nitrate-water from 0° to 100°. E. CORNEC and A. NEUMEISTER (Caliche, 1929, 11, 488—491).—The solubility of sodium nitrate is increased slightly by the addition of potassium perchlorate, and that of the latter to a large extent by the addition of sodium nitrate. A saturated solution at 0° contains sodium nitrate and potassium perchlorate in the ratio 4.4:95.6. When saturated solutions are cooled, mixtures of the two salts separate in which the percentage of potassium perchlorate is greater the higher is the initial temperature. Separation of the two salts by a cyclic process may be readily effected.

H. F. GILLBE.

System potassium perchlorate-sodium chloride-water from 0° to 100°. E. CORNEC and A. NEUMEISTER (Caliche, 1929, 11, 492—494).—Potassium perchlorate and sodium chloride diminish the solubility of each other in water. A solution saturated with both salts yields on cooling a mixture which always contains a greater proportion of perchlorate. Separation of the two salts may be effected by a cyclic process.

H. F. GILLBE.

System sodium nitrate-sodium chloride-potassium perchlorate-water from 0° to 100°. E. CORNEC and A. NEUMEISTER (Caliche, 1929, 11,

494—499).—A single cycle is described whereby the three salts may be separated from a solution saturated with regard to sodium nitrate and sodium chloride, but unsaturated with regard to potassium perchlorate.

H. F. GILLBE.

Ternary system: water, sodium sulphate, sodium nitrate. A. CHRÉTIEN (Compt. rend., 1929, 188, 1047—1050).—The double salt $\text{Na}_2\text{SO}_4 \cdot \text{NaNO}_3 \cdot \text{H}_2\text{O}$ identical with darapskite can exist as a solid phase between 13° and 74° . No other double salt was detected. The three solid-phase equilibria observed were: (1) Na_2SO_4 — $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ —darapskite at 24.3° ; (2) NaNO_3 — Na_2SO_4 —darapskite at 74° ; (3) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ — NaNO_3 —darapskite at 13° .

J. GRANT.

Double salt isotherms. R. M. CAVEN and W. JOHNSTON (J. Roy. Tech. Coll. Glasgow, 1929, 2, [i], 30—35).—See A., 1928, 1191.

System $\text{Fe}(\text{NO}_3)_3$ — HNO_3 — H_2O at 25° . G. MALQUORI (Atti R. Accad. Lincei, 1929, [vi], 9, 324—325).—The system has been investigated in the region of high nitric acid concentrations. The compounds $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were identified. The latter may be prepared by the action of nitric anhydride on a saturated solution of the former in nitric acid of d 1.52.

F. G. TRYHORN.

System $\text{Fe}(\text{NO}_3)_3$ — KNO_3 — HNO_3 — H_2O . G. MALQUORI (Atti R. Accad. Lincei, 1929, [vi], 9, 414—416; cf. preceding abstract).—A portion of the 25° isotherm for this system has been investigated with reference to the fractional crystallisation of the liquor obtained by the extraction of leucite with nitric acid. The following sets of solid phases are stable in contact with solutions of the compositions given by the figures in parentheses, which refer respectively to the percentages of ferric nitrate, potassium nitrate, nitric acid, and water: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ + $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (28.2, 0, 54.23, 17.75); $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ + $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ + $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{KNO}_3 \cdot 4\text{H}_2\text{O}$, (27.0, 17.30, 39.11, 16.59); $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ + KNO_3 , (39.05, 11.02, 0, 49.03); $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ + KNO_3 + $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{KNO}_3 \cdot 4\text{H}_2\text{O}$, (24.91, 26.50, 26.71, 21.88); $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{KNO}_3 \cdot 4\text{H}_2\text{O}$ + KNO_3 , (7.80, 43.95, 46.15, 2.10). The compound $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{KNO}_3 \cdot 4\text{H}_2\text{O}$ is the first example of a double nitrate of an alkali metal and tervalent iron.

F. G. TRYHORN.

Systems: strontium oxide-phosphorus pentoxide-water, and barium oxide-phosphorus pentoxide-water at 25° (acid region). H. V. TARTAR and J. R. LORAH (J. Amer. Chem. Soc., 1929, 51, 1091—1097).—The isotherms for 25° have been determined for the above two systems.

S. K. TWEEDY.

Double decomposition in the absence of a solvent. VII. Equilibrium in the systems formed from thallous sulphate and mercury halides. N. K. VOSKRESSENSKAJA (J. Russ. Phys. Chem. Soc., 1929, 61, 79—87).—The systems thallous sulphate—mercuric chloride, bromide, or iodide have been examined in reference to the conditions of equilibrium. Their behaviour resembles that of binary systems. Thallous sulphate forms no complexes with either the bromide or the iodide, but with the chloride it combines to form a complex $3\text{Tl}_2\text{SO}_4 \cdot \text{HgCl}_2$, m. p. 269° .

The composition cannot, however, be regarded as definitely settled on account of experimental difficulties. The reaction between thallous sulphate and the three mercuric salts in water was also examined. In the case of mercuric chloride a compound of the approximate composition $5\text{HgCl}_2 \cdot 2\text{Tl}_2\text{SO}_4$ is formed, but no double decomposition appears to take place.

A. FREIMAN.

Double decomposition in the absence of a solvent. VIII. Unusual irreversible system $\text{TlNO}_3 + \text{KBr} \rightarrow \text{TlBr} \rightarrow \text{KNO}_3$. A. P. ROSTKOVSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 89—107).—The equilibrium relations are described. It has been found that the reaction goes irreversibly in the direction of the formation of thallous bromide. The critical temperature of complete miscibility of the components is 535° . Complex formation occurs only in the case of potassium nitrate and potassium bromide: the compound $\text{KNO}_3 \cdot \text{KBr}$ has m. p. 342° (decomp.).

A. FREIMAN.

Carbon dioxide-carbon monoxide equilibrium over copper. F. HALLA (Z. anorg. Chem., 1929, 180, 83—88).—The equilibrium pressure for the system $\text{Cu}_2\text{O} \rightleftharpoons 2\text{Cu} + 0.5\text{O}_2$ indicated by the experimental data of Ishikawa and Kimura (A., 1928, 246) is, contrary to the assumption made by Brody and Millner (A., 1927, 939), much less than the pressure corresponding with the equilibrium $2\text{CuO} \rightleftharpoons \text{Cu}_2\text{O} + 0.5\text{O}_2$ at the same temperature. By means of the new figures, the constant for the equilibrium $2\text{Cu} + \text{CO}_2 \rightleftharpoons \text{Cu}_2\text{O} + \text{CO}$ between 200° and 700° has been recalculated.

R. CUTHILL.

Heterogeneous equilibrium of tungsten and its oxides with carbon monoxide and carbon dioxide. Z. SHIBATA (Tech. Rep. Tohoku, 1929, 8, 129—144).—The reduction of tungsten trioxide by mixtures of carbon monoxide and dioxide takes place in three stages through the intermediate oxides W_2O_5 and WO_2 ; between each oxide and the next lower and between WO_2 and metal there is a limited series of solid solutions. The constants for the successive stages of equilibrium have been determined.

A. R. POWELL.

Heterogeneous equilibrium of tungsten and its oxides with hydrogen and water vapour and the dissociation pressure of the oxides. Z. SHIBATA (Tech. Rep. Tohoku, 1929, 8, 145—151).—Equations have been derived which express the equilibria in the successive stages of the reduction of tungsten trioxide by hydrogen, and the dissociation pressure of the three oxides of tungsten have been calculated. The heats of formation of WO_3 and WO_2 are respectively 138.2 and 199.9 g.-cal. and the heat of the reaction $2\text{WO}_2 + 0.5\text{O}_2 = \text{W}_2\text{O}_5$ is 62.9 g.-cal. These values are in close agreement with those found by earlier investigators.

A. R. POWELL.

Heat of dissociation of nitrogen. J. KAPLAN (Proc. Nat. Acad. Sci., 1929, 15, 226—229).—Theoretical. Arguments are presented in support of Gaviola (cf. A., 1928, 1075) and others, that the heat of dissociation of nitrogen is less than the accepted value of 11.4 volts. The value 9.0 volts seems to be indicated.

N. M. BLIGH.

Specific heats of sodium and potassium hydroxide solutions [at 18°]. T. W. RICHARDS and L. P. HALL (J. Amer. Chem. Soc., 1929, 51, 707—712).—Experiments already recorded were repeated and extended, the results previously obtained being confirmed (cf. Richards and Gucker, A., 1925, ii, 848; Richards and Rowe, A., 1913, ii, 920). The method of determining sodium as a chloride residue is subject to error on account of the retention of water by the crystals; only fusion of the salt will remove this water. Sodium hydroxide may be completely freed from potassium by two crystallisations. S. K. TWEEDY.

Heats of dilution of sodium hydroxide, acetic acid, and sodium acetate, and their bearing on heat capacities and heat of neutralisation. T. W. RICHARDS and F. T. GUCKER, jun. (J. Amer. Chem. Soc., 1929, 51, 712—727).—The method previously described was improved and used to determine the specific heats and heats of dilution at 16° and 20° of sodium acetate, sodium hydroxide, and acetic acid (Richards and Rowe, A., 1921, ii, 380). Dilution of sodium acetate and acetic acid is attended by evolution of heat; the same applies to sodium hydroxide at concentrations below 1 mol. of salt in 400 mols. of water, at which concentration the heat of dilution changes sign. Dilution of concentrated acetic acid solutions is accompanied by an increase in heat capacity. The heat of neutralisation of acetic acid increases with the dilution, but for all acids the value 13,600 g.-cal./mol. is approached at infinite dilution.

S. K. TWEEDY.

Heats of dilution and heat capacities of hydrochloric acid solutions. T. W. RICHARDS, B. J. MAIR, and L. P. HALL (J. Amer. Chem. Soc., 1929, 51, 727—730).—The specific heats at 18° and the heats of dilution at 16° and 20° of some hydrochloric acid solutions were measured, and from the results the specific heats at other dilutions were calculated. The values for the heats of dilution substantially agree with those previously found (cf. Richards and Rowe, A., 1920, ii, 584).

S. K. TWEEDY.

Thermochemical behaviour of weak electrolytes. T. W. RICHARDS and B. J. MAIR (J. Amer. Chem. Soc., 1929, 51, 740—748).—The heats of dilution of citric acid, sodium citrate, and the two sodium hydrogen citrates were determined over a wide range of dilution. The replacement of hydrogen by sodium does not produce any regular effect on the heat of dilution, and the latter decreases for each compound as the ionisation increases. Each replacement of hydrogen in citric acid by sodium is accompanied by an almost regular increase in the loss of heat capacity of the solution, which latter quantity seems to depend very largely on the degree of dissociation. Contrary to the behaviour of strong inorganic acids, the heat capacities of the solutions decrease as hydrogen is replaced by sodium. The heats of neutralisation of citric acid and the two hydrogen citrates are recorded; they are smaller, and their temperature coefficients are smaller, than the corresponding values for strong acids.

S. K. TWEEDY.

Heats of dilution and specific heats of barium and calcium chloride solutions. T. W. RICHARDS

and M. DOLE (J. Amer. Chem. Soc., 1929, 51, 794—802).—The specific heats increase between 20° and 25°. As required by the Debye-Hückel theory (Bjerrum, A., 1926, 476), both calcium and barium chlorides have positive heats of dilution at very small concentration. The heats of dissolution of calcium, strontium, and barium chlorides show a regular decrease in magnitude as the at. wt. of the metal increases.

S. K. TWEEDY.

Thermolysis of solid salts (Ludwig-Soret phenomenon). H. REINHOLD (Z. physikal. Chem., 1929, A, 141, 137—140).—Continuing earlier work on thermo-electric phenomena in solid salts, thermolytic experiments were carried out with mixed crystals of cuprous and silver iodides. Cylinders containing 25% of cuprous iodide and 75% of silver iodide were prepared and made homogeneous, being heated for some time at 250° in an atmosphere of nitrogen. Two cylinders with their ends in contact were then heated for 4 days so that the temperature difference between one end and the other was in the neighbourhood of 100—120°. There was a change in weight of the cylinders, the hotter cylinder becoming heavier. The total weight of the two remained unchanged. By transposing the hot and cold cylinders the change was made to take place in the reverse direction, the cylinders regaining their original weights. There is an exchange of ions from one cylinder to the other. Copper ions travel with the temperature gradient; silver ions travel against it. Hence the colder cylinder will become lighter as the silver ions are replaced by the lighter copper ions. In the case of silver and copper ions with their abnormally high mobilities the effect is considerable.

A. J. MEE.

Superconducting mixture made up of non-superconducting elements. W. J. DE HAAS, E. VON AUBEL, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 226—230).—The resistance of a eutectic mixture of gold and bismuth (17.9% Au) has been determined down to 2.041° Abs. The mixture appears to be superconducting. There are two possibilities. In the first place, either gold or bismuth may be superconducting at very low temperatures, or, secondly, the superconductivity may be due to impurities. The transition point from ordinary to superconduction, however, does not agree with that of any known superconductor. The temperature-resistance curve has the same character as that for ordinary superconductors.

A. J. MEE.

Variation of the conductivity of coloured solutions during decolorisation. N. ZCHODRO (J. Chim. phys., 1929, 26, 117—119).—The electrical resistance of solutions of cyanine and of gallocyanine in benzene decreases when the solution is exposed to light. On removing the source of light the resistance slowly returns to its initial value. Monochromatic light is effective only within the limits of the absorption band of a solution of cyanine in benzene.

O. J. WALKER.

Conductometric titrations and the measurement of the resistances of electrolytes by a visual method. G. JANDER and O. PFUNDT (Z. Elektrochem., 1929, 35, 206—208).—An alternating-current method is described which dispenses with the

use of a telephone and the adjustment of the position of the sliding contact on the wire of the Wheatstone bridge at each stage of the titration. In this method the sliding contact is first placed in a suitable position and a transformer is inserted in the position normally occupied by the telephone. A "thermocross" is placed in the secondary circuit of the transformer and is also included in the circuit of a mirror-galvanometer. The variation in current produced in the main Wheatstone bridge circuit by the addition of reactant to the titration cell results in the heating of the "cross" in the galvanometer circuit, giving rise to a thermoelectric current, which causes the galvanometer needle to be deflected in such a way that the deflexion bears a simple relation to the conductivity of the liquid undergoing titration. Details are also given of the procedure to be adopted to use the apparatus as a null-point instrument for the exact measurement of conductivity.

H. T. S. BRITTON.

Electrode potential of nickel. II. Effect of occluded hydrogen on the electrode potential of nickel. III. Mechanism of the reactivation of the passive state of nickel. K. MURATA (Tech. Rep. Tohoku, 1929, 8, 71—82, 83—94).—II. Prolonged cathodic polarisation of nickel in dilute sulphuric acid solution causes a slight decrease in the initial value of the *E.M.F.* of the cell $\text{Ni}|\text{NiSO}_4(0.05M)||\text{KCl}(0.1N), \text{Hg}_2\text{Cl}_2|\text{Hg}$; the decrease is attributed to the introduction of traces of free acid. The potential of a nickel electrode in an atmosphere of nitrogen and hydrogen is the same as that in nitrogen. These results indicate that occluded hydrogen has no effect on the potential of nickel; the true value of this potential can be determined only in the complete absence of oxygen, however, as even traces of oxygen reduce the potential by 30 millivolts.

III. The reactivation of passive nickel electrodes by hydrogen is explained on the assumption that nickel acts as a catalyst in the combination of hydrogen and oxygen. From thermodynamic considerations the equilibrium conditions in the nickel half cells have been deduced to be such that the activity product ($a_{\text{Ni}} \times a_{\text{OH}^-}$) reaches the solubility product of nickel hydroxide when the partial pressure of hydrogen is 0.22 atm. The free energies of several reactions in the system nickel-oxygen-hydrogen have been determined.

A. R. POWELL.

***E.M.F.* of silver-silver chloride-calomel cells.** W. M. MAZEL (Amer. Electrochem. Soc., May 1929. Advance copy, 8 pp.).—The dependence of the potential of the silver-silver chloride electrode on the mode of preparation of the silver and the silver chloride has been investigated. Coarsely crystalline silver prepared by electrolysis of a 20% silver nitrate solution shows a more positive potential against silver nitrate solution than silver prepared in other ways and this potential is unchanged by heating at 400—500°, whereas other samples all change in potential on such treatment. Of several preparations of silver chloride the least soluble was that made by fusing a carefully washed sample. Using the coarsely crystalline electrodeposited silver and the least soluble preparation of silver chloride, the *E.M.F.* of the cell

$\text{Hg}|\text{Hg}_2\text{Cl}_2, 0.1N\text{-KCl}, \text{AgCl}|\text{Ag}$ is 0.0466 volt at 25° and is reproducible to 0.1 millivolt. Values as low as 0.0422 volt were obtained with silver chloride prepared in other ways.

H. J. T. ELLINGHAM.

***E.M.F.* of the reversible cell in a non-aqueous solution.** T. YOSHIDA (Sci. Rep. Tohoku, 1928, 7, 1279—1287).—Reversible cells of the type $\text{Cd amalgam}|\text{saturated solution}, \text{CdI}_2|\text{HgI}|\text{Hg}$ were prepared with water, acetone, methyl, ethyl, and propyl alcohols as solvents. Measurements at various temperatures show that the *E.M.F.* is independent of the solvent.

C. J. SMITHELLS.

Solubility of galena and some lead concentration cells. L. F. NIMS and W. D. BONNER (J. Physical Chem., 1929, 33, 586—590).—The *E.M.F.* of cells of the type $\text{Pb}(\text{Hg})|\text{PbX}_2(\text{sat.}), \text{PbY}_2(\text{sat.})|\text{Pb}(\text{Hg})$ have been determined at 25°. When X and Y respectively are Cl and Br, Cl and I, Br and I, Cl and 0.5SO₄, Br and 0.5SO₄, I and 0.5SO₄, and 0.5SO₄ and S, the *E.M.F.* are 0.0077, 0.0495, 0.0420, 0.1030, 0.0955, 0.0530, and 0.0670 volt, respectively. For the first three cells, the observed values agree with those calculated; from the value of the last, the solubility of galena is found to be approximately 0.94×10^{-6} g.-mol./1000 g. of water at 25°.

L. S. THEOBALD.

Reversible *E.M.F.* of electrolysis. J. VUILLERMOZ (Compt. rend., 1929, 188, 1098—1099).—The *P.D.* between 2*N*-sulphuric acid and a platinum electrode polarised negatively with a current density of 0.2—2.0 milliamp./cm.² has been determined at the instant of interruption of the current and for the first half second of spontaneous depolarisation. Interruption produces no instantaneous variation in *P.D.* unless it is accompanied by a static discharge across the electrode-electrolyte contact, when the variation increases with the intensity of the discharge. The resulting depolarisation curves, which are divisible into two types each tending asymptotically towards the same straight line, indicate that normal depolarisation is the superposition of an electrostatic and a chemical effect.

J. GRANT.

Electrochemical behaviour of substances in very dilute solutions. F. JOLLOT (Compt. rend., 1929, 188, 1106—1108).—The rate of deposition of small quantities of substances from dilute solutions may be measured continuously by means of a photoelectric cell from the increase in optical density of a glass cathode on which a transparent deposit of gold or platinum (20—40 μ in thickness) is produced by cathodic sputtering. If *i* is the cell current, *x* the thickness of metal deposited, and *A* and *B* are constants, $\log i = A - Bx$. The deposition potentials of bismuth and tellurium were determined, and the method was shown to be capable of detecting a change in weight of the deposit of 10^{-7} g.

J. GRANT.

Kucera's anomalies in electrocapillary curves. P. HERASYMENKO (Chem. Listy, 1929, 23, 121—124).—Polemical against Teige (this vol., 402).

R. TRUSZKOWSKI.

Photo-voltaic cells with silver-silver bromide electrodes. I. W. VANSELOW and S. E. SHEPPARD (J. Physical Chem., 1929, 33, 331—353).—Photo-

voltaic cells of Ag|AgBr electrodes in solutions of potassium bromide have been studied using a new vacuum tube voltmeter which is described. The shape of the *P.D.*-time curves depends on the thickness of the silver bromide layer and on the crystal size of the bromide particles, but, in general, the curve is the resultant of an initial negative effect superimposed on a positive. The *E.M.F.* between the illuminated and dark electrodes increases with an increase in concentration of the potassium bromide solution surrounding the electrodes. The results are explained by an extension of the hypothesis of Sheppard and Trivelli (cf. B., 1922, 79A) and Fajans and Frankenburg (A., 1923, ii, 109) in terms of the liberation of electrons and bromine atoms from bromide ions on absorption of light. This is supported by experiments in which the positive effect shown in the *P.D.*-time curves has been suppressed and the negative effect made more pronounced by the addition of bromine acceptors. The positive effect is also shown to be similar to that produced by allowing bromine to diffuse through the silver bromide layer to the silver. The preparation of trustworthy silver|silver bromide electrodes is described.

L. S. THEOBALD.

Electrolytic polarisation. VII. Complex cyanides: (a) silver. VIII. Complex cyanides: (b) copper. S. GLASSTONE (J.C.S., 1929, 690—702, 702—713; cf. A., 1927, 422).—VII. The variation with current density of the cathode potential and current efficiency for the deposition of silver from solutions of silver cyanide in sodium cyanide solutions with a silver cathode and a platinum anode has been investigated. When equivalent amounts of the two cyanides are present, the cathode potential increases fairly rapidly with increasing current density, since, as is shown by measurements of the static electrode potential, the potential at the equivalence point varies considerably with slight variations in the ratio of silver ions to cyanide ions. If, on the other hand, an excess of alkali cyanide is present, the cathode potential does not at first change very much with rise in current density, for in such solutions the static electrode potential is much less sensitive to variations in the relative amount of silver. In all solutions, with increasing current density a state is ultimately reached in which silver ions are deposited as rapidly as they are brought up to the electrode by diffusion and other processes. Further increase causes discharge of hydrogen ions on the electrode, resulting in the efficiency dropping below 100%, but owing to overvoltage effects gas is not evolved until a considerably higher potential is reached. Raising the temperature or stirring the solution increases the maximum current density for 100% efficiency, whereas diluting the solution has the opposite effect. Substitution of potassium cyanide for sodium cyanide has no material influence on the results. Addition of alkali carbonate renders the electrode potential for the higher current densities somewhat more negative, but the effect seems to be due mainly to the altered cathodic environment; under the conditions used technically the carbonate would have little influence. The electrodeposition of silver from argentocyanide solutions is best explained by assuming the presence

in solution of complex cations such as Ag_3CN^+ and $\text{Ag}_3\text{CN}^{2+}$, which on discharge at the cathode break down into neutral silver atoms and cyanide and silver ions.

VIII. Electrometric titration of cuprous cyanide with sodium cyanide using a copper electrode indicates that the cuprocyanide solution contains both $\text{Cu}(\text{CN})_2^+$ and $\text{Cu}(\text{CN})_3^{2-}$ ions in comparable amounts, which agrees with the observation that about 1.5 equivalents of alkali cyanide are required to dissolve 1 equivalent of cuprous cyanide. Similar results are obtained using potassium cyanide instead of sodium cyanide. When sodium cuprocyanide solutions are electrolysed with a copper cathode, the cathodic potential increases quite rapidly with increase in current density, since the static electrode potential also increases rather rapidly with decrease in the ratio of copper to cyanide when this is below about 1:2. The current efficiency for the deposition of copper is almost always below 100%, largely because the reversible copper potential soon becomes more negative than the reversible potential for hydrogen evolution. Stirring the solution much reduces the polarisation and increases the efficiency, indicating that the complex ions present dissociate rapidly, a view which accords with the relatively slight effect of rise in temperature. The solution probably contains complex cations such as Cu_2CN^+ and $\text{Cu}_3\text{CN}^{2+}$, which on discharge at the cathode yield copper. Potassium cuprocyanide solutions give results similar to the foregoing.

R. CUTHILL.

Inflammability of hydrogen. VII. Dew point, density, and range of inflammability of treated hydrogen. Y. TANAKA and Y. NAGAI (Proc. Imp. Acad. Tokyo, 1929, 5, 80—81; cf. A., 1928, 847).—Density, dew point, and range of inflammability values for hydrogen treated with various explosion suppressors are tabulated. Tin tetramethyl is considered to be the best explosion suppressor for hydrogen to be used in airships. Methyl selenide and ethyl bromide are also good, but ethyl ether and acetone are not suitable.

O. J. WALKER.

Combustion of rigidly dried carbon monoxide-oxygen mixtures. W. A. BONE (Nature, 1929, 123, 644).—Explanatory.

A. A. ELDRIDGE.

Thermal formation of hydrogen chloride. J. A. CHRISTIANSEN (Z. physikal. Chem., 1929, B, 2, 405—427).—The formation of hydrogen chloride from its elements in the dark is investigated. A new type of micro-burette used in the work is described, and it is mentioned that in an electrical thermostat with iron-mercury contact the iron must be negative. The velocity of the reaction at 200° is practically independent of the hydrogen pressure at a definite oxygen pressure, approximately proportional to the chlorine pressure, and inversely proportional to the oxygen pressure. The theory of the reaction is also considered. The Nernst atom-chain mechanism can be used to interpret the results obtained if it is assumed that the reaction chains begin only on the walls of the vessel. Various phenomena, especially the low-temperature coefficient of the reaction, support this assumption. It may also explain, in part, the differences between the results of some

earlier experiments. The presence of hydrogen chloride appears to inhibit the reaction somewhat. The effect of bromine on the reaction was also studied. As Polanyi and others have already observed, bromine does not inhibit the thermal formation of hydrogen chloride.

A. J. MEE.

Reaction of atomic hydrogen with hydrocarbons. H. S. TAYLOR and D. G. HILL (*Z. physikal. Chem.*, 1929, B, 2, 449—450).—Ethylene with an excess of hydrogen and in the presence of excited mercury atoms gives practically entirely ethane. If, however, relatively high concentrations of ethylene are used, the saturated hydrocarbons formed are more complex. The reaction may also furnish liquid condensation products of the composition $(CH_2)_n$. Methane is also formed and is acted on by hydrogen atoms under the influence of excited mercury atoms. The effect of atomic hydrogen on the saturated hydrocarbons varies with the mol. wt., being the more rapid the greater is the mol. wt. The velocity of the reaction between ethylene and hydrogen is accelerated considerably by increase in the hydrogen atom concentration, other things being equal. The reaction is therefore started by hydrogen atoms. With large excess of ethylene, acetylene is formed in considerable quantity, but with excess of hydrogen no acetylene is formed. The results are not in complete agreement with those of Bonhoeffer and Harteck (this vol., 409), which could, however, be repeated at low pressures and with large excess of hydrogen. The pressures used in the present work were up to atmospheric, and under these conditions all possible kinds of reaction product are formed.

A. J. MEE.

Low-temperature oxidation of hydrocarbons.
I. Pressure-temperature curves of amylene-oxygen mixtures. J. S. LEWIS (*J.C.S.*, 1929, 759—767).—Pressure-temperature curves of mixtures of amylene and oxygen show that a slight chemical action occurs up to 220—230°, followed by a more vigorous reaction up to 237—241° which is characterised by a fall of pressure to a minimum varying with the concentration of the gases in the mixture. Continued heating above the point of minimum pressure results in a rapid increase in pressure due to the oxidation of products formed in the preceding stage. The curves in this oxidation region are comparable with those of the paraffins (cf. Brunner and Rideal, *A.*, 1928, 1350). The reaction products in the case of amylene appear to be primarily peroxides, the rate of formation of which is increased by a rise in temperature, which also increases their rate of decomposition into aldehydes etc. which polymerise and so account for the fall in pressure. At temperatures above the minimum points in the curves the unstable compounds present set up chain reactions and rapid oxidation. This oxidation can be accelerated by the presence of catalysts such as pumice or active charcoal, which cause detonation at the critical point in the curves. Inhibitors such as lead tetraethyl almost eliminate the contraction part of the curve. These results suggest that the second step in the combustion of a paraffin hydrocarbon is the oxidation of the primarily-formed unsaturated compound to a readily decomposed peroxide the energy of decomposition of which assists the further

oxidation of the aldehydes formed during its decomposition.

A. R. POWELL.

Kinetics of the oxidation of organic compounds by bromine. I. Action of bromine on oxalic acid. E. JOSÉFOWICZ (*Bull. Acad. Polonaise*, 1929, A, 39—63).—See *A.*, 1928, 715.

Unimolecular reaction in aqueous solution which can be followed thermometrically. W. O. ROTH (*Z. Elektrochem.*, 1929, 35, 186—189).—Dihydroxyacetone undergoes a keto-enol transformation. When freshly-distilled dihydroxyacetone was burnt its heat of combustion was 3810.3 ± 0.7 g.-cal. per g., but on keeping this value became slowly diminished. This transformation readily takes place in aqueous solution and if placed in a calorimeter its course may be followed by observing the variations in temperature with a Beckmann thermometer with time. Calculations based on the corrected temperatures showed the reaction to be unimolecular. The rate depends on the age of the preparation; thus a freshly-distilled product underwent a 50% change in 0.5 min., whilst an old sample suffered about 30% transformation in that time. The heat of the keto-enol change is about $+0.43$ kg.-cal. per mol.

H. T. S. BRITTON.

Nitric acid. IV. System nitric acid-nitrous acid during oxidation. Activation of nitric acid. A. KLEMENC and L. KLIMA (*Z. anorg. Chem.*, 1929, 179, 379—412).—The nitric acid in an aqueous solution of nitric and nitrous acids possesses towards the stannous ion a definite oxidising power, which, however, gradually falls to zero; on dilution the oxidising value again increases. This effect is ascribed to the production of activated nitric acid according to the equation $3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$; decomposition of the activated acid follows the unimolecular law. A direct relationship between reaction and activation has thus been established.

H. F. GILLBE.

Velocity of hydrolysis of esters and lactones by sodium hydroxide in mixtures of two and three solvents. J. F. M. CAUDRI (*Rec. trav. chim.*, 1929, 48, 422—460; cf. Tasman, *A.*, 1928, 138).—The velocity of ring-opening of phthalide by sodium hydroxide at 25° in water and mixtures of water and methyl alcohol, water and ethyl alcohol, water and acetone, and water, ethyl alcohol, and ether was determined. In general the addition of an organic solvent decreases the velocity, except in the case of acetone, when a minimum is reached. The velocity of hydrolysis of ethyl acetate by sodium hydroxide at 25° in water and in mixtures of water and ethyl alcohol, water and methyl alcohol, water and acetone, and water, ethyl alcohol, and ether, and also of methyl acetate in a mixture of methyl alcohol and water, was also determined. The hydrolysis curves for the esters and phthalide were drawn and were found to agree fairly well.

A. FREIMAN.

Velocities of esterification of alcohols in formic acid. A. KAILAN and G. BRUNNER (*Monatsh.*, 1929, 51, 334—368).—The velocity of the uncatalysed esterification of *tert.*-butyl and *isopropyl* alcohols, glycolmonoformin, and glycerol- α -diformin in formic

acid containing various concentrations of water (w , 0.1–1.2 mols./litre), and in some cases with hydrogen chloride catalysis, has been determined at 25° and 15°. The progress of the esterification was followed by the increase in the f.p. depression of the mixture. The values of the coefficients k_1+k_2w and k_1 (k_1 =esterification coefficient, k_2 =hydrolysis coefficient) for a reversible, unimolecular reaction are calculated and are expressed by interpolation formulae as functions of w . In the uncatalysed reaction the effect of the concentration of water is greatest with *tert.*-butyl alcohol and least with the secondary alcohols, an increase in w from 0.30 to 1.37 mols./litre depressing the value of k_1+k_2w and k_1 by, respectively, 46% and 43% with the tertiary alcohol, 15% and 11%, and 21% and 20%, respectively, for isopropyl alcohol and glyceroldiformin, and 30% and 25% with glycolmonoformin. The velocity of esterification is greatest with isopropyl alcohol, the values of k_1+k_2w and k_1 for *tert.*-butyl alcohol with almost anhydrous formic acid being, respectively, 64% and 51% ($w=0.3$) and 41% and 32% ($w=1.37$) of the corresponding values for isopropyl alcohol. With glycolmonoformin the velocity of esterification at $w=0.3$ is slightly less, and at $w=1.37$, slightly higher, than that of *tert.*-butyl alcohol, whilst the value of the velocity coefficient for glycerol- α - γ -diformin is only about 0.1 of that for isopropyl alcohol, the effect of substitution of the two methyl groups by the group $\text{CH}_2\cdot\text{O}\cdot\text{CH}$ being very great. The presence of 0.0085 mol./litre of hydrogen chloride quadruples the velocity of esterification in the case of glyceroldiformin, and doubles it with the other alcohols studied, whence it is concluded that steric effects play less part in the catalysed than in the uncatalysed esterification. The mean values (for $w=0.30$ –1.37) of the temperature coefficients of k_1+k_2w and k_1 between 15° and 25° are, respectively, 3.2 and 3.5 for the uncatalysed esterification with *tert.*-butyl alcohol, and 2.4 and 2.5 for catalysis with 0.0085–0.01*N.* hydrogen chloride ($w=0.22$). The degree of esterification is 70–80% with *tert.*-butyl alcohol and glyceroldiformin, 80–90% with glycolmonoformin, and 92–100% with isopropyl alcohol. The significance of the results is discussed. J. W. BAKER.

Oxidation [by potassium permanganate] of benz-*o*-toluidide at a benzene-water interface with special reference to the temperature coefficient of the reaction rate. L. S. KASSEL and N. K. SCHAFER (J. Amer. Chem. Soc., 1929, 51, 965–974).—The kinetics of the above reaction, which is influenced by the rate of stirring and the presence of some catalyst, was investigated at 15–45°. The activation energy increases with temperature, indicating that more than one reaction is occurring. The temperature coefficient is 2; Bell (A., 1928, 848) found 13 for this quantity. The mechanism suggested by Bell is not in disagreement with the data, but other mechanisms are possible. S. K. TWEEDY.

Decomposition of triphenylacetic acid by sulphuric acid. H. R. DITTMAR (J. Physical Chem., 1929, 33, 533–556).—The decomposition of triphenylacetic acid, in the form of its sodium salt, by sulphuric acid has been investigated by means of

measurements of the rate of evolution of carbon monoxide. The reaction is unimolecular and at 12° $k=30.7\times 10^{-3}$. Water inhibits the reaction and its effect can be represented by the equation $\log k\times 10^3=-0.544M+3.4688$. Sodium and potassium sulphates, acetic, benzoic, *o*-toluic, and crotonic acids, phenol, acetone, dimethylpyrone, *p*-cresol, and acetophenone also act as inhibitors; in general, the inhibitory effect increases exponentially with an increase in concentration and the inhibitors form an additive compound with the sulphuric acid. Hydrogen chloride in low concentration has no effect on k , but phosphoric acid at high concentration slightly inhibits the reaction. Although the temperature coefficients are affected irregularly by the presence of inhibitors, $k^2/k^{12}=2$ approx. Indirect evidence of the formation of an additive compound between triphenylacetic and sulphuric acids has been obtained and leads to an explanation of the decomposition based on the formation of an intermediate unstable additive complex, and the effect of inhibitors may be to disturb the equilibrium of the reaction by which this complex is formed. The results support Taylor's theory of the mechanism of negative catalysis. The relative ease with which sulphuric acid decomposes oxalic, formic, malic, or triphenylacetic acid is given by the critical increments of the reactions, and the similarity of these decompositions is pointed out, with the suggestion that the mechanism in each case is practically the same. Sodium triphenylacetate monohydrate forms efflorescent needles. The additive compound, $\text{C}_6\text{H}_5\cdot\text{OH}\cdot 4\text{H}_2\text{SO}_4$, has been isolated during a concentration-temperature study of the system triphenylcarbinol-sulphuric acid. The solubility of triphenylacetic acid in acetic acid at 25° has also been determined. L. S. THEOBALD.

Reactions with very large apparent temperature coefficients. L. S. KASSEL (J. Amer. Chem. Soc., 1929, 51, 1136–1145).—Examination of the available data in light of the author's reaction rate theory (A., 1928, 715; Rice and Ramsperger, *ibid.*, 484) indicates that the dehydration of calcium carbonate hexahydrate in presence of liquid water is not a single reaction. The experimental results can be accounted for, however, on the basis of the general reaction rate theory on the supposition that the change occurs in a series of steps (perhaps 5). If the temperature coefficients of the intermediate dissociation reactions are assumed to be about 3, and those of the association reactions to be about 1.5, then the observed abnormal temperature coefficient of 12 is accounted for.

The abnormal temperature coefficients of the decomposition of menthyl and bornyl benzene-sulphonates in organic solvents (Patterson and McAlpine, *ibid.*, 1253) are due to autocatalysis by the acid formed during the decomposition together with an accompanying homogeneous uncatalysed reaction and a heterogeneous catalysed reaction (? wall reaction). The nature of the solvent influences the predominance of one or other of the first two of these reactions, according as it forms complexes with hydrogen ions or not, and according to its electric moment. S. K. TWEEDY.

Kinetics of the dissolution of aluminium and cadmium in hydrochloric acid. K. JABŁCZYŃSKI, E. HERMANOWICZ, and H. WAJCHSELFISZ (*Z. anorg. Chem.*, 1929, 180, 184—192).—The rates of dissolution of aluminium and of cadmium in hydrochloric acid are independent of the rate of stirring. The temperature coefficients are 2.26 and 2.02, respectively. The dissolution process is therefore purely chemical and is not dependent on diffusion. In the case of aluminium, the rate of dissolution is directly proportional to the acid concentration. Dissolution is considered to take place by the following stages: $\text{Al} + \text{H}^+ = \text{Al}^+ + \text{H}_2$; $\text{Al}^+ + \text{H}^+ = \text{Al}^{2+} + \text{H}_2$; $\text{Al}^{2+} + \text{H}^+ = \text{Al}^{3+} + \text{H}_2$; $2\text{H} = \text{H}_2$. The velocity of the first stage is the lowest and is the velocity which is measured. If aluminium is activated by means of mercuric chloride it reacts much more readily with hydrochloric acid, and the reaction is converted into a true diffusion process. O. J. WALKER.

Velocity of dissolution of tin and some tin-copper alloys in acids. M. CENTNERSZWER (*Z. physikal. Chem.*, 1929, A, 141, 167—179).—Tin will only dissolve with measurable velocity in hydrochloric acid of concentration greater than 6*N*. The reaction is complicated, the velocity indicating that it is of the fourth order. The effect of stirring and of temperature on the velocity was determined. Diffusion had only a subordinate effect on the velocity of dissolution. The temperature coefficient of the reaction is comparable with that for the dissolution of cadmium in hydrochloric acid, which is a fourth order reaction. Alloys of tin and copper dissolved more readily than tin itself, but only the tin went into solution, leaving behind the copper, or a compound of copper and tin. This increase in velocity is due to local action, and the reaction is accelerated by stirring. A. J. MEE.

Kinetics of the contact sulphuric acid process and modern views on adsorption. M. BODENSTEIN.—See B., 1929, 354.

Influence of nitrogen peroxide on the combination of hydrogen and oxygen. H. W. THOMPSON and C. N. HINSHELWOOD (*Proc. Roy. Soc.*, 1929, A, 124, 219—227).—The accelerating effect of traces of nitrogen peroxide on the union of hydrogen and oxygen has been further investigated (cf. Gibson and Hinshelwood, A., 1928, 1334), with the object of constructing a definite theory of the mechanism of the reaction. A study of the influence of temperature, pressure, proportion of oxygen to hydrogen, presence of nitrogen, and nature of the reaction vessel on the critical concentrations of nitrogen peroxide shows that (a) the lower critical concentration is raised and the upper lowered as the total pressure of hydrogen and oxygen is increased, (b) for a given total pressure the upper limit is lowered by an increase in the proportion of oxygen to hydrogen, (c) the upper limit is lowered by the presence of nitrogen, the lower limit being only slightly affected, and (d) the results are essentially the same in porcelain as in silica vessels. These results are interpreted in terms of a theory of "reaction chains" (cf. this vol., 403). The nitrogen peroxide reacts with hydrogen, yielding activated hydrogen peroxide which in turn reacts with hydrogen in the gas phase, giving rise to a cycle of processes

whereby ultimately α (probably two) molecules of active hydrogen peroxide arise from each of the original ones. The reaction chain thus "branches," and the reaction velocity will increase indefinitely, and explosion ensue, except in so far as various deactivation processes keep the effect of the branching chains in check. The balancing of these various influences determines the critical limits of concentration between explosion and slow reaction. The interruption of the chains may be due to decomposition or reaction with hydrogen at the walls of the vessel, to mutual destruction of two hydrogen peroxide molecules, or to destruction of hydrogen peroxide by nitrogen peroxide. The latter mechanism is analogous to that which recent studies in combustion have indicated for the action of "anti-knocks."

L. L. BIRCUMSHAW.

Inhibiting action of catalysts on the decomposition of hydrogen peroxide. S. DUNAIEVA (*Pharm. J. Russia*, 1928, No. 3, 23—24; *Chem. Zentr.*, 1928, ii, 2323).—The decomposition of hydrogen peroxide is prevented by "luminal" or quinine sulphate (0.02%) for a much longer period than by phenacetin, antifebrin, or aspirin.

A. A. ELDRIDGE.

Autoxidation of quinol catalysed by managanous salts in acid solutions. V. K. LA MER and J. W. TEMPLE (*Proc. Nat. Acad. Sci.*, 1929, 15, 191—194).—A cell in which, by measuring the rate of change of *E.M.F.*, the kinetics of the quinol oxidation reaction can be followed, is described. Side reactions are eliminated. The values of the reaction velocity are plotted against a function of the percentage of quinol oxidised, proportional to the free energy content of the system, and a linear relation is obtained. The case is stated to be the first in which the velocity of a homogeneous reaction has proved to be proportional to the logarithms of the concentrations of the initial and final states, i.e., to the energy levels of the system. N. M. BLIGH.

Influence of protein on the catalytic properties of inorganic catalysts. M. J. GALVIAŁO and R. DOBROTVORSKAJA (*Biochem. Z.*, 1929, 207, 146—150).—Experiments on the oxidation of tincture of guaiacum and on the decomposition of hydrogen peroxide by inorganic catalysts in the presence of egg-albumin show that the latter has considerable influence on the processes. The decomposition of the peroxide by salts of manganese, nickel, gold, and platinum (but not that by salts of iron, cobalt, and copper) is accelerated by albumin, the reaction proceeding most rapidly when the salts are present in concentrations 0.001*M* to 0.0001*M*. Nothing is known of the influence on the anions. It is concluded that the albumin acts by holding the metal in suspension. W. MCCARTNEY.

Decomposition of aqueous bromine and bromic acid solutions by charcoal. I. M. KOLTHOFF (*Rec. trav. chim.*, 1929, 48, 291—297).—In the adsorption of bromine by charcoal, part of the bromine may react according to the equations $2\text{Br}_2 + 2\text{H}_2\text{O} = 4\text{HBr} + \text{O}_2$, $\text{Br}_2 + \text{H}_2\text{O} = \text{HBr} + \text{HBrO}$. Experiment shows that 33—40% of the bromine in a 0.015*N*-solution is decomposed in con-

tact with charcoal in a few minutes, according to the first equation. Hypobromous acid is not formed as an end-product, since this substance, as well as hypiodous acid, is very rapidly decomposed in contact with charcoal. Consequently determinations of the adsorption isotherm of bromine by charcoal, and measurements of the effect of charcoal on the velocity of reactions in which bromine is involved, are subject to error. Iodine, on the other hand, does not react when adsorbed by charcoal from aqueous solution. Reaction is slight, or absent, when bromine is adsorbed from carbon tetrachloride solution. Bromic acid is rapidly decomposed when adsorbed by charcoal from acid solutions, and slowly decomposed even in weakly alkaline solutions, with the formation of hydrogen bromide. F. G. TRYHORN.

Influence of charcoal on the velocity of the reaction among iodide, iodate, and hydrogen ions, decomposition of thiosulphuric acid, and reaction between phenol and bromine. I. M. KOLTHOFF (Rec. trav. chim., 1929, 48, 298—309).—When adsorbed on charcoal, hydrogen iodide does not react with iodate and hydrogen ions in aqueous solution. Ash-free charcoal adsorbs only hydrogen iodide from a solution of an alkali iodate and iodide. Measurements indicate a retardation by charcoal of the reaction $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightleftharpoons 3\text{I}_2 + 3\text{H}_2\text{O}$. The inhibition is only apparent, since if allowance is made for the strong adsorption of hydrogen and iodide ions, and especially of free iodine, calculation shows that the above reaction is actually accelerated by the charcoal. Great acceleration of the decomposition of a weakly acid solution of sodium thiosulphate was observed in the presence of charcoal. This was shown to be due to the instability of the undissociated thiosulphuric acid which is formed. The decomposition is rapid even in a neutral buffer solution. Little evidence was found of reaction between phenol and bromine in the adsorbed state, but reaction is rapid in the case of iodine and quinol.

F. G. TRYHORN.

Conversion of water and iodine into hydriodic acid in the presence of charcoal. P. T. DANILITSCHENKO and M. I. RAVITSCH (J. Russ. Phys. Chem. Soc., 1929, 61, 123—130).—When a mixture of iodine and water vapour is passed through a heated quartz tube containing a layer of wood charcoal hydriodic acid is formed. The temperature for the maximum yield (98%) is 795°. The maximum temperature is lowered if the porosity of the charcoal is increased.

A. FREIMAN.

Influence of some physical and chemical factors on the activity of charcoal. E. V. ALEXSEVSKI and A. I. AVGASTINIK (J. Russ. Phys. Chem. Soc., 1929, 61, 131—141).—Commercial wood and animal charcoals were impregnated with solutions of uranyl nitrate, thorium nitrate, or radium bromide and any change in their adsorptive powers towards acetic acid and acetylene was noted. Thorium nitrate was the least affected in that it retained its adsorptive powers unimpaired. Samples of birchwood were treated with solutions of uranyl nitrate, potassium nitrate, potassium carbonate, potassium hydroxide, potassium silicate, zinc chloride, ferric

nitrate, cobaltous nitrate, and nickelous nitrate for 20 hrs., then burnt, and the charcoal was investigated for any changes in its adsorptive powers towards acetic acid, acetylene, benzene, phenol, and 1% indocarmine solution. Different solutions affect the adsorptive powers of the charcoal for the various substances differently. The effect of exposure of both wood and animal charcoal to ultra-violet light was also investigated.

A. FREIMAN.

Influence of the curvature of solids on chemical and electrolytic phenomena. L. R. LUCE (Ann. Physique, 1929, [x], 11, 167—250).—The curvature of the surface of a solid reactant influences considerably the nature of the reaction, especially in liquid media. Reboul's formula for the thickness of deposits on silken threads has been verified quantitatively, and quantitative investigations show that in general the activity of a surface increases with its curvature. Two explanatory hypotheses have been developed, the one having regard to diffusion phenomena and the other to selective forces of adhesion or of affinity in the interface.

H. F. GILLBE.

"Electrolysis with fluorine." W. D. BANCROFT and N. C. JONES (Amer. Electrochem Soc., May 1929. Advance copy, 13 pp.).—It is claimed that any anode reaction not involving a time factor can be duplicated by the action of fluorine, except in so far as the hydrofluoric acid formed introduces a complication, and that any cathode reaction not involving a time factor can be duplicated by the action of a suitable metal, except in so far as the corrosion product introduces a complication. Experimental evidence is cited in support of these contentions and in opposition to statements made by Fichter (A., 1926, 925; 1927, 741; 1928, 382). It is concluded that oxidation with fluorine can be used with advantage instead of anodic oxidation in many cases where the solutions are poor conductors or where it is desirable to avoid having to deal with cathode reaction products. It is shown that the reason why lead peroxide is not obtained by the action of fluorine on acidified lead nitrate solution is that the lead tetrafluoride which is formed does not hydrolyse appreciably in slightly acid solutions. Lead peroxide is produced, however, by the action of fluorine on neutral or slightly alkaline solutions or suspensions of lead salts. When fluorine attacks organic substances it must displace the least negative radical or combine with the most positive radical, and it is suggested that this opens up a new method for studying organic compounds. A difficulty is that in reactions with fluorine an induction period may be followed by an explosive reaction, and methods of slowing down the reaction are being studied. The fluorine used was made by electrolysis of fused potassium hydrogen fluoride in a Mathers cell consisting of a magnesium pot as cathode with a magnesium diaphragm surrounding a graphite anode.

H. J. T. ELLINGHAM.

Reaction between manganese dioxide and ammonium chloride. C. DROTSCHMANN (Z. Elektrochem., 1929, 35, 194—198).—Several series of experimental Leclanche cells were set up and discharged for different times through known resist-

ances. The behaviour of different types of manganese dioxide—natural and artificial—was compared as regards (a) the amounts of manganese which dissolved in the electrolyte during the discharge of the cell, and (b) the attack on the zinc electrode. Abnormal amounts of manganese were found in the electrolytes in which artificial pyrolusite was used, although the dissolution of manganese did not appear to be a direct consequence of the depolarising action of the manganese dioxide. The enhanced chemical action of the artificial variety caused a greater attack on the zinc. The development of free ammonia in the electrolyte of a cell when kept for 14 days was greater when the zinc electrode was completely immersed than when it was partly exposed to the air. Less hydrogen was developed by a cell containing artificial manganese dioxide than by one containing the natural product when kept on open circuit. H. T. S. BRITTON.

Effect of the electric discharge on gases containing hydrocarbons at reduced pressure. F. FISCHER and K. PETERS (Z. physikal. Chem., 1929, 141, 180—194).—An apparatus which is suitable for studying the effect of the electric discharge on gaseous mixtures at low pressures is described. A gas containing initially 0.4% H_2 and 93.6% CH_4 after being subjected to the discharge contained 92.1% H_2 and 3.3% CH_4 . The methane was decomposed into acetylene and hydrogen according to the equation $2CH_4 = C_2H_2 + 3H_2$. 97% of the mixture of gases condensed by liquid air after the discharge consisted of acetylene, the remaining 3% being hydrocarbons with 2, 3, or 4 carbon atoms. Using a mixture with a very much smaller methane content, there was still a large amount of acetylene formed, together with some hydrocyanic acid from nitrogen present in the original mixture. A. J. MEE.

Integration of light by photo-electrolysis. W. R. G. ATKINS and H. H. POOLE (Sci. Proc. Roy. Dublin Soc., 1929, 19, 159—164).—A Burt vacuum sodium cell was found suitable for the integration of light. The photo-electrolytic production of alkali in a dilute hydrogen carbonate solution and the photo-electric deposition of copper under various conditions of daylight and season are described.

N. M. BLIGH.

Temperature coefficients of some photochemical reactions. G. B. KISTIAKOWSKY (Proc. Nat. Acad. Sci., 1929, 15, 194—197).—Having regard to Semenov's thermal reaction chain theory (cf. A., 1928, 847), a study was made of the non-sensitized photochemical hydrogen-oxygen and oxygen-carbon monoxide reactions. The temperature coefficient is tabulated over sets of intervals from 25° to 527°. The results diverge widely from the Arrhenius equation and increase rapidly with rise of temperature, this being attributed to an increasing quantum yield. Semenov's theory is supported, and a general theory of the reaction mechanism is outlined.

N. M. BLIGH.

Photochemical equilibrium between hydrogen, bromine, and hydrogen bromide. R. W. ARMOUR and E. B. LUDLAM (Proc. Roy. Soc. Edin., 1929, 49, 91—96).—A mixture of hydrogen and bromine was subjected to light of the shortest wave-

length possible with quartz apparatus (185 μ), using an aluminium spark, which closely approximates to monochromatic light. At equilibrium, it was found that somewhat less than 1% by weight of bromine combines to give hydrogen bromide. N. M. BLIGH.

Photochemical formation of ammonium [type] salts. A. K. PLISOV (Gazzetta, 1929, 59, 200—206).—Some preliminary experiments have been performed on the photochemical formation of salts of aromatic amines with alkyl halides in an attempt to determine whether the activation of the amine or of the halide is the determining factor in the reaction. Photochemical action is more evident in the combination of aniline with benzyl chloride than in the case of *o*-toluidine and benzyl chloride. In the former case, the yield in 3 hrs. increased from 15% for the dark reaction to 82% when illuminated in a quartz vessel by an electric arc. F. G. TRYHORN.

Photochemical decomposition of solutions of metallic salts in organic solvents. E. PUXEDDU (Gazzetta, 1929, 59, 160—164).—Solutions of mercuric chloride, lead chloride, and titanium tetrachloride in anhydrous ether were exposed to sunlight for prolonged periods in sealed vessels. Little photochemical action was observed with the lead chloride solutions, but with mercuric chloride solutions, after 5½ months, a greyish-white precipitate separated which on heating was found to consist of mercury and calomel. In the solution remaining the presence of aldehydes and chloro-compounds as well as of hydrogen chloride was detected. Photochemical action was much more rapid in the titanium chloride solution. In two or three days the original clear yellow solution became deep brown, and later, clear green in colour. Attempts at crystallisation by evaporation of this solution at low temperatures were unsuccessful, although a colour change from green to violet occurred. F. G. TRYHORN.

Action of optically excited mercury atoms on hydrocarbon molecules. W. FRANKENBURGER and R. ZELL (Z. physikal. Chem., 1929, B, 2, 395—398).—It was sought to discover whether when optically excited mercury atoms came into contact with hydrocarbon molecules there was any chemical reaction such as the breaking of the C-C linking or the C-H linking. A mixture of pentane vapour with some other gas (air, nitrogen, or carbon dioxide) was saturated with mercury vapour at 50°, and the radiation from a mercury-vapour lamp was passed through it. The products formed varied with the nature of the gas mixed with the pentane. With air a certain amount of hydrogen peroxide and aldehyde was formed, and the iodoform test gave a positive result. With nitrogen some higher hydrocarbons were produced, and with carbon dioxide the resulting mixture gave the aldehyde reactions. The primary reaction in all these cases can be traced to the breaking of a C-C or a C-H linking. The final products are the results of secondary reactions. In indifferent atmospheres (e.g., nitrogen and, to a certain extent, carbon dioxide), the residues may combine with each other, forming hydrogen and higher or lower hydrocarbons. In the presence of air or carbon dioxide the hydrogen could form hydrogen

peroxide, and organic compounds containing oxygen will be produced.

A. J. MEE.

Photochemical reaction between mercury vapour and oxygen. W. A. NOYES, jun. (Z. physikal. Chem., 1929, B, 2, 445—448; cf. Leipunsky and Sagulin, this vol., 155).—The results obtained are compared with those of Leipunsky and Sagulin. The points of agreement are: (1) the oxygen pressure in a mixture of mercury vapour and oxygen decreases if the mixture is exposed to radiation containing the resonance wave-length of mercury (λ 2537 Å.); (2) a certain amount of mercury oxide is formed during the exposure, the layer being thickest on the side of the vessel nearest the lamp; (3) a decrease in the intensity of the λ 2537 Å. radiation causes a diminution in the velocity of decrease of pressure. The chief difference in the results of the two observations lies in the action of short wave-length radiation. Short wave-length radiation which causes direct formation of ozone influences the reaction. This was not found by Leipunsky and Sagulin. This difference may be due to the different apparatus used. Apart from this there is almost complete agreement. The mechanism of the reaction is discussed, and it is shown that that put forward by Leipunsky and Sagulin is probably incorrect. A series of reactions is proposed which will give a satisfactory explanation of all the results, but a definite decision is not possible. A. J. MEE.

Retarding action of heat on photochemical reactions of coloured solutions in benzene. N. ZHODRO (J. Chim. phys., 1929, 26, 178—181).—The rates of decolorisation of a solution of cyanine in benzene at 15°, 32°, and 45°, and of gallocyanine in benzene at 14.8° and 43.5°, have been measured. In each case rise in temperature retards the reaction.

C. W. GIBBY.

Phototropic mercury compounds. S. V. R. RAO and H. E. WATSON (J. Indian Inst. Sci., 1929, 12A, 1—16).—The following compounds, which, with the exception of the last two, are phototropic, have been prepared, in most cases by crystallisation or precipitation from mixed solutions of the appropriate salts of potassium and mercury: *mercuric halogenocyanates*, XHgCNO ($\text{X}=\text{Cl}, \text{Br}, \text{I}$), *thiocyanates*, XHgCNS , and *selenocyanates*, XHgCNSe ; *mercuric hydrosulphoselenocyanate*, $\text{HS}\cdot\text{Hg}\cdot\text{CNSe}$; *trimercuric disulphodihalide*, $\text{HgX}_2\cdot 2\text{HgS}$; *trimercuric disulphodithiocyanate*, $\text{Hg}(\text{CNS})_2\cdot 2\text{HgS}$; *trimercuric disulphodiselenocyanate*, $\text{Hg}(\text{CNSe})_2\cdot 2\text{HgS}$; *trimercuric diselenodihalide*, $\text{HgX}_2\cdot 2\text{HgSe}$; *trimercuric dioxidithiocyanate*, $(\text{HgCNS})_2\cdot 2\text{HgO}$; *mercuric hydroselenoselenocyanate*, $\text{HSe}\cdot\text{Hg}\cdot\text{CNSe}$; *mercuric hydroselenothiocyanate*, $\text{HSe}\cdot\text{Hg}\cdot\text{CNS}$. By spectroscopic examination of ten of the more sensitive of these compounds it has been found that with one exception they all are darkened by exposure to light of wave-length of the order of 5500 Å. or less, slight sensitivity extending into the ultra-violet to the limit of transmission of quartz. A broad but well-defined maximum of sensitivity is found, usually in the green, of which the position for related compounds tends to move towards the red with increase in the mol. wt. of the compound.

Reversal can be effected by exposure to red light in compounds previously darkened by exposure to

light of shorter wave-length. There was a limiting wave-length on the short-wave side capable of producing reversal, but no evidence was found of a maximum efficiency in reversal. In several cases the limiting wave-length was too far in the red to be detected. A neutral zone in which no action occurs was found between the wave-lengths effective in reversal and those producing darkening. The effect of the medium in which the compound was suspended for examination was determined, and in most cases darkening was accelerated and reversal retarded by a medium such as gelatin. By suitably dyeing the compounds the region of sensitivity can be extended towards the red. For two compounds the mean temperature coefficients of the dark and light reactions were found to be 1.9 and 1.0, respectively. No induction period was observed, and the time of exposure required to produce a given effect was inversely proportional to the light intensity.

F. G. TRYHORN.

Primary process in the formation of the latent photographic image. F. C. TOY and G. B. HARRISON (Nature, 1929, 123, 679—680).—The photo-conductivity effect in layers of silver bromide made under conditions such that the bromine cannot escape is simply an expression of the primary photographic process (decomposition of silver bromide into silver and bromine), completely isolated from secondary chemical processes (removal of the bromine). The photo-current, due to liberated valency electrons when light passes through a thin layer of silver bromide fused between quartz plates, starts instantaneously on illumination and quickly reaches its final value.

A. A. ELDRIDGE.

Effect of photographic reactions on the Weigert effect in photochloride. H. ZOCHER and K. COPER (Z. physikal. Chem., 1929, 141, 217—218).—It has been stated that the Weigert effect can be obtained only by the use of red light. The authors claim to have obtained it with white light.

A. J. MEE.

Helium. VI. Helium content of "moldavites" and artificial glasses. F. PANETH, K. W. PETERSEN, and J. CHLOUPEK (Ber., 1929, 62, [B], 801—809).—The rare gases are present in the products evolved when moldavites are ignited or fused with sodium carbonate, the proportion of helium being greater than that corresponding with its relationship to argon and neon in atmospheric air. Fresh determinations show the presence of 2.19×10^{-5} c.c. of neon + helium in 1 c.c. of air. If the relationship of the rare gases were the same as in atmospheric air, the amount of neon and helium must be derived from the amount of argon by multiplication by 2.35×10^{-3} . Three moldavites of different origin exhibited an excess of helium above this value equal as an average to 1.6×10^{-5} c.c. per g. of material. The preponderance of helium can be detected qualitatively by observation of the neon-helium spectrum. The excess of helium in the gas from the moldavites is a direct consequence of their glassy nature, since artificial glasses have the power of concentrating helium greatly in comparison with neon; under rather less than atmospheric pressure they dissolve in equal

times at the ordinary temperature approximately ten times as much helium as neon. In spite of the very small partial pressure of helium in atmospheric air, this action is sufficient to explain at any rate the greater part of the helium content of moldavites, since artificial glass, in which the helium cannot be of radioactive origin, but is necessarily derived from the air, has a "helium excess" amounting to 4.2×10^{-6} c.c. per g. It is therefore beyond doubt that the helium excess in moldavites is conditioned by the establishment of an equilibrium in the distribution of helium between the material and the atmosphere and does not depend in a simple manner on the geological age. Determination of the age of moldavites and other types of textites or of natural glassy products by the helium method is, in principle, impossible.

H. WREN.

Preparation of sodium-potassium alloy. T. MIDGLEY, jun., and A. L. HENNE (Ind. Eng. Chem. [Anal.], 1929, 1, 751).—Freshly cut sodium and potassium are placed in slightly wet ether and gently agitated. Association with ether is less dangerous than association with benzene, the cooling effect of evaporation of the ether reducing the tendency for spontaneous ignition in the air.

J. S. CARTER.

Decomposition of alkali carbonates in aqueous solution. B. L. VANZETTI (Gazzetta, 1929, 59, 219—223; cf. A., 1925, ii, 421).—By passing a current of hydrogen free from carbon dioxide through a boiling solution of potassium or sodium carbonate (about 0.2*N*) as much as 70% of the carbonic acid may be removed in 5—6 days with the formation of free alkali. The amount of carbonate decomposed is proportional to the square root of the time. Analogous results are obtained if the solutions are boiled in open vessels by a current of superheated steam, the bulk of the solution being maintained with water free from carbon dioxide. At lower temperatures, under reduced pressure, the smaller yield of carbonic acid through reduced hydrolysis, and the lower dissociation pressure of the carbonic acid solution so formed, inhibit the loss of carbon dioxide. The decomposition increases with, but less quickly than, the concentration of the carbonate.

F. G. TRYHORN.

Complex sulphites. G. JANTSCH and K. ABRESCH (Z. anorg. Chem., 1929, 179, 345—356).—Lithium cobaltisulphite, $\text{Li}_3[\text{Co}(\text{SO}_3)_3] \cdot 4\text{H}_2\text{O}$, has been prepared by treating a solution containing lithium nitrite and cobalt nitrate with acetic acid, and adding the resulting solution to a boiling solution of lithium sulphite. The complex salt crystallises out readily if the solution is kept hot (80—90°) for a short time. On exposure of the solution to air cobaltic hydroxide gradually precipitates. The insoluble potassium salt, crystallising with 6 mols. of water, may be obtained by direct precipitation. A solution of the lithium salt yields no precipitate when treated with cold ammonia solution, whereas with sodium hydroxide solution all the cobalt is precipitated as hydroxide. The solution has a very low conductivity and exhibits the Tyndall effect; after ultrafiltration the conductivity remains very small, and the Brownian movement is observable. The true solubility of the complex salt thus appears to be very small. Trans-

port observations indicate the presence in the solution of the $\text{Co}(\text{SO}_3)_3'''$ ion.

H. F. GILLBE.

Alkali perborates in the solid state. M. LE BLANC and R. ZELLMANN (Z. anorg. Chem., 1929, 180, 127—128).—Polemical against Menzel (A., 1928, 32).

R. CUTHILL.

Double carbonate of cobalt and potassium. F. DE CARLI (Atti R. Accad. Lincei, 1929, [vi], 9, 417—419).—The salt $\text{CoCO}_3 \cdot \text{K}_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ is obtained as rose-coloured crystals from a mixed solution of cobalt nitrate and potassium carbonate. By dehydration at 100—120° in a current of carbon dioxide it is converted into the deep violet anhydrous compound. From measurements of the dissociation pressures at temperatures between 220° and 318°, a mean value of 13.74 kg.-cal. is obtained for the heat of dissociation. This figure includes the heat of dissociation of cobalt carbonate as well as that of the dissociation of the double carbonate.

F. G. TRYHORN.

Action of potassium ferrocyanide on silver and several sparingly soluble silver compounds. E. BEUTEL and A. KUTZNIGG (Monatsh., 1929, 51, 309—380).—When finely-divided silver is boiled with a solution of potassium ferrocyanide in a current of air it passes into solution with the formation of potassium silver cyanide, ferric hydroxide is precipitated, the solution becoming alkaline, and some hydrogen cyanide is evolved. Quantitative examination shows that the amount of silver dissolved is not equivalent to the precipitated iron. Decomposition of the potassium ferrocyanide into ferric hydroxide and potassium cyanide occurs on boiling its solution, the potassium cyanide reacting with the silver, and a portion being hydrolysed with liberation of hydrogen cyanide. A similar reaction occurs with silver chloride, bromide, cyanide, ferrocyanide, oxide, carbonate, and chromate, the solution in these cases remaining neutral. Similar dissolution of silver and its sparingly soluble salts occurs more slowly in cold saturated potassium ferrocyanide solution, the ferric hydroxide formed remaining in colloidal solution. By measurements of the *P.D.* of concentration cells the solubility of silver ferrocyanide (which, contrary to statements in the literature, is readily soluble in hot, concentrated hydrochloric acid) is intermediate between that of the chloride and bromide. When well washed, precipitated silver cyanide is shaken with an equivalent quantity of dilute potassium ferrocyanide solution, the orange colour formed with nitric acid shows the presence of $\text{Ag}_4\text{Fe}(\text{CN})_6$. If a slight excess of saturated potassium ferrocyanide is now added and shaking continued, the precipitate becomes definitely crystalline and consists of the compound $\text{KAg}_3\text{Fe}(\text{CN})_6$, intermediate in the formation of potassium silver cyanide, and in the third stage of the reaction dissolves in the excess of potassium ferrocyanide, the total reaction being represented by the equation " $4\text{AgCN} + 2\text{K}_4\text{Fe}(\text{CN})_6 + 5\text{H}_2\text{O} = 4\text{KAg}(\text{CN})_2 + 2\text{Fe}(\text{OH})_3 + 4\text{HCN}$." The application of these results to photographic processes, and the explanation of the processes involved in a silvering solution and in a ferrocyanide silver plating bath are discussed on the basis of these results.

J. W. BAKER.

Red phosphorescent alkaline-earth compounds. L. VANINO and F. SCHMID (J. pr. Chem., 1929, [ii], 121, 374—376).—The red luminescence of the alkali sulphide compounds obtained by Vanino and Zumbusch (A., 1909, ii, 731) is improved by partial substitution of caesium for rubidium carbonate, but the most intense red phosphorescence is obtained by heating together 40 g. of barium oxide, 9 g. of sulphur, 0.7 g. of lithium phosphate, and 3.2 c.c. of a copper nitrate solution containing 0.38 g. of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 100 c.c. of alcohol. J. W. BAKER.

Action of calcium carbonate and of dolomite on zinc sulphate solutions. L. CAMBI, G. BOZZA, and D. MASPERI.—See B., 1929, 354.

Sulphoaluminates of calcium. W. LERCH, F. W. ASHTON, and R. H. BOGUE (U.S. Bur. Stand. Res. Paper, 1929, No. 54, and Bur. Stand. J. Res., 1929, 2, 715—731).—The existence of calcium sulphoaluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$, d^{20} 1.48; refractive indices w_D 1.464, e_D 1.458, has been confirmed. The compound is stable in aqueous solution except in the presence of magnesium salts or carbonates. A new calcium sulphoaluminate, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$, d^{20} 1.95, refractive indices 1.504, e_D 1.488, has been isolated. It is much less stable than the former and under conditions occurring in concrete it is transformed into the more stable sulphoaluminate. In solution the transformation is retarded by hydroxyl ions. The existence of the calcium sulphosilicoaluminate of Lafuma (Ciment, 1925, 30, 175) has not been confirmed. F. J. WILKINS.

Germanium. XXVII. Germanium dichloride. L. M. DENNIS and H. L. HUNTER (J. Amer. Chem. Soc., 1929, 51, 1151—1154).—Germanium tetrachloride vapour reacts with metallic germanium at 350° to form germanium dichloride, a light yellow solid, which dissociates at 74.6°. The dichloride is insoluble in, or reacts with, many of the common solvents, although it does not attack 95% ethyl alcohol or chloroform. It is soluble in germanium tetrachloride, is hydrolysed by water, and is converted by ammonia solution into an orange-coloured substance. Concentrated hydrochloric acid converts it into trichloromonogermene. In dry oxygen, the reaction $2\text{GeCl}_2 + \text{O}_2 = \text{GeO}_2 + \text{GeCl}_4$ occurs; in wet oxygen, germanochloroform is formed. The dichloride is converted by hydrogen sulphide into germanium sulphide, GeS , and bromine reacts with it to form a mixture of germanium tetrachloride and tetrabromide. Withdrawal of the elements of hydrogen chloride from germanochloroform does not produce germanium dichloride, nor does reduction of the tetrachloride with powerful reducing agents. S. K. TWEEDY.

Phosphorous oxide. L. WOLF and H. SCHMAGER (Ber., 1929, 62, [B], 771—786).—When heated in a sealed tube, phosphorous oxide undergoes slow but sensible decomposition at 150°; with rising temperature, the rate of decomposition increases rapidly. The effect is due in part to temperature, in part to the vapour tension of the trioxide, which is greater than that of its decomposition products. Distillation of phosphorous oxide through a heated tube under greatly diminished pressure (0.01—0.001 mm.) shows

that incipient decomposition takes place at 340—475°; below 500° the rate of change is slow but increases rapidly above this temperature. Favourable results in the preparation of phosphorous oxide depend on a favourable compromise between the period during which the trioxide remains in the flame and the lengthening of the flame. The yellow phosphorus is contained in a twice-bent quartz tube immersed in a vessel of water. A mixture of oxygen and nitrogen (25 and 75 vol.-%), dried by calcium chloride, soda-lime, phosphoric oxide, and sulphuric acid or carbon dioxide can be passed through the apparatus, the pressure of the gas being regulated by suitable pumps. The collecting apparatus consists of coarse and fine dust chambers followed by three U-tubes cooled respectively by ice and salt, carbon dioxide and acetone, and liquid air. Entry of dust into the pump is prevented by a long glass tube loosely packed with glass wool and connected with a U-tube cooled in liquid air. After the apparatus has been filled with carbon dioxide, the phosphorus is introduced. After evacuation, the phosphorus is warmed to about 50° and the water evolved is condensed in a subsidiary U-tube immersed in liquid air. The phosphorus is ignited and the quartz tube immersed in water at 46—50°. During the complete change, the pressure of the gas is maintained at 90 mm.; the rate of passage is 30 litres per hr. The product, which collects mainly in the coarse and fine dust chambers, is distilled at above 1 mm. into the U-tubes, a very slow current of carbon dioxide being helpful. It is contaminated by phosphoric oxide, probably phosphorus tetroxide, red and yellow phosphorus, from which (with the exception of yellow phosphorus) it can be freed by filtration through glass wool or a glass crucible in an atmosphere of carbon dioxide. Distillation from a special apparatus yields phosphorous oxide containing, as impurity, yellow phosphorus in amount not exceeding 0.2%. H. WREN.

Attempts to prepare phosphorus trioxide by a method other than by burning phosphorus. W. P. JORISSEN and A. TASMAN (Rec. trav. chim., 1929, 48, 324—327; cf. Druten, this vol., 540).—Unsuccessful attempts have been made to prepare phosphorus trioxide by the action of phosphorus trichloride on phosphorous acid, or by the action of the same reagent on acetic, trichloroacetic, and butyric acids, and on sodium formate. F. G. TRYHORN.

Difluorophosphoric acid and its analogy to perchloric acid in salt formation. Monofluorophosphoric acid and the similarity of its salts to the sulphates. W. LANGE (Ber., 1929, 62, [B], 786—792; 793—801).—Hydrolysis of phosphoryl fluoride by cold, dilute alkali hydroxide results in the production of difluorophosphoric acid, HPO_2F , conveniently isolated as the nitron salt (cf. A., 1927, 532). More conveniently, phosphoric oxide is heated with 3 mols. of ammonium fluoride in a copper or nickel crucible at 135°; ammonium difluorophosphate, m. p. 213°, is obtained by extracting the cold product with alcohol. Addition of the requisite salts to dilute, aqueous solutions of ammonium difluorophosphate gives the corresponding tetramethylammonium, strychnine, brucine, morphine, and cocaine compounds; from

very concentrated solutions the *potassium* and *cæsium* salts are prepared. Other salts are obtained by treating a hot solution of nitron difluorophosphate with the metallic nitrate, separation of nitron nitrate, and evaporation of the filtrate over sulphuric acid in a vacuum. They crystallise poorly, are hygroscopic, and, in part, become decomposed by hydrolysis during evaporation. The crystalline difluorophosphates are stable in air. They yield neutral solutions in water, in which they slowly undergo hydrolysis. Distillation of them with concentrated sulphuric acid does not afford difluorophosphoric acid, which has been prepared in dilute aqueous solution from the nitron salt and nitric acid or the silver salt and hydrochloric acid. Difluorophosphoric acid exhibits, in part, the properties of perchloric acid in a weakened form. The solubilities of its characteristic salts are generally considerable in comparison with those of the corresponding perchlorates; certain of them (*o*-toluenediazonium, pyridine, methylene-blue, malachite-green) cannot be prepared by precipitation, although the sparingly soluble perchlorates exist.

Salts of difluorophosphoric acid are completely hydrolysed by protracted heating with concentrated alkali hydroxide, whereas boiling, very dilute potassium hydroxide yields potassium fluoride and potassium monofluorophosphate. Addition of much solid silver nitrate to the resultant solution causes the separation of *silver monofluorophosphate*, $\text{Ag}_2\text{PO}_3\text{F}$, from which, by double decomposition with the requisite chloride, the corresponding *sodium*, *potassium*, and *ammonium* (monohydrate and anhydrous) salts are derived; the ammonium compound loses ammonia at 220° , yielding *ammonium hydrogen monofluorophosphate*, m. p. 225.5° . Aqueous solutions of the alkali salts are neutral to phenolphthalein but alkaline to methyl-orange, in the presence of which 1 mol. of salt requires 1 equivalent of acid for neutralisation. The salts are remarkably stable in neutral or alkaline solution, but are rapidly decomposed in hot acid solution. All cations which give sparingly soluble sulphates give characteristic monofluorophosphates. Other cations, including magnesium, zinc, and copper which yield sparingly soluble phosphates or fluorides, give freely soluble salts which have not been investigated further. The similarity is attributed to the identical valency of the anions co-ordination number and similar radii of the central atoms.

Monofluorophosphoric acid is present in the product of the action of phosphoric oxide and ammonium fluoride, from which it can be partly extracted by alcohol as the ammonium hydrogen salt. The optimal proportion of the reactants is the same as for the production of difluorophosphate, so that the change is formulated: $\text{P}_2\text{O}_5 + 3\text{NH}_4\text{F} = (\text{NH}_4)\text{PO}_2\text{F}_2 + (\text{NH}_4)_2\text{PO}_3\text{F}$. The mono-acid is also formed when phosphoric oxide is dissolved in 40% hydrofluoric acid or when metaphosphoric acid is treated with hydrofluoric acid or ammonium fluoride.

Treatment of silver monofluorophosphate with concentrated sulphuric acid causes the evolution of small quantities of a readily condensable gas, possibly the oxyfluoride, PO_2F . *Monofluorophosphoric acid* is readily prepared in dilute aqueous solution from the silver salt and hydrochloric acid; it is slowly but

completely hydrolysed to orthophosphoric and hydrofluoric acid.

The *calcium* ($+2\text{H}_2\text{O}$), *strontium* ($+ \text{H}_2\text{O}$), *barium*, *mercurous*, *lead*, and *benzidine monofluorophosphates* are described.

H. WREN.

Combination of phosphorus pentachloride with bromine. V. A. PLOTNIKOV and S. I. JAKUBSON (*J. Russ. Phys. Chem. Soc.*, 1928, 60, 1513—1515).—See this vol., 158.

Double sulphates and their components. III. Chromic sulphate. F. KRAUSS, H. QUERENGASSER, and P. WEYER (*Z. anorg. Chem.*, 1929, 179, 413—417).—The existence of the following hydrates of chromic sulphate has been established: 18, 9, 3, anhydrous (violet); 6 (probably), and anhydrous (green, crystalline). The water in the green, amorphous form is in zeolitic combination.

H. F. GILLBE.

Sulpho-salts. VIII. Persulpho-salts. L. FERNANDES (*Atti R. Accad. Lincei*, 1919, [vi], 9, 409—414; cf. this vol., 525).—The formulæ of the type $\text{S}_3\text{Mo}\cdot\text{S}\cdot\text{S}\cdot\text{S}\cdot\text{NH}_4$, proposed by Hoffmann, for salts derived from the acids HMoS_5 and HMoS_6 are untenable. Instead, co-ordination formulæ of the type $(\text{NH}_4)_2[\text{Mo}_2\text{S}_7(\text{S}_6)]$ are suggested for the following compounds which have been prepared, chiefly by the action of hydrogen sulphide or ammonium polysulphide on solutions of the normal sulpho-salts of molybdenum and vanadium: NH_4MoS_6 ;

$\text{NH}_4\text{MoS}_6\cdot\text{H}_2\text{O}$; $[\text{NH}_4\text{C}(\text{NH}_2)_2]\text{MoS}_6$;
 $(\text{NH}_4)_3\text{VS}_9\cdot 5\text{H}_2\text{O}$; $(\text{NH}_4)_3\text{HV}_2\text{S}_9\cdot 5\text{H}_2\text{O}$;
 $[\text{NH}_4\text{C}(\text{NH}_2)_2]_3\text{HV}_2\text{S}_9\cdot 6\text{H}_2\text{O}$; $\text{Ti}_3\text{HV}_2\text{S}_9\cdot 3\text{H}_2\text{O}$;
 $\text{K}_3\text{HV}_2\text{S}_9\cdot 8\text{H}_2\text{O}$; $(\text{NH}_4)_2\text{H}_2(\text{VS}_5)_6\cdot 10\text{H}_2\text{O}$;
 $[\text{NH}_4\text{C}(\text{NH}_2)_2]_4\text{H}_2(\text{VS}_5)_6\cdot 10\text{H}_2\text{O}$. F. G. TRYHORN.

Aminosulphonic acid and its trisubstituted derivatives. P. BAUMGARTEN (*Ber.*, 1929, 62, [B], 820—826).—Trisubstituted derivatives of aminosulphonic acid, O , form neutral solutions in

water, without immediately suffering hydrolysis. Their stability towards water depends on the nature of the group R. They are decomposed more readily by alkali hydroxide, usually into tertiary amine and sulphate. With acids they are able to form salts and they can also yield complex compounds, as instanced by the substances $[\text{NMe}_3\cdot\text{SO}_3\text{H}]\text{ClO}_4\cdot\text{H}_2\text{O}$ and $[\text{NMe}_3\cdot\text{SO}_3]_2\text{KI}\cdot\text{I}_5\cdot 2\text{H}_2\text{O}$. The structure $\text{NH}_2\cdot\text{SO}_3\text{H}$ for aminosulphonic acid rests mainly on the properties of its aqueous solution. Its high m. p., non-hygroscopicity, and limited solubility in water indicate a constitution differing from that of other sulphonic acids. Dissolution in water may be considered to cause the changes $\text{NH}_2\cdot\text{SO}_3\cdot\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{HO}\cdot\text{NH}_2\cdot\text{SO}_2\cdot\text{OH} \rightleftharpoons \text{NH}_2\cdot\text{SO}_2\cdot\text{OH}$; the hypothesis receives support from the observation that aminosulphonic acid is precipitated from its solutions by mineral acids. The presence of the betaine form to a small extent in aqueous solution is deduced from the differing degree of stability of the sulphur-nitrogen linking towards hydrolytic agents in aminosulphonic acid and its alkali salts. The free acid passes in aqueous solution into ammonium hydrogen sulphate under conditions which do not affect the alkali salts.

H. WREN.

Action of gases on metals. I. Kinetic study of the phenomena. G. VALENSI (J. Chim. phys., 1929, 26, 152—177).—Measurements have been made on the amounts of nitrogen absorbed by iron, chromium, and manganese when heated at a fixed pressure, and on the dissociation pressures. Evidence is found for the formation of a nitride, CrN, in the case of chromium. The compositions of the mixtures of gases, mainly hydrogen and nitrogen, given off when the three metals are heated in a vacuum have been investigated. C. W. GIBBY.

Supposed sesquisulphide of molybdenum. V. MONTORO (Atti R. Accad. Lincei, 1929, [vi], 9, 331—337).—An X-ray examination has been made of specimens of molybdenite which had been desulphurised by heating in an arc furnace until the sulphur content varied between 0 and 36%. Specimens containing 36—28% of sulphur gave photograms of the molybdenite lines superposed on others less distinct. The relative intensities of these two sets of lines were reversed in photograms of samples containing less than 20% S. The second set of lines disappeared after treating the specimens with dilute aqua regia. The substance to which these lines are due has been identified with a molybdenum carbide (or solid solution of carbon in molybdenum) of composition corresponding with Mo₂C. An analysis of the substance extracted from the roasted molybdenite by aqua regia agrees closely with the composition deduced from the X-ray lines. The structure assigned to the substance is that of a hexagonal lattice with $a=2.992$ Å. and $c/a=1.581$. F. G. TRYHORN.

Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. VIII. Tungstates, isopoly- and heteropoly-tungstic acids. G. JANDER, D. MAJERT, and T. ADEN (Z. anorg. Chem., 1929, 180, 129—149; cf. this vol., 281).—When aqueous solutions of alkali tungstates are gradually acidified, amorphous precipitates of hydrated forms of tungsten trioxide are finally obtained. Before the precipitate is actually formed, however, polymerisation changes occur in the dissolved tungstic acid, and these changes have been investigated by the two methods already used in the case of stannates, viz., by means of measurements of diffusion coefficients and of absorption coefficients of visible and ultra-violet light. The gradual addition of hydrochloric acid to a solution of an alkali tungstate produces first a polymerisation to hexatungstic acid, without the formation of any intermediate acid, as follows: $6\text{WO}_4^{''} + 6\text{H}^+ \rightleftharpoons \text{W}_6\text{O}_{21} + 3\text{H}_2\text{O}$. The salts of hexatungstic acid are identical with the paratungstates of the literature. With the addition of more acid there is a further polymerisation to metatungstic acid, which is probably a diparatungstic acid, and in presence of other acids, such as arsenic or phosphoric acids, heteropolytungstic acids are formed. The changes $\text{H}_2\text{WO}_4 \rightarrow \text{H}_6[\text{W}_6\text{O}_{21}] \rightarrow \text{H}_8[\text{As}_2(\text{W}_2\text{O}_7)_6]$ are described in detail. O. J. WALKER.

Fluorine and chlorine, an explosive gaseous mixture. K. FREDENHAGEN and O. T. KREFFT (Z. physikal. Chem., 1929, 141, 221—222).—Since chlorine forms no ions in liquid hydrogen fluoride, it was concluded that there must be considerable affinity

between chlorine and fluorine. A mixture of chlorine and fluorine was sparked in a specially constructed tube. On the passage of the spark a yellowish-red flame spread through the tube followed by an explosion. On completely drying the gases and the apparatus no reaction occurred, but on admitting moisture the flame and explosion were once more obtained.

A. J. MEE.

Purification of gases, especially chlorine, by repeated liquefaction. R. WASMUTH.—See B., 1929, 392.

[Reaction between] sulphuric and hydriodic acids. (Miss) F. BUSH (J. Physical Chem., 1929, 33, 613—620).—Qualitative experiments are described and discussed. With a relatively low concentration of hydriodic acid the sulphuric is reduced to sulphurous acid, and with a high concentration to hydrogen sulphide. The relative amounts of sulphurous acid, hydrogen sulphide, and sulphur produced vary considerably with the size of the crystals of potassium iodide dropped into the concentrated sulphuric acid and with the rate of stirring of the solution.

L. S. THEOBALD.

Action of chlorine on iron oxide. W. KANGRO and R. FLUGGE (Z. Elektrochem., 1929, 35, 189—194).—Theoretical considerations show that it should be possible for chlorine to react with ferric oxide to form ferric chloride and oxygen at higher temperatures without the use of carbon. Experiments were carried out by passing chlorine through a silica tube, in which a boat containing ferric oxide was inserted at various temperatures, any ferric chloride formed distilling off. One set of experiments, which show the amounts of iron oxide that had been so acted on when subjected to the action of chlorine by passage at a fixed rate for a given time at different temperatures, reveal that whilst little action occurs at temperatures below 700° the amounts of ferric chloride formed increased rapidly with rise of temperature. Iron-bearing minerals, e.g., magnetite, hæmatite, and pyrites, on treatment with chlorine at 900—1000° yielded up nearly all their iron as the volatile chloride. H. T. S. BRITTON.

Mixed halogen complexes of tervalent iron. F. KRAUSS and T. VON HEIDELBERG (J. pr. Chem., 1929, [ii], 121, 364—368).—A series of mixed halogen complex salts of tervalent iron was prepared by the action of ferric chloride or bromide on various alkali halides in solutions strongly acidified with the corresponding hydrogen halide. All these salts are very hygroscopic and undergo fission into their components in aqueous solution. Thus from the appropriate components are obtained the complex *rubidium* salts, $\text{Rb}_2[\text{FeBr}_2\text{Cl}_2 \cdot \text{H}_2\text{O}]$ and $\text{Rb}[\text{FeCl}_2\text{Br}_2 \cdot \text{H}_2\text{O}]$, and the two corresponding complex *caesium* salts, the *triethylammonium* complex salts, $[\text{Et}_3\text{NH}][\text{FeClBr}_3]$, m. p. 39.5° (decomp.), and $[\text{Et}_3\text{NH}][\text{FeCl}_2\text{Br}]$, and the complex *pyridinium* salt, $[\text{C}_5\text{H}_5\text{NH}][\text{FeCl}_2\text{Br}]$, m. p. 84°. J. W. BAKER.

Ferrous bromide enne- and di-hydrate. F. SCHMIDEL (Ber., 1929, 62, [B], 963—966).—The solubility in water of ferrous bromide, prepared by dissolving pure iron in aqueous hydrobromic acid, has been determined over the range -60° to $+132^\circ$.

The *ennea-* and *di-hydrates* have been isolated. The cryohydric point of the solution lies at -43.6° with 42.25% of ferrous bromide. The transition temperatures of *ennea-* to *hexa-*, *hexa-* to *tetra-*, and *tetra-* to *di-hydrate* are $+29.3^\circ$, $+49.0^\circ$, and $+83^\circ$, respectively. The saturated solution has b. p. 132° and contains 70.2% of ferrous bromide. All the hydrates have a pure green colour; the "red, hygroscopic powder" of commerce owes its colour to ferric salts.

H. WREN.

Chromatocobaltiammines. II. Dichromato-tetramminecobaltates and the maximum co-ordination number of cobalt. S. H. C. BRIGGS (J.C.S., 1929, 685—690).—Addition of a solution of a diaquotetramminecobaltic salt to a large excess of a concentrated solution of an alkali chromate affords green or brown crystals of the corresponding alkali dichromato-tetramminecobaltate, $M[Co, 2CrO_4, 4NH_3]$. The green form corresponds with the *trans*-configuration and the brown form with the *cis*-configuration of the chromate radicals; the formation of the brown form is favoured by the presence of a large quantity of dichromate in the solution. Sodium *trans*-dichromato-tetramminecobaltate, $Na[Co, 2CrO_4, 4NH_3]$, separates as a green, microcrystalline precipitate, whereas the corresponding *cis*-compound forms greenish-brown crystals with $1H_2O$. Lithium *cis*-dichromato-tetramminecobaltate, $2Li[Co, 2CrO_4, 4NH_3] \cdot 3H_2O$, and the potassium *trans*-salt, $K[Co, 2CrO_4, 4NH_3]$, have also been prepared. With magnesium chromate a mixture of brown and green crystals is obtained, the brown crystals being the compound

$(Mg, 2H_2O)[Co, 2CrO_4, 4NH_3]_2$ and the green crystals the compound $(Mg, 6H_2O)[Co, 4NH_3, 2CrO_4, 2H_2O]_2$, in which the cobalt atom has the co-ordination number eight. Dehydration of the green salt in a vacuum over sulphuric acid and treatment of the residue with cold water affords the brown *hexahydrate*,

$(Mg, 6H_2O)[Co, 2CrO_4, 4NH_3]_2$. Addition of diaquotetramminecobaltic salts to a large excess of neutral sodium chromate affords a dark chocolate compound, $Co_2(CrO_4)_3 \cdot 8NH_3 \cdot 2.5H_2O$, which gives the *monohydrate* in a vacuum desiccator. Using sodium dichromate in this reaction the compound $Co_2(Cr_2O_7)_3 \cdot 9NH_3 \cdot 4H_2O$ is obtained in brownish-black crystals, whilst ammonium chromate affords the compound

$(NH_4)_2CrO_4 \cdot [Co, 5NH_3, CrO_4]CrO_4$ in dark reddish-brown crystals.

A. R. POWELL.

Nickel hydride, NiH . T. WEICHSSELFELDER [with M. Kossodo] (Ber., 1929, 62, [B], 769—771; cf. A., 1924, ii, 189; 1926, 372).—The assumption that the very unstable nickel diphenyl is formed as an intermediate product in the action of magnesium phenyl bromide on anhydrous nickel chloride and is converted by 2 mols. of hydrogen into nickel hydride and benzene is supported by the following observations. In absence of hydrogen, the products of the change are nickel and diphenyl. If admission of hydrogen follows 4 hrs. after completion of the first action, 70% of the nickel is converted into the hydride but benzene is not produced; if shorter periods elapse before treatment with hydrogen, benzene is formed in amount which increases as the period decreases. If exactly 2 mols. of hydrogen are present from the

beginning of the change, the tension of the gas sinks to zero.

Nickel hydride, suspended in ether, can yield a considerable proportion of its hydrogen to an excess of ethylene within a few days at the atmospheric temperature. It is immaterial whether the nickel hydride has nearly the theoretical content of hydrogen or less than half this amount. Complete loss of hydrogen never occurs. The hydride (hydrogen content=80% of theoretical), suspended in ether, causes the union of a mixture of hydrogen and ethylene to ethane within a few hours. When the hydride in ethereal suspension has been treated with alcohol so that it has apparently lost 25% or more of its hydrogen, it causes almost complete union of ethylene with hydrogen in a few minutes. After almost complete decomposition by water, the hydride reacts more slowly but smoothly with the mixture. Nickel, free from hydrogen, does not appear to unite with or adsorb ethylene.

H. WREN.

Double sulphates and their components. IV. Rhodium sulphate and its hydrates. F. KRAUSS and H. UMBACH (Z. anorg. Chem., 1929, 180, 42—56; cf. this vol., 663).—By dissolving rhodium hydroxide precipitated in the cold in dilute sulphuric acid, evaporating over concentrated acid, and precipitating the alcoholic solution of the residue with ether, a yellow *hydrate* of rhodium sulphate, $Rh_2(SO_4)_3 \cdot 15H_2O$, is obtained. On isobaric dehydration, the first three molecules of water prove to be zeolitically combined, and then there are indications of hydrates with 12, 9, and 6 mols. of water, the last 6 mols. also being in zeolitic combination. The aqueous solution gives the normal precipitation reactions of rhodium and sulphate ions, but on evaporation yields a red *hydrate*, $Rh_2(SO_4)_3 \cdot 4H_2O$, the aqueous solutions of which, when freshly prepared, do not react in this way. The whole of the water in this hydrate is held zeolitically.

R. CUTHBERT.

Cyanogen compounds of the platinum metals.

V. Cyanides and thiocyanates of rhodium. F. KRAUSS and H. UMBACH (Z. anorg. Chem., 1929, 179, 357—368).—The complex ion $Rh(CN)_6'''$ is, contrary to previous reports in the literature, extremely stable. By heating potassium rhodicyanide with concentrated sulphuric acid to above 100° a brown precipitate, which on partial drying has the composition $2Rh(CN)_3 \cdot 7H_2O$, is formed; complete desiccation is not possible without decomposition; by treatment of the cyanide with concentrated ammonia solution the salt $4Rh(CN)_6 \cdot 7NH_3 \cdot 7H_2O$ has been prepared. Rhodium cyanide is insoluble in potassium cyanide solution and is decomposed by concentrated potassium hydroxide solution. The following complex *cyanides* have been prepared: $Cu_3Rh(CN)_6 \cdot xH_2O$ (blue), $Cu_3Rh(CN)_6 \cdot 5NH_3 \cdot 5H_2O$ (deep blue), $Cu_3Rh(CN)_6 \cdot 5C_5H_5N \cdot 5H_2O$ (deep blue), $Ni_3Rh(CN)_6 \cdot xH_2O$ (green), and $Ni_3Rh(CN)_6 \cdot 4NH_3 \cdot 10H_2O$ (violet). Solutions of aluminium, ferric, chromic, stannous, lead, palladium, and mercuric salts do not give precipitates with potassium rhodocyanide solution. Attempts to prepare the free acid and salts corresponding with the nitroprussides have been unsuccessful. Rhodium thiocyanate,

$\text{Rh}(\text{CNS})_3 \cdot x\text{H}_2\text{O}$, has been prepared by the addition of concentrated sulphuric acid to a cold solution containing rhodium chloride and potassium thiocyanate: on concentration of the solution in a vacuum desiccator an orange precipitate is produced which is soluble in water but precipitated by sulphuric acid solution. Complex rhodium thiocyanates could not be prepared.

H. F. GILLBE.

Ultra-violet colorimetry with the aid of fluorescent substances. I. EISENBRAND (Z. angew. Chem., 1929, 42, 445—448).—A simple means for carrying out colorimetric determinations with ultra-violet light consists of a narrow (0.5 cm.) tube containing a solution which is fluorescent in ultra-violet light (e.g., 0.0001*N*-quinine sulphate in 0.1*N*-sulphuric acid) which is immersed perpendicularly in the solution under investigation and projects above the surface. When a parallel beam of ultra-violet light is directed through the solution at right angles to this tube the solution in the latter exhibits unaltered fluorescence if the test solution does not absorb ultra-violet light. If slight absorption occurs, the immersed portion of the fluorescent solution is darker than that projecting above the liquid, becoming quite invisible where strong absorption occurs. For quantitative measurements the method has a maximum error of 33%, and its application to the detection and determination of nitrites and certain alkaloids is described.

J. W. BAKER.

Critical consideration of some schemes of fractionation. A. A. SUNIER (J. Physical Chem., 1929, 33, 577—585).—Four schemes are discussed and it is concluded that (i) a scheme of fractionation should, in general, be carried outwards as far as possible in both directions, (ii) the number of rows worked should be large, and (iii) the more important factors to be considered in any scheme are yield, g. evaporated per g. yield, and quantity of original material needed to produce a required yield.

L. S. THEOBALD.

Influence of shaking on various precipitation reactions. G. THANHEISER and P. DICKENS.—See B., 1929, 392.

Differential potentiometric titration. III. Improved apparatus and its application to precision measurements. D. A. MACINNES and M. DOLE (J. Amer. Chem. Soc., 1929, 51, 1119—1127).—The retarded electrode (cf. A., 1927, 35) is surrounded by a glass tube having a capillary opening at the bottom and an aperture near the top, a "gas-lift" being sealed mid-way between these openings. When gas is passed down the lift (which is preferably controlled by the burette tap) solution is circulated over the enclosed electrode, whereas this electrode becomes an "isolated" electrode when no gas is passing. The improved apparatus offers several advantages. Ferrous ions may be accurately titrated with potassium dichromate in an atmosphere of carbon dioxide, and chloride ions may be determined with great precision by titration with silver nitrate. An analysis of constant-boiling hydrochloric acid by the improved method gave results agreeing with those of Foulk and Hollingsworth (A., 1923, ii, 482).

S. K. TWEEDY.

Chart of indicators useful for p_{H} measurements. C. E. DAVIS and H. M. SALISBURY (Ind. Eng. Chem. [Anal.], 1929, 1, 92).—Fourteen indicators covering the p_{H} range 1—10 are tabulated together with their optimum concentrations, appropriate solvents, individual ranges of applicability, and a chart illustrating the dependence of colorations on the p_{H} value.

J. S. CARTER.

Yatren, a mono-colour, amphoteric indicator. H. W. VAN URK (Z. anal. Chem., 1929, 77, 12—14).—Yatren, 7-iodo-8-hydroxyquinoline-5-sulphonic acid, is a mono-colour, amphoteric indicator, the intensity of the yellow coloration of aqueous solutions being dependent on the p_{H} value. The colour disappears at p_{H} 8. Determination of the dissociation curve shows that the ions are colourless and that the coloration is due to the neutral ampholyte.

J. S. CARTER.

Berry-juice indicator. L. MOSENDZ (Z. anal. Chem., 1929, 77, 37—38).—The colouring matter of the juice of the black mulberry (*Morus nigra*, L.) may be used as an indicator in acidimetry, the colorations in acid and alkaline media being red and green, respectively. The most accurate results are obtained when acids are titrated with alkalis.

J. S. CARTER.

Determination of the acidity of undissociated acids with dimethylaminoazobenzene as indicator. A. HANTZSCH and W. VOIGT (Ber., 1929, 62, [B], 975—984).—The acidity of acids cannot be calculated from their conductivities in aqueous solution on account of the production of hydroxonium salts, but is deduced chemically from the differing stabilities of their salts. Yellow dimethylaminoazobenzene is a suitable base, since it gives red salts owing to the conversion of the azoid amine into quinonoid salts. The position of the equilibrium $\text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 + \text{HX} \rightarrow \text{NHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2\text{X}$ depends primarily on the strength of the acid, secondarily on the nature of the solvent. Only the saturated hydrocarbons and (approximately) their halogeno-derivatives, particularly carbon tetrachloride and to a somewhat smaller extent chloroform, are almost indifferent solvents. All media containing oxygen react chemically with acids in a degree which increases with the strength of the acid. For practical reasons, measurements are made in chloroform and ether. The dimethyl-yellow salts, or equimolar solutions of base and acid, are dissolved in the solvent and diluted until the change of colour shows the practically quantitative fission into the components. The process is less sensitive than the conductivity method, its indefiniteness increasing with the weakness of the acids. As the strength of the latter increases, the method becomes more accurate and is superior to the conductivity process for the strongest carboxylic acids. In dry chloroform, the order of acidity is generally parallel with the dissociation constant, but the acidities increase much more rapidly and markedly than the dissociation constants. The values for the acidity have about ten times as wide a range as those of the dissociation constants, due to the levelling effect of water; this latter influence is obvious in a smaller degree when moist chloroform is used as solvent.

All salts of dimethyl-yellow are completely decomposed by dilution in anhydrous ether much more rapidly than in chloroform, giving dimethyl-yellow and the acid etherate. Addition of water has little influence except that it represses slightly the values for the strongest acids. The salts of the strongest inorganic acids are not completely dissociated in anhydrous chloroform even at very great dilutions. For their investigation, they are dissolved in a little chloroform and the solutions are diluted with ether. The sequence of acidities is $\text{HClO}_4 > \text{HBr} > \text{HCl} > \text{HNO}_3$. With a weaker base (dianisylideneacetone), the activities of hydrogen bromide, hydrogen chloride, and trichloroacetic acid can be compared in anhydrous chloroform. By means of these salts, also, it is shown that the halogeno-derivatives of saturated hydrocarbons are less inactivating than benzene or toluene.

H. WREN.

Determination of water by means of difficultly inflammable liquids. F. FRIEDRICHS (Chem.-Ztg., 1929, 53, 287).—The substance is heated with tetrachloroethane in a small flask fitted with a glass stopper carrying a long vertical tube bent over at its upper end to meet a small condenser the lower end of which is connected through a capillary tube with a small burette filled with tetrachloroethane. An overflow tube from the lower end of the burette returns excess of the liquid to the distillation flask. The water vapour condenses as an emulsion with the tetrachloroethane in the condensers and is thus forced into the burette, where the water rises to the surface of the organic liquid and its volume can then be measured.

A. R. POWELL.

Microtitration of iodides [alone] and in the presence of large quantities of nitrites. J. F. REITH (Rec. trav. chim., 1929, 48, 386—390).—Details are given of a titration method, using sodium thiosulphate solution, by which from 0.01 to 0.0015 mg. of iodine ion can be determined with an accuracy of from 5 to 2%.

By the application of the sodium azide method 0.005 mg. of iodine ion may be determined with an accuracy of about 2% in the presence of several times that quantity of nitrite. F. G. TRYHORN.

Absorption of oxygen by dilute alkaline solutions of pyrogallol. T. J. DRAKELEY and H. NICOL.—See B., 1929, 355.

Determination of gases in metals, particularly of oxygen in steel. W. HESSENBRUCH.—See B., 1929, 358.

Separation and determination of nitrous acid by esterification. W. M. FISCHER and A. SCHMIDT (Z. anorg. Chem., 1929, 179, 332—338).—Owing to the high esterification velocity of nitrous acid, and to the volatility of the esters, the acid may be readily and quantitatively separated from a mixture by conversion into ethyl or methyl nitrite and removal of the ester in a current of carbon dioxide; after passage of the vapour into potassium iodide solution the liberated iodine may be titrated with sodium thiosulphate solution. Hydrazine, hydroxylamine, aniline salts, and bromates, sulphites, ferrocyanides, and permanganates interfere.

H. F. GILLBE.

Detection of nitrites in the forensic study of gunshot wounds. C. GORONCY (Deut. Z. ges. gerichtl. Med., 1928, 11, 482—486; Chem. Zentr., 1928, ii, 2047).—Lunge's reagent is used, after dissolution with alcoholic potassium hydroxide, for the detection of nitrite from black or smokeless powder.

A. A. ELDRIDGE.

Use of liquid amalgams in volumetric analysis. XI. **Determination of phosphoric acid by using zinc or cadmium amalgam.** K. SOMEYA (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 1289—1298).—Molybdic acid is completely reduced to the tervalent state by treatment with zinc or cadmium amalgam in dilute sulphuric acid. Molybdenum can then be determined by titration with potassium permanganate solution. The method is extended to the determination of phosphorus, the usual precipitate of phosphomolybdate being reduced and titrated, assuming 24 mols. of MoO_3 for each mol. of P_2O_5 .

C. J. SMITHELLS.

Separation and determination of ortho- and pyro-phosphoric acids. W. STOLLENWERK and A. BAURLE (Z. anal. Chem., 1929, 77, 81—111).—Ortho- and pyro-phosphoric acids cannot be quantitatively separated by precipitation of the latter with silver nitrate in the presence of sodium acetate and acetic acid, as an excess of the precipitant results in the gradual conversion of the silver pyrophosphate into orthophosphate; a similar reaction occurs with copper nitrate. Separation of the two acids by precipitation with aluminium, beryllium, magnesium, or lead salts is always incomplete either because of adsorption or owing to the too great solubility of the precipitate. Alkaline-earth salts precipitate completely both acids in the tri- or tetra-basic form respectively. Either acid alone may therefore be determined by titrating its solution with an excess of barium hydroxide in an atmosphere free from carbon dioxide and then determining the total alkalinity of a portion of the filtrate by acidimetric titration or the excess of barium as sulphate gravimetrically; both methods give good results. If both acids are present in the same solution the sum is obtained by the above method and the total P_2O_5 is determined as usual. From these results the proportion of each acid present is readily calculated by the indirect method.

A. R. POWELL.

Analytical studies of pyrophosphoric acid. [Determination of pyrophosphate in presence of orthophosphate.] R. DWORZAK and W. REICH-ROHRWIG (Z. anal. Chem., 1929, 77, 14—37).—The method of Berthelot and André (A., 1897, ii, 158) yields trustworthy results except when orthophosphate is the predominating constituent. Under these latter conditions, however, satisfactory results are obtained by titration with a solution of uranyl acetate, until a permanent precipitate of orthophosphate indicates the completion of the reaction $\text{UO}_2(\text{OAc})_2 + 2\text{Na}_4\text{P}_2\text{O}_7 = \text{Na}_6[\text{UO}_2(\text{P}_2\text{O}_7)_2] + 2\text{NaOAc}$. In accurate work it is desirable to add a trace of ammonia and varying amounts of a solution of uranyl acetate to each of several aliquot parts of the solution to be tested and to keep for several hours. The true titration is the mean of the values which just produce, or

do not produce, turbidity. The indirect method of Aoyama (*J. Pharm. Soc. Japan*, 1925, No. 520, 7), with certain modifications, gives trustworthy results and should be used if metaphosphate is also present.

J. S. CARTER.

Volumetric determination of arsenic in organic and inorganic compounds in presence of halogens and heavy metals. P. VILLECZ (*Ber. Ungar. pharm. Ges.*, 1928, 4, 313—337; *Chem. Zentr.*, 1928, ii, 2173).—The substance is decomposed by heating with concentrated sulphuric acid and 30% hydrogen peroxide; a macro- and a micro-procedure are described. If a brown coloration appears, hydrogen peroxide is again added. Arsenic acid is reduced at the b. p. by hydrazine sulphate in concentrated sulphuric acid, which removes the excess of hydrazine sulphate. The arsenious acid is then titrated with potassium bromate solution. The determination of arsenic in presence of calcium, strontium, barium, iron, lead, mercury, or silver is described.

A. A. ELDRIDGE.

Determination of arsenic by Smith's method. J. GNESSIN (*Pharm. J. Russia*, 1928, 89, 442—444; *Chem. Zentr.*, 1929, ii, 2269).—Gadamer's method (*Lehrb. d. Chem. Tox.*, 1924, 166) is modified, the arsenic hydride being produced in a Marsh-Lockemann apparatus and then passed into the solution containing mercuric chloride, potassium iodide, and sodium hydrogen carbonate.

A. A. ELDRIDGE.

Test for boric acid and borates. A. S. DODD (*Analyst*, 1929, 54, 282—285).—To about 10 c.c. of an acid aqueous solution of the substance to be tested are added methyl-red or Sofnol indicator 1, and the solution is neutralised with sodium hydroxide. After boiling (filtering if necessary), the liquid is acidified with dilute sulphuric acid and just neutralised with 0.1*N*-sodium hydroxide solution, when 0.5 g. of mannitol is added. If on shaking a reddish-pink colour appears, borates are present. Small quantities of carbon dioxide do not interfere if 0.01 g. of boric acid is present. A reaction is given with 0.2 mg. of boric acid and a very distinct one with 0.3 mg. The following substances gave negative results with the test and did not interfere when present with borates: Metallic radicals: aluminium, ammonium, antimony, barium, bismuth, cadmium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, potassium, silver, sodium, strontium, tin, titanium, and zinc. Acid radicals: acetates, benzoates, bromates, bromides, chlorates, chlorides, citrates, formates, iodates, iodides, lactates, molybdates, nitrates, nitrites, oxalates, salicylates, sulphates, sulphides, sulphites, tartrates, and tannates. Tungstates gave a colour similar to that produced by boric acid.

D. G. HEWER.

Detection of alkali metals in mixtures of salts and in silicates. N. A. TANANAEV (*Z. anorg. Chem.*, 1929, 180, 75—82).—If a mixture of chlorides and nitrates is converted into oxides, carbonates, and free metals by ignition with oxalic acid, then treated with ammonium carbonate to change any calcium oxide into carbonate, the aqueous extract of the residue can contain only alkali metals and a little magnesium carbonate, so that if the latter is

decomposed by evaporating the solution and igniting, an alkaline reaction in the aqueous extract of the residue proves the presence of alkali metals. If, however, the original mixture contained arsenite or arsenate, this solution will contain arsenite, which must be precipitated as sulphide by addition of ammonium sulphide and oxalic acid, the residue left on evaporation of the filtrate being ignited, and then dissolved in water and its alkalinity examined. Any sulphate present in the mixture is converted into chloride by addition of excess of barium chloride before ignition with oxalic acid, whilst silicates require a preliminary treatment with hydrofluoric acid, the fluorides then reacting with oxalic acid in the same way as chlorides.

R. CUTHILL.

Determination of metals as sulphates using silica crucibles. A. A. GUNTZ and J. BARBIER (*Chim. et Ind.*, 1929, 21, 711—712).—The determination of various metals as sulphates using vitreous crucibles in an electric furnace with temperature control was investigated, with results as follows. Sodium: the method is accurate between 700° and 950° (m. p. of sodium sulphate, 880°). Magnesium: accurate between 600° and 850°. Lithium: accurate from 500° to 950° (m. p. of lithium sulphate, 580°). Cadmium: accurate between 450° and 800°. It is impracticable to heat further and determine as oxide. Lead and manganese can be determined between limits 450° and 800° and 400° and 750°, respectively. Zinc requires close temperature control as the limits are 400° and 600°; by heating to above 900° in a closed crucible it may be weighed as oxide. Cobalt and nickel: the method is unsuitable.

C. IRWIN.

Zirconium. III. Influence of lithium, rubidium, caesium, and magnesium on the detection of potassium by zirconium sulphate. R. D. REED and J. R. WITTHROW (*J. Amer. Chem. Soc.*, 1929, 51, 1062—1065; cf. A., 1928, 858).—Zirconium sulphate will detect 1.0 mg. or more of potassium in 2 c.c. of solution containing 50 mg. of lithium sulphate, 16.6 mg. of rubidium sulphate, or 11.6 mg. of caesium sulphate. It will also detect 0.5 mg. or more of potassium in 2 c.c. of a solution which are free from interfering ions or contain 50 mg. of magnesium sulphate.

S. K. TWEDDY.

Determination of small quantities of beryllium in rocks. B. E. DIXON (*Analyst*, 1929, 54, 268—274).—The determination of beryllium present in silicate rocks has been hampered by lack of a suitable way of separating from titanium. This may be brought about by precipitating the weak hydroxide of titanium with *p*-chloroaniline, and subsequently the beryllium with ammonia. The hydroxides of iron, aluminium, etc. are separated from the solution of chlorides by two precipitations with boiling ammonia, with evaporation of the filtrate to recover any unprecipitated traces. The precipitates are dried and ignited with the residue from the silica determination, ground and mixed with 5 g. of sodium carbonate, and heated for 2.5—3 hrs., first in the molten condition. The mass is digested with water, filtered, and washed with sodium carbonate solution. Any chromium can be determined colorimetrically in the filtrate. The solution is then acidified with 15 c.c.

of hydrochloric acid, evaporated to dryness, a few c.c. of hydrochloric acid are added, then 100 c.c. of hot water, and the liquid is filtered. The precipitate is ignited and weighed, and the weight of silica determined by loss in weight on evaporation with hydrofluoric and sulphuric acids. Aluminium can be determined in the filtrate and a correction made for any chromium and phosphorus which are also precipitated. Ten c.c. of hydrochloric acid are put into the sodium carbonate fusion crucible, and the extract is used to dissolve the precipitate of iron, titanium, and beryllium on the filter paper. The paper is ashed and any residue is dissolved in hydrochloric acid and added to the main solution, which is neutralised with ammonia and 10 g. of solid sodium hydrogen carbonate are added per 100 c.c., the solution is boiled for 1 min., cooled, filtered, the residue washed with 50 c.c. of hot 10% sodium hydrogen carbonate solution, redissolved in hydrochloric acid, neutralised, and the precipitation repeated. The final precipitate of ferric and titanous hydroxides is ignited. The united filtrates are acidified with 30 c.c. of hydrochloric acid, the solution is boiled, and a preliminary separation of beryllium and titanium hydroxides made by dissolving in hydrochloric acid, treating with ammonia until a turbidity but not flocculation is present. *p*-Chloroaniline (1—1.5 g.) is then added, the solution is boiled for 3 min. and filtered, and the precipitate redissolved and reprecipitated, ignited, and weighed. A slight excess of ammonia is added to the filtrate, the solution boiled and filtered after uniting with the filtrate from the final separation, and the beryllium hydroxide washed free from chlorides, ignited, and weighed.

D. G. HEWER.

Detection of magnesium in silicates. H. LEITMEIER and F. REIGL (*Tsch. Min. Petr. Mitt.*, 1928, 29, 323).—The test by fusing with cobalt nitrate is unsatisfactory and a quick test for magnesium is wanting. Silicates are treated with hydrofluoric acid, or with potassium hydrogen fluoride and sulphuric acid, and the solution is heated with an alkaline alcoholic solution of diphenylcarbazide. In the presence of magnesium a bluish-violet colour results (cf. A., 1928, 1108).

L. J. SPENCER.

Rapid electrolytic determination of lead as peroxide. H. TOPELMANN (*J. pr. Chem.*, 1929, [ii], 121, 289—319).—Various physico-chemical factors affecting the electrolytic determination of lead have been investigated and on the basis of the results the following procedure is recommended. The solution of lead nitrate (100 c.c.) containing 0.3—0.5 g. of lead, 8—10 c.c. of nitric acid, *d* 1.4, and 1—2 g. of copper nitrate is electrolysed at the ordinary temperature with a platinum gauze anode and a rotating platinum cathode for 1—2 min. with a current of 0.5 amp., the current strength then being increased to 2 amp. in the course of 0.25 hr. After a further 0.25 hr. the anode is washed with distilled water before interrupting the current and dried under conditions elaborated below. Complete precipitation of the lead is affected by the evolution of oxygen, which sets in towards the end of the electrolysis and by the solvent action of the nitrous acid produced, but with the above procedure these errors amount to less than

0.1 mg. The varying factors recorded for conversion of the weight of dried lead peroxide into lead (usually more than 1% below the theoretical value) are shown to be due, not to the presence of higher oxides, nor, entirely, to the presence of nitrate (which never exceeds 1%), but to occlusion of varying amounts of water depending on the method of drying and on the physical state of the deposit, the latter, in turn, depending on the temperature of electrolysis and current density. The best results are obtained by drying in a described apparatus at 260° for 2 hrs., for which a constant conversion factor (independent of the quantity of lead) 0.8628 is found. Constant conversion factors are also obtained by drying for 0.5 hr. (0.8580) or 1 hr. (0.8589) at 230°, but previous washing with alcohol and ether is not to be recommended. Thermal dissociation of lead peroxide occurs slowly at 320—350°, but is not appreciably accelerated by diminution of the partial pressure of the oxygen. Contrary to some results of earlier investigators, the presence of ammonium or alkali nitrates (in concentration 0.32*N*) does not affect the electrolytic determination of lead, but by altering the anode and cathode potentials small concentrations (0.00455*N*) of chloride ion have a relatively large effect and must be avoided. The adaptation of the method to the micro-determination of lead is described.

J. W. BAKER.

Volumetric determination of thallous salts using potassium permanganate in a medium containing hydrochloric acid. A. JILEK and J. LUKAS (*Chem. Listy*, 1929, 23, 124—129).—The accuracy of the following gravimetric methods for the determination of thallium salts is examined. The experimental errors of Werther and Willm's method (*Z. anal. Chem.*, 1865, 4, 432) are from −10 to +3%. of Browning and Palmer's method (A., 1909, ii, 620) about +2%, of Browning's method (A., 1900, ii, 247) from −20 to +2%, of Werther's method (*Z. anal. Chem.*, 1864, 3, 2) only +0.1%, of Willm's method (*Z. anal. Chem.*, 1865, 4, 432) −0.3%, of Crookes' method (*Chem. News*, 1863, 8, 255) +3%, and of Carstenjen's method (*Z. anal. Chem.*, 1867, 8, 73) from −3 to +7%. Willm's volumetric method (*Bull. Soc. chim.*, 1863, 5, 532) gives fairly accurate results (99.5—102.4%), using 0.02*N*-solutions of thallous salts and of potassium permanganate, and in the presence of potassium chloride, 1 c.c. of permanganate being equivalent to 2.078 mg. of thallium.

R. TRUSZKOWSKI.

Cupric oxide as a standard in iodometry. T. F. BUEHRER and C. M. MASON (*Ind. Eng. Chem. [Anal.]*, 1929, 1, 68—70).—Since impurities in metallic copper are unevenly distributed, the use of copper oxide as an iodometric standard is recommended. After a copper compound has been evaporated to dryness with sulphuric acid it is unnecessary to neutralise with ammonia and re-acidify with acetic acid before adding potassium iodide.

J. S. CARTER.

Determination of copper. H. F. BRADLEY.—See B., 1929, 359.

Ceric sulphate in volumetric analysis. V. Potentiometric study of the reaction between

ferrocyanide and ceric ions. N. H. FURMAN and O. M. EVANS (J. Amer. Chem. Soc., 1929, 51, 1128—1133).—Ferrocyanide ions may be accurately titrated potentiometrically with ceric sulphate. If a small quantity of ferric iron is present in the ceric solution there is produced a green coloration of ferric ferrocyanide which disappears at a point which practically coincides with the potentiometric end-point. The reverse titration is accurate only if most of the ferrocyanide is added very rapidly. S. K. TWEEDY.

Confirmatory test for aluminium. R. GEMMILL, R. BRACKETT, and C. R. McCROSKY (J. Amer. Chem. Soc., 1929, 51, 1165).—An asbestos wad looped in platinum wire is dipped in 0.05*N*-cobalt nitrate solution, ignited, dipped in the aluminium nitrate solution, and again ignited (cf. Panganiban and Soliven, A., 1928, 1206). The test is sensitive to 0.2 mg. of aluminium; sodium salts do not interfere. 0.5 Mg. of zinc may be readily detected in a similar manner. S. K. TWEEDY.

Behaviour of certain zeolites. G. GRASSI-CRISTALDI and F. SCAFILE (Annali Chim. Appl., 1929, 19, 136—140).—Besides in the ordinary mineral acids, the two zeolites, analcime and mesolite, are soluble, with decomposition, in certain organic acids. Thus, aqueous 5% oxalic acid dissolves analcime when hot and mesolite when cold, and the oxalic acid solutions may be employed for the separation and determination of the constituents.

T. H. POPE.

Determination and separation of rare from other metals. XV. Determination of gallium. II. L. MOSER and A. BRUKL (Monatsh., 1929, 51, 325—333; cf. A., 1928, 1347).—Gallium may be determined and quantitatively separated from aluminium, chromium, indium, uranium, and cerium by means of its compound with "cupferron." The neutralised solution (containing 0.01—0.3 g. of gallium) is diluted to 200—300 c.c. with 2*N*-sulphuric acid (the precipitate is somewhat soluble in more concentrated acid) and treated with a 6% aqueous cupferron solution at the ordinary temperature (only 0.1 g. of cupferron for each 0.1 g. of gallium). The precipitate is washed free from chloride ion (gallium oxide being volatile in the presence of ammonium chloride) and ignited to gallium oxide. The filtrate, after addition of hydrogen peroxide, is evaporated to fuming and redissolved in water, and the other metal determined in the usual manner. In the separation from indium a little cupferron solution is added to the 2*N*-sulphuric acid used in washing the precipitate, great care being required in this operation, whilst in the separation from uranium any reduction must be avoided, since quadrivalent uranium is quantitatively precipitated by cupferron. In the quantitative separation of gallium from iron three cases are considered: (1) a small quantity of gallium with much iron, (2) a small quantity of each, (3) much gallium in the presence of a small amount of iron. In (1) the neutralised solution (free from ammonium salts) is treated in the cold with sodium thiosulphate solution until the violet colour of the ferric salt is destroyed, heated to boiling for 0.25 hr., and 10 c.c. of aniline are added at 5 min. intervals to the boiling solution.

The precipitated gallium hydroxide is filtered hot, washed free from sodium with hot water, and ignited to gallium oxide. The latter contains a little ferric oxide and is fused with potassium pyrosulphate, the mass dissolved in very dilute sulphuric acid, and the gallium determined by method (2) or (3). In (2) the solution is treated with sulphosalicylic acid followed by sufficient ammonia to yield a clear red solution and the iron is separated as ferrous sulphide by passing hydrogen sulphide into the hot solution. The filtrate is acidified with acetic acid, boiled to expel hydrogen sulphide, ammonium acetate added, and the gallium precipitated with tannin (*loc. cit.*). In (3), the neutral solution is poured slowly with stirring into a hot solution of ammonia and the precipitated ferric hydroxide, which adsorbs some gallium, washed with hot water, and treated as in (2). Gallium is determined in the united filtrates by the tannin method. J. W. BAKER.

Two reversible oxidimetric indicators and the manganometric determination of hydroferrocyanic acid. J. KNOP (Z. anal. Chem., 1929, 77, 111—125).—The triphenylmethane dyes, erio- and erio-green B, are completely reversible indicators in titrations with permanganate but not with dichromate. The former in acid solution gives a green colour which becomes bluish-red on addition of a slight excess of permanganate; as these colours are almost complementary, the end-point in a titration is characterised by a change from green to a pale grey or almost colourless. Erio-green B gives a yellow colour to acid solutions which becomes deep orange-yellow on the addition of a drop of permanganate. In both cases the colour changes are more sensitive than the pink colour which permanganate imparts to water. For the titration of ferrocyanide with permanganate 1 g. is dissolved in 400 c.c. of water and 20 c.c. of 8*N*-sulphuric acid, 1 c.c. of erio- or 2 c.c. of erio-green (0.1% solution) are added, and the solution is titrated with 0.05*N*-permanganate until the colour changes from yellowish-green to brownish-orange in the first case or from deep yellow to orange-yellow in the second case. The results are correct to within 0.02 c.c.

A. R. POWELL.

Permanganate titration of iron with erio- and erio-green B as indicator. J. KNOP and O. KUBELKOVA (Z. anal. Chem., 1929, 77, 125—130).—Ferrous salts may be determined accurately by macro- or by micro-titration with permanganate, using erio- and erio-green B as indicator (cf. preceding abstract). For the micro-titration 2 c.c. of the iron solution are treated with 0.5 c.c. of 1 : 4 sulphuric acid and 0.1 c.c. of indicator solution and titrated with 0.005*N*-permanganate; the results are correct to within 0.5% of the iron present.

A. R. POWELL.

Prussian-blue and Turnbull's blue reactions. H. W. VAN URK (Z. anal. Chem., 1929, 77, 39—41; cf. Szebellédy, A., 1928, 1347).—The influence of ammonium fluoride in repressing the Prussian-blue and Turnbull's blue reactions is due to the depression of the hydrogen-ion concentration below that necessary for their occurrence. J. S. CARTER.

Iodometric determination of chromic oxide in potassium chromium alum. J. E. S. HAN.—See B., 1929, 391.

Separation of thorium from uranium by means of ether. P. MISCIATELLI (Phil. Mag., 1929, [vi], 7, 670—674).—The anhydrous ternary system uranyl nitrate-thorium nitrate-ether has been examined. It is shown that thorium nitrate is undissolved only in ether solutions saturated with the uranyl salt at temperatures above 20°. The results are important in connexion with the analytical separation of thorium from uranium by extraction of the mixed nitrates with ether. A. E. MITCHELL.

Determination of tin by rapid electrolysis. J. ŠVĚDA and R. UZEL (Coll. Czech. Chem. Comm., 1929, 4, 203—222).—The most suitable conditions for the electrolytic determination of tin in stannous or stannic salt solutions are obtained by the addition of ammonium oxalate, oxalic acid, and hydroxylamine hydrochloride to the solution and electrolysis for 25 min. (5 amp. at 2.5—3.5 volts) at 60—70° while the solution is rapidly stirred. For solutions of ammonium thioannate, sodium sulphite and the ammonium salt of a strong acid must be added. The method is not applicable to sodium thio-salt solutions.

A. I. VOGEL.

Titration of tin with "chloramine." E. RUPP and F. LEWY (Z. anal. Chem., 1929, 77, 1—3; cf. A., 1928, 387).—Reduction of stannic to stannous salts in acid media is conveniently effected by electrolytic iron foil. Oxidation during manipulations is avoided by allowing a solution of sodium hydrogen carbonate to drip into the reduction flask. J. S. CARTER.

Determination of bismuth in bismuth hydroxyiodide. G. BUMMING and K. FERREIN.—See B., 1929, 355.

Separation of niobium and tantalum by electrolytic hydrolysis. L. F. YNTEMA (Amer. Electrochem. Soc., May 1929. Advance copy, 3 pp.).—The niobate-tantalate mixture obtained by fusing tantalite with potassium hydroxide was dissolved in water and enough sulphuric acid added to cause a slight turbidity. Electrolysis in a diaphragm cell with 0.07 amp./cm.² at the platinum anode yielded a granular precipitate around the anode. Analysis of successive portions of this precipitate showed an excess of niobium in the earlier fractions, and it is concluded that the method could be used for concentrating either niobium or tantalum, although it does not lead to a complete separation. H. J. T. ELLINGHAM.

Separation of ruthenium and osmium, and the use of benzene in the iodometric titration of osmium. S. SARTO (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 164—179).—The separation of osmium and ruthenium under various conditions is described. Osmium can be completely removed by distillation with nitric acid of concentration greater than 6N, if it is present in a soluble form. Ruthenium obtained by evaporation of an aqua regia solution of the sulphide does not distil; it distils slightly if present as the oxide RuO₄, whilst the product obtained by fusion with sodium peroxide is almost completely distilled. Osmium distils completely, but ruthenium

not at all, on boiling with N-hydrochloric acid solution. The residual ruthenium in both cases can be completely distilled as RuO₄ by making the acid solution strongly alkaline with sodium hydroxide, passing in chlorine, and heating the solution. Small quantities of osmium are most accurately determined from the colour of the sodium hydroxide solution in the receiver on distilling with hydrochloric acid. Benzene is a suitable indicator of the end-point in the iodometric titration of osmium. C. J. SMITHELLS.

X-Ray tube with detachable ends and electrodes for X-ray spectroscopy. W. BAND and A. J. MADDOCK (J. Sci. Instr., 1929, 6, 160—161).—Detailed directions are given for the construction of an X-ray tube. The ends are made of brass, with soldered joints, and are clamped to the porcelain tube which forms the body by plates fitting on rubber washers. C. W. GIBBY.

Optical method for analysing photographs of α -ray tracks. J. M. NUTTALL and E. J. WILLIAMS (Nature, 1929, 123, 799).—A method similar to that of Curtiss (this vol., 534) has already been used for the study of β -ray tracks. A. A. ELDRIDGE.

Calibration of sixty-five 35-yellow Lovibond glasses. I. G. PRIEST, D. B. JUDD, K. S. GIBSON, and G. K. WALKER (Bur. Stand. J. Res., 1929, 2, 793—819).—The glasses are used as precision colour standards, but it is shown that in the sixty-five specimens examined there are many imperfections which make them unsuitable for this work. Accurate calibration would therefore serve no useful purpose. The data reported include for each glass: (1) the equivalent in terms of standard Lovibond yellow and red, and (2) the sunlight transmission. Directions are given for using the equivalents in practice. Special comments are made on seven glasses which have strikingly abnormal transmissions or badly marred surfaces. The application of the results to the colour-grading of oils and the conditions of observation necessary for the highest obtainable accuracy are given. The sources of discrepancies in the colour grading of oil may be traced to: (1) unstandardised, non-uniform, and insensitive methods of comparing the oil samples with the glasses, (2) the grading of oils by observers having abnormal colour sense or low power of hue discrimination, and (3) errors in the red glasses. A. J. MEE.

Device for identifying colours. W. C. HOLMES (Chemicals, 1928, 30, No. 21, 31).—The spectrophotometer gives better results than the colorimeter. The former is applied to the examination of dyes and gases, and to the determination of p_H and dissociation constants of indicators. CHEMICAL ABSTRACTS.

Simple interferometer for the measurement of small thicknesses. H. FROMHERZ and W. MENSCHICK (Z. physikal. Chem., 1929, B, 2, 399—404).—A simple interferometric method is described for the measurement of thicknesses of 200—1 μ . The optical arrangement is described in detail. The method is of use in the determination of the absorption of light by strongly absorbing solutions where only very thin layers can be used. A. J. MEE.

Sensitive micromanometer. J. L. HODGSON (J. Sci. Instr., 1929, 6, 153—156).—Differences in pressure cause the movement of an oil meniscus in a tube inclined at a small angle. The meniscus is brought back to zero by raising or lowering a plunger actuated by a screw with a graduated head and vernier. Pressure differences of 10^{-5} in. of water can be measured.

C. W. GIBBY.

Measurement of small pressures with an external indicator. A. SIMON and F. FEHER (Z. Elektrochem., 1929, 35, 162—165).—A method has been devised by which small pressures may be measured at a distance from the reaction vessel; it is particularly useful for reactions that are apt to be explosive, e.g., in the measurement of the dissociation pressure of manganese heptoxide. The gas is led into one limb of a U-tube tensimeter containing mercury, whilst within the other limb and very close to, and above, the mercury level is fixed a glass rod, thus confining the movement of the mercury to the space between the glass wall and the central glass obstruction. Outside the manometer tube at this point a sheet of tin-foil is folded, so that, in effect, a condenser is formed between the mercury in the manometer and the tin-foil. An increase in gas pressure causes the mercury to rise inside the space surrounded by the tin-foil sheath and thereby alters the capacity of the condenser. This is included in a system containing two valves, oscillating in resonance, and a milliammeter in the plate circuit, so that any change in the capacity disturbs the state of the valves, which after readjustment enables a current to be measured which can be calibrated in terms of pressure. The glass-blowing technique involved is difficult. Pressures of the order of 0.05 mm. of mercury may thus be measured. A less sensitive modification of the manometer device is also described, in which a glass rod, around which is wound a constantan wire of 16 ohms resistance, is placed in the central portion of the remote arm immediately above the mercury level. An increase in pressure causes the mercury to rise over a portion of the wire and so reduces the resistance of the wire, which is registered by means of a milliammeter in the anode circuit of a valve in the filament circuit of which the resistance is connected. By using wire of greater resistance, 160 ohms, the use of a valve was unnecessary.

H. T. S. BRITTON.

Gravimeter for recording rapid changes of density in gases. A. BLACKIE and B. H. WILLIAMS (J. Sci. Instr., 1929, 6, 157—160).—A Ranarex carbon dioxide recorder has been adapted to measure small differences in the densities of gases considerably lighter than air. The standard gas and that under test are driven through two similar cylinders by two fans rotating at identical speeds, and the torques produced on two free fans at the other ends of the cylinders are balanced against one another by a connexion which actuates a pointer. The pressures of the gases on the entry sides must be kept the same. The sensitivity varies with the density of the gas used.

C. W. GIBBY.

Extraction apparatus and "perforators" for liquid extraction. P. H. PRAUSNITZ (Oesterr.

Chem.-Ztg., 1929, 32, 71—73).—Descriptions of various modifications of Soxhlet's extractor and "perforators" are given.

A. J. MEE.

Apparatus for electrolytic analysis. H. J. S. SAND (Analyst, 1929, 54, 275—282).—The apparatus described is based in general purpose and design on that used previously (J.C.S., 1907, 91, 374). The new designs of electrodes achieve reduction in the weight of platinum required. A rotating anode to be used in conjunction with a revolving partition (a parchment-paper thimble) when the anode and electrolyte must not come in contact is also described. A special mounting of the electrodes on a rubber and glass frame is useful for zinc and similar determinations.

D. G. HEWER.

Air separator for the laboratory. R. E. ZINN (Ind. Eng. Chem. [Anal.], 1929, 1, 112).—The powder to be separated is carried by an air stream into the annular space between two cylindrical containers, where the velocity is depressed sufficiently to cause deposition of coarser particles. The air then enters the inner container, where finer particles are deposited. Escaping dust is arrested by a muslin etc. filter.

J. S. CARTER.

Receiver for vacuum distillation. E. J. POTH (Ind. Eng. Chem. [Anal.], 1929, 1, 111—112).—By using float check valves sealed against mercury and suitably coupling these with levelling bulbs the use of stopcocks is avoided.

J. S. CARTER.

Continuous still for conductivity water. C. C. DE WITT and G. G. BROWN (Ind. Eng. Chem. [Anal.], 1929, 1, 109—111).—Vapour from the first still, which contains a permanganate solution, passes up a packed column and reflux condenser into the column of a second still. The second still is charged with pure distilled water. The final product is drawn from the base of the second column. All parts are made of tin and heating is effected by steam coils.

J. S. CARTER.

Containers for caustic solutions. B. A. SOULE (Ind. Eng. Chem. [Anal.], 1929, 1, 109).—Solutions of sodium hydroxide may be stored safely over reasonably long periods in bottles coated with rubber paint. The use of such paint as a protection for glass against hydrofluoric acid is unsatisfactory.

J. S. CARTER.

Heavy-duty thermostat. D. F. OTHMER (Ind. Eng. Chem. [Anal.], 1929, 1, 97).—A single heating circuit thermostatic system used to maintain the temperature of a small boiler constant to 0.02° is described.

J. S. CARTER.

Utility shaking machine. W. M. SHAW (Ind. Eng. Chem. [Anal.], 1929, 1, 93).—The shaker consists of a system of trays, each accommodating six containers, and overhead clamps arranged radially every 60° about the centre shaft.

J. S. CARTER.

Electrically-heated thermocirculator for hot leaching and digesting. M. G. RAEDER (Ind. Eng. Chem. [Anal.], 1929, 1, 88).—The apparatus consists of a glass bulb connected with a reflux condenser at the top and a circulation tube, with an electrically-heated portion, between the bottom and the upper portion. Circulation is not continuous

but pulsating, and material being leached is brought into vigorous circulation. J. S. CARTER.

Coated spiral fractionating columns. T. MIDGLEY, jun. (Ind. Eng. Chem. [Anal.], 1929, 1, 86—88).—Improved fractionation is effected by coating spirals, Hempel columns, etc. with carborundum. Obvious precautions must be taken in choosing a suitable binding material. Shellac is a satisfactory binding material for use with hydrocarbons etc.

J. S. CARTER.

Automatic pipette. L. N. MARKWOOD (Ind. Eng. Chem. [Anal.], 1929, 1, 82).—The apparatus consists of a bulb with overflow arrangement and a valve rod passing down the pipette and ground in at the exit orifice to make a liquid-tight seal.

J. S. CARTER.

Self-regulating gas flow-meter. L. CHALKLEY, jun. (Ind. Eng. Chem. [Anal.], 1929, 1, 74—75).—The arrangement consists essentially of an electrically-operated gas valve, a capillary tube flow-meter with

a mercury manometer connected across it, and suitable connexions for operating the valve by changes in the manometer level.

J. S. CARTER.

Glass electrode. D. A. MACINNES and M. DOLE (Ind. Eng. Chem. [Anal.], 1929, 1, 57—59).—The usual bulb electrode is replaced by a glass tube, to the bottom of which is fused a very thin (0.001 mm.) glass diaphragm. The inner electrolyte is 0.1N-hydrochloric acid and the inside electrode Ag|AgCl. Using two such electrodes it is possible to perform titrations by the differential method (A., 1927, 35) with considerable accuracy. Glass electrodes respond to changes in hydrogen-ion concentration only and are independent of oxidation-reduction potentials existing in the solution.

J. S. CARTER.

Intermittent extraction apparatus. C. W. EDDY (Chemist-Analyst, 1929, 18, 15—16).

Thermostat. V. ČUPR (Pub. Facs. Sci. Univ. Masaryk, No. 108, 1929, 8 pp.).—See A., 1928, 1348.

Geochemistry.

Determination of nitrides in Etna projections. D. GRASSI-CRISTALDI and A. GIAMMONA (Annali Chim. Appl., 1929, 19, 128—135).—When hydrolysed, the nitrides present in Etna lava yield ammonia, which may be determined by means of Nessler's solution. Decomposition of the material with potassium hydroxide does not always give trustworthy results and the disaggregation is best effected by sulphuric acid and potassium fluoride, which, unlike hydrofluoric acid, is always free from ammonia. The percentages of ammonia obtained from the upper, central, and lower (in contact with the soil) portions of the lava from the eruption of 1669 are 0.0738, 0.0403, and 0.0252, respectively.

T. H. POPE.

Paragenetic classification of the minerals of Franklin, New Jersey. C. PALACHE (Amer. Min., 1929, 14, 1—18).

Phosphorescence and fluorescence of Franklin minerals. C. PALACHE (Amer. Min., 1928, 13, 330—333).

Seligmanite from Bingham, Utah. C. PALACHE (Amer. Min., 1928, 13, 402—405).—Crystallographic data are recorded.

CHEMICAL ABSTRACTS.

Beryllonite and other phosphates from Newry, Maine. C. PALACHE and E. V. SHANNON (Amer. Min., 1928, 13, 392—396).—The composition and optical characters of beryllonite (*d* 2.806), herderite, and eosphorite are recorded.

CHEMICAL ABSTRACTS.

Rosy muscovite from Suizawa and a dark grey muscovite from Doi. S. IMORI and J. YOSHIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 221—223).—Analyses are given of a rosy muscovite from Suizawa, the colour of which is probably due to colloidal copper, and of a dark grey muscovite from Doi.

C. W. GIBBY.

Radioactive constituents of hokutolites and other minerals of Japan. J. YOSHIMURA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 223—227, and Bull. Chem. Soc. Japan, 1929, 4, 91—96).—The radium and thorium contents of four Japanese minerals were found to be as follows: hokutolite from Hokuto $1.73 \times 10^{-7}\%$ Ra, 0.02% ThO₂; hokutolite from Shibukuro $1.22 \times 10^{-7}\%$ Ra, 0.01% ThO₂; allanite from Kyoto $4.87 \times 10^{-9}\%$ Ra, 1.05% ThO₂, 0.017% U₃O₈; xenotime from Ishikawa $6.98 \times 10^{-7}\%$ Ra and 2.42% U₃O₈. The uranium content was calculated from the radium content.

C. J. SMITHELLS.

Quartz-porphyry and granite-porphyry from Teplitz, Bohemia. J. E. HIBSCH (Tsch. Min. Petr. Mitt., 1928, 39, 320—322).—New analyses of the fresh rocks differ appreciably from earlier analyses.

L. J. SPENCER.

Makite and hanksite. R. WEGSCHEIDER (Tsch. Min. Petr. Mitt., 1928, 39, 316—319).—The formula of hanksite has been variously given as $4\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ and $9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$. The chloride is no doubt present as an impurity, and perhaps also some of the sulphate. The suggestion is made that hanksite is identical with the artificial double salt, $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ (A., 1926, 664), or with the double sulphate and carbonate of sodium from salt lakes of Armenia, described under the name makite by Abich in 1846. The formula of the latter is then deduced as $4\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ with some admixed $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (thermonatrite).

L. J. SPENCER.

Rocks from the Stubalp, Styria. F. ANGEL and A. RUSCH (Tsch. Min. Petr. Mitt., 1928, 39, 254—303).—Nine analyses of gneisses of different types show a range in silica from 44.15 to 73.30%.

L. J. SPENCER.

Spinel. L. PASSERINI (Atti R. Accad. Lincei, 1929, [vi], 9, 338—343).—An X-ray examination of

seven spinels has been made by the powder method, and the results for two, magnesium chromite, MgCr_2O_4 , and nickel ferrite, NiFe_2O_4 , are detailed. A more accurate examination is promised of the others, which have previously been examined by Holgersson (Lunds Univ. Årsskrift, 1927, [ii], (2), 23, 9). The two spinels mentioned above were prepared by calcination at about 800° of the mixed nitrates in the case of magnesium chromite and of the mixed hydroxides in the case of nickel ferrite. Both substances form cubic crystals with the typical spinel lattice, a fact confirmed by the agreement of the observed intensities of the X-ray lines with those calculated from the postulated structure. For MgCr_2O_4 and NiFe_2O_4 the width and volume of the unit cell, and the calculated d , were, respectively: $a=8.290 \pm 0.005$, 8.340 ± 0.005 Å.; 569.72×10^{-24} , 580.09×10^{-24} c.c.; d 4.49, 5.268.

F. G. TRYHORN.

Thucholite. H. V. ELLSWORTH (Amer. Min., 1928, 13, 419—439).—Thucholite, a black, lustrous mineral from Parry Sound, Ont., has H 3.5—4, $d^{17.74}$ 1.777, and is of variable composition, containing about 50% C, 13% H_2O , and 28% of ash, of which half is thorium dioxide. The radioactivity of the ash and the gas content are high.

CHEMICAL ABSTRACTS.

Heulandite of Monastir. G. MARTINEZ (Atti R. Accad. Lincei, 1929, [vi], 9, 428—433).—Microscopical,

chemical, and crystallographic analyses have been made of specimens of heulandite obtained from the basaltic and trachitic regions of Monastir. The presence of the following minerals was recognised: plagioclase, olivine, monoclinic pyroxene, serpentine amphibole, basaltic hornblende, serpentine, muscovite, epidote, chlorite, and iron oxide. The excess of iron oxide was the cause of the red colour of the heulandite.

Chemical analysis gave the following results: SiO_2 47.77, TiO_2 0.57, Al_2O_3 19.01, Fe_2O_3 8.88, FeO 2.0, MnO 0.01, MgO 4.23, CaO 8.70, Na_2O 3.00, K_2O 1.59, H_2O 3.97, total 99.72%. The Lowinson-Lessing magmatic formula is RO 1.46, R_2O_3 1, SiO_2 3.23, $\alpha=1.60$, $\beta=76$, $\text{R}_2\text{O}:\text{RO}=1:4.27$, $\text{K}_2\text{O}:\text{Na}_2\text{O}=1:2.5$. The triangular representation of Osann is given by $S=62.64$, $A=5.24$, $C=9.56$, $F=22.26$, $a=4.25$, $c=7.75$, $f=18.00$, $n=7.14$, and the tetrahedral representation of Niggli by $al=28.26$, $fm=37.56$, $c=23.76$, $alk=10.10$, $si=120.26$, $k=0.28$, $mg=0.43$, $c/fm=0.63$. The forms $b\{010\}$, $c\{010\}$, $t\{201\}$, $s\{201\}$, $m\{110\}$, and $u\{111\}$ were recognised among the monoclinic crystals of heulandite.

Analysis of the purest crystals (d 2.19) gave SiO_2 57.40, Al_2O_3 17.10, CaO 7.80, H_2O 17.67.

F. G. TRYHORN.

Minerals. IX, X, XI, XII. H. COLLINS (Chem. News, 1929, 138, 82—84, 184—186, 273—275, 369—371.)

Organic Chemistry.

Condensation of ethylene with sulphuric acid in presence of mercurous and copper sulphates.

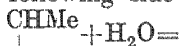
J. BOESEKEN and N. MAX (Rec. trav. chim., 1929, 48, 486—488; cf. Ormandy and Craven, B., 1929, 462).—When ethylene is passed into 93—95% sulphuric acid containing 5% of anhydrous copper sulphate and 2% of mercurous sulphate, saturated and unsaturated hydrocarbons are produced. The saturated hydrocarbons of low b. p. appear to be paraffins, whilst the mixture of unsaturated substances contains a fraction, b. p. 184—196°, resembling dipentene.

H. BURTON.

Ozonisation of gaseous unsaturated hydrocarbons. III. Butenes, aldehydes, and acetone.

E. BRINER and R. MEIER (Helv. Chim. Acta, 1929, 12, 529—553).—When Δ^2 -butene dissolved in methyl chloride is treated with ozone at -80° , the liquid ozonide, d^{21} 1.081, 1.4120 , obtained contains only traces of hydrogen peroxide. Decomposition with water at 70 — 75° gives, in addition to acetaldehyde and acetic acid, methane, formic acid, and small amounts of oxides of carbon. The following side-

reaction presumably occurs:



$\text{Me}\cdot\text{CO}_2\text{H} + \text{H}\cdot\text{CO}_2\text{H} + \text{CH}_4$. Decomposition of the ozonide with cold water is slow: a small amount of formic acid is again produced. The ozonide from a Δ^2 -butene containing 20% of the Δ^3 -isomeride gives hydrogen on hydrolysis. This is formed by decomposition of the intermediate hydroxymethyl- α -hydroxypropyl peroxide (cf. Briner and Schnorf, this vol., 290). The ozonide, d^{20} 1.05, n_D^{25} 1.4081, from isobutene

decomposes rapidly even in absence of water, yielding acetone peroxide and formaldehyde. With water at 70° these products, together with acetone, formic acid, hydrogen, and oxides of carbon, are produced. Propene ozonide also gives hydrogen, methane, and oxides of carbon. In all the above cases the amount of acid products formed during decomposition of the ozonides by water exceeds that of aldehydes. Ozonisation of the isomeric butenes has also been carried out in the gaseous state by the method previously described (*loc. cit.*). An excess of acid products is again formed: hydrogen and formaldehyde are also obtained in varying amounts. Application of this method to a mixture of butenes obtained by "cracking" gives results similar to those obtained with the individual hydrocarbons. Ozone reacts only slowly with formaldehyde, yielding traces of formic acid and carbon monoxide. Acetaldehyde furnishes formaldehyde, formic acid, and carbon monoxide in varying amounts. Propaldehyde yields carbon monoxide, formic acid, acetaldehyde, and a trace of formaldehyde. Formaldehyde and formic acid are also obtained by the action of ozone on acetone.

H. BURTON.

Natural and synthetic rubber. II. Reduction of isoprene by $\text{Na}\cdot\text{NH}_3$. III. Dimethyloctadiene.

T. MIDDLEY, jun., and A. L. HENNE (J. Amer. Chem. Soc., 1929, 51, 1293—1294, 1294—1296).—The volatile product obtained by adding isoprene to sodium dissolved in liquid ammonia consists entirely of β -methyl- Δ^2 -butene (60% of the theoretical) which is not reduced to isopentane by excess of the reagent.

Isoprene is reduced and polymerised by potassium and ethyl alcohol to a mixture, b. p. 163—167°, 0.769, n_D^{20} 1.4457, of $\beta\gamma$ - and $\gamma\delta$ -dimethyl- Δ^2 -octadienes, identified by hydrogenation to a mixture of the corresponding dimethyloctanes and by oxidation with chromic and acetic acids to acetone, hexane- $\beta\epsilon$ -dione, and lævulic and succinic acids.

H. E. F. NOTTON.

Low-temperature oxidation of hydrocarbons.
I. Pressure-temperature curves of amylene-oxygen mixtures. J. S. LEWIS.—See this vol., 655.

Preparation of acetylenic hydrocarbons from epidibromohydrins. R. LESPIEU and WIEMANN (Compt. rend., 1929, 188, 998—1000).—When treated with magnesium methyl bromide epidibromohydrin yields mainly γ -bromo- Δ^2 -hexene, b. p. 34°/16 mm., d_4^{21} 1.197, n_D^{21} 1.459, converted by bromine into $\gamma\gamma\delta$ -tribromohexane, b. p. 105—106°/9 mm., d_4^{20} 1.9434, n_D^{20} 1.5508, yielding with alcoholic sodium hydroxide $\gamma\delta$ -dibromo- Δ^2 -hexene, b. p. 60—61°/9 mm., d_4^{20} 1.6128, n_D^{20} 1.514. With zinc dust and alcohol the latter yields mainly Δ^2 -hexinene, m. p. —51°, b. p. 79—80°/770 mm., d_4^{20} 0.724, n_D^{20} 1.4115, together with a very little γ -methyl- Δ^2 -pentinene, b. p. 65—70°/770 mm. The epidibromohydrin accordingly probably possesses the structure $\text{CH}_2\text{Br}\cdot\text{CBr}\cdot\text{CHEt}$ and not $\text{CH}_2\cdot\text{CBr}\cdot\text{CHEtBr}$, as Bouis suggests from considerations of b. p. The b. p. of Δ^2 -hexinene lies between that of the Δ^2 - and Δ^3 -isomerides.

R. BRIGHTMAN.

Action of acetylene on selenium. F. P. MAZZA and L. SOLAZZO.—In the abstract under this title (this vol., 290) the b. p. of selenophen should be 113—114°. The b. p. 207—209° given is that of selenonaphthen, m. p. 53—54°.

Law of periodicity. P. PETRENKO-KRITSCHENKO (Ukraine Chem. J., 1928, 3 [Sci.], 445—455).—See A., 1927, 713; 1928, 614.

Law of periodicity. P. PETRENKO-KRITSCHENKO [with A. RAVIKOVITSCH, V. OPOTSKI, E. PUTJATA, and M. DIAKOVA] (J. Russ. Phys. Chem. Soc., 1929, 61, 29—40).—See A., 1928, 614.

Ferric ethoxide (preparation and properties). P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1929, 180, 65—74).—From a mixed solution of ferric chloride and sodium ethoxide in absolute alcohol ferric ethoxide separates in dark brown crystals which do not contain alcohol of crystallisation. The solubility in alcohol has been measured between 11° and 58°, the mol. wt. of the solute, as determined from the b. p. elevation, corresponding with the formula $\text{Fe}(\text{OEt})_3$.

R. CUTHILL.

Action of Grignard reagent on highly branched carbonyl compounds. J. B. CONANT and A. H. BLATT (J. Amer. Chem. Soc., 1929, 51, 1227—1236).—The yields of *sec.*- and *tert.*-alcohols obtainable from aliphatic aldehydes and ketones, respectively, by the Grignard reaction are decreased by the introduction of branched or lengthy alkyl radicals into either reagent, whilst products formed by concurrent reactions such as reduction, enolisation, and intermolecular condensation of the carbonyl compound appear to a greater extent. Attempts to prepare *tert.*-carbinols containing more than two *sec.*- or *tert.*-alkyl radicals

were unsuccessful. Thus, under standard conditions using excess of Grignard reagent, magnesium *tert.*-butyl chloride gives with acetaldehyde methyl*tert.*-butylcarbinol (80% of the theoretical); with *isobutaldehyde*, *isobutyl alcohol* (20%) and *isopropyl-tert.*-butylcarbinol (44%), but no $\beta\beta\delta$ -trimethyl-pentane- $\alpha\gamma$ -diol (cf. Favorski. A., 1913, i, 1146); with diethyl ketone, no definite products; with methyl *tert.*-butyl ketone, a small yield of condensation products of high b. p.; with diisopropyl ketone, diisopropylcarbinol (80%); with *isopropyl tert.*-butyl ketone, *isopropyl-tert.*-butylcarbinol (90%); with di*tert.*-butyl ketone, di*tert.*-butylcarbinol (69%), and with ethyl trimethylacetate, no reaction. Magnesium *isopropyl bromide* gives with *isobutaldehyde* diisopropylcarbinol (78%); with methyl *tert.*-butyl ketone, condensation products of high b. p.; with diisopropyl ketone, diisopropylcarbinol (78%); with *isopropyl tert.*-butyl ketone, *isopropyl-tert.*-butylcarbinol (88%), and with ethyl phenylacetate, ethyl $\alpha\gamma$ -diphenyl-acetoacetate (94%). Magnesium *n*-butyl bromide yields with diethyl ketone diethyl-*n*-butylcarbinol (60%), b. p. 116—118°/105 mm., d_4^{20} 0.8409, n_D^{20} 1.4360, but no diethylcarbinol (3:5-dinitrobenzoate, m. p. 101°); with methyl *tert.*-butyl ketone, methyl-*n*-butyl-*tert.*-butylcarbinol (25%), b. p. 84—87°/13 mm., d_4^{20} 0.8487, n_D^{20} 1.4409, and methyl*tert.*-butylcarbinol (30%), and with diisopropyl ketone, diisopropyl-*n*-butylcarbinol (40%), b. p. 115—118°/45 mm., d_4^{20} 0.8487, n_D^{20} 1.4435, and diisopropylcarbinol (13%). Magnesium methyl iodide gives with *isopropyl tert.*-butyl ketone methylisopropyl*tert.*-butylcarbinol (60%), b. p. 56—57°/6 mm., d_4^{20} 0.8564, n_D^{20} 1.4430, and with di*tert.*-butyl ketone, methyl*di**tert.*-butylcarbinol (78%), m. p. 39—41°, b. p. 184—191°. Magnesium *isopropyl chloride* and this ketone give a small yield of di*tert.*-butylcarbinol.

H. E. F. NOTTON.

Isomerisation of acetylenic carbinols to ethylenic ketones. A. WILLEMART (Compt. rend., 1929, 188, 1172—1174).—The conversion of various acetylenic carbinols $\text{CR}^1\text{R}^2(\text{OH})\cdot\text{C}\cdot\text{CR}^3$ into the ethylenic ketones $\text{CR}^1\text{R}^2\text{CH}\cdot\text{C}\cdot\text{OR}^3$ is effected by heating with alcoholic sulphuric acid, whilst the corresponding chloro-compounds, $\text{CR}^1\text{R}^2\text{Cl}\cdot\text{C}\cdot\text{CR}^3$, are similarly converted by heating with alcohol alone. Thus the following: diphenylheptylcarbinol, b. p. 179—180°/1 mm.; diphenyl- β -p-tolylolethylcarbinol, m. p. 68—69°; phenyl- α -naphthyl- β -phenylethylcarbinol, m. p. 137—138° (only through its chloro-compound); di- α -naphthyl- β -phenylethylcarbinol, m. p. 70—71°; diphenyl- β -naphthylethylcarbinol, m. p. 99—100°, are converted, respectively, into β -phenylstyryl *n*-amyl ketone, m. p. 7—8°, b. p. 173°/1 mm.; p-tolyl- β -phenylstyryl *n*-amyl ketone, m. p. 74—75°; phenyl- β -(1-naphthyl)styryl ketone, m. p. 107—108°; phenyl $\beta\beta$ -di-(1-naphthyl)vinyl ketone, m. p. 170—171°; and 2-naphthyl β -phenylstyryl ketone, m. p. 168—169°.

J. W. BAKER.

Electronic conception in organic chemistry.
II. Interpretation of the rearrangements of trisubstituted α -glycols. M. MIGITA (Bull. Chem. Soc. Japan, 1929, 4, 57—65).—An explanation in terms of the electronic theory of the rearrangements following the dehydration of trisubstituted α -glycols

by dilute or concentrated sulphuric acid is given. It is assumed that the dilute acid acts catalytically, the concentrated acid substitutively. Semihydrobenzoin rearrangement takes place, when dilute acid is used, if the tertiary hydroxyl group has negative polarity and the hydrogen of the secondary hydroxyl group is induced (by the presence of a negative group) more positive than that bound to the secondary carbon atom: $\text{CRR}'(\text{OH})\cdot\text{CHAr}\cdot\text{OH} \longrightarrow \text{CRR}'\cdot\text{CHAr}(\text{O}) \longrightarrow \text{CRR}'\text{Ar}\cdot\text{CHO}$. Vinyl dehydration results either with the dilute acid when the tertiary hydroxyl has negative polarity and the hydrogen attached to the secondary carbon atom is induced (by the presence of a positive group) more positive than that of the secondary hydroxyl group: $\text{CRR}'(\text{OH})\cdot\text{CHR}''\cdot\text{OH} \longrightarrow \text{CRR}'\cdot\text{CR}''\cdot\text{OH} \longrightarrow \text{CHRR}'\cdot\text{CO}\cdot\text{R}''$, or with concentrated acid when the tertiary hydroxyl group is markedly negative: $\text{CRR}'(\text{OH})\cdot\text{CHR}''\cdot\text{OH} \longrightarrow \text{CRR}'(\text{SO}_3\text{H})\cdot\text{CHR}''\cdot\text{OH} \longrightarrow \text{CRR}'\cdot\text{CR}''\cdot\text{OH} \longrightarrow \text{CHRR}'\cdot\text{CO}\cdot\text{R}''$. Semipinacolin rearrangement results, using dilute or concentrated acid, in the few cases of glycols having a negatively polarised secondary hydroxyl group: $\text{CRR}'(\text{OH})\cdot\text{CHR}''\cdot\text{OH} \longrightarrow \text{CRR}'(\text{O})\cdot\text{CHR}'' \longrightarrow \text{R}\cdot\text{CO}\cdot\text{CHR}'\text{R}''$, and also by action of the concentrated acid on glycols with feebly negative tertiary hydroxyl groups, as steric hindrance here plays a part.

B. W. ANDERSON.

Affinity of hydrocarbon radicals for oxygen.

I. R. LYDEN (Finska Kemistsamf. Medd., 1928, 37, 53—75; Chem. Zentr., 1928, ii, 2133).—Ethereal components of a reaction system may exercise a mutual influence which can result in a marked diminution of reactivity; this is especially so when the system contains a simple aliphatic ether and an aromatic ether containing an aliphatic group differing from that of the simple aliphatic ether. As the carbon content of the alkyl groups is increased the activity of the aromatic aliphatic ether component is diminished. If the system consists of a mixed aliphatic ether and an aromatic aliphatic ether containing a common alkyl group, the reactivity of the aromatic aliphatic ether has an intermediate value. By heating the components with acetyl bromide in a sealed tube and submitting the products to fractional distillation, the following molecular reactivities were obtained: ethyl ether-phenyl isoamyl ether, 1:0.0113; isoamyl ether-phenyl isoamyl ether, 1:0.528; phenetole-phenyl isoamyl ether, 1:0.335; ethyl isoamyl ether-phenyl isoamyl ether, 1:1.58; ethyl isoamyl ether-phenetole, 1:0.852; *n*-propyl ether-phenyl *n*-propyl ether, 1:0.753; *n*-butyl ether-phenyl *n*-butyl ether, 1:0.528.

A. A. ELDRIDGE.

Organic cyclic polysulphides. Condensation of ethyl mercaptan with di- and tri-chloroacetic acids. G. C. CHAKRAVARTY and J. M. SAHA (J. Indian Inst. Sci., 1928, 11A, 226—230).—See A., 1928, 1214.

Octa- [and hexa-]decoic acids and their bactericidal action towards *B. leprae*. XV. W. M. STANLEY, M. S. JAY, and R. ADAMS (J. Amer. Chem. Soc., 1929, 51, 1261—1266; cf. A., 1928, 754, 990, 1003).—The bactericidal activity of the series of acids obtained by introducing a carboxyl group successively into each position in the pentadecane

and heptadecane molecules shows that the effect is not connected with the presence of a ring. The first member of each series (palmitic and stearic acids) is much less active than the others, and, of the two acids with a common alkyl radical, the pentadecane is more active than the heptadecane derivative. A general review of the acids tested suggests that the physical properties and not the chemical constitutions of the individual acids are primarily responsible for their bactericidal power. The effect of six of the acids on *B. tuberculosis* is similar to, but considerably less than, that on *B. leprae*. The toxicity of two natural, and three synthetic acids towards eight different strains of *B. leprae* is tabulated. The following are described, b. p., d_4^{25} , and being given in that order: *ethyl dialkylmalonates*: methylpentadecyl-, 179—183°/5 mm., 0.9119, 1.4453; ethyltetradecyl-, 172—177°/3 mm., 0.9163, 1.4461; propyltridecyl-, 183—187°/5 mm., 0.9048, 1.4475; butyldodecyl-, 175—180°/3.5 mm., 0.9104, 1.4473; amylundecyl-, 180—185°/5 mm., 0.9124, 1.4509; hexyldecyl-, 185—188°/2.5 mm., 0.9118, 1.4476; heptylnonyl-, 193—197°/5 mm., 0.9118, 1.4471; dioctyl-, 192—195°/3 mm., 0.9135, 1.4471; isopropyltridecyl-, 179—183°/5 mm., 0.9144, 1.4491; isobutyldodecyl-, 180—185°/5 mm., 0.9115, 1.4481; sec.-butyldodecyl-, 180—184°/5 mm., 0.9163, 1.4501; sec.-amylundecyl-, 175—178°/4 mm., 0.9155, 1.4509; methyltridecyl-, 167—170°/3 mm., 0.9181, 1.4418; ethyldodecyl-, 181—183°/4 mm., 0.9249, 1.4422; propylundecyl-, 178—179°/4 mm., 0.9186, 1.4422; butyldecyl-, 181—183°/4 mm., 0.9220, 1.4424; amylnonyl-, 185—186°/5 mm., 0.9282, 1.4462; hexyloctyl-, 175—178°/4 mm., 0.9168, 1.4458; diheptyl-, 178—180°/3 mm., 0.9169, 1.4459; isobutyldodecyl-, 160—162°/2 mm., 0.9207, 1.4428; sec.-butyldecyl-, 196—198°/10 mm., 0.9253, 1.4454; and *dialkylacetic acids*: methylpentadecyl (m. p. 34—35°), 179—183°/5 mm.; ethyltetradecyl- (m. p. 23—24°), 167—170°/2.5 mm., 0.8767, 1.4531; propyltridecyl- (m. p. 31—32°), 179—183°/5 mm.; butyldodecyl- (m. p. 23—24°), 180—184°/4 mm., 0.8743, 1.4528; amylundecyl-, 180—185°/4 mm., 0.8829, 1.4519; hexyldecyl-, 182—184°/5 mm., 0.8741, 1.4527; heptylnonyl-, 180—183°/5 mm., 0.8747, 1.4528; dioctyl- (m. p. 35—36°), 183—185°/5 mm.; isopropyltridecyl- (m. p. 58—59°), 178—182°/5 mm.; isobutyldodecyl- (m. p. 26—27°), 175—180°/4 mm.; sec.-butyldecyl- (m. p. 38—39°), 178—183°/6 mm.; -amylundecyl-, (m. p. 37—38°), 175—178°/5 mm.; methyltridecyl- (m. p. 24°), 172—173°/2.5 mm., 0.8765, 1.4453; ethyldodecyl- (m. p. 23°), 178—179°/3 mm., 0.8808, 1.4460; propylundecyl- (m. p. 16.5—17°), 178—179°/3 mm., 0.8808, 1.4460; butyldecyl- (m. p. 13—14°), 175—176°/3 mm., 0.8789, 1.4458; amylnonyl- (m. p. 9—10°), 178—179°/3 mm., 0.8887, 1.4518; hexyloctyl-, 165—168°/2 mm., 0.8768, 1.4495; diheptyl- (m. p. 26—27°), 187—189°/4 mm., 0.8771, 1.4497; isobutyldodecyl-, (m. p. 17.5—18°), 187—188°/9 mm., 0.8763, 1.4448; and sec.-butyldecyl- (m. p. 38—39°), 185—186°/9 mm. (cf. Morgan and Holmes, A., 1927, 539; Guthzeit, A., 1880, 871; Jourdan, A., 1880, 313).

H. E. F. NOTTON.

Acid sodium palmitates. P. EK WALL and W. MYLIUS (Ber., 1929, 62, [B], 1080—1084).—By crystallisation of suitable mixtures of the components

from ethyl alcohol the following *acid sodium palmitates* have been isolated: $2C_{16}H_{31}O_2Na, C_{16}H_{32}O_2$, m. p. 115—117°; $C_{16}H_{31}O_2Na, C_{16}H_{32}O_2$, m. p. 97—98°; $C_{16}H_{31}O_2Na, 2C_{16}H_{32}O_2$, m. p. 81—82°. The individuality of the substances is confirmed by microscopical examination and determinations of mol. wt. in camphor. H. WREN.

Use of methyl-alcoholic barium hydroxide. C. NEUBERG (Helv. Chim. Acta, 1929, 12, 304).—A claim of priority (Neuberg and Behrens, A., 1926, 542) against Escher (this vol., 294). J. W. BAKER.

Action of hydrazine on some unsaturated acids, $C_nH_{2n-4}O$, $C_nH_{2n-6}O_2$. J. HANUS and J. VOŘÍŠEK (Coll. Czech. Chem. Comm., 1929, 4, 223—227).—The interaction between hydrazine hydrate and oleic acid in the cold affords the *hydrazide* of oleic acid as a gelatinous mass which after several days at the ordinary temperature yields a solid mass, from which a 50% yield of stearic acid, m. p. 69—69.5°, is obtained on decomposition with dilute sulphuric acid. Interaction at 100° gives the *hydrazide* of stearic acid (I), m. p. 114°, whilst the reaction between potassium oleate and hydrazine hydrate at 100° yields stearic acid mixed with a little of its hydrazide. Elaidic acid and hydrazine hydrate at 100° similarly give the hydrazide of stearic acid (*acetyl* derivative, m. p. 138.7°); under similar conditions the mixture of linoleic and linolenic acids isolated from linseed oil gives a 50% yield of I. A. I. VOGEL.

Removal of halogen from halogenated elæostearic acid. D. HOLDE, W. BLYBERG, and M. A. AZIZ (Z. angew. Chem., 1929, 42, 283—284).—The ease with which hydrogen halide is removed from halogenated elæostearic acid suggests the possibility of the formation of an *o*-disubstituted aromatic compound which should yield phthalic acid on oxidation; none could be found, however, on carrying out a test. The fluorescein test for phthalic acid is not specific unless the condensation with resorcinol is conducted at 205—210° without sulphuric acid; in the presence of the latter many other compounds give fluorescent condensation products. A. R. POWELL.

Determination of lactic acid. T. E. FRIEDEMANN and A. I. KENDALL (J. Biol. Chem., 1929, 82, 23—43).—The yield of acetaldehyde obtainable from lactic acid by oxidation with potassium permanganate or with manganese dioxide is increased by diluting the oxidising agent and by working in the presence of large amounts of manganese sulphate and at a low acidity (about 0.1M-phosphoric acid). A modification of the method of Friedemann, Cotonio, and Shaffer (A., 1927, 800) is described which is based on a consideration of the factors mentioned and by which a yield of 97—99% of acetaldehyde is obtainable from pure solutions of lactic acid. The determination of lactic acid in various biological fluids is discussed.

C. R. HARRINGTON.

Determination of pyruvic acid. B. H. R. KRISHNA and M. SREENIVASAYA (J. Indian Inst. Sci., 1929, 12A, 41—51).—A method, applicable to quantities of pyruvic acid between 0.5 and 15 mg. in solutions of concentration 0.1—0.05%, is based on determination of acetaldehyde formed by permang-

anate oxidation of lactic acid produced by reduction of pyruvic acid by the zinc-copper couple in sulphuric acid solution. The probable error of a single determination is about 1.1%. The method may be used for biological fluids, provided that proteins be first removed by precipitation and all preformed acetone, acetaldehyde, etc. driven off by distillation in a vacuum. Pyruvic acid is then extracted from the nearly dry residue with sodium hydrogen sulphite solution and determined. R. J. W. LE FEVRE.

Hydroxypolymethylenecarboxylic acids with eight to twenty-one carbon atoms. P. CHUIT and J. HAUSSEY (Helv. Chim. Acta, 1929, 12, 463—492).— ω -Hydroxyaliphatic acids, $OH \cdot [CH_2]_n \cdot CO_2H$ ($n=7-20$), have been prepared by reduction of alkyl or alkyl hydrogen polymethylenedicarboxylates, oxidation of polymethylene glycol monoacetates or bromides (with subsequent replacement of bromine by hydroxyl), from bromohydrins by treatment with potassium cyanide and subsequent hydrolysis, and by oxidative fission of unsaturated alcohol acetates. Thus, reduction of potassium ethyl suberate with sodium and alcohol and subsequent treatment with a mixture of acetic and hydrochloric acids give η -*acetoxyoctoic acid*, b. p. 155—158°/1.5 mm., m. p. 9—10°, d^{20}_D 1.042, hydrolysed to η -*hydroxyoctoic acid*, m. p. 58° (methyl ester, b. p. 137—138°/8 mm., d^{20}_D 0.992). Treatment of this with an acetic acid solution of hydrogen bromide yields η -*bromo-octoic acid*, b. p. 147—150°/2 mm., m. p. 38.5—39°. Similar reduction and treatment of potassium ethyl azelate affords the acetyl derivative, b. p. 192—193°/10 mm., m. p. 1°, d^{20}_D 1.025, of θ -hydroxynonoic acid (I), m. p. 51—51.5° (methyl ester, b. p. 147—150°/13 mm., d^{20}_D 0.978), also obtained in 8% yield by reduction of ethyl azelate. Oxidation of ι -*bromononan- α -ol*, b. p. 125—126°/2 mm., m. p. 33.5°, with potassium dichromate and sulphuric acid in presence of benzene yields θ -*bromononoic acid* (II), b. p. 160—161°/2 mm., m. p. 36—36.5°, together with ι -*bromononyl θ -bromononoate* (III), b. p. 228—232°/2 mm., m. p. 5°, d^{15}_D 1.237. Treatment of II with potassium acetate at 200° and subsequent hydrolysis furnishes I: during this reaction the *substance* (IV), $OAc \cdot [CH_2]_8 \cdot CO_2 \cdot [CH_2]_8 \cdot CO_2H$, m. p. 40°, is also produced. Similar treatment of III gives a *diacetate*, b. p. 222—223°/1 mm., d^{20}_D 0.988, hydrolysed by alcoholic potassium hydroxide to I and nonane- α -diol. When θ -acetoxynonoic acid is heated with a small amount of potassium acetate at 200—210°, IV results: this is also hydrolysed to I. Oxidation of nonane- α -diol monoacetate, b. p. 159—161°/10 mm., d^{20}_D 0.955, with chromic and acetic acids, and subsequent hydrolysis gives I. The dimeric intermolecular *acid*, $OH \cdot [CH_2]_8 \cdot CO_2 \cdot [CH_2]_8 \cdot CO_2H$, m. p. 60—61°, is obtained when I is heated at 100°/vac.; at 200°/vac. the *substance* $CO_2H \cdot [CH_2]_8 \cdot \{CO_2 \cdot [CH_2]_8\}_2 \cdot OH$, m. p. 71—72°, results. When the methyl ester of ι -hydroxydecoic acid (Grün and Wirth, A., 1922, i, 804; Chuit and others, A., 1927, 40) (ι -*bromo-acid*, b. p. 163—165°/2 mm., m. p. 42—42.5°) is heated at 220—230°, methyl alcohol is eliminated and the dimeric *methyl ester*, $OH \cdot [CH_2]_9 \cdot CO_2 \cdot [CH_2]_9 \cdot CO_2Me$, m. p. 56—56.5°, is formed. The acid itself gives small amounts of complex condensation products. κ -Hydr-

oxyundecic acid (Walker and Lumsden, J.C.S., 1901, 79, 1193) (*acetyl* derivative, b. p. 184—185°/2 mm., m. p. 34°; *methyl* ester, b. p. 168—169°/8 mm., m. p. 27—27·5°), is obtained by hydrolysis of the corresponding *nitrile*, b. p. 186—187°/13 mm., m. p. 12—13°, d_{20}^{20} 0·910, or by condensing ι -bromononan- α -ol and ethyl sodiomalonate, with subsequent thermal decomposition of the intermediate dicarboxylic acid.

[With G. MALET.]— λ -Hydroxydodecic acid [sabinic acid] (Bougault and Bourdier, A., 1909, i, 82; Lycan and Adams, this vol., 423) (*methyl* ester, m. p. 34—34·5°) is obtained by the malonic ester method from κ -bromodecan- α -ol, and by the hydrolysis of λ -acetoxydodecic acid, m. p. 45°, formed together with λ -acetoxydodecaldehyde, b. p. 143—145°/0·5 mm., m. p. 8—9°, d_{15}^{15} 0·9436 (*semicarbazone*, m. p. 85—86°), by the action of ozone on tridecenyl acetate (Chuit and others, A., 1927, 445). λ -Bromododecic acid has m. p. 52—52·2°. Hydrolysis of the waxy residue obtained during the reduction of ethyl brassylate (cf. A., 1926, 499) with aqueous-alcoholic sodium hydroxide gives an insoluble *sodium* salt of μ -hydroxytridecic acid (V) (*acetyl* derivative, b. p. 202—205°/1·5 mm., m. p. 49—49·2°; *methyl* ester, b. p. 192—193°/10 mm., m. p. 44·5°). ι -Bromotridecic acid, m. p. 59—59·2°, is prepared by the action of hydrobromic acid on V, or by oxidation of ν -bromotridecan- α -ol, m. p. 59°. ν -Bromotridecanyl μ -bromotridecoate has m. p. 38—39°. ν -Hydroxytetradecic acid, m. p. 91—91·5° (*acetyl* derivative, b. p. 215°/3 mm., m. p. 54—54·5°; *methyl* ester, b. p. 196—198°/10 mm., m. p. 47°; ν -bromo-acid, m. p. 61·8—62°), is formed by hydrolysis of the corresponding *nitrile*, b. p. 205°/4 mm., m. p. 53°, by reduction of methyl dodecane- α - μ -dicarboxylate, and by the malonic ester method from μ -bromodecan- α -ol. By methods similar to the last two ξ -hydroxypentadecic acid, m. p. 84·8—85·2° (lit. 82—82·5°; *acetyl* derivative, b. p. 219—221°/2 mm., m. p. 59·4—59·6°; *methyl* ester, b. p. 180—182°/2 mm., m. p. 52—52·5°; ξ -bromo-acid, m. p. 65·2—65·5°), is prepared. Oxidation of *hexadecane- α , π -diol monoacetate*, b. p. 217—218°/8 mm., m. p. 54—54·5° (*diacetate*, b. p. 193—194°/1·5 mm., m. p. 47°), with chromic and acetic acids gives *o*-acetoxyhexadecic acid, m. p. 62°, hydrolysed to *o*-hydroxyhexadecic acid (VI) [juniperic acid] (*methyl* ester, b. p. 194—196°/2 mm., m. p. 55—55·5°; *o*-bromo-acid, m. p. 70—70·5°), prepared also by reduction of methyl tetradecane- α , ξ -dicarboxylate. When VI is heated at 125°/vac. a tetrameric intermolecular acid, $C_{64}H_{122}O_9$, m. p. 87·5—88°, results. τ -Hydroxyheptadecic acid, m. p. 87·5—88° (lit. 84—85°; *acetyl* derivative, b. p. 223—225°/1 mm., m. p. 67·6—68°; *methyl* ester, b. p. 210°/3 mm., m. p. 58·6—59°; π -bromo-acid, b. p. 219—220°/1 mm., m. p. 70·5—71°), ρ -hydroxyoctadecic acid, m. p. 96·6—97·2° (*acetyl* derivative, b. p. 228—231°/1·5 mm., m. p. 70—70·5°; *methyl* ester, m. p. 61·5—62°; ρ -bromo-acid, b. p. 240—241°/4 mm., m. p. 75·2—75·8°), σ -hydroxynonadecic acid, m. p. 91—91·5° (*acetyl* derivative, b. p. 225—229°/2·5 mm., m. p. 70—70·2°; *methyl* ester, m. p. 65·6—66°; σ -bromo-acid, b. p. 225—228°/2·5 mm., m. p. 73—74°), τ -hydroxyeicosic acid, m. p. 97·4—97·8° (*acetyl* derivative, b. p. 235—240°/3 mm., m. p. 77°; *methyl* ester, m. p. 68—68·5°; τ -bromo-acid, b. p. 245—247°/3 mm., m. p. 77—78°),

and ν -hydroxydocosic acid, m. p. 92·5—93° (*acetyl* derivative, b. p. 239—242°/3 mm., m. p. 73·8—74·2°; *methyl* ester, m. p. 70—71°; ν -bromo-acid, m. p. 75—76°), are prepared by reduction of the requisite polymethylenedicarboxylate.

The m. p. of the hydroxy-acids alternate, the even-numbered series being the less fusible. The m. p. of the methyl esters approximate to a curve which ascends with increasing number of carbon atoms. There is no simple relationship between m. p. and number of carbon atoms in the acetoxy- and bromo-derivatives.

H. BURTON.

Complex oxalates of quadrivalent molybdenum. H. M. SPITTLE and W. WARDLAW (J.C.S., 1929, 792—799).—When molybdenum trihydroxide, carefully freed from ammonia and ammonium salts, is treated with oxalic acid and then evaporated rapidly in absence of air, a deep brown solution is obtained, which is oxidised by ammonia-free air, giving a bright red solution (A) of molybdenyl oxalate. Addition of a large amount of alcohol to this and treatment with the appropriate base affords amorphous, bluish-pink, *dipyridinium*, *dipotassium*, and *diammonium trimolybdenumtetraoxytrioxalates*, $B_2[Mo_3O_4(C_2O_4)_3, 5H_2O]$ ($B = C_5H_5N$, K, and NH_4 , respectively). These salts dissolve readily in water, giving bright red solutions, in which the oxalate ion cannot be detected. Addition of alkali in the cold does not give an immediate precipitate of molybdenum hydroxide, and the solutions possess marked reducing properties. When A is concentrated on the water-bath and then treated with alcohol and solid ammonium oxalate the purplish-red salt, $(NH_4)_2[Mo_3O_4(C_2O_4)_3, 5H_2O] \cdot 1\frac{1}{2}EtOH$, is obtained. Molybdenyl oxalate, $MoO(C_2O_4) \cdot 3H_2O$, is best formulated as the compound $H_2[Mo_3O_4(C_2O_4)_3, 2H_2O]$, containing a polynuclear complex of three molybdenum atoms, and not as $H_2[MoO_2(C_2O_4) \cdot 2H_2O]$. This is supported by molecular conductivity measurements at 0° of the above dipyridinium and ammonium salts, which indicate that they are ternary electrolytes. When A is concentrated by boiling and then treated with acetone *pentamolybdenum hexaoxytetraoxalate*, $Mo_5O_6(C_2O_4)_4$ (purple), is precipitated. Extraction of this with aqueous alcohol at the ordinary temperature gives *tetramolybdenum pentaoxytrioxalate*, $Mo_4O_5(C_2H_4)_3 \cdot 10H_2O$ (brown), also obtained by atmospheric oxidation of a suspension of molybdenum oxyoxalate (A., 1925, i, 893) in water or aqueous oxalic acid. Both these complex salts are converted by treatment with appropriate concentrations of oxalic acid into molybdenyl oxalate.

H. BURTON.

Stability of complex metallic salts. F. G. MANN (J.C.S., 1929, 651—658).—The stability of complex metallic salts is usually considered to be dependent on the electronic structure of the co-ordinated metal, since during co-ordination the metal endeavours to increase the number of its electrons to that of the next inert gas. This explains the great stability of the complex trivalent cobalt salts (inert gas configuration), and accounts for the instability of potassium ferricyanide (electron deficiency) when compared with the ferrocyanide. Where two types of salts are obtained, e.g., nickel tetrammino- and hexammino-series, the excess of electrons in the latter

series causes a greater instability. A second factor is now considered, namely, the case with which a polyamine molecule can arrange itself around a complex (square, tetrahedron, octahedron, or cube, according to the co-ordination number). Thus, $\alpha\beta\gamma$ -triaminopropane (I) $=[\text{ptn}]$, when treated with zinc nitrate and potassium iodide gives the very stable *bistriaminopropanezinc iodide* $[\text{Zn ptn}_2]\text{I}_2$, decomp. 255—270°, where the metal has a co-ordination number of 6 (cf. Mann and Pope, A., 1925, i, 373; 1926, 1233; Mann, A., 1928, 622), and an excess of 4 electrons over the inert gas configuration. Bivalent palladium also adopts the abnormal co-ordination number 6 (cf. Mann, *loc. cit.*) in order to provide the necessary octahedron for maximum stability. Thus, the reaction product from ammonium chloropalladite and I, when treated with potassium iodide, yields *bistriaminopropanepalladous iodide*, m. p. 230° (decomp.), where the metal has an excess of 2 electrons. If the above reaction product is treated with potassium thiocyanate and acetic acid *bis(triaminopropane-monothiocyanate)palladous dithiocyanate*, m. p. 166—168° (decomp.), is obtained; here the metal shows the normal co-ordination number of 4. The same co-ordination number is shown by cadmium in all its complex salts with I. *Tetrakis(triaminopropanetriscadmium hexaiodide)*, $[\text{Cd}_3 \text{ptn}_4]\text{I}_6$ (hexabromide + $3\text{H}_2\text{O}$), is converted by boiling with water into *monoiidotriaminopropanecadmium monoiiodide*, m. p. 210—213°. *Monobromotriaminopropanecadmium monobromide*, m. p. 221—223° (decomp.), is obtained similarly. *Dithiocyanato(triaminopropane - monohydrochloride) - cadmium*, m. p. 150—154° (decomp.), when exposed to air loses hydrogen chloride yielding *monothiocyanatotriaminopropanecadmium monothiocyanate*, $[\text{SCN ptn Cd}]\text{SCN}$, m. p. 201—202° (decomp.).

H. BURTON.

Preparation of maleic acid by catalytic oxidation of benzene. T. YABUTA and R. SIMOSE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 197—205).—The method of preparation of the catalyst, the effect of acid oxides on the vanadium oxide (catalyst?), and the influence of the diluent gas in the reaction mixture of benzene and air have been studied. H. BURTON.

Supposed $\alpha\beta\gamma$ -trimethylglutaric acid of Noyes and Skinner. F. E. RAY (J. Amer. Chem. Soc., 1929, 51, 930—932).—Prolonged hydrolysis of ethyl α -cyano- $\alpha\beta\gamma$ -trimethylglutarate (Perkin and Thorpe, J.C.S., 1899, 75, 65) with boiling aqueous 50% potassium hydroxide affords α -carboxy- $\alpha\beta\gamma$ -trimethylglutaric acid (I), m. p. 189—190° (decomp.), which is decarboxylated at 200° to $\alpha\beta\gamma$ -trimethylglutaric acid. The tricarboxylic acid obtained by Noyes and Skinner (A., 1918, i, 65) from *isoaminocamphonan* acid has a mol. wt. of 192—194 and not 218 as previously stated. It cannot be identical with I, since it appears to be decarboxylated to $\alpha\beta\gamma$ -trimethylglutaric acid (A., 1928, 394).

H. E. F. NOTTON.

α -isoPropylglutaconic acid. K. V. HARIHARAN, K. N. MENON, and J. L. SIMONSEN (J. Indian Inst. Sci., 1928, 11, A, 207—214).—See A., 1928, 395.

Determination of configuration in the terpene series. II. Optically active forms of β -isopropyladipic acid and their relationship to the

optically active limonenes. J. VON BRAUN and G. WERNER (Ber., 1929, 62, [B], 1050—1058).—*p*-isopropylphenol is readily hydrogenated in the presence of nickel at about 150° to a mixture of the *cis*- and *trans*-forms of *p*-isopropylcyclohexanol, which is oxidised by alkaline permanganate at a temperature not exceeding 10° to *dl*- β -isopropyladipic acid, m. p. 75° (yield 50%) (ethyl ester, b. p. 145—150°/12 mm., d_4^{20} 0.9776). The acid is resolved by strychnine in aqueous solution, thus giving *d*- β -isopropyladipic acid, m. p. about 66°, $[\alpha]_D^{20} +5.4^\circ$ (as sodium salt). *d*- β -isopropyladipyl chloride, b. p. 145—146°/15 mm., d_4^{20} 1.1023, $[\alpha]_D^{20} +1.134^\circ$, *d*- β -isopropyladipamide, m. p. 169.5°, $[\alpha]_D^{20} +9.5^\circ$ in water, and ethyl *d*- β -isopropyladipate, b. p. 145—150°/13 mm., d_4^{20} 0.9776, $[\alpha]_D^{20} -1.534^\circ$, are described.

The initial step in establishing the connexion between α -limonene and β -isopropyladipic acid consists in the saturation of the Δ^1 -linking of the hydrocarbon. Treatment with hydrogen chloride is unsatisfactory, since it induces marked racemisation at the C^4 atom and the activity of the limonene hydrochloride depends greatly on the duration of the action. The hydrocarbon is, however, readily hydrogenated in the presence of platinum-black to dihydrolimonene, $[\alpha]_D^{25} +118^\circ$, whereas when palladium is used as catalyst a mixture of dihydrolimonene, *p*-menthane, and limonene is produced. Ozonisation of dihydrolimonene in glacial acetic acid followed by reduction of the ozonide with zinc dust and water gives ϵ -keto- β -isopropylheptaldehyde, b. p. 130—132°/12 mm., d_4^{20} 0.9393, $[\alpha]_D^{20} -6.97^\circ$ (semicarbazone, m. p. 182—183°), oxidised to ϵ -keto- β -isopropylheptic acid, b. p. 188°/12 mm., d_4^{20} 1.020, $[\alpha]_D^{20} +2.5^\circ$, converted by alkaline hypobromite into $+\beta$ -isopropyladipic acid.

H. WREN.

Potassium permanganate oxidation of carotinoids. P. KARRER (Helv. Chim. Acta, 1929, 12, 558).—A question of priority (cf. Kuhn, Winterstein, and Karlovitz, this vol., 425).

H. BURTON.

Effect of heat on malic acid. F. W. MORSE (J. Amer. Chem. Soc., 1929, 51, 1276—1279).—In order to ascertain the cause of the decrease in free acid content observed in cranberries dried at 85°, samples of the two principal acid constituents (cf. Nelson, A., 1927, 798), citric and *dl*-malic acids, have been heated at 65—95°. The former remains unchanged, but the latter is slowly dehydrated at temperatures above 75°, giving finally an anhydride (?) $\text{C}_6\text{H}_6\text{O}_4(\text{CO}_2\text{H})_2$ (cf. Walden, A., 1900, i, 10). This is almost completely hydrolysed when its neutralised solution is boiled for several hours, and the same effect is observed with extracts of the dried cranberries.

H. E. F. NOTTON.

Aconitic acids. I. R. MALACHOVSKI and M. MASLOVSKI (Rocz. Chem., 1929, 9, 49—55).—See this vol., 172.

Osones for the synthesis of ketouronic acids. T. KITASATO and C. NEUBERG (Biochem. Z., 1929, 207, 230—231).—Sufficient alkali-free lead carbonate to remove all hydrochloric acid is added with stirring to the solution obtained from the hydrolysis of an osazone with concentrated hydrochloric acid, free phenylhydrazine hydrochloride having first been

removed by cooling with ice and filtration. As much lead chloride as possible is separated by preserving the cold liquid, part of the colouring matter which is also present being thus carried down. The filtered solution is then decolorised by shaking with animal charcoal at the ordinary temperature and can be used directly for the preparation of ketouronic acids (cf. following abstract). W. MCCARTNEY.

Further syntheses of α -keto-acids of the carbohydrate series. α -Keto-*D*-galactonic acid and α -ketomaltobionic acid. T. KITASATO (Biochem. Z., 1929, 207, 217—229).—Osones of disaccharides can be oxidised by bromine to α -keto-acids in the same way as are those of monosaccharides (cf. A., 1927, 544). *D*-Galactosone gives α -keto-*D*-galactonic acid, $[\alpha]_D^{20} -7.8^\circ$ [barium salt + H_2O ; calcium salt; brucine salt, m. p. 175° (decomp.), $[\alpha]_D^{20} -24.55^\circ$ in water]. The acid readily reduces alkaline copper solutions and ammoniacal silver nitrate solutions. Similarly, maltosone gives α -keto-*D*-maltobionic acid, $[\alpha]_D^{20} +54.9^\circ$ [brucine salt, + $2H_2O$, and anhyd., m. p. $150-160^\circ$ (decomp.), $[\alpha]_D^{20} +11.4^\circ$ in water; barium salt, $[\alpha]_D^{20} +54.8^\circ$ in water]. The acid reduces Fehling's solution and is hydrolysed by sulphuric acid and by maltase. W. MCCARTNEY.

Dithioformic acid. II. T. G. LEVI (Atti R. Accad. Lincei, 1929, [vi], 9, 170—175; cf. A., 1923, i, 996).—Dithioformic acid, $(CH_2S_2)_3$, m. p. $55-60^\circ$ (decomp.), forms the following derivatives: *potassium*, m. p. 193° (decomp.); *ammonium*; *methyl*, m. p. 105.5° ; *ethyl*, liquid; *propyl*, m. p. $38-39^\circ$, two *benzyl*, probably *cis-trans*-isomerides, m. p. 154° and 77° , respectively; *monosulphide*, $C_2H_2S_3$, m. p. 195° (decomp.). When heated, the acid decomposes, giving hydrogen sulphide, carbon disulphide, carbon, and sulphur. The trimeric constitution of the acid and its esters indicates a cyclic structure with alternating carbon and sulphur atoms. T. H. POPE.

Constitution of high molecular substances. H. STAUDINGER (Naturwiss., 1929, 17, 141). K. H. MEYER (*ibid.*, 255).—Polemic. R. A. MORTON.

Formation of acetaldehyde from alanine in presence of pyrocatechol. F. SCHAAF (Biochem. Z., 1929, 205, 449—450).—Equivalent amounts of pyrocatechol and alanine shaken with oxygen yield small amounts of acetaldehyde, detected by its compound with dimethyldihydroresorcinol. This confirms the author's theory of the mechanism of the formation of melanin by oxidation of 3:4-dihydroxyphenylalanine. J. H. BIRKINSHAW.

Trimethyl- and dimethylethyl-acetaldehydes. J. B. CONANT, C. N. WEBB, and W. C. MENDUM (J. Amer. Chem. Soc., 1929, 51, 1246—1255).—Magnesium *tert*-butyl chloride and excess of formaldehyde give, in addition to *tert*-butylcarbinol, *methylene ditert-butyl ether*, b. p. $182-185^\circ$. Magnesium *tert*-amyl chloride gives similarly *tert*-amylcarbinol and *methylene ditert-amyl ether*, b. p. $220-224^\circ$. The carbinols are dehydrogenated by the method of Bouveault (A., 1908, i, 117) to trimethyl- and dimethylethyl-acetaldehydes, which autoxidise in air or oxygen to the corresponding acids (cf. Samec, A., 1907, i, 286). The change is retarded by quinol, but not to the same

extent as with benzaldehyde. The photochemical decomposition of trimethylacetaldehyde into carbon monoxide and isobutane (cf. Hinterberger, Diss., Vienna, 1923) is effected mainly by light of wavelength $2950-3200 \text{ \AA}$. Dimethylethylacetaldehyde behaves similarly. The proportions of (a) primary, (b) secondary alcohol formed from (A) trimethyl- and (B) dimethylethyl-acetaldehydes and excess of the following Grignard reagents are: magnesium *n*-propyl bromide: A (a) a trace, (b) 50% of the theoretical; B (a) 15%, (b) 45%; magnesium *iso*-propyl bromide: A (a) 10%, (b) 33%; B (a) 33%, (b) 27%; and magnesium *tert*-butyl chloride: A (a) 66%; B (a) 60%. These reactions illustrate the effect of branched chains on the course of the reaction (cf. this vol., 675). Trimethylacetaldehyde undergoes the Cannizzaro reaction to the extent of 60% in presence of alcoholic (but not aqueous) potassium hydroxide. H. E. F. NORTON.

Derivatives of glycollaldehyde and methylglyoxal. H. O. L. FISCHER and L. FELDMANN (Ber., 1929, 62, [B], 854—865; cf. A., 1927, 857).—Full details are given of the preparation of glycollaldehyde, m. p. 76° , by ozonisation of allyl or cinnamyl alcohol in glacial acetic acid and reduction of the ozonides by zinc dust. The yields are 20—25% and 6%, respectively; the poor yield in the latter case is due in part to the volatility of glycollaldehyde with steam. *Methyl allyl carbonate*, b. p. $38^\circ/18 \text{ mm.}$, $n_D^{20} 1.4118$, prepared from allyl alcohol and methyl chloroformate in pyridine, is converted by successive treatment with ozone and zinc dust into *O*-carbomethoxyglycollaldehyde, $CO_2Me \cdot O \cdot CH_2 \cdot CHO$, b. p. $78-79^\circ/17 \text{ mm.}$, $n_D^{20} 1.4171$ (yield 39%), transformed by ethyl orthoformate in presence of ethyl alcohol and ammonium chloride into the corresponding *diethylacetal*, b. p. $72-75^\circ/0.3-0.4 \text{ mm.}$, $n_D^{20} 1.4105$. Ozonisation and subsequent reduction of allylglucoside tetra-acetate affords *glycollaldehydeglucoside tetra-acetate*, $C_2H_3O \cdot O \cdot C_6H_7O_5Ac_4$, which could not be caused to crystallise; it is hydrolysed by sulphuric acid to dextrose and glycollaldehyde; the amorphous substance is converted by methyl-alcoholic hydrogen chloride and subsequent re-acetylation by acetic anhydride and pyridine into its *dimethylacetal*, m. p. 84° after softening, $[\alpha]_D^{20} -20.48^\circ$ in methyl alcohol, also obtained from acetobromoglucose, glycollaldehyde dimethylacetal, and silver carbonate in chloroform.

[With G. DANGSCHAT.]—Vinyl acetate, dissolved in glacial acetic acid, is converted into its dibromide, which is transformed by potassium acetate into *glycollaldehyde triacetate*, m. p. 52° , also obtained by protracted ebullition of crystalline glycollaldehyde with acetic anhydride. *Diacetoxylacetone*, from dihydroxyacetone and boiling acetic anhydride, has m. p. $46-47.5^\circ$. Treatment of anhydrous, monomeric methylglyoxal with acetic anhydride affords the *diacetate*, $COMe \cdot CH(OAc)_2$, b. p. $115-116^\circ/13 \text{ mm.}$, converted by concentrated hydrogen peroxide into a substance, $C_7H_{10}O_6$, m. p. $78-79^\circ$ after softening, the nature of which has not been fully elucidated. Two mols. of the compound liberate 2 atoms of iodine from hydriodic acid and Freudenberg's method indicates the presence of three acetyl groups,

obviously due to oxidation of the methylglyoxal residue during the determination. With an excess of phenylhydrazine acetate it yields methylglyoxal-phenylosazone.

Full details are given of the preparation of methylglyoxal from dihydroxyacetone and phosphoric oxide, the apparatus being designed so that collection and re-distillation of the sensitive product are effected without exposing it to air. The oxidation of tartaric acid to dihydroxymaleic acid is described at length.

H. WREN.

Methylations with diazomethane in the presence of catalysts. II. H. MEERWEIN, T. BERSIN, and W. BURNELEIT [with P. POHLS] (Ber., 1929, 62, [B], 999—1009; cf. A., 1928, 1217; Arndt and others, this vol., 328).—Acetone, undiluted or dissolved in ether, toluene, heptane, acetonitrile, chloroform, or acetic anhydride, does not react appreciably with diazomethane at 0° as shown by the rate of evolution of nitrogen and the diminution of the diazomethane content as indicated by titration with ethereal benzoic acid. Formation of an additive product of acetone and diazomethane does not appear to occur. Experiments with chloral and diazomethane show that such additive compounds are not decomposed by ethereal benzoic acid, which thus indicates only free diazomethane. The reaction of the last-named compound with ketones is greatly influenced by catalysts, both electrolytes and compounds of marked dipolar character such as water and alcohols. Acetone reacts fairly energetically with diazomethane in the presence of 70% of formamide, giving mainly *as*-dimethylethylene oxide; methyl ethyl ketone is produced to some extent, whereas the formamide is scarcely methylated.

Chloral hydrate is transformed by ethereal diazomethane mainly into $\gamma\gamma$ -trichloropropylene $\alpha\beta$ -oxide, b. p. 41—42°/10 mm., with small amounts of chloral dimethylacetal, methyl alcohol, methyl ether, and a nitrogenous compound, b. p. 98—103°/3 mm. Chloral hydrate must therefore have the constitution $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ and its methylation is ascribed to its acidic character. The interaction of diazomethane with solutions of chloral alcoholates in the corresponding alcohols proceeds similarly, yielding $\gamma\gamma$ -trichloropropylene $\alpha\beta$ -oxide and the unsymmetrical chloral methylalkylacetals. Simultaneously a more or less considerable proportion of the alcohol (except *tert*.-butyl alcohol) passes, under the influence of the acidic alcoholate, into its methyl ether. The alcoholates are therefore normal valency compounds which are partly dissociated into their components in alcoholic solution at 0°. The percentage yield of $\gamma\gamma$ -trichloropropylene $\alpha\beta$ -oxide in presence of the various alcohols is ethyl (10.9), *n*-propyl (9.6), *iso*-propyl (23.4), *n*-butyl (16.6), *tert*.-butyl (88.8).

In the presence of 25% of $\beta\beta\beta$ -trichloroethyl alcohol, acetone reacts vigorously with diazomethane, with formation of *as*-dimethylethylene oxide and methyl ethyl ketone, whilst a portion only of the alcohol is transformed into its methyl ether. Since reaction between acetone and diazomethane is not, in general, induced by organic acids, the process appears influenced by the nature of the anion as well as by the strength of the acid.

H. WREN.

Methyl ethers of diacetyldioxime. E. THILO (Ber., 1929, 62, [B], 866—871).—The monomethyl ether (Charrier, A., 1907, i, 829) and dimethyl ether (Avogadro and Tavola, A., 1925, i, 1040) of diacetyldioxime are shown to be *O*-compounds. Treatment of the dimethyl ether with fuming hydrochloric acid at about 60° results in the production of diacetyl and *O*-methylhydroxylamine (isolated as the hydrochloride) with unchanged di-ether. Similarly, the mono-ether affords diacetyl, diacetyldioxime, hydroxylamine, and *O*-methylhydroxylamine. With 1% hydrochloric acid at about 60° the mono-ether is partly unchanged, partly converted into diacetylmonoxime methyl ether and diacetyldioxime. One part of the mono-ether loses the oximino-group, whilst another portion loses the methylated oximino-group; if the mixture is cooled the products interact, giving mono-ether and diacetyldioxime and its di-ether in equivalent amounts. The disproportionation of the mono-ether into diacetyldioxime and its dimethyl ether shows that the alkyl group in the former is analogously linked to those in the latter, and this conclusion is confirmed by the formation of the di- from the mono-ether and methyl sulphate in feebly alkaline solution. Diacetylmonoxime is transformed by a slight excess of *O*-methylhydroxylamine into the monomethyl ether (yield 80%). Similarly, diacetylmonoxime methyl ether and *O*-methylhydroxylamine give the di-ether in almost theoretical yield.

H. WREN.

Compounds of sugars with sulphuric acid. II. Reaction for the differentiation of ring-isomeric, acylated halogeno-sugars. H. OHLE, W. MARECEK, and W. BOURJAU (Ber., 1929, 62, [B], 833—854; cf. A., 1925, i, 634).—All acylated 1-halogeno-sugars containing a 1:5-oxygen bridge give esters of the type $\text{R}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{N}(\text{C}_5\text{H}_5)\cdot\text{R}$ [R = acylated sugar residue] when treated with pyridine in the presence of silver sulphate. Furoid compounds appear to give salts of the type $\text{R}\cdot\text{N}(\text{C}_5\text{H}_5)\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{N}(\text{C}_5\text{H}_5)\cdot\text{R}$, but the available material is not sufficiently diverse in character to enable a decision to be reached with regard to the specificity of ester formation.

Benzyl chloride, pyridine, and silver sulphate give *benzylpyridinium sulphate*, $\text{C}_{24}\text{H}_{24}\text{N}_2\text{SO}_4$, m. p. 117—118°. Chloroacetic acid similarly affords *carboxymethylpyridinium sulphate*, m. p. 177° (decomp.), whereas ω -bromoacetophenone yields *phenacylpyridinium sulphate*, m. p. (indef.) 210—225° (probably an equimolecular mixture of the normal and hydrogen salts). Chlorodiethyl ether and pyridine yield pyridine hydrochloride and acetaldehyde diethylacetal.

The acylated 1-halogeno-sugars are obtained by the established method or by Pacsu's process (A., 1928, 1118), using titanium tetrachloride or tetrabromide. The halogen compound and silver sulphate (mol. ratio, 2:1) are shaken with the fivefold to tenfold weight of pyridine over-night at the atmospheric temperature. Tetra-acetyl-*l*-arabinose, b. p. 178°/1.5 mm., $[\alpha]_D^{25} + 41.78^\circ$ in chloroform, could not be caused to crystallise when prepared by treatment of *l*-arabinose with acetic anhydride in pyridine. It is converted

into acetochloroarabinose, m. p. 146° , $[\alpha]_D^{25} +242.61^{\circ}$ in chloroform, and thence into *triacetyl- α -l-arabinose-1-pyridinium triacetyl- α -l-arabinose-1-sulphate*, $C_{27}H_{35}O_{18}NS$, m. p. 153° , $[\alpha]_D^{25} +27.97^{\circ}$ in chloroform. Similarly, tetra-acetyl- α -l-xylose, m. p. 124.5° , $[\alpha]_D^{25} -24.8^{\circ}$ in chloroform, is transformed into acetochloroxylose, m. p. $100-101^{\circ}$, $[\alpha]_D^{25} +167.85^{\circ}$ in chloroform, and *triacetyl- α -l-xylose-1-pyridinium triacetyl- α -l-xylose-1-sulphate*, m. p. 143° , $[\alpha]_D^{25} -41.71^{\circ}$ in chloroform and alcohol. Tetra-acetyl-rhamnose is transformed by Pacsu's method into crystalline acetochloro-rhamnose, m. p. 72.5° , $[\alpha]_D^{25} -127.03^{\circ}$ in chloroform, and thence into *triacetyl- α -l-rhamnose-1-pyridinium triacetyl- α -l-rhamnose-1-sulphate*, m. p. 142° , $[\alpha]_D^{25} -51.38^{\circ}$ in chloroform, and, probably, the β -ester. Acetodibromoglucose, silver sulphate, and pyridine afford 5-bromo-2:3:4-triacetyl- β -d-glucose-1-pyridinium (+2EtOH), m. p. $62-69^{\circ}$. 3-p-Toluenesulphonyl-2:4:6-triacetyl- β -d-glucose-1-pyridinium 3-p-toluenesulphonyl-2:4:6-triacetyl- β -d-glucose-1-sulphate, m. p. $145-146^{\circ}$, $[\alpha]_D^{25} -4.47^{\circ}$ in chloroform, is described. The furoid 3-p-toluenesulphonyl-2:5:6-triacetyl-1-bromo-d-glucose yields a non-crystalline syrup in which sulphur is present entirely in the form of sulphate. Benzobromoglucose gives *tetrabenzoyl- β -d-glucose-1-pyridinium tetrabenzoyl- β -d-glucose-1-sulphate*, m. p. $193-194^{\circ}$, $[\alpha]_D^{25} +15.47^{\circ}$ in chloroform. Acetobromogalactose, readily prepared from penta-acetyl-galactose and hydrogen bromide in glacial acetic acid, is transformed into *tetra-acetyl- β -d-galactose-1-pyridinium tetra-acetyl- β -d-galactose-1-sulphate*, m. p. $172-173^{\circ}$, $[\alpha]_D^{25} \pm 0^{\circ}$ in chloroform, and *tetra-acetyl- β -d-galactose-1-pyridinium sulphate*, m. p. about 170° (decomp.). Acetochloromannose, when prepared from penta-acetylmannose, aluminium chloride, and phosphorus pentachloride in chloroform, does not react with pyridine and silver sulphate, whereas the compound (or the corresponding bromo-derivative) prepared by Pacsu's method is converted into a syrup consisting mainly of the ester salt; in this instance, as with rhamnose, the sugars and their products belong to the same series. β -Penta-acetylfructose is transformed by Pacsu's method directly into *tetra-acetylchloro- β -d-fructose*, m. p. 82° , $[\alpha]_D^{25} -160.47^{\circ}$ in chloroform, which with pyridine and silver sulphate appears to give a mixture of the ester salts of the α - and β -series in which the α -form preponderates (m. p. $97-109^{\circ}$, $[\alpha]_D^{25} -8.48^{\circ}$ in chloroform). Acetobromocellobiose affords *hepta-acetyl-d-cellobiose-1-pyridinium hepta-acetyl-d-cellobiose-1-sulphate* (+2.5H₂O and anhydrous), m. p. $194-195^{\circ}$ (decomp.). *Hepta-acetyl- β -d-lactose-1-pyridinium hepta-acetyl- β -d-lactose-1-sulphate*, m. p. $185-186^{\circ}$, $[\alpha]_D^{25} -9.44^{\circ}$ in chloroform, is described. Acetobromoglucose and dimethylaniline at the ordinary temperature give phenyltrimethylammonium bromide, m. p. $213-214^{\circ}$, whereas the sugar product could not be caused to crystallise. In the presence of silver sulphate, acetobromoglucose is transformed by dimethylaniline into phenyltrimethylammonium tetra-acetyl- β -d-glucose-1-sulphate, m. p. $163-164^{\circ}$.

H. WREN.

Constitution of chinovose. E. VOTOČEK (Coll. Czech. Chem. Comm., 1929, 4, 234-238).—Oxidation

of chinovose with bromine water gave an acid which readily passed into a lactone; reduction of the latter with sodium amalgam furnished chinovose. This is regarded as proof that chinovose is an aldose (cf. Fischer and Liebermann, A., 1894, i, 4).

A. I. VOGEL.

Identity of chinovose with d -glucomethylose (isorhodoose). E. VOTOČEK and F. RAC (Coll. Czech. Chem. Comm., 1929, 4, 239-244).—Reduction of chinovose with sodium amalgam (solution maintained acid with sulphuric acid) gave a syrupy sugar-alcohol which yielded with benzaldehyde a product, m. p. $193-194^{\circ}$, identical with that similarly prepared from isorhodoose, thus indicating that chinovose is a d -glucomethylose (cf. Freudenberg and Raschig, this vol., 427).

A. I. VOGEL.

Fission of β -glucosan with titanium tetrachloride. G. ZEMPLÉN and Z. CSÜROS (Ber., 1929, 62, [B], 993-996).—A method is described which permits the preparation of glucose derivatives with a free hydroxyl in the ζ -position. Triacetyl- β -glucosan is converted by an excess of titanium tetrachloride in chloroform into α -1-chloro-2:3:4-triacetylglucose, m. p. $124-125^{\circ}$, $[\alpha]_D^{25} +191.5^{\circ}$ in chloroform, smoothly transformed by acetic anhydride and pyridine into α -chloroacetoglucose, m. p. 73° , $[\alpha]_D^{25} +165.3^{\circ}$ in chloroform. It is converted by methyl alcohol and silver carbonate into 2:3:4-triacetyl- β -methylglucoside, m. p. $131-132^{\circ}$, $[\alpha]_D^{25} -13.59^{\circ}$ in chloroform. With silver carbonate in benzene it gives a tetra-acetyl derivative converted into 1:2:3:4-tetra-acetyl-6-p-toluenesulphonyl- β -d-glucose (cf. Helferich and Klein, A., 1926, 386). Tribenzoyl- β -glucosan is not affected by titanium tetrachloride under these conditions, whereas pentabenzoylglucose smoothly yields 1-chlorotetrabenzoyl- α -glucose. Trimethyl- β -glucosan yields amorphous products containing relatively little halogen. Penta-acetylgluconic acid and hexa-acetylmannitol are unaffected. 2:3:4:6-Tetramethylglucose is decomposed into ill-defined products.

H. WREN.

Oxidation of dextrose and glycine by means of alkaline copper solutions. H. LUNDIN (Biochem. Z., 1929, 207, 91-106, 107-119).—Glycine (and also other amino-acids) if present in sufficient quantity interfere (at least at p_H 9.1-9.8) with the oxidation of dextrose by alkaline copper solutions such as those of Folin and of Folin and Wu, the interference being the greater the lower is the p_H . Increased time of boiling (standard time 10 min.) reduces the extent of interference. If the oxidation is carried out at p_H 9.8 or more the total reduction of copper is approximately the same as the sum of the reductions due to the dextrose and the glycine separately unless the alkalinity is very high. The extent of oxidation of glycine by the copper solutions increases rapidly with increase of p_H and with increased time of boiling and decreases with low carbonate contents. The optimum alkalinity for the oxidation of dextrose by alkaline copper solutions is p_H 9.2-9.8. When quantities of buffering substances are present in the sugar solutions these must be brought to the p_H of the copper reagent by the addition of sodium hydroxide. Boric acid interferes (at least at p_H 9.1-10.5) in the same way

as does glycine with the oxidation of dextrose by alkaline copper solutions, and if very large proportions (400—500 : 1) of it are present the dextrose is not oxidised at all (boiling time 6—7 min.). Alkaline copper solutions containing borate oxidise amino-acids to the same extent as do similar solutions free from borate. A copper solution having the same p_H as the reagent of Folin and Wu and containing 56 g./litre of boric acid (or 86 g./litre of borax) scarcely oxidises small amounts of dextrose, but oxidises amino-acids to the same extent as does the Folin-Wu reagent. The difference in the values obtained when solutions containing glycine (up to 8 g./litre) or creatinine (up to 0.5 g./litre) and dextrose (up to 0.2 g./litre) are oxidised with the Folin-Wu reagent and with this reagent containing borate represents the concentration of dextrose present. The p_H values given are only approximate and refer to the reaction mixtures before heating. The p_H of sugar solutions containing quantities of buffering substances must be brought to the same value as that of the copper solution by the addition of sodium hydroxide before determinations are made.

W. McCARTNEY.

Formation of carbon monoxide by the action of oxygen or air on dextrose in alkaline solution. Influence of temperature and alkalinity. M. NICLOUX (Compt. rend. Soc. Biol., 1928, 98, 1548—1551; Chem. Zentr., 1928, ii, 1668).—For a 0.5% solution of dextrose, the optimal temperature for the formation of carbon monoxide is 84—85°, and the optimal alkalinity about 0.1N. A. A. ELDRIDGE.

Compounds of dextrose and phosphoric acid. B. HELFERICH and H. DU MONT (Z. physiol. Chem., 1929, 181, 300—308).—1 : 2 : 3 : 4-Tetra-acetyl- β -glucose reacts with phosphoryl chloride in pyridine giving tri-(β -tetra-acetyl-*D*-glucose)-6-phosphate, m. p. 236—237°, $[\alpha]_D^{20} + 30.2^\circ$. Under different conditions the same substances give β -tetra-acetyl-*D*-glucose-6-chlorohydrin. Hydrolysis of the tri(acetylglucose)-phosphate yields an amorphous product in which phosphoric acid is organically combined, but reacetylation gives back only a small amount of the original ester and secondary changes must have largely taken place. Triacetyl- α -methylglucoside reacts similarly in pyridine to give tri(triacetyl- α -methylglucoside)phosphate, m. p. 185°, $[\alpha]_D^{20} + 151.9^\circ$. This substance on hydrolysis gives tri-(α -methyl-*D*-glucoside)-6-phosphate, which readily reacetylates and also when heated with sodium iodide in a sealed tube gives the corresponding 6-iodohydrin. P. W. CLUTTERBUCK.

Walden inversion in the hexose series. P. A. LEVENE, A. L. RAYMOND, and A. WALT (J. Biol. Chem., 1929, 82, 191—195).—Lævulose- γ -phosphoric acid yielded an osazone, m. p. 165—168° after softening at 160°, $[\alpha]_D^{20} - 138^\circ$, which was thus different from the osazone prepared by Fischer and Zach (A., 1912, i, 678) from γ -anhydroglucose; the new osazone is regarded as γ -anhydroallosazone, Walden inversion having occurred during hydrolysis of the phosphoric acid group. C. R. HARRINGTON.

Syntheses in the carbohydrate group with the aid of sublimed ferric chloride. I. Preparation of biosides of the α -series. G. ZEMPLÉN

(Ber., 1929, 62, [B], 985—990).—Octa-acetyl- α -cellobiose is converted by sublimed ferric chloride in chloroform containing ethyl alcohol into hepta-acetyl- α -ethylcellobioside, m. p. 169—170° after softening, $[\alpha]_D^{18} + 49.7^\circ$ in chloroform. The bioside is transformed by hydrogen bromide in glacial acetic acid into acetobromocellobiose, m. p. about 180° (decomp.), $[\alpha]_D^{19} + 90.5^\circ$ in chloroform. Its specific rotation is increased to +52.6° by treatment with titanium tetrachloride, thus showing that it is not completely homogeneous. In the absence of alcohol, octa-acetyl- α -cellobiose is not affected by ferric chloride in chloroform. Octa-acetyl- β -maltose yields the amorphous hepta-acetyl- α -ethylmaltoside, m. p. about 90—100° after softening at 80—85°, $[\alpha]_D^{17} + 122.2^\circ$ in chloroform (changed to +124.4° by treatment with titanium tetrachloride). The method is not available for the synthesis of α -phenylbiosides. Replacement of aliphatic alcohols by tetra-acetyl derivatives of hexoses or hepta-acetyl compounds of bioses leads to the production of higher sugars from completely acetylated sugars in presence of ferric chloride.

H. WREN.

Action of metallic aluminium and mercury salts on acetohalogeno-sugars. I. Syntheses of α -biosides. G. ZEMPLÉN (Ber., 1929, 62, [B], 990—996).—Acetobromocellobiose is rapidly converted by aluminium filings and dry mercuric acetate in benzene into hepta-acetylcellobiose; reduction in presence of ethyl alcohol affords hepta-acetyl- β -ethylcellobioside, m. p. 186°, $[\alpha]_D^{18} - 19.44^\circ$ in chloroform. If phenol is added to the benzene solution, hepta-acetyl- α -phenylcellobioside, m. p. 217°, $[\alpha]_D^{18} + 81.10^\circ$ in chloroform, results, the specific rotation of which is unchanged after treatment with titanium tetrachloride; the compound is converted by hydrogen bromide in glacial acetic acid into acetobromocellobiose, m. p. about 178° (decomp.), $[\alpha]_D^{18} + 92.0^\circ$ in chloroform, and decomposed by sodium hydroxide with production of phenol. Hepta-acetyl- α -cyclohexylcellobioside, m. p. 203.5°, $[\alpha]_D^{20} + 63.4^\circ$ in chloroform, is prepared in a similar manner.

H. WREN.

Synthesis of sucrose. G. ZEMPLÉN and A. GERECES (Ber., 1929, 62, [B], 984; cf. Pictet and Vogel, A., 1928, 510, 741).—The condensation of tetra-acetyl- γ -fructose with tetra-acetylglucose in the presence of phosphoric oxide causes the production of 10—15% of a disaccharide from which octa-acetyl-sucrose could not be obtained crystalline. The acetylated sucrose does not crystallise when seeded from mixtures of 50% of it with 50% of tetra-acetyl- γ -fructose or 50% of tetra-acetylglucose. The conditions for the synthesis of sucrose appear particularly subtle.

H. WREN.

Condensation of dextrose and lævulose; iso-sucrose. J. C. IRVINE, J. W. H. OLDHAM, and A. F. SKINNER (J. Amer. Chem. Soc., 1929, 51, 1279—1293).—Freshly prepared ethyl- γ -fructoside is converted by acetic anhydride and sodium acetate into ethyl- γ -fructoside tetra-acetate, $[\alpha]_D^{20} + 39.0^\circ$ to +47.9° in chloroform, n_D^{20} 1.4528—1.4542. When this is treated with hydrogen chloride in acetyl chloride and the resulting chloro-derivative hydrolysed with moist silver oxide in benzene γ -fructose tetra-acetate, $[\alpha]_D^{20}$

+31.5° in chloroform, +38.7° in benzene, n_D 1.4645, is obtained. It is formed similarly, together with a little crystalline *anhydrofructose triacetate*, $[\alpha]_D$ +37.8° in chloroform, n_D 1.4662, from inulin triacetate. The tetra-acetate, now obtained pure for the first time, differs in rotatory power and solubility from that described by Pictet (A., 1928, 510, 741). It is characterised by its quantitative hydrolysis by 2*N*-sodium hydroxide and by its conversion through methyl- γ -fructoside tetra-acetate and tetramethyl-methyl- γ -fructoside into tetramethyl- γ -fructose, $[\alpha]_D$ 26.4°, changing to +30.1°, the behaviour of which in several reactions followed polarimetrically is identical with that of a sample, $[\alpha]_D$ +31.8°, changing to 34.1°, prepared from octamethylsucrose. Of the ten possible disaccharide octa-acetates obtainable from the tetra-acetate and syrupy (α - and β -)glucose tetra-acetates in benzene in presence of phosphoric anhydride, only *isosucrose octa-acetate*, m. p. 131–132°, $[\alpha]_D$ +19.9° in chloroform, –2.0° in benzene, has been obtained crystalline, although *isotrehalose octa-acetate* is also present. The former is converted by dimethylamine in absolute ethyl alcohol into *isosucrose*, decomp. 194°, sintering from 152°, $[\alpha]_D$ +50.0° in methyl alcohol, +34.2° in water, which may be identical with Pictet's *sucrose-D* (A., 1928, 1223). It reduces Fehling's solution to a slight extent on prolonged boiling and is more easily hydrolysed by acid and alkali than is sucrose. The same *isosucrose* is obtained from the condensation product of *chloro- γ -fructose tetra-acetate* (87% pure) with glucose tetra-acetate in chloroform in presence of silver carbonate and sodium sulphate. The crude mixtures of disaccharides obtained from the products of the above condensations have, coincidentally, the same rotatory power, both before and after inversion, as sucrose and must therefore contain a disaccharide more dextrorotatory than sucrose. This is regarded as α -glucosido- β (γ)-fructose and *isosucrose* as β -glucosido- β (γ)-fructose (cf. Pictet, *loc. cit.*), so that sucrose is α - or β -glucosido- β (γ)-fructose, probably the latter. Chloro- or bromo-glucose tetra-acetate does not condense with γ -fructose tetra-acetate in presence of bases.

H. E. F. NOTTON.

Cardiac glucoside from *Convallaria majalis*, L. W. KARRER (Helv. Chim. Acta, 1929, 12, 506–511).—The flowers are extracted with much water, and after treatment with lead acetate, the active principle is adsorbed on charcoal. Extraction of the adsorbate with chloroform and subsequent purification of the residue from alcohol affords *convallatoxin*, m. p. 212–213°. This gives Molisch's test, reduces Fehling's solution after hydrolysis with dilute acid, and yields a red colour changing to green when subjected to Liebermann's cholesterol reaction. *Convallatoxin* is about 1.5 times as toxic as ouabain.

H. BURTON.

Solanine. G. ODDO (Gazzetta, 1929, 59, 155–160).—See this vol., 299.

[**Lignin and cellulose.**] K. HESS (Ber., 1929, 62, [B], 924–927).—A reply to Freudenberg (this vol., 430). The "insoluble" methylcellulose of Freudenberg is dissolved by water at 0° after being shaken with water or dissolved in methyl alcohol and chloroform (1 : 1). The non-identity of an anhydride of $\beta\gamma$ -trimethylglucose with trimethylcellulose for

which the depression in dilute solution corresponds with that of a trimethylglucosan is not an argument for or against the main valency chain structure of cellulose. The high acetyl content of Freudenberg's preparations of the author's hexa-acetylbiosan is solely due to the presence of known products of acetolysis.

H. WREN.

Selective action of three hydroxyl groups of cellulose. T. NAKASHIMA and I. SAKURADA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 272–276).—When cellulose mono-*p*-toluenesulphonate is heated with anhydrous hydrazine at 100° for 15–16 hrs. fission occurs, affording *p*-toluenesulphonic acid, a soluble product (4.55% N), and an insoluble product (2.28% N) (monohydrazine derivative of cellulose requires 16.1% N); both products absorb bromine, but it is not clear whether this is due to unsaturation or to the hydrazine group. The above result indicates the partial formation of a hydrazine derivative of cellulose at the former point of esterification, which is considered to be the secondary hydroxyl group in position 2 or 3 in the $C_6H_{10}O_5$ unit.

The preparation of *tribenzylcellulose* by heating dibenzylcellulose with benzyl chloride and silver oxide is described.

C. W. SHOPPEE.

Cellulose benzyl ethers. T. NAKASHIMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 261–264).—By treatment of cotton paper, which has been steeped in 40–50% sodium hydroxide solution, with sufficient benzyl chloride in benzene or toluene, dibenzylcellulose is obtained in quantitative yield in a single operation. If 10–20% sodium hydroxide solution is employed, a mixture of *monobenzylcellulose* and unchanged cellulose is obtained, from which the latter may be removed by treatment with ammoniacal copper oxide solution.

C. W. SHOPPEE.

Celluloseamine and celluloseaniline. I. SAKURADA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 265–271).—Cellulose mono-*p*-toluenesulphonate (A) (Kita, Nakashima, and Sakurada, B., 1926, 944), when heated with concentrated aqueous ammonia at 100° for 24 hrs., affords a product (1 mol. celluloseamine + 1 mol. cellulose + $\frac{1}{2}$ mol. A); the proportion of celluloseamine in the product is not raised by heating for a longer period. Treatment with ammonia in dry ethyl alcohol at 0° for 20 hrs. yields a preparation (1 mol. celluloseamine + 1 mol. cellulose + $\frac{1}{2}$ mol. A). Aniline heated with A in glycerol at 100° for 20 hrs. furnishes a product (2 mols. celluloseaniline + 1 mol. cellulose + 2 mols. A) and after 100 hrs. a product (2 mols. celluloseaniline + $\frac{1}{2}$ mol. cellulose + 1 mol. A); methylaniline behaves similarly. By hydrolysis of any unchanged I in the above products, followed by removal of all cellulose with ammoniacal copper oxide solution, *celluloseamine*, $C_{12}H_{19}O_5 \cdot NH_2$, and *celluloseaniline*, $C_{17}H_{14}O_5 \cdot NHPH$, are obtained.

C. W. SHOPPEE.

Identification of amines. IV. **Methanesulphonamides.** C. S. MARVEL and J. P. BELSLEY (J. Amer. Chem. Soc., 1929, 51, 1272–1274).—Methanesulphonyl chloride (Carius, Annalen, 1860, 114, 142), prepared by an improved method, gives with amines (2 mols.) in benzene methanesulphonamides, which are readily hydrolysed by boiling for

6 hrs. with 60% sulphuric acid. The following derivatives of methanesulphonanilide, m. p. 100.5° (cf. Duguet, A., 1902, i, 428), are described: *o*-methyl-, m. p. 103°; *p*-methyl-, m. p. 102.5°; *o*-methoxy-, m. p. 115.5°; *p*-methoxy-, m. p. 116°; *p*-ethoxy-, m. p. 125°; *o*-chloro-, m. p. 90.5°; *p*-chloro-, m. p. 148°; *p*-bromo-, m. p. 136°; 2:5-dichloro-, m. p. 174°; *N*-methyl-, m. p. 76.5°; *N*-ethyl-, m. p. 59°; *N*-*n*-propyl-, m. p. 76°; *N*-*n*-butyl-, m. p. 73°; *N*-benzyl-, m. p. 122°; oily *p*-methyl-*N*-ethyl-, oily *o*-methyl-*N*-ethyl-, and *N*-sec.-butyl-, also methanesulphon- α -naphthylamide, m. p. 125.5°; β -naphthylamide, m. p. 153.5°; δ -phenoxybutylamide, m. p. 79.5°, and oily 1-menthylamide, diethylamide, di-*n*-butylamide, and di-*n*-propylamide. The separation of known mixtures of primary, secondary, and tertiary amines is satisfactorily effected by means of methanesulphonyl chloride and alkali, but with mixtures of unknown composition it is difficult completely to remove primary and secondary amines without converting the former into alkali-insoluble diacyl derivatives.

H. E. F. NOTTON.

Additive compound containing oxygen obtained by the action of ozone on tetramethylammonium hydroxide. W. TRAUBE and F. KUHBIER (Ber., 1929, 62, [B], 809—820; cf. A., 1927, 342).—Tetramethylammonium hydroxide, when exposed in successive thin layers to the action of ozonised oxygen, absorbs 6—8% of its weight of oxygen, yielding an intensely red compound; repeated successive trituration and ozonisation permits the oxygen content to be raised to 9—10%. Better results are obtained if the product is dried from time to time in a high vacuum, whereby ultimately the hydroxide may absorb 20% of its weight of oxygen. Optimal results are obtained by using tetramethylammonium hydroxide containing 25—28% of water at 20—25°. The best specimens obtained contain 37—41% of their oxygen in evolvable form and contain up to 46% (or 60% if the water content is disregarded) of tetramethylammonium hydroxyoxide, $[\text{NMe}_4\text{OH}]_2\text{O}_2$; the remainder is carbonate, partly present in the original material and partly produced by unavoidable oxidation, and small amounts of formate and non-identified oxidation products of the ammonium hydroxide. Nitrite or nitrate is not present. Tetramethylammonium hydroxyoxide is remarkably stable and can probably be preserved indefinitely at the ordinary temperature. At about 75° it decomposes without explosion into oxygen and colourless tetramethylammonium hydroxide. It is converted by water or alcohol into "indifferent" oxygen (which does not liberate bromine from acidified potassium bromide) and tetramethylammonium hydroxide, the proportion of gas being identical with that obtained by thermal decomposition. The solution contains a small amount of hydrogen peroxide which is not connected with the liberation of oxygen from the red compound, since its amount is not increased if the latter is brought directly into acidified potassium iodide solution; it is due to the presence of an ozonide or peroxide formed by the oxidising action of ozone on tetramethylammonium hydroxide. This action is also observed under conditions such that the formation of the red compounds is excluded, for example, when ozone is

passed through an aqueous solution of the ammonium hydroxide; in this case, also, the products are formic and carbonic acids. Other ammonium hydroxides give intensely coloured, oxygen adducts with ozone provided they do not offer too great opportunity to the oxidising action of the gas. Tetra-alkylarsonium hydroxides behave similarly, but the behaviour of phosphonium hydroxides is uncertain. H. WREN.

s-Methylisopropylhydrazine and methylisopropyl-di-imide. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1929, 51, 918—921).—Attempts to hydrogenate acetone-methylhydrazine and acetaldazine in presence of colloidal platinum were unsuccessful. $\alpha\beta$ -Dibenzoylisopropylhydrazine (cf. Lochte, A., 1922, i, 329) is converted by methyl sulphate and sodium hydroxide in alcohol into dibenzoylmethylisopropylhydrazine, m. p. 76.2—76.7°. This is hydrolysed by hydrochloric acid at 100° to α -methyl- β -isopropylhydrazine, b. p. 79.5—79.7°/371 mm., d 0.7959, heat of vaporisation 9150 g.-cal./mol. (hydrochloride), which is oxidised by hydrogen peroxide at 0° to faintly yellow methyl- β -azopropane, b. p. 45.5—46.5°/760 mm., heat of vaporisation 7350 g.-cal./mol. This is the first known simple unsymmetrical aliphatic azo-derivative; its chemical and physical properties are intermediate between those of azomethane and azoisopropane (A., 1928, 254, 255). Its thermal decomposition at 300° is a homogeneous unimolecular reaction.

H. E. F. NOTTON.

Determination of amino-acids formed by hydrolysis of proteins. II. Esters of acetylated amino-acids. E. CHERBULEZ and P. PLATTNER (Helv. Chim. Acta, 1929, 12, 317—329).—As a preliminary investigation on the separation of amino-acids obtained by hydrolysis of proteins, acetylated esters have been prepared by esterifying amino-acids with alcoholic hydrogen chloride, and after removal of volatile products the residue is treated with acetic anhydride and sodium acetate. The acetylated ester can then, with one exception (cystine), be obtained by vacuum distillation. If hydroxyl groups are present these are acetylated also. Partial racemisation occurs during the distillation but the b. p. of the *r*-ester is the same as that of the active form. The acetamido-acids are obtained by hydrolysis of the esters with barium hydroxide solution. The following are described: ethyl acetamidoacetate, b. p. 145°/11 mm.; ethyl *r*- α -acetamidopropionate, b. p. 96°/1 mm., m. p. 38—39°; ethyl α -acetamidoisohexanoate, b. p. 114°/2 mm.; ethyl α -acetamidosuccinate, b. p. 180°/15 mm.; ethyl α -acetamidoglutarate, b. p. 142°/2 mm.; ethyl *r*- α -acetamido- β -phenylpropionate, b. p. 155—157°/2 mm., m. p. 68°; ethyl 1- α -acetamido- β -*p*-acetoxypheylpropionate, b. p. 184°/2 mm., m. p. 90°, $[\alpha]_D^{25}$ —16.3° in alcohol (the *r*-ester has b. p. 184°/2 mm., m. p. 102—103°); ethyl *N*-acetylpyrrolidine-2-carboxylate, b. p. 155°/13 mm., $[\alpha]_D^{25}$ —80.43° in alcohol; ethyl *N*-acetyl-4-acetoxypyrrolidine-2-carboxylate, b. p. 142°/2 mm.; ethyl di-(α -acetamido- β -thiopropionate), m. p. 123°, $[\alpha]_D^{25}$ —102.3° in alcohol, and ethyl α -acetamido- β -thiopropionate, b. p. 150—151°/3 mm. H. BURTON.

Curtius and Goebel's glycine anhydride silver. T. ASAHINA (Bull. Chem. Soc. Japan, 1929, 4, 75—77).—A greyish-white compound, $\text{C}_4\text{H}_4\text{O}_2\text{N}_2\text{Ag}_2$,

apparently identical or isomeric with the glycine anhydride silver compound of Curtius and Goebel (A., 1888, 576), is formed when freshly precipitated silver oxide is agitated with a concentrated aqueous solution of glycine anhydride in presence of ammonia.

B. W. ANDERSON.

Preparation of lysine, histidine, and arginine from hydrolysed blood-corpuscles by electrical transport. G. J. COX, H. KING, and C. P. BERG (J. Biol. Chem., 1929, 84, 755—764).—The solution obtained by hydrolysing red blood-corpuscles with sulphuric acid, removal of the latter, and concentration, is subjected, after removal of leucine and tyrosine by filtration, to electrolysis at 110 volts, 0.5 amp., in a three-compartment cell divided by parchmentised paper (compare Foster and Schmidt, A., 1926, 802). By separation of the solution in the cathode compartment at three appropriate stages, and by re-electrolysis of the middle fraction, two solutions are obtained, one containing arginine and lysine and the other histidine. The amino-acids are isolated by the usual methods, 4 kg. of blood-corpuscles yielding histidine monohydrochloride 51 g., arginine monohydrochloride 21 g., and lysine dihydrochloride 62 g.

C. R. HARRINGTON.

Carnitin. W. LINNEWIEH (Z. physiol. Chem., 1929, 182, 8—12; cf. Tomita and Sendju, A., 1927, 1058).—Krimberg's chloroaurate of γ -butyrobetaine, m. p. 201—203° (A., 1908, i, 41), is shown to be impure crotonobetaine chloroaurate, m. p. 214—216°. Crotonobetaine chloroaurate crystallises in different forms according to the source from which it is derived.

C. C. N. VASS.

Reactions of carbon monoxide with metallic compounds of cysteine. W. CREMER (Biochem. Z., 1929, 206, 228—239).—Iron forms with cysteine and isocysteine carbonyl compounds containing 1 g.-atom of iron to 2 mols. of carbon monoxide. These compounds are reversibly dissociated by light. Cobalt forms a carbonylcobalt-cysteine with 1 mol. of carbon monoxide, insensitive to light. Carbonylferrocysteine from *D*-cysteine has $[\alpha]_D^{20} +600^\circ$; the cobalt compound is inactive. The catalytic action of iron in the oxidation of cysteine is inhibited by carbon monoxide owing to formation of the complex.

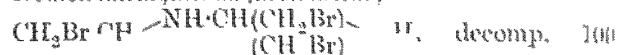
J. H. BIRKINSHAW.

Physiological activity of -onium compounds. Phosphoric ester derivatives of choline. VIII. R. R. RENSHAW and C. Y. HOPKINS (J. Amer. Chem. Soc., 1929, 51, 953—954).—Phosphoryl β -chloroethoxydichloride, b. p. 108—110°/15 mm., from phosphoryl chloride and ethylene chlorohydrin in carbon tetrachloride, gives with trimethylamine the product (?) $\text{Cl}_2\text{PO}\cdot\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{NMe}_3\text{Cl}$, and with methyl alcohol dimethyl β -chloroethyl phosphate, b. p. 95—96°/4 mm. This yields with trimethylamine in toluene at the ordinary temperature the choline ester, $(\text{MeO})_2\text{PO}\cdot\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{NMe}_3\text{Cl}$, m. p. 136.5—137°, which is a powerful nicotine-like stimulant, but has little muscarine action.

H. E. F. NOTTON.

Action of ammonia on monobromoacetaldehyde and preparation of pyrazine from the latter substance. A. E. TSCHITSCHIBABIN and M. N. SCHTSCHUKINA (Ber., 1929, 62, [B], 1075—1080).—

The action of an excess of dry ammonia on monobromoacetaldehyde in benzene at 10—15° affords tri-bromotrimethylhexahydrotriazine,



(yield 17%), probably formed by polymerisation of monobromoacetaldehyde. Under other conditions, bromoacetaldehyde and ammonia yield aminoacetaldehyde hydrobromide, which undergoes further change, yielding substances with completely ionisable bromine. Thus in anhydrous ether at -10° to -5°, a crystalline product is formed the composition of which is not always the same but generally agrees with the formula $(\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NH})_3\cdot 3\text{HBr}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$ (I), although in some cases it more closely approximates to $(\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NH})_3\cdot 3\text{HBr}$. If the passage of ammonia is very protracted, a viscous oil is formed which, as the temperature rises, evolves ammonia and gives the compound I. The formation of glyoxal-phenylosazone from the products confirms the conclusion that they are aminoacetaldehyde derivatives. Conversion of monobromoacetaldehyde into pyrazine is effected by treatment with ammonia in ether at -10° to -5°, followed by addition of sulphuric acid and then of water. The aqueous portion is treated with potassium hydroxide and a mercury salt and then distilled with steam. The yield is about 15.5%.

H. WREN.

Action of magnesium ethyl bromide on succintetraethyldiamide. M. HUAN (Compt. rend., 1929, 188, 1174—1176).—Magnesium ethyl bromide reacts in ether with succintetraethyldiamide (or ethyl succindiethylamate) to yield mainly (63%) γ -keto-*n*-hexodiethylamide (I), b. p. 142—143°/12 mm. (semicarbazone, m. p. 138°; phenylhydrazone, m. p. 107°; *p*-nitrophenylhydrazone, m. p. 165°) (hydrolysed with boiling 48% hydrobromic acid to the corresponding acid), together with 3% of γ -diketo-*n*-octane (II). The action of excess of magnesium ethyl bromide on I yields mainly γ -hydroxy- γ -ethyl-*n*-hexodiethylamide (III), b. p. 166—168°/13 mm., 5% of II, and 2:2:5-trimethyldihydrofuran (IV), b. p. 55—56°/11 mm., the last being obtained by elimination of 1 mol. of water from the unstable γ -ketol, which would be the normal product if both carbonyl groups of I reacted with the Grignard reagent. With alcoholic semicarbazide, however, IV yields the semicarbazone, m. p. 95°, of ethyl γ -hydroxy- γ -ethyl-*n*-amyl ketone. Acetic anhydride eliminates a molecule of diethylamine as acetdiethylamide from III, converting it into γ -ethyl-*n*-hexolactone (Hepworth, J.C.S., 1919, 115, 1203) (additive compound with hydrazine hydrate, m. p. 78°).

J. W. BAKER.

Determination of cyanide in small amounts. R. G. SMITH (J. Amer. Chem. Soc., 1929, 51, 1171—1174).—Quantities of about 0.1 mg. of cyanide ion may be determined with an accuracy of 1% by observing the colour developed in 5 min. at 100° with excess of sodium picrate and carbonate solution. Sodium hydroxide and some reducing agents must be absent, but the method is applicable to tissue distillates obtained by Bischoff's method (A., 1883, 1020). Qualitatively 1 part of cyanide ion in 50,000,000 parts may be detected.

H. E. F. NOTTON.

Constitution of Grignard's magnesium compounds. W. SCHLENK and W. SCHLENK, jun. (Ber., 1929, 62, 920—924).—Dioxan precipitates magnesium halides and organohalides quantitatively from all Grignard solutions. The precipitates are not decomposition products which alter the nature of the organomagnesium compounds, since they bring about the same changes as the original solutions. The filtrates contain only magnesium dialkyls or diaryls, which must therefore be present, in addition to other magnesium organic compounds, in all Grignard solutions. Solutions of organomagnesium compounds which are not too dilute deposit the "Grignard compound" as etherates which melt at the atmospheric temperature in a coarsely crystalline form when cooled with carbon dioxide and acetone. By repeatedly freezing, decanting, and dissolving it is possible to obtain solutions in which $Mg : \text{halogen} = 1 : 1$. If such pure solutions are precipitated with dioxan, the filtrates contain magnesium dialkyl or diaryl, which under these conditions are formed spontaneously from the crystalline, homogeneous organomagnesium halide. The precipitates contain magnesium and halogen in the atomic ratio $Mg : \text{Hal} < 1$. The occurrence of an equilibrium (I) $2R \cdot MgHal + MgR_2 + MgHal_2$ or (II) $R_2Mg, MgHal_2 \rightleftharpoons MgR_2 + MgHal_2$ is thus indicated, and is confirmed by the determination of the ratio $Mg : Br$ in the precipitates obtained by the fractional addition of dioxan to an ethereal solution of pure magnesium α -naphthyl bromide. The decision in favour of I is based on the observation that the precipitates obtained from ethereal magnesium ethyl iodide and dioxan are independent in composition of the concentration of the ethereal solution. The part played by the ether in the formation of Grignard solutions is due to its solvent power, not only for the organo-metallic compounds, but also for the magnesium halides. The position of the equilibrium depends on the nature of the halide; in the case of ethyl iodide, 43% of the total magnesium is present as magnesium ethyl iodide, whereas in that of bromobenzene about 80% of the metal exists as magnesium phenyl bromide. As indicated by the behaviour of bromobenzene and magnesium towards benzophenone and fluorenone, respectively, both organomagnesium compounds and organomagnesium halides are agents of the Grignard synthesis. The establishment of equilibrium between organomagnesium halide and magnesium dialkyl or diaryl is not an instantaneous process. H. WREN.

Mercury dialkyls from organomagnesium halides. H. GILMAN and R. E. BROWN (J. Amer. Chem. Soc., 1929, 51, 928—930).—Improvements in the method of preparation of mercury diethyl (88% of the theoretical yield) and di-*n*-butyl (66%) (cf. Marvel and Gould, A., 1922, i, 329), involving (a) continuous introduction of the mercuric chloride by means of a Soxhlet extractor and (b) increases in the amount of solvent and time of heating, are described. H. E. F. NOTTON.

Benzene model on a basis of the electron theory and the substitution laws. M. ULMANN (Z. angew. Chem., 1928, 41, 674—680).—A benzene model is proposed in which alternate carbon atoms

hold complete electron octets, these CH groups thus having each a resultant charge of -3 , at the expense of the remaining CH groups, which therefore have each a resultant charge of $+3$. The reasons for this arrangement and its relation to the substitution laws are discussed. A. DAVIDSON.

Action of acetylene on benzene in presence of aluminium chloride. J. BÖESEKEN and A. A. ADLER (Rec. trav. chim., 1929, 48, 474—485).—Acetylene condenses with benzene in presence of freshly-prepared aluminium chloride (prepared by heating aluminium in a current of chlorine) at 20° , in approximately molecular proportions, forming an insoluble powder which, when heated at 310° /cathode vac., gives a small amount of styrene (cf. Cook and Chambers, A., 1921, i, 332). Since styrene is polymerised by treatment with aluminium chloride in benzene solution, it is concluded that the small amount obtained is not an intermediate, but arises from an activated form (termed protostyrene). Normally the protostyrene polymerises, but the small amount protected by the micelle of the polymeride is stabilised, giving styrene. Using aluminium chloride (prepared other than by direct synthesis) or an aluminium-mercury couple in the above condensation gives polymerised styrene. With chlorobenzene the condensation product is polymerised *p*-chlorostyrene. This does not yield *p*-chlorostyrene when heated in a cathode vacuum, and it resembles the product obtained by treating the styrene derivative with aluminium chloride in chlorobenzene solution. The difference in the above condensations is ascribed to the smaller reactivity of chlorobenzene. The results are also explicable by the author's dislocation theory (A., 1926, 806; 1927, 1150). H. BURTON.

Chlorine additive products of toluene. W. QVIST [with U. SAHLBERG and O. JANSSON] (Finska Kemistsamf. Medd., 1928, 37, 45—52; Chem. Zentr., 1928, ii, 1876).—In addition to mono-, di-, and trichlorotoluene, tetra-, hexa-, and possibly also penta-chloro-additive products are obtained on chlorination of toluene. A. A. ELDRIDGE.

Action of nitrogen trichloride on toluene and cyclohexene. N. STOLL (Bull. Soc. chim. Belg., 1929, 38, 71—96).—When a 6.35% solution of nitrogen trichloride in toluene is allowed to decompose in the dark at 17 — 19° in presence of iodine as a catalyst, a mixture of *p*-chlorotoluene, benzyl chloride, a product corresponding with a trichlorotoluene, nitrogen, ammonium chloride, and hydrochloric acid is obtained in addition to unchanged toluene. The ratio $Cl : N$ for the total reaction products is 8.22 as compared with the value 7.61 for nitrogen trichloride. The decomposition is complete after about 2 hrs., but in absence of catalyst it proceeds for several days. After 5 days the composition of the resulting products is very similar to the above; the amount of benzyl chloride formed increases somewhat at the expense of the *p*-chlorotoluene. Decomposition in sunlight causes a much larger increase in the amount of benzyl chloride, and indications of the formation of chloroamines were obtained (cf. Coleman and Noyes, A., 1922, i, 133). The following reactions are presumed to occur: $2NCl_3 + 3C_6H_8 = N_2 + 3HCl + 3C_6H_7Cl$

and $\text{NCl}_3 + 3\text{C}_7\text{H}_8 = \text{NH}_3 + 3\text{C}_7\text{H}_7\text{Cl}$, the former predominating.

Treatment of cyclohexene with nitrogen trichloride in benzene solution at 7–12° gives essentially 1 : 2-dichlorocyclohexane, b. p. 186–188°/762 mm., d_4^{20} 1.1738, n_D^{20} 1.49006, formed thus: $2\text{NCl}_3 + 3\text{C}_6\text{H}_{10} = \text{N}_2 + 3\text{C}_6\text{H}_{10}\text{Cl}_2$. Small amounts of monochlorinated (substitution) derivatives are also formed.

H. BURTON.

Tetra-*p*-tolylethylene. H. GILMAN and F. B. FLICK (Rec. trav. chim., 1929, 48, 461–463).—Tetra-*p*-tolylethylene, m. p. 151° (Staudinger and Goldstein, A., 1916, i, 850), is obtained by (a) heating di-*p*-tolylmethyl chloride or bromide, either alone or with pyridine, (b) the action of copper on the thioketone from di-*p*-tolyl ketone (I) and phosphoric sulphide, (c) treating the compound from di-*p*-tolylketen and quinoline with I, (d) reducing a mixture of *p*-tolylpinacol and I by Steinkopf and Wolfram's method (A., 1923, i, 216). Oxidation of the ethylene with chromic and acetic acids gives a 67% yield of I.

H. BURTON.

s-Diphenyltetra-*tert*.-butylethynylethane. S. S. ROSSANDER and C. S. MARVEL (J. Amer. Chem. Soc., 1929, 51, 932–936).—The Grignard reagent from *tert*.-butylacetylene and magnesium ethyl bromide yields with ethyl benzoate *phenylditert*.-butylethynylcarbinol, $\text{CPh}(\text{C}:\text{C}:\text{CMe}_3)_2\text{OH}$, m. p. 46–47°, which is converted by sulphuric acid into an isomeric ketone, m. p. 108–110°, and by phosphorus tribromide in ether into *phenylditert*.-butylethynylmethyl bromide (I), m. p. 58–59° (by-product, m. p. 169–174°). With "molecular" silver in ether this affords *s*-diphenyltetra-*tert*.-butylethynylethane, m. p. 98–99°. In presence of oxygen the debromination is accompanied by oxidation and no crystalline products are obtained (cf. A., 1928, 1365). Solutions of the ethane are stable towards oxygen; when heated at 100–140° they acquire a yellow, or in presence of air a red colour, which persists on cooling. The ethane linking is broken by sodium-potassium alloy or 40% (but not 1%) sodium amalgam and the resulting *sodio*-derivative gives with carbon dioxide *phenylditert*.-butylethynylacetic acid, m. p. 154–156°, which is also formed from the bromide, I, magnesium or sodium, and carbon dioxide in ether. H. E. F. NOTTON.

Benzopolymethylene compounds. XIV. Isomerisation of 1- to 2-arylindenes by heat. J. VON BRAUN and G. MANZ (Ber., 1929, 62, [B], 1059–1065).—In accordance with the procedure of Mayer, Sieglitz, and Ludwig (A., 1921, i, 554), 1-phenylindene is passed in an atmosphere of carbon dioxide over red-hot pumice, whereby a hydrocarbon is produced, identified as 2-phenylindene. Contrary to these authors, it is readily transformed by hydrogen in the presence of palladised charcoal and alcohol into 2-phenyldihydroindene, b. p. 162–163°/10 mm., d_4^{18} 1.0821, n_D^{20} 1.5955; it readily gives the dibromide, $\text{C}_{15}\text{H}_{12}\text{Br}_2$, m. p. 130–131°. 2-Hydrindone is converted by magnesium phenyl bromide into the carbinol, $\text{C}_6\text{H}_5\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CPh}\cdot\text{OH}$, b. p. 160–165°/0.5 mm., transformed by boiling 20% sulphuric acid into 2-phenylindene, m. p. 167°. 2-Phenylindanone

is converted into its oxime, m. p. 157°, which is reduced by sodium amalgam and dilute acetic acid to 1-amino-2-phenyldihydroindene, b. p. 180–184°/10 mm. (picrate, decomp. 121–123°). The base is converted into the corresponding, very hygroscopic, quaternary iodide, which, when boiled with 50% potassium hydroxide, gives trimethylamine and 2-phenylindene. 1-Hydrindone is converted by treatment with magnesium *p*-tolyl bromide and subsequent distillation of the product under diminished pressure into 1-*p*-tolylindene, b. p. 184–188°/11 mm., isomerised by heat to 2-*p*-tolylindene, m. p. 183–184°. The last-named hydrocarbon is also obtained from 2-hydrindone through 2-hydroxy-2-*p*-tolylhydryndene, b. p. 155–160°/0.2 mm. 2-*m*-Tolylindene, m. p. 99–100°, is obtained analogously through 2-hydroxy-2-*m*-tolylhydryndene, b. p. 165–170°/0.5 mm.

H. WREN.

1 : 2- and 2 : 3-Diphenylindenes. A. GARCÍA BANUS and F. CALVET (Anal. Fis. Quím., 1929, 27, 49–59).—Benzylhydrobenzoin ($\alpha\beta\gamma$ -triphenylpropane- $\alpha\beta$ -diol) (Orékhoff, A., 1919, i, 205) is converted by boiling with excess of commercial acetyl chloride, or acetyl chloride to which sulphuryl chloride has been added, into 1 : 2-diphenylindene, m. p. 173–175° (Orékhoff and Tiffeneau, A., 1922, i, 458). 1-Oximino-2 : 3-diphenylindene, obtained by the action of amyl nitrite and alcoholic sodium ethoxide on 1 : 2-diphenylindene (cf. Thiele and Ruggli, A., 1912, i, 866; Orékhoff, A., 1920, i, 225), is reduced to 1-amino-2 : 3-diphenylindene (hydrochloride; chloroplatinate) by zinc and acetic acid. 2 : 3-Diphenylindene, m. p. 110°, is obtained by the isomerisation of 1 : 2-diphenylindene by boiling with alcoholic potassium ethoxide. It yielded on ozonolysis, not the expected "diphenylisochroman hydrate" (this vol., 324), but benzoyl-(*o*-benzoylphenyl)carbinol, m. p. 121–123° (monophenylhydrazone, m. p. 143–145°; dioxime, m. p. 178–180°), which yielded *o*-benzoylbenzil when oxidised by permanganate in acetone solution. This reaction confirms the constitution of 2 : 3-diphenylindene. Homophthalaldehyde, an alternative starting-point for the synthesis of "diphenylisochroman hydrate," could not be obtained by ozonolysis of indene.

R. K. CALLOW.

Stereochemistry of aromatic ring systems. II. W. SCHLENK and E. BERGMANN (Ber., 1929, 62, [B], 745–750).—Further examples are cited of the isolation of isomerides, the existence of which cannot be explained by the classical theory of stereochemistry and for which the hypothesis is adopted that the single rings of condensed systems are inclined to one another in space. 9-Benzoylfluorene, m. p. 180°, is obtained by the action of benzoyl chloride on the lithium derivative of fluorene; phenyldi-9-fluorenylcarbinol, m. p. 290°, is simultaneously produced. 9-Phenyl-9-benzoylfluorene, m. p. 125–126°, is prepared with the isomeride, m. p. 139° (cf. Gomberg and Cone, A., 1906, i, 822), from sodium 9-phenylfluorene and benzyl chloride; it is converted into the form of m. p. 139° by treatment with chromic acid in cold, glacial acetic acid. Benzylidenefluorene, m. p. 153°, and *p*-anisylidenefluorene, m. p. 145°, are present in addition to the forms described previously (cf. Thiele and Henle, A., 1906, i, 571) in the condensation products of

fluorene with benzaldehyde and *p*-anisaldehyde. 4 : 4' - *Tetramethyldiaminodiphenylmethylenefluorene*, red prisms, m. p. 238—240°, is obtained in addition to the isomeride, yellow needles, m. p. 239—240° (cf. Rodd and Linch, A., 1927, 1067), by the action of sodium on a mixture of Michler's ketone and fluorene. The two varieties show marked depression of m. p. when mixed. They are not interconvertible by seeding in solution or when molten. The orange is transformed into the yellow variety by addition of sodium and treatment of the product with mercury.

H. WREN.

Explanation of Schlenk's isomerism. E. BERGMANN and H. MARK (Ber., 1929, 62, [B], 750—757).—In order to depart as little as possible from the classical assumption of stereochemistry, the existence of Schlenk's isomerides (preceding abstract) has been explained by the hypothesis of the inclination of the rings in complex ring systems. An attempt is now made to establish a theory on a less hypothetical, physical basis founded on the "puckered" ring of W. H. and W. L. Bragg. Detailed consideration is given to benzene, naphthalene, anthracene, phenanthrene, and fluorene.

H. WREN.

Two supposed instances of isomerism in the aromatic series. O. BLUM (Ber., 1929, 62, [B], 881—893).— $\beta\beta$ -Diphenylvinyl bromide slowly forms a red solution when treated with sodium powder in ether and, on addition of alcohol, 1 : 2 : 4-triphenyl-1 : 4-dihydronaphthalene, m. p. 142.5—144°, is obtained in 10% yield; two compounds, $C_{28}H_{20}$, b. p. 283—285°/13 mm., and $C_{14}H_{13}$, m. p. 82—84°, are isolated as by-products. Treatment of the organo-metallic derivative with carbon dioxide affords 1 : 2 : 4-triphenyl-1 : 4-dihydronaphthalene-1-carboxylic acid, m. p. 238—239° (decomp.), whilst with phenylthiocarbimide the compound $C_6H_4 \begin{smallmatrix} \text{CPh}(\text{CS}\cdot\text{NPh}) \\ \text{CHPh} \end{smallmatrix} \text{CH} \text{CPh}$, m. p. 243—244°, is produced. The last-named compound is also derived by the action of phenylthiocarbimide on the product of the action of sodium on 1 : 2 : 4-triphenyl-1 : 4-dihydronaphthalene, thus proving that the hydrocarbon undergoes substitution instead of addition. Catalytic hydrogenation of 1 : 2 : 4-triphenyl-1 : 4-dihydronaphthalene in presence of palladium affords 1 : 2 : 4-triphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 126—129°. The constitution of the dihydro-compound is established by its oxidation to *o*-dibenzoylbenzene, m. p. 146—148°, whereby under milder conditions 1 : 2 : 4-triphenyl-naphthalene, m. p. 158—159°, and the *keto-acid*, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{Bz}$, m. p. 232—233° (decomp.), are produced. 1 : 2 : 4-Triphenylnaphthalene is unaffected by hydrogen in the presence of palladised barium sulphate, but is reduced by sodium and boiling amyl alcohol to 1 : 2 : 4-triphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 125—129°, and an isomeride, m. p. 186—187°. 1 : 2 : 4-Triphenyl-naphthalene, m. p. 158°, is identical with the second form of $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\beta\gamma}$ -butatriene described by Purdie and Arup (J.C.S., 1910, 97, 1537) and by Buttenberg. The supposed isomerism with Brand's authentic compound (A., 1921, i, 783) does not therefore exist.

The action of lithium on $\beta\beta$ -diphenylvinyl bromide is rather more complicated than that of sodium, yielding 1 : 2 : 4-triphenyl-1 : 4-dihydronaphthalene, m. p. 143—144°, in very small amount, particularly if the action is very protracted. The normal reaction consists of stabilisation of the primary diphenylvinyl residues by production of the compound

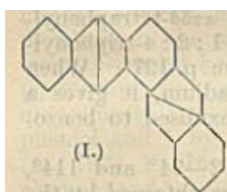
$\text{CPh}_2\text{Li}\cdot\text{CH}\cdot\text{CH}\cdot\text{CLiPh}_2$, hydrolysed by alcohol to $\alpha\alpha\delta\delta$ -tetraphenyl- Δ^{β} -butene, m. p. 139—140°, and converted by iodine or phenylthiocarbimide into tetraphenylbutadiene, m. p. 200—201°. If the reaction is curtailed, the tetraphenylbutene is accompanied by an isomeric hydrocarbon, $C_{28}H_{24}$, m. p. 126.5—127.5°, not identical with $\alpha\alpha\delta\delta$ -tetraphenyl- Δ^{β} -butene, m. p. 126—127°, or 1 : 2 : 4-triphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 127°. When hydrogenated in presence of palladium, it gives a dihydro-derivative, $C_{28}H_{26}$; it is oxidised to benzophenone and benzoic acid.

Two 9-methylacridines, m. p. 92—94° and 114°, respectively, have been described as obtained by the action of diphenylamine on glacial acetic acid in the presence of zinc chloride. It is shown that the compound of higher m. p. (now 117—118°) is the true 9-methylacridine, whereas that of lower m. p. (now 99—100°) is an additive compound of 1 mol. of 9-methylacridine and 1 mol. of diphenylamine. The compound of m. p. 117—118° adds 2 atoms of sodium and the product is hydrolysed to 9-methyl-9 : 10-dihydroacridine, m. p. 124—125.5° (cf. Sastry, J.C.S., 1916, 109, 270). The substance of m. p. 99—100° gives a transitory red solution with sodium and ether, from which, after addition of alcohol, 9-methyl-9 : 10-dihydroacridine and diphenylamine are obtained. The two substances last named combine in light petroleum, giving the compound of m. p. 99—100° in quantitative yield.

H. WREN.

Polynuclear, aromatic hydrocarbons and their derivatives. II. 2' : 3'-Naphtho-1 : 2-anthracene, its homologues and oxidation products. E. CLAR, F. JOHN, and B. HAWRAN. III. Anthracenoanthracenes and their quinones. E. CLAR, H. WALLENSTEIN, and R. AVENARIUS (Ber., 1929, 62, [B], 940—950, 950—955; cf. this vol., 435).—II. The action of magnesium *o*-tolyl bromide on terephthalyl chloride in benzene and ether yields a mixture of 1 : 4-di-*o*-toluylbenzene, m. p. 82°, and 4-*o*'-toluylbenzoic acid, m. p. 177° (corresponding chloride) oxidised by alkaline permanganate to benzophenone-2 : 4'-dicarboxylic acid, m. p. 234°. *s*-Phthalyl chloride gives similarly the non-crystalline 1 : 2-di-*o*-toluylbenzene. 1 : 3-Di-2' : 4'-dimethylbenzoylbenzene, b. p. 243°/12 mm., is obtained from isophthalyl chloride and *m*-xylene in the presence of aluminium chloride; 1 : 4-di-2' : 4'-dimethylbenzoylbenzene, m. p. 128°, is analogously prepared. Contrary to the literature, 2-2' : 5'-dimethylbenzoylbenzoic acid, m. p. 147.5°, is readily prepared from phthalic anhydride, excess of *p*-xylene, and aluminium chloride. It is converted by zinc and 80% acetic acid into 3-*p*-xylylphthalide, leaflets, m. p. 112°, or needles, m. p. 115°, transformed by magnesium *p*-xylyl bromide into the non-crystalline 1 : 3-di-*p*-xylylisobenzofuran, oxidised by chromic acid to 1 : 2-di-2' : 5'-dimethylbenzoyl-

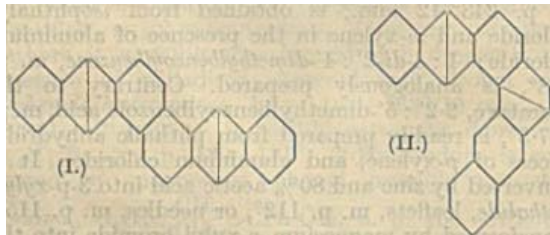
benzene, m. p. 138.5° (corresponding azine, m. p. 136.5°). Condensation of the crude but ash-free diketones to hydrocarbons is effected by distillation with a free flame. Water and a little oil at first volatilise, followed by anthracene or 2-methylanthracene. The distillation is then rapidly completed and the distillates are purified by crystallisation from xylene, sublimation, or crystallisation from benzene in presence of picric acid, if much anthracene or β -methylanthracene is present. The yields from *o*-diketones are small owing to rupture of the molecules, but attain 20—25% with *m*- and *p*-compounds. The following substances are described: 2':3'-naphtho-



1:2-anthracene (I), m. p. 265°; 6':7'-dimethyl-2':3'-naphtho-1:2-anthracene (II), m. p. 265—266°; 7:7'-dimethyl-2':3'-naphtho-1:2-anthracene (III). Compound II is oxidised by chromic acid to 1' (14')-keto-6':7'-dimethyl-1':4'-dihydro-2':3'-naphtho-1:2-anthraquinone, m. p. 323°, whereas III affords 1' (14')-keto-7:7'-dimethyl-1':4'-dihydro-2':3'-naphtho-1:2-anthraquinone, m. p. 332°. 2':3'-Naphtho-1:2-anthracene is oxidised by chromic acid to 1:2-phthalylanthraquinone, m. p. 322—323°, whereas dimethylphthalylanthrone affords 1':4'-diketo-6':7'-dimethyl-1':4'-dihydro-2':3'-naphtho-1:2-anthraquinone, m. p. 338°, converted by hydrazine hydrate in boiling pyridine into the azine of dimethyl-1:2:3:4-diphthalylbenzene, which does not melt below 380°. Dimethylphthalylanthrone is oxidised by dilute nitric acid at 190—200° to 1:2:3:4-diphthalylbenzene-4':4''-dicarboxylic acid, not molten below 380°.

III. In the production of anthracenoanthracenes by the action of heat on suitable diketones, the yields are severely restricted by the decomposition of the ketones into smaller fragments, notably benzaldehyde and benzoic acid. The method appears to reach its limit of applicability with the production of hydrocarbons with seven condensed benzene nuclei.

1:5-Dibenzoyl-2:6-dimethylnaphthalene is produced in good yield by the action of aluminium chloride on benzoyl chloride and 2:6-dimethylnaphthalene in cold carbon disulphide. Under similar conditions, acetic anhydride affords 1-acetyl-2:6-dimethylnaphthalene, m. p. 70—71° (picrate, m. p. 139—140°). 2:7-Dimethylnaphthalene appears to be converted by an excess of benzoyl chloride into a mixture of 1:5- and 1:8-dibenzoyl-2:7-dimethylnaphthalenes. 9:10-Dihydroxy-9:10-di-*o*-tolylacenaphthene, m. p. 164°, prepared from magnesium *o*-tolyl bromide and



acenaphthenequinone, is oxidised by chromic acid in glacial acetic acid to 1:8-di-*o*-toluoylnaphthalene, m. p.

238°. The diketones are converted by heat respectively into 2':1'-anthraceno-1:2-anthracene (I), m. p. about 400°, and 1':2'-anthraceno-1:2-anthracene (II), m. p. 308°. Oxidation of the hydrocarbons affords 2':1'-anthraquinono-1:2-anthraquinone [1:2:5:6-diphthalyl-naphthalene], m. p. about 395°, and 1':2'-anthraquinono-1:2-anthraquinone [1:2:7:8-diphthalyl-naphthalene], not molten below 360°, respectively.

H. WREN.

Absorption spectra of rubrenes. A. WILLEMART (Compt. rend., 1929, 188, 988—990).—Rubrene, dimethylrubrene, and dibenzorubrene have similar absorption spectra with three bands having maxima 4650 Å., 4950 Å., and 5300 Å., the spectra differing only in the intensity of the absorption. Accordingly the two naphthalene residues present in dibenzorubrene are not an integral part of the chromophoric group, but are present as univalent substituents. The mechanism of formation of rubrenes previously suggested (A., 1928, 996) thus finds support in their absorption spectra.

R. BRIGHTMAN.

Rubicene. A. ECKERT (J. pr. Chem., 1929, [ii], 121, 278—280).—Exposure of an acetic acid solution of di(diphenylene)ethylene to sunlight gives di(diphenylene)ethane and fluorenone. When fluorenone is subjected to prolonged thermal decomposition using Meyer's method (A., 1917, i, 641), small amounts of rubicene (cf. Schlenk and Karplas, A., 1928, 1235) and a substance, m. p. 218°, are obtained.

H. BURTON.

Double salts of aniline hydrohalides with metallic halides. G. D. BYRKIT and W. M. DEHN (J. Amer. Chem. Soc., 1929, 51, 1167—1171).—The known compounds of the general formula $(\text{PhNH}_3\text{Hal})_x(\text{MHal}_n)_y$ have been classified into 17 types, $x:y$ being: 1:2; 1:1 (also $+\text{H}_2\text{O}$), 4:3, 3:2, 2:1 (also $+1, 2, \text{ or } 3\text{H}_2\text{O}$), 3:1 (also $+1 \text{ or } 2\text{H}_2\text{O}$), 4:1, 6:1 (also $+\text{H}_2\text{O}$), and 8:1. No theory accounts for the composition and properties of all the compounds. The simpler compounds are formed at higher temperatures. All the salts readily dissociate into simple ions in aqueous solution. The following new double salts are described ($\text{A}=\text{NH}_3\text{Ph}$): $8\text{ACl}_2\text{HgCl}_2$, m. p. 231.5°; $3\text{ACl}_2\text{HgCl}_2$, m. p. 167°, softening from 160°; $\text{ABr}_2\text{HgBr}_2$, m. p. 156°; AlHgI_2 , m. p. 61°; $2\text{ACl}_2\text{CoCl}_2$, m. p. 135°; $2\text{ACl}_2\text{AuCl}_2$, m. p. 95°, softening from 85°; $\text{ACl}_2\text{BiCl}_3$, decomp. 210°; $\text{ACl}_2\text{MnCl}_2$; $2\text{ACl}_2\text{MnCl}_2\cdot 2\text{H}_2\text{O}$, m. p. above 230°; $3\text{ACl}_2\text{AlCl}_3$; $3\text{ACl}_2\text{SnCl}_4$; $3\text{ABr}_2\text{AsBr}_3$; also PhNH_3HgBr , m. p. 127°, and $\text{PhNH}_3\text{PbCl}_2$.

H. E. F. NOTTON.

Action of aromatic amines on alkyl nitrates. H. RYAN and M. T. CASEY (Sci. Proc. Roy. Dubl. Soc., 1928, 19, 101—111).—Primary aromatic amines react with alkyl nitrates to yield the nitrate of the base and the appropriate alkylamine; no trace of the alcohol corresponding with the alkyl nitrate is formed. Aniline heated with ethyl nitrate (I) for several days at 70°, butyl nitrate (II) for 24 hrs. at 100°, or amyl nitrate (III) for 8 hrs. at 100° gives aniline nitrate, m. p. 198° (decomp.), butylaniline being isolated in the second case; with mannitol hexanitrate (IV) at 80—90° a violent reaction with charring occurs. *p*-Toluidine with I for 4—5 hrs. at

100°, II for 8 hrs. at 100°, or III for 4 hrs. at 100° affords *p*-toluidine nitrate, m. p. 202° (decomp.). Similarly, *o*-toluidine with I, II, or III at 100° yields *o*-toluidine nitrate, m. p. 189° (decomp.), and *m*-xylylidine with I, II, or III at 100° gives *m*-xylylidine nitrate, m. p. 208—209° (decomp.). The chief reaction between a secondary amine and an alkyl nitrate appears to be one of oxidation, accompanied by slight nitration; methylaniline heated with I at 100° or with IV in alcoholic solution at 78° yields red, viscous products, whilst diphenylamine with I or II at 100° affords a green, amorphous solid together with some diphenylnitrosoamine. Tertiary amines are also oxidised by alkyl nitrates with production of a reddish-violet coloration which appears to be independent of the nature of the alkyl group. If the relative decomposition velocities of alkyl nitrates be measured by the colorations produced with dimethylaniline by heating for 40 hrs. at 60—70° the velocities for ethyl, butyl, amyl, and cellulose nitrates and mannitol hexanitrate are in the ratio 1, 2.85, 0.17, 9.4, and 22.9, respectively.

C. W. SHOPPEE.

Nitration of phenylbenzylamine derivatives. J. REILLY, P. J. DRUMM, and T. V. CREEDON (J.C.S., 1929, 641—644).—Nitrosobenzylaniline gives, on nitration with nitric acid (*d* 1.42, at 0—5°), nitroso-4-nitrophenylbenzylamine accompanied by smaller quantities of the nitroso-2-nitro-compound. Nitration in acetic acid solution gives slightly greater yields.

The conclusion of Schultz, Rohde, and Bosch (A., 1904, i, 992) that benzyloethylaniline is nitrated in sulphuric acid solution in the benzyl ring (cf. Gnehm and Scheutz, A., 1901, i, 519) is supported by the isolation of mainly *phenyl-3-nitrobenzyl-n-butylamine*, m. p. 44—45°, from the mixed-acid nitration of phenylbenzyl-*n*-butylamine dissolved in sulphuric acid. Nitration of dibenzylaniline (m. p. 69—70°; lit. 67°, 71°) in sulphuric acid solution gives no *op*-nitro-compounds, only *phenyldi-m-nitrodibenzylamine*, m. p. 128—129°, being obtained. Treatment of aniline with *m*-nitrobenzyl chloride affords the same substance. The experimental evidence suggests that direct nitration of phenylbenzylamines leads to the formation of nitro-derivatives substituted in the aniline ring, whereas nitration through the salt promotes substitution in the benzyl nucleus.

R. J. W. LE FEVRE.

Complex compounds of aromatic diamines. **Compounds of *o*-phenylenediamine with metallic salts.** W. HIEBER, C. SCHLIESZMANN, and K. RIES (Z. anorg. Chem., 1929, 180, 89—104).—By interaction of *o*-phenylenediamine and the following salts in aqueous or alcoholic solution, complex compounds containing the salt molecule combined with 1, 2, 3, 4, or 6 mols. of base have been obtained: with 1 mol., zinc, cupric, and cobalt chlorides, and cadmium chloride, bromide, and iodide; with 2 mols., chlorides, bromides, and iodides of cadmium and nickel, cupric, cobalt, nickel, zinc, and cadmium sulphates, and cupric nitrate; with 3 mols., nickel iodide, zinc bromide and iodide, and cadmium sulphate; with 4 mols., chlorides, bromides, and iodides of cobalt and nickel, nickel sulphate, and zinc iodide and perchlorate; with 6 mols., cobalt, nickel, and zinc chlorides. In general, these compounds are com-

paratively unstable in aqueous solution, being readily oxidised in air. By utilising their property of adding ammonia with simultaneous loss of diamine, it has been shown that in those compounds containing 4 and 6 mols. of base the secondary valency of the diamine is 1 and the same is also true for most of the other compounds.

R. CUTHILL.

Constitution of compounds of metallic salts with *p*-phenylenediamine and benzidine. W. HIEBER and K. RIES (Z. anorg. Chem., 1929, 180, 105—109).—Cobalt chloride and the chlorides, bromides, iodides, and sulphates of zinc and cadmium react with *p*-phenylenediamine in aqueous or alcoholic solution to form compounds, the molecules of which contain an equal number of molecules, apparently two, of salt and base, and zinc chloride forms a similar compound with benzidine, and also a compound containing twice this amount of benzidine. The secondary valency of the base is two, i.e., both amino-groups are linked with the metal, in all these compounds except the last, in which it is one. Cobalt chloride also appears to form a compound, $2\text{CoCl}_2 \cdot 3\text{C}_6\text{H}_4(\text{NH}_2)_2$.

R. CUTHILL.

Catalytic reduction of phenol and naphthol ethers with hydrogen and platinum. E. WASER, H. SOMMER, C. LANDWEER, and C. GAZA (Helv. Chim. Acta, 1929, 12, 418—443).—Reduction of the following phenol ethers (Ph·OR), anisole, b. p. 152.2—152.4°/728 mm. (all b. p. are corr.), phenetole, b. p. 168.1—168.6°/731 mm., d_4^{20} 0.9689, n_D^{20} 1.50845, phenyl *n*-propyl ether, b. p. 190—191°/725 mm., phenyl *iso*-propyl ether, b. p. 170—172°/720 mm., phenyl *n*-butyl ether, b. p. 198—200°/721 mm., phenyl *isobutyl* ether, phenyl *isoamyl* ether, b. p. 215—217°/718 mm., and phenyl *n*-hexyl ether, b. p. 240—241°/721 mm., with hydrogen in presence of platinum-black and acetic acid shows that about one third of the ether is converted into the cyclohexyl derivative $\text{C}_6\text{H}_{11}\cdot\text{OR}$. Two other courses of reduction also occur: (a) elimination of R with the production of the hydrocarbon R·H, and cyclohexanol, (b) elimination of OR and formation of the alcohol R·OH and cyclohexane. In the change (a) cyclohexanone is produced as an intermediate, since reduction in presence of semicarbazide hydrochloride affords cyclohexylsemicarbazide. The amount of hydrogen absorbed varies from 3.57 to 3.8 mols. (limits). Reduction of α -naphthyl ethyl ether gives about 50% of α -decahydronaphthyl ethyl ether, b. p. 236—238°/728 mm., d_4^{20} 0.9446, n_D^{20} 1.47824, together with ethyl alcohol, a small amount of ethane, decahydronaphthalene, and α -decahydronaphthol. β -Naphthyl ethyl ether yields about 50% of β -decahydronaphthyl ethyl ether, b. p. 239—240°/713 mm., d_4^{20} 0.9542, n_D^{20} 1.47718, *cis*- β -decahydronaphthol, and *cis*- β -decahydronaphthalene. Methane, methyl alcohol, cyclohexane, cyclohexanol, and hexahydroguaiacol, b. p. 175—180°/730 mm., d_4^{20} 0.9775, n_D^{20} 1.45687, are obtained from guaiacol. The following ethers appear to be new: cyclohexyl *n*-propyl ether, b. p. 170.5—171.5°/728 mm., d_4^{20} 0.8665, n_D^{20} 1.43936; cyclohexyl *isopropyl* ether, b. p. 168—169°/716 mm., d_4^{20} 0.9285, n_D^{20} 1.48332; cyclohexyl *n*-butyl ether, b. p. 193.5—194.5°/734 mm., d_4^{20} 0.8664, n_D^{20} 1.43853; cyclohexyl *isobutyl* ether, b. p. 175—177°/719 mm., d_4^{20} 0.8618, n_D^{20}

1.44137; cyclohexyl isoamyl ether, b. p. 206—207°/718 mm., d_4^{20} 0.8523, n_D^{20} 1.44136, and cyclohexyl *n*-hexyl ether, b. p. 222.5—224.5°/728 mm., d_4^{20} 0.8515, n_D^{20} 1.44275. H. BURTON.

***m*-Hydroxytolylsulphones and *m*-cresolsulphonic acids.** J. ZEHENTER, H. BOHUNCK, and E. NOWOTNY (J. pr. Chem., 1929, [ii], 121, 223—236).—*α*-*m*-Hydroxytolylsulphone [5 : 5'-dihydroxy-di-*o*-tolylsulphone] (I) (A., 1920, i, 544), when treated with boiling sodium carbonate solution yields a *monosodium* derivative (+4H₂O); the *disodium* derivative (+EtOH) is obtained by the action of sodium on an alcoholic solution of I. Concentrated sulphuric acid converts I at the ordinary temperature into a *disulphonic acid* (II), m. p. 65—66° [*dipotassium* (+4H₂O) salt; the *barium* (+9.5H₂O) and *lead* (+8H₂O) salts contain 1.5 atoms of metal in 1 mol.], whilst at 100—120°, *m*-cresol-6-sulphonic acid (potassium +2H₂O, barium +5H₂O, and *lead* +4H₂O, salts) and II are obtained. At 180° cresol-mono- and -di-sulphonic acids are produced. When a mixture of *m*-cresol, *m*-cresol-6-sulphonic acid, and phosphoric oxide is heated at 170°, I is obtained, thus indicating its constitution. β-*m*-Hydroxytolylsulphone [3 : 3'-dihydroxydi-*p*-tolylsulphone (?)] (III) (*loc. cit.*), also gives a *monosodium* derivative when treated with sodium carbonate solution. Treatment with concentrated sulphuric acid at the ordinary temperature yields a *disulphonic acid* (+4.5H₂O), m. p. 139—140° (*tetrapotassium* salt +4.5H₂O); at 100—120° cresol-mono- and -di-sulphonic acids result. Bromination of III in ethereal solution gives a *tetrabromo*-derivative, m. p. 220° (decomp.). Treatment of *m*-cresol-6-sulphonic acid with an excess of bromine water affords 2 : 4 : 6-tribromo-*m*-cresol (IV) together with a small amount of another substance which contains bromine and no sulphur. Bromination of the acid in acetic acid solution and in ethereal suspension, or of the potassium salt in water, gives IV as the sole product. *m*-Cresol-4-sulphonic acid, m. p. 109—110° (copper salt +3H₂O), is converted by an excess of bromine water into a mixture of IV and 2(or 6) : 4 : 5-tribromo-*m*-cresol, m. p. 131° (decomp.), whilst the potassium salt yields IV and the *potassium* salt of a dibromo-*m*-cresol-4-sulphonic acid. H. BURTON.

Condensation of *o*-aminophenol and oxalic acid. I. A. A. LEVINE and L. WEHMHOF (J. Amer. Chem. Soc., 1929, 51, 1243—1246; cf. Kehrman and Bener, A., 1925, i, 443).—*o*-Aminophenol (2 mols.) and anhydrous oxalic acid (1 mol.) at 180—200° give a red substance, (C₁₄H₁₂O₄N₂)_n, m. p. 271—272°, which is recovered unchanged from its sulphuric acid solution. At 130—140° a little *o*-hydroxy-oxanilide is also formed. The red product loses 1 mol. of carbon dioxide at 280°, and gives yellow *disodium* and *potassium* salts. With methyl sulphate and alkali it yields a *trimethyl* (?) ester, m. p. 246—247°; with acetic anhydride an impure red *acetyl* derivative, m. p. 189°, which decomposes in boiling benzyl alcohol into *oo'*-diacetoxyoxanilide; and with aniline a *monoanilide*, m. p. 250°. H. E. F. NOTTON.

Methylurethanes of isomeric α-hydroxyphenylethyldimethylamines and their miotic activity. EDGAR STEDMAN and ELLEN STEDMAN (J.C.S., 1929,

609—617).—α-*o*-Hydroxyphenylethyldimethylamine methylurethane, m. p. 90° [methiodide, m. p. 148° (efferv.)], α-*m*-hydroxyphenylethyldimethylamine methylurethane, m. p. 86° [hydrochloride, m. p. 169° (efferv.); methiodide, m. p. about 130° (efferv. and after previous sintering)], and α-*p*-hydroxyphenylethyldimethylamine methylurethane, an oil [hydrochloride, m. p. 203° (after previous sintering); methiodide, m. p. 173° (efferv.)] are prepared from the appropriate methoxybenzaldehydes through the methoxyphenylmethylcarbinols, the carbinyl bromides, and the α-methoxyphenylethyldimethylamines. The last-named are demethylated by hydrobromic acid and the resulting phenols converted into the methylurethanes by interaction with methylcarbimide; in the case of the *m*-compound condensation was directly effected in an inert solvent, but with the *o*- and *p*-isomerides addition of metallic sodium to the reactants in benzene or ether solution was necessary.

The miotic actions of the urethane hydrochlorides and methiodides (tested by instillation of 1.5% solutions of substances in physiological saline into cat's eyes) were estimated as: *m*-HCl > *o*-MeI > *p*-HCl, *o*-HCl, *m*-MeI > *p*-MeI. This order of relative strengths does not agree with those found for similar salts of the hydroxybenzyl dimethylamines, where the order is *o* > *p* > *m*. In both series conversion of the tertiary bases into quaternary ammonium salts increases the miotic activity of the *o*- and diminishes that of the *m*- and *p*-isomerides, the methiodides of the *p*-compounds being inactive at the concentrations employed.

The following compounds are described incidentally: α-*m*-methoxyphenylethyldimethylamine methiodide, m. p. 142°, α-*m*-hydroxyphenylethyldimethylamine hydrochloride, m. p. 197—198°, and methiodide, m. p. 160° (with sintering at 145°), α-*o*-methoxyphenylethyldimethylamine methiodide, m. p. 136—137°, α-*o*-hydroxyphenylethyldimethylamine hydrochloride, m. p. 136—137°, α-*p*-methoxyphenylethyldimethylamine hydrochloride, m. p. 213°, and methiodide, m. p. 128—130°, di-(α-*p*-methoxyphenylethyl)dimethylammonium bromide monohydrate, m. p. 109°, and α-*p*-hydroxyphenylethyldimethylamine hydrochloride, m. p. 183°.

It is concluded that the physiological properties of the urethanes investigated are due to the common phenylcarbamate structure coupled with a necessary basic group. R. J. W. LE FÈVRE.

Dehydrogenation of *ar*-1 : 3-dibromo-β-tetralol with bromine. M. JAKES (Coll. Czech. Chem. Comm., 1929, 1, 245—256).—Treatment of *ar*-1 : 3-dibromo-β-tetralol with 2 mols. of bromine and subsequent heating at 180—185° gave a mixture of two dibromo-β-naphthols, b. p. 195—229°/10 mm., m. p. 112—142°, separated by fractional crystallisation from carbon tetrachloride into two compounds, m. p. 181—183° (I) and m. p. 124—125° (II), respectively. The constitution of I was established as 3 : 7-dibromo-β-naphthol by reduction with sodium amalgam to 7-bromo-β-naphthol, m. p. 132—133° (mixed m. p. with 6-bromo-β-naphthol, 100—105°), identical with 7-bromo-β-naphthol, m. p. 132—133°, produced from 7-hydrazino-β-naphthol and cupric bromide, whilst that of II as 3 : 6-dibromo-β-naphthol follows from its reduction with sodium amalgam to 6-bromo-

β -naphthol, m. p. 126–127°, identical with that obtained by the reduction of 1 : 6-dibromo- β -naphthol with tin and hydrochloric acid, by the production of 1 : 3 : 6-tribromo- β -naphthol, m. p. 133°, with bromine and acetic acid, and by its formation from 3 : 6-dibromo- β -naphthylamine through the diazonium compound and decomposition of the latter with aqueous cupric sulphate. The compound described by Franzen and Stauble (A., 1922, i, 450) as 3 : 6-dibromo- β -naphthol is probably 4 : 6-dibromo- β -naphthol. Dehydrogenation of 1 : 3-dibromo-2-acetoxy-naphthalene by heating with 2 mols. of bromine at 185° followed by hydrolysis of the product with alcoholic potassium hydroxide gave a mixture of I and II; 1 : 3 : 6-tribromo- β -naphthol, m. p. 133° (reduced by tin and hydrochloric acid in the presence of alcohol to 3 : 6-dibromo- β -naphthol), is formed when excess of bromine is employed in the dehydrogenation.

A. I. VOGEL.

Manufacture of *o*-nitro- and *o*-amino-diaryl ethers. I. G. FARBERIND. A.-G.—See B., 1929, 349.

Manufacture of hydrogenated aromatic amino-compounds. I. G. FARBERIND. A.-G.—See B., 1929, 350.

Action of diazo-hydrates on azoxyphenols. D. BIGIARI and S. STEFANIC (Atti R. Accad. Lincei, 1929, [vi], 9, 326–331).—Various reactions showing the differences in behaviour between the two isomeric *p*-hydroxyazoxybenzenes and the analogy of the β -isomeride with *p*-nitrophenol are cited. The statement that *p*-bromobenzeneazo-*p*-nitrophenol (cf. Dimroth and Hartmann, A., 1909, i, 66) does not yield salts with aqueous alkali hydroxide is inaccurate, as a red sodium salt, easily reconvertible into the original compound, is readily obtainable. When treated with *p*-bromodiazobenzene hydrate: (1) α -benzeneazoxyphenol yields the corresponding oxyazo-compound, $\text{ONPh}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br}$, m. p. 178–180°, which gives aniline, *p*-bromoaniline, and 2 : 4-diaminophenol when reduced with tin and hydrochloric acid and forms the derivatives: copper, deflagrating at 285°, nickel, altering at about 290°, ethyl ether, m. p. 163.5°, acetyl, m. p. 154–156°, benzoyl, m. p. 175°. (2) β -Benzeneazoxyphenol yields the diazo-ether, $\text{NPh}\cdot\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br}$, m. p. about 110° (decomp.), which may be coupled with sodium β -naphthol-3 : 6-disulphonate or β -naphthol, and at 80–90° is converted into the azo-derivative, $\text{NPh}\cdot\text{NO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br}$, m. p. 157°, this forming the following derivatives: sodium salt, copper salt, m. p. 266–270° (decomp.), ethyl, m. p. 118°, acetyl, m. p. 149–150°. T. H. POPE.

Neutral reduction of nitro-compounds. W. M. CUMMING and G. S. FERRIER (J. Roy. Tech. Coll. Glasgow, 1929, 2, [1], 40–43).—Reduction of nitrobenzene with zinc dust and ammonium chloride in alcoholic solution yields chiefly phenylhydroxylamine with small quantities of aniline and occasionally a little azoxybenzene, but no hydrazobenzene. Nitrosobenzene under the same conditions gives a 60% yield of hydrazobenzene, phenylhydroxylamine affords aniline, and azoxybenzene a 77% yield of hydrazobenzene together with traces of azobenzene.

A. R. POWELL.

Neutral reduction and double basic zinc salts. W. M. CUMMING and G. HOWIE (J. Roy. Tech. Coll. Glasgow, 1929, 2, [1], 43–49).—When a nitro-compound or one of its reduction products is reduced with zinc and ammonium chloride in boiling alcohol an organo-zinc compound is formed as an intermediate product, but in most cases this decomposes rapidly, with the formation of a basic zinc salt; the salt formed in the reduction to the azoxy-stage is always the white, crystalline compound, $2\text{NH}_4\text{Cl}\cdot 5\text{Zn}(\text{OH})_2$, and conversely reduction to the azoxy- and hydrazo-stage takes place only in the presence of this compound. Reduction of 1 : 1'-azoxynaphthalene to the hydrazo-stage by means of zinc and ammonium chloride affords the compound $9\text{Zn}(\text{OH})_2\cdot 4\text{NH}_4\text{Cl}\cdot 6\text{H}_2\text{O}$; under similar conditions *p*-nitrophenol affords *p*-aminophenol and the compound $\text{ZnCl}_2\cdot \text{Zn}(\text{NH}_3)_2\cdot \text{NH}_4\text{Cl}$. In the case of *m*-nitrobenzaldehyde, the azoxy-compound formed by reduction is obtained in combination with a zinc complex as the compound

$\text{ZnCl}_2\cdot 3\text{NH}_4\text{Cl}\cdot 2\text{C}_{14}\text{H}_{10}\text{O}_3\text{N}_2\cdot 9\text{Zn}(\text{OH})_2$, from which the azoxy-compound can be isolated only by treatment with acids or alkalis. From *p*-nitrotoluene a complex zinc compound of *p*-toluidine, $4\text{C}_6\text{H}_4\text{Me}\cdot \text{NH}_2\cdot \text{NH}_4\text{Cl}\cdot \text{ZnCl}_2$, m. p. 250°, was obtained in the reduction to hydrazotoluene. By the reduction of nitronaphthalene with zinc and calcium chloride in alcoholic solution a 98% yield of naphthylamine is obtained but no azoxynaphthalene.

A. R. POWELL.

Action of the Grignard reagent on azoxybenzene. W. M. CUMMING and G. S. FERRIER (J. Roy. Tech. Coll. Glasgow, 1929, 2, [1], 49–51).—An attempt has been made to determine the best conditions for the interaction between magnesium methyl iodide and azoxybenzene. The reaction products were azobenzene and a brown oil which had the odour of ethylaniline but could not be identified as such.

A. R. POWELL.

Esters of aminoazobenzenesulphonic acids, $\text{NR}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{SO}_2\cdot\text{OC}_2\text{H}_5$. A. HANTZSCH (Ber., 1929, 62, [B], 966–968).—Diethylhelianthin is converted by diazomethane in ether into methyl diethylaminoazobenzenesulphonate, m. p. 125°, which is slowly attacked by cold sodium hydroxide, readily by hydrochloric acid. Methyl dimethylaminoazobenzenesulphonate, decomp. about 280°, is obtained similarly in very poor yield. Methyl methylaminoazobenzenesulphonate, decomp. 113°, and methyl dimethylamino-*o*-tolueneazobenzenesulphonate, m. p. 77–78°, are described. Aminoazobenzenesulphonic acid is converted mainly into violet helianthin, the methyl ester being formed only in traces. Yellow and red helianthins do not exhibit any fundamental difference in their behaviour towards diazomethane. The methyl esters of dimethyl- and diethyl-helianthin are also prepared from the sodium salts and methyl sulphate in boiling toluene.

H. WREN.

Aminoazobenzenes and their salts. A. HANTZSCH and W. VOIGT (Ber., 1929, 62, [B], 968–975; cf. preceding abstract).—To the yellow and red salts of aminoazobenzenes, the azoid and quinonoid structures, $\text{PhN}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2\cdot\text{HX}$ and $\text{PhNH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2\cdot\text{X}$, have been ascribed by

Hantzsch and Hilscher (A., 1908, i, 484). The assumption of the existence of more strongly absorbing and therefore quinonoid yellow salts is rendered unnecessary by the observation of the dissociation (etherolysis) of the oxalate, trichloroacetate, and monochloroacetate of dimethyl-yellow in ether into base and acid or their etherates (cf. Thiel, Fortschr. Chem., Phys., u. physikal. Chem., 1924, 18, 112). Similarly, alcoholysis also occurs to a marked extent; solutions of amino- and dimethylamino-azobenzene hydrochlorides have a close optical resemblance to those of the free base and become optically constant only after addition of widely varying amounts of hydrochloric acid. It is remarkable that amino- and diethylamino-azobenzene yield primarily yellow salts, whereas dimethyl- and dipropyl-aminoazobenzene afford red compounds (*dipropylaminoazobenzene hydrochloride* has m. p. 86°). As expected, water causes hydrolysis, whereas "solvolytic" is observed even in indifferent media. To the yellow and red helianthins, the structures $\text{HN}(\text{R}_2)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3$ and

$\text{NR}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3$ are now ascribed. The

absorption spectrum of methyl diethylaminazo-benzenesulphonate is closely similar to that of the corresponding yellow azoid sodium salt. Helianthin closely resembles aminoazobenzene in alcohol and therefore exists in solution mainly in the open form, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3[\text{H}_2\text{O} \cdot \text{OEt}]$. Dimethylamino-*o*-tolueneazobenzenesulphonic acid exists in alcohol as the internal azoid salt $\text{HNMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3$

even in acid solution it remains yellow and undergoes only partial conversion into the open benzenoid salt. Its stability is imputed to the *o*-methyl group. The yellow helianthins evolve nitrogen from diazoacetic ester, whereas the red compounds do not react or cause the change very much more slowly.

H. WREN.

Absorption spectra and composition of azo-dyes. I. Effect of position isomerism on absorption of methyl derivatives of benzeneazo-phenol. W. R. BRODE (J. Amer. Chem. Soc., 1929, 51, 1204—1213).—The absorption spectra of 4-hydroxyazobenzene and its mono- and di-methyl derivatives, which have only one methyl group on each ring, have been measured in approximately 0.00015*M*. solutions in 3% sodium hydroxide. All show an intense band at frequency 670—750 and a weaker one at 1125—1200, the former being composed of two overlapping bands, A and B. Observed and calculated values for A, B, and A+B are tabulated. In the parent compound A and B are of nearly equal intensity. The effect of the introduction of methyl groups in various positions on (a) A/B, (b) A+B (calc.) are: 3', (a) and (b) no change; 4', (a) no change, (b) increased; 2', (a) and (b) considerably decreased; 3-, (a) increased; 2-, (a) decreased. The disubstituted derivatives show the combined effects of the two substituents. The results are regarded as indicating the presence of two tautomerides in proportions [given by A/(A+B)] varying from 68% of A in the 3-methyl to 41% in the 2:3'-dimethyl derivative.

H. E. F. NOTTON.

Constitutional influences on the conversion of azonaphthols into their azo-sulphites and their bearing on the structure of α - and β -naphthol. A. T. KING (J.C.S., 1929, 601—609).—The conversion of azonaphthols into their azo-sulphites occurs more readily with β -naphthol derivatives than with α -naphthol derivatives and is materially affected by the orientation of substituent sulphonic groups. Thus *p*-sulphobenzeneazo- α -naphthol reacts with concentrated aqueous sodium hydrogen sulphite less readily than *p*-sulphobenzeneazo- β -naphthol and 4-sulpho- α -naphthaleneazo- α -naphthol less readily than the corresponding β -naphthol compound. Sulphonation of the naphthol component enhances the reactivity of the β -naphthol derivatives (probably by increasing their solubility) in contradistinction to the α -naphthol series, the reactivities of which are diminished. The following derivatives of the former class are described: sodium salts of benzene- and 4-sulpho- α -naphthaleneazo-6-sulpho- β -naphthyl sulphite, sodium benzene-, *m*-xylene-, *o*-carboxybenzene-, α -naphthalene-, and 4-sulpho- α -naphthalene-azo-3:6-disulpho- β -naphthyl sulphite, sodium 4-sulpho- α -naphthaleneazo-6:8-disulpho- β -naphthyl sulphite, and sodium 4-sulpho- α -naphthaleneazo-3:6:8-trisulpho- β -naphthyl sulphite. The non-reactivity conferred by a sulphonated α -naphthol component prevents formation of sulphites from α -naphthaleneazo- α -naphthol-4:8- and -3:6-disulphonic acids, 4-sulpho- α -naphthaleneazo- α -naphthol-4- and -5-sulphonic acids, and 6-sulpho- β -naphthaleneazo- α -naphthol-4-sulphonic acid, although α -naphthaleneazo- α -naphthol-5-sulphonic acid gives sodium α -naphthaleneazo-5-sulpho- α -naphthyl sulphite.

The mechanism of azo-sulphite formation is discussed. The explanations of Spiegel (A., 1885, 987) and Voroshekov (A., 1911, i, 819) (namely, that rate of addition is controlled by steric hindrance or ketonisation of the naphthol residue, respectively) are not in accord with present facts. It is suggested that in the α -naphthol type there is a disability to assume the ketonised form, whereas the β -naphthol type readily ketonises. This contrast is explained on the ordinary unsymmetrical naphthalene formula by assuming that in the β -naphthol type the ring tends to stabilise with a double linking across the 1:2-positions, but in the α -naphthol type with only a single linking. Such an explanation agrees with the opposing directions in which reduction of α - and β -naphthol to their tetrahydro-derivatives occurs.

The azo-sulphites are regarded as additive products with hydrazone structures (since the nitrogen linking is stable to hydrogen sulphite) which analyses show not to have reverted to azo-compounds by loss of water.

R. J. W. LE FÈVRE.

Purification of picric acid. S. R. BENEDICT.—See this vol., 730.

Occurrence of ergosterol in phytosterols. I. M. HEILBRON and W. A. SEXTON (Nature, 1929, 123, 567).—It is suggested that, concurrently with its reduction to sitosterol, oxidation of sitosterol (possibly γ -) to ergosterol may occur. The fact that neither of the two known tetrahydroergosterols is identical with the isomeric γ -sitosterol is not remarkable.

A. A. ELDRIDGE.

Preparation of ethers of aromatic alcohols by catalytic action of alkali hydrogen sulphates. J. B. SENDERENS (Compt. rend., 1928, 183, 1073—1076).—Benzyl alcohol and β -phenylethyl alcohol are converted into the corresponding ethers when heated at 120—180° in contact with potassium hydrogen sulphate or, better, sodium hydrogen sulphate, which act as dehydrating catalysts. Mixtures of benzyl alcohol and aliphatic alcohols similarly treated yield the respective mixed ethers as well as dibenzyl ether, but never the aliphatic ether.

B. W. ANDERSON.

Action of sulphur dioxide on the halogeno-magnesium derivatives of carbinols. W. SCHMIDT-NICKELS (Ber., 1929, 62, [B], 917—919).—The product obtained by the action of magnesium phenyl bromide on benzophenone in ether readily absorbs sulphur dioxide with production of *magnesium triphenylmethyl sulphite*, m. p. 186°; at 200° the compound loses the whole of its sulphur dioxide, leaving a magnesium compound converted by dilute sulphuric acid into triphenylcarbinol. *Magnesium phenyldiphenylenemethyl sulphite*, from sulphur dioxide and the product from magnesium, bromobenzene, and fluorenone in ether, is more thermostable, but loses sulphur dioxide at about 320°. The product derived from magnesium methyl iodide and benzophenone is converted by the successive action of sulphur dioxide and hot water into $\alpha\alpha\gamma\gamma$ -tetraphenyl- Δ^a -butene, m. p. 113—114°.

9-Chloro-9-phenylfluorene is transformed by magnesium phenyl bromide into diphenyldibiphenylene-ethane, identified as the peroxide, m. p. 192°.

H. WREN.

Occurrence of free, substituted methylenes in chemical reactions. E. BERGMANN and J. HERVEY (Ber., 1929, 62, [B], 893—916).—The isolation of the disodium compound of tetraphenylallene by Schlenk and Bergmann (A., 1928, 1031) establishes the possibility of the existence of free, substituted methylenes under certain conditions and indicates their, probably, extraordinary reactivity. For the proof of their production, for example, during the conversion of *p*-nitrobenzyl chloride into a mixture of *cis*- and *trans*-*pp'*-dinitrostilbene under the influence of alcoholic alkali, it is necessary to work in the presence of a compound which unites readily with the free methylene. For this purpose, aromatic aldehydes, α -diketones, fluorenone, thioketones, and nitroso-compounds are suitable, whereas substances containing the C:C and C:N linkings are unsuitable. Free substituted methylenes have been obtained from *p*- and *o*-nitrobenzyl chlorides, 9-chlorofluorene, benzyl chloride, and 9-bromoanthrone, but not from diphenylmethyl bromide, di-*p*-anisylmethyl chloride, or 10-chloro-9 : 9-diphenyl-9 : 10-dihydroanthracene. Two groups of aromatically substituted methyl halides appear to exist, one of which yields primarily the corresponding methylene when treated with alcoholic alkali, whereas the other undergoes double decomposition with production of the corresponding alkyl ether.

9-Chlorofluorene and *p*-nitrobenzaldehyde in boiling methyl alcohol in the presence of solid potassium carbonate afford *p*-nitrobenzylidenefluorene oxide, m. p.

153° (in an isolated instance, a substance, decomp. 217° after softening, was obtained). In one experiment the oxide, $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{C} \begin{array}{c} \text{O} \\ \text{CHPh} \end{array}$ m. p. 131—132°, was obtained from 9-chlorofluorene and benzaldehyde under the influence of potassium hydroxide; particularly when potassium carbonate is employed, the chief product is 9- α -hydroxybenzylfluorenyl methyl ether, m. p. 187—188°, obtained also by addition of benzaldehyde to the product of the action of sodium on fluorenone dimethylacetal. *p*-Nitrobenzyl chloride and *p*-nitrobenzaldehyde in presence of potassium carbonate afford the two isomeric *pp'*-dinitrostilbene oxides, m. p. 200—201° and 153—154°, respectively; both are converted by potassium iodide and boiling glacial acetic acid into *pp'*-dinitrostilbene. Similarly, *p*-nitrobenzyl chloride with *o*-nitrobenzaldehyde gives the two *op'*-dinitrostilbene oxides, m. p. 158—160° and 112°, respectively, and with *m*-nitrobenzaldehyde the *mp'*-dinitrostilbene oxides, m. p. 148° and 116°, respectively. *p*-Nitrostilbene oxide, m. p. 125—126°, is converted by potassium iodide in boiling glacial acetic acid into *p*-nitrostilbene, m. p. 157°. With anisaldehyde, *p*-nitrobenzyl chloride affords *p*-nitro-*p'*-methoxystilbene oxide, m. p. 138°, and with diphenylacetaldehyde the isomeric α -*p*-nitrophenyl- β -benzylidenethylenes, m. p. 147° and 188°, respectively. *o*-Nitrobenzyl chloride and *p*-nitrobenzaldehyde give the isomeric *op'*-dinitrostilbene oxides, m. p. 160—161° and 111° (see above). The reaction between benzyl chloride and *o*-nitrobenzaldehyde occurs less smoothly than the changes described above, chiefly owing to the preponderating formation of methyl *p*-nitrobenzyl ether, b. p. 145—147°/17 mm.; *p*-nitrostilbene oxide, m. p. 187—189°, is produced only in minimal amount. 9-Bromoanthrone and benzaldehyde yield a very difficultly separable mixture of anthraquinone and benzylideneanthrone oxide; with anisaldehyde, the only isolable compound is anthraquinone. *p*-Nitrobenzyl chloride is converted by benzil in presence of potassium carbonate and methyl alcohol into the *p*-nitrobenzylidene ether of stilbenediol, $\begin{array}{c} \text{CPh O} \\ \text{CPh O} \end{array} > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, m. p. 138°, and by phenanthraquinone into the *p*-nitrobenzylidene derivative of phenanthraquinol, m. p. 153°. 9-Chlorofluorene and fluorenone afford dibiphenylene-ethylene and dibiphenylene-ethylene oxide, m. p. 234° (decomp.), whilst *p*-nitrobenzyl chloride and the ketone give *p*-nitrobenzylidenefluorene oxide, m. p. 149°. 2 : 7-Dibromofluorenone, m. p. 202°, prepared by oxidising 2 : 7-dibromofluorene, and *p*-nitrobenzyl chloride yield *p*-nitrobenzylidene-2 : 7-dibromofluorene oxide, m. p. 230°. *o*-Nitrobenzylidenefluorene oxide, m. p. (indef.) 111°, and biphenylenemethyleneanthrone oxide, m. p. 252—254°, are described.

9-Chlorofluorene and *p*-nitrobenzyl chloride with *p*-nitrosodimethylaniline yield respectively *p*-dimethylaminosulphenyldiphenylenemethylenenitrone, $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{C} \begin{array}{c} \text{O} \\ \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \end{array}$ m. p. 223—224°

and the *p*-dimethylaminoanil of *p*-nitrobenzaldehyde, m. p. 206°; an isomeric of the latter compound, m. p. 221°, is obtained from *p*-aminodimethylaniline and *p*-nitrobenzaldehyde. *p*-Nitrobenzylidene-*p'*-amino-

diethylaniline, m. p. 136°, *o*-nitrobenzylidene-*p*'-amino-dimethylaniline, m. p. 94—95°, and anthraquinone-mono-*p*-dimethylaminoanil, m. p. 238°, are described.

The action of hydrogen sulphide and hydrogen chloride on a solution of fluorenone in alcohol yields *dimeric thiofluorenone*, m. p. 232°, instead of the desired monomeride. *p*-Nitrobenzyl chloride and Michler's thioketone in presence of potassium carbonate and boiling propyl alcohol yield α -*p*-nitrophenyl- $\beta\beta$ -*di-p*-dimethylaminophenylethylene, m. p. 175—176° (from primarily formed ethylene sulphide). Under similar conditions, 9-chlorofluorene affords *di-p*-dimethylaminophenylmethylenefluorene, m. p. 238—240°, *tetra-p*-dimethylaminodibenzhydryl disulphide, $[\cdot\text{S}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2]_2$, and *di-9*-fluorenyl disulphide, m. p. 169—170°. The last-named compound has been obtained by Smedley (J.C.S., 1905, 87, 1249, 1253) from 9:9-dichlorofluorene and potassium hydrosulphide and regarded as dimeric thiofluorenone. Its constitution follows from its solubility in alcoholic alkali and from its synthesis from 9-chlorofluorene and sodium disulphide. The trustworthiness of the method is established by the production of dibenzyl disulphide, m. p. 74°, from benzyl chloride under analogous conditions. Chlorofluorene and sodium hydrosulphide in alcohol yield exclusively *di-9*-fluorenyl sulphide, m. p. 250° after becoming discoloured at 238°.

p-Nitrobenzyl chloride could not be caused to condense with benzophenone, *di-p*-anisyl ketone, xanthone, 9-methoxy-9-phenylanthrone, 9:9-diphenylanthrone, benzoin ethyl ether, benzylideneacetophenone or its oxide, benzophenonephenylhydrazone, benzylideneaniline, *as*-diphenylethylene, or benzylidenefluorene. 9-Chlorofluorene does not react with benzophenone.

Diphenylmethyl bromide is transformed by boiling methyl-alcoholic potassium hydroxide into *benzhydryl methyl ether*, b. p. 147—148°/17 mm., the constitution of which is established by conversion into diphenylthioacetanilide, m. p. 187°, by successive treatment with sodium in ether and phenylthiocarbimide. The ether is also obtained when the reaction is performed in the presence of *m*-nitrobenzaldehyde. Anisyl chloride, b. p. 140—141°/14 mm., from the acid and thionyl chloride, is converted by anisole and aluminium chloride in carbon disulphide into *di-p*-anisyl ketone (yield 88%), reduced by zinc dust in alcoholic, alkaline solution to *pp*'-dimethoxybenzhydrol, m. p. 70—72°, which is transformed by thionyl chloride in presence of toluene into *di-p*-anisylmethyl chloride, m. p. 83—84°; the last-named compound exchanges chlorine for methoxyl when treated with methyl-alcoholic potassium hydroxide. 9:9-Diphenylanthrone, in boiling 95% alcohol, is reduced by aluminium amalgam to 10-hydroxy-9:9-diphenyl-9:10-dihydroanthracene, m. p. 142°, converted by hydrogen chloride in glacial acetic acid into 10-chloro-9:9-diphenyl-9:10-dihydroanthracene, m. p. 226°; simple exchange of groups occurs when the last-named compound is treated with potassium carbonate and benzaldehyde in boiling methyl alcohol, 10-methoxy-9:9-diphenyl-9:10-dihydroanthracene, m. p. 147°, being produced; the corresponding *ethyl ether*, m. p. 163°, is formed analogously. H. WREN.

Resin acids. G. ROUTIN (Bull. Inst. Pin, 1928, 167—172, 173—175; Chem. Zentr., 1928, ii, 2015).—The dihydrobromide (m. p. 146—151°) of abietic acid from Aleppo colophony appears to be identical with that (m. p. 170—175°) from American colophony.

A. A. ELDRIDGE.

Does anthranilyl chloride exist? L. ANSCHUTZ and H. BOEDEKER (Ber., 1929, 62, [B], 826—830).—*Sodium anthranilate* (+H₂O) is converted by thionyl chloride into *o*-aminobenzoylanthranilic anhydride, m. p. 160° (cf. Schroeter, A., 1909, i, 576), and, apparently, an *isomeride*, m. p. 136—139°. Barium anthranilate combines with 1 mol. of water, which is very firmly retained. The anhydrous silver or lead anthranilate is converted by thionyl chloride in presence of anhydrous ether into *o*-thionylaminobenzoyl chloride, $\text{COCl}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{S}\cdot\text{O}$, b. p. 98°/0.07 mm., m. p. 34—35°. In contact with atmospheric moisture it is converted into sulphur dioxide and amorphous products. With *p*-toluidine it affords *p*-toluidine hydrochloride and anthranil-*p*-toluidide. Lead *p*-aminobenzoate and thionyl chloride yield *p*-thionylaminobenzoyl chloride, but the corresponding *m*-compound cannot be prepared analogously.

H. WREN.

Hydrogenation of anthroic acid and the question of the existence of two isomeric 9:10-dihydroanthracene-9-carboxylic acids. H. MEERWEIN and A. MIGGE (Ber., 1929, 62, [B], 1046—1050).—The action of hydrogen on a boiling solution of anthroic acid in isopropyl alcohol in the presence of palladised barium sulphate leads to the evolution of carbon dioxide. 1:2:3:4-Tetrahydroanthracene, m. p. 104—105°, and octahydroanthracene, m. p. 72—74°, are isolated from the portion of the product insoluble in sodium carbonate. The soluble portion yields small amounts of dihydroanthroic acid, m. p. 203.5—204.5° (methyl ester, m. p. 97—98°), identical with the so-called " α " acid obtained by Schlenk and Blum (A., 1928, 1036) by the action of carbon dioxide on the monosodium additive compound of anthracene. The main product is 1:2:3:4-tetrahydroanthracene-9-carboxylic acid, m. p. 204.5—205.5° (methyl ester, m. p. 67—68°), oxidised to 1:2:3:4-tetrahydroanthraquinone, m. p. 157—158°. Dihydroanthroic acid is also formed. Schlenk and Blum's " β -9:10-dihydroanthroic acid" is therefore regarded as a mixture of products and an instance of "superfluous" isomerism is disproved.

H. WREN.

Action of carbon dioxide on sodium β -naphthoxide. The Kolbe-Schmitt synthesis. E. SCHWENK [with M. KNOB and H. STEIN] (Chem.-Ztg., 1929, 53, 297—299, 333—336).—The mechanism of the Kolbe synthesis of phenolcarboxylic acids is investigated by a study of the action of carbon dioxide on sodium β -naphthoxide under varying conditions. When carbon dioxide is passed under slight pressure over carefully dried sodium β -naphthoxide at 18—20° the additive compound, $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CO}_2\text{Na}$, is formed which is decomposed by water in accordance with the equation $2\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CO}_2\text{Na} + \text{H}_2\text{O} = \text{C}_{10}\text{H}_7\cdot\text{ONa} + \text{C}_{10}\text{H}_8\text{O} + \text{CO}_2 + \text{NaHCO}_3$, and by heating in a sealed tube at 120—130° yields, after acidification of the product,

β -naphthol-1-carboxylic acid. The sodium salt of this acid (obtained by the action of alcoholic sodium ethoxide), after very careful drying over phosphoric oxide and finally by heating at 105—110°/8 mm., does not absorb dry ammonia (cf. Tijmstra and Eggink, A., 1906, i, 179) and when heated in a sealed tube at 250—260° is converted into β -naphthol and β -naphthol-3-carboxylic acid, the carboxyl group migrating from the 1 to the 3 position. The mechanism of this reaction involves the initial decomposition of the sodium salt into sodium β -naphthoxide and carbon dioxide, these products then interacting according to temperature conditions to yield either β -naphthol-1- or -3-carboxylic acid. The liberation of carbon dioxide during the reaction is proved by the partial conversion of sodium phenoxide, placed in an open second tube inside the sealed tube, into sodium salicylate. When in the latter experiment the tube is heated only at 150—160°, the conversion of the sodium phenoxide into sodium salicylate is more complete, and the sole reaction products are β -naphthol and a little β -naphthol-1-carboxylic acid. Potassium β -naphthol-1-carboxylate is stable up to 200° (the sodium salt begins to decompose at 130°) and by heating in a sealed tube at 230° is converted into β -naphthol and β -naphthol-3-carboxylate, but no -6-carboxylate is obtained. Similarly, substitution of potassium β -naphthoxide for sodium phenoxide in the earlier sealed tube experiments (above) yields only a small quantity of the -3-carboxylic acid, but again no 6-acid. Thus the β -naphthol-6-carboxylic acid said to be obtained in G.P. 436524 cannot be formed from the potassium β -naphthol-1-carboxylate, but is produced in some other way. J. W. BAKER.

p-Methoxycinnamylidenecetic acid. D. VORLÄNDER and K. GIESELER (J. pr. Chem., 1929, [ii], 121, 247—254).—Condensation of *p*-methoxycinnamaldehyde and malonic acid in presence of acetic acid at 50—60°, or aqueous-alcoholic ammonia at 100°, gives *p*-methoxycinnamylidenemalonic acid (anhydrous and +H₂O), m. p. 182° (decomp.). Elimination of carbon dioxide from this by heating with pyridine and a small amount of piperidine first at 100° and then over a free flame affords mainly the crystalline-liquid form (*trans-trans*) of *p*-methoxycinnamylidenecetic acid (I), m. p. 179° and 222—223° (corr.) [tetra-bromide, m. p. 180° with elimination of hydrogen bromide; methyl ester, m. p. 126°; ethyl ester, m. p. 66—68°; *n*-propyl ester, m. p. 47—49°; acid chloride, m. p. about 110°; *p*-ethoxyphenyl ester, m. p. 150° and 211° (corr.); anilide, m. p. 189° (corr.); *p*-toluidide, m. p. 214° (corr.); *p*-aniside, m. p. 193° and 218° (corr.); *p*-phenetide, m. p. 182° and 220° (corr.); piperide]. Exposure of a solution of the sodium salt of I to ultra-violet light causes the formation of salts of two acids (or mixtures of acids), m. p. 90—96° and 106—110°, respectively, both of which regenerate I in benzene solution containing iodine exposed to sunlight. When the thermal decomposition is effected in presence of acetic anhydride at 130° or quinoline at 160° some allo(*trans-cis*)-*p*-methoxycinnamylidenecetic acid, m. p. 128—131° (corr.) [tetra-bromide, m. p. about 165° (decomp.)], is also obtained. This is also converted into I by exposing a benzene solution containing iodine to sunlight.

Reduction of I and II with sodium amalgam and water yields the same δ -*p*-methoxyphenyl- Δ^{β} -pentenoic acid, m. p. 57°, oxidised by alkaline potassium permanganate to oxalic and anisic acids, and converted by boiling with 10% sodium hydroxide solution into β -*p*-methoxyphenylpropylidenecetic acid, m. p. 136—138°.

p-Methoxycinnam-*p*-aniside and -*p*-phenetide have m. p. 184—185° (corr.) and 180°, respectively.

H. BURTON.

γ -Resorcylic acid [2 : 6-dimethoxybenzoic acid]. F. MAUTHNER (J. pr. Chem., 1929, [ii], 121, 259—265).—When 6-nitro-2-methoxybenzonitrile (Lobry de Bruyn, Rec. trav. chim., 1883, 2, 205) is treated with methyl-alcoholic potassium hydroxide solution, 2 : 6-dimethoxybenzonitrile, m. p. 118°, results. Hydrolysis of this with concentrated sulphuric acid at 60—65° gives 2 : 6-dimethoxybenzamide, m. p. 207—208°, whilst prolonged treatment with boiling concentrated potassium hydroxide solution yields a small amount of the amide together with 2 : 6-dimethoxybenzoic acid (methyl ester, m. p. 88°, obtained either with diazomethane or by esterification with methyl alcohol and hydrogen chloride). Treatment of the acid with aluminium chloride in boiling chlorobenzene solution affords resorcinol.

H. BURTON.

Reaction of thiocarbimides and hydrogen chloride with polyhydric phenols. P. KARRER and E. WEISS (Helv. Chim. Acta, 1929, 12, 554—557).—Substituted thiobenzamides are obtained by treating a mixture of a phenol and a thiocarbimide in dry ether with hydrogen chloride in presence of zinc chloride. Reaction occurs through the intermediate thio-carbamyl chloride. The following are described: 2 : 4-dihydroxythiobenzethylamide, m. p. 96°; 2 : 4 : 6-trihydroxythiobenzethylamide, m. p. 152°; 2 : 3 : 4-trihydroxythiobenzallylamide, m. p. 206° (decomp.); 2 : 4-dihydroxythiobenzanilide, m. p. 176°; 4-hydroxythionaphthanilide (?), m. p. 206° after sintering at 198°, and 2 : 4-dihydroxythiobenz- β -naphthylamide, m. p. 177—179° after sintering at 167°. H. BURTON.

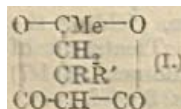
Halogen derivatives of thyronine (deiodo-thyroxine). K. SCHUEGRAF (Helv. Chim. Acta, 1929, 12, 405—414).—Bromination of 3 : 5-di-iodothyronine (cf. Harington, this vol., 313) gives 3' : 5'-dibromo-3 : 5-di-iodothyronine, m. p. 245—246° (decomp.) [3' : 5'-dichloro-derivative, m. p. 262° (decomp.)]. 3 : 5-Dibromo-4-iodonitrobenzene reacts with quinol monomethyl ether in presence of methyl ethyl ketone and anhydrous potassium carbonate yielding 3 : 5-dibromo-4-*p*-methoxyphenoxynitrobenzene, m. p. 151—152°. Reduction of this with stannous chloride and hydrogen chloride in acetic acid gives the corresponding amine, m. p. 117°, converted by the usual method into the corresponding nitrile, m. p. 107°. This is converted by Stephen's method into 3 : 5-dibromo-4-*p*-methoxyphenoxynitrobenzaldehyde, m. p. 98°, which condenses with hippuric acid in presence of acetic anhydride and sodium acetate, yielding the corresponding azlactone, m. p. 195°. Treatment of this with red phosphorus and hydriodic acid (*d* 1.7) in acetic anhydride solution affords 3 : 5-dibromothyronine, m. p. 257° (decomp.), brominated further to 3 : 3' : 5 : 5'-tetrabromothyronine, m. p. 241—242°.

(decomp.). 3':5'-Dichloro-3:5-dibromo-, m. p. 234° (decomp.), and 3:5-dibromo-3':5'-di-iodo-thyronine, m. p. 229° (decomp.), are described. 3:5-Dichloro-4-p-methoxyphenoxy-nitrobenzene, m. p. 147°, is converted as above through the corresponding amine, m. p. 144°, and nitrile, m. p. 97°, into 3:5-dichloro-4-p-methoxyphenoxybenzaldehyde. The azlactone, m. p. 191°, from this affords 3:5-dichlorothyronine, m. p. 266° (decomp.) [3':5'-dibromo-derivative, m. p. 240° (decomp.); 3':5'-di-iodo-derivative, m. p. 229° (decomp.)]. 3:3':5:5'-Tetrachlorothyronine has m. p. 231° (decomp.). H. BURTON.

Modified Curtius synthesis of primary amines. R. H. F. MANSKE (J. Amer. Chem. Soc., 1929, 51, 1202—1204).—When direct hydrolysis of alkyl-carbamides and -urethanes to primary amines is difficult, they may be converted by phthalic anhydride into alkylphthalimides, which are then hydrolysed by means of hydrazine (cf. A., 1926, 1132). Thus, α , ω -dimethylurethano-octane and phthalic anhydride at 230° give α , ω -diphthalimido-octane, m. p. 138° (corr.), which with hydrazine gives α , ω -diamino-octane. γ -Phenoxybutyrylhydrazide is converted through the azide into *s*-di- γ -phenoxypropylcarbamide, m. p. 150°, which with phthalic anhydride gives γ -phenoxypropylphthalimide. Similarly, *s*-di- β -indolylethylcarbamide yields 3-3'-indolylethylphthalimide, m. p. 164—165°, quantitatively hydrolysed by hydrazine to tryptamine. H. E. F. NOTTON.

Keto-lactol tautomerism. II. Influence of the cyclohexane ring on the tautomeric character of cyclohexane-1-acetone-1-malonic acid, a comparison with cyclopentane-1-acetone-1-malonic acid, and synthesis of the corresponding δ -ketomonobasic acids. M. QUDRAT-KHODA (J.C.S., 1929, 713—721).—Condensation of cyclohexenylacetone with cyanoacetamide in alcoholic sodium ethoxide solution gives cyclohexanespirocyclo-3-hydroxy-6-cyano-3-methyl-5-piperidone, m. p. 258°, hydrolysed by aqueous potassium hydroxide to cyclohexane-1-acetone-1-malonic acid, m. p. 116°, decomp. 118° [semicarbazone, m. p. 183° (decomp.); ethyl ester, b. p. 192°/14 mm., d_4^{19} 1.0681, n_D^{19} 1.46984; ethyl ester semicarbazone, m. p. 104°]. Analogous treatment of cyclopentenylacetone affords cyclopentanespirocyclo-3-hydroxy-6-cyano-3-methyl-5-piperidone, m. p. 282°, whence cyclopentane-1-acetone-1-malonic acid, m. p. 106°, decomp. about 130° (semicarbazone, m. p. 177°; ethyl ester, b. p. 179°/13 mm., d_4^{19} 1.0767, n_D^{19} 1.4632; ethyl ester semicarbazone, m. p. 109°), is prepared.

The behaviour of cyclohexane- and cyclopentane-1-acetone-1-malonic acids supports the views previously advanced by the Thorpe-Ingold school; in particular, the second acid resembles α -carboxy- γ -acetyl- β -dimethylbutyric acid (this vol., 295). In the liquid state the two acids exist as an equilibrium mixture of the keto- and lactol forms. When heated they decompose similarly: cyclohexane-1-acetone-1-malonic acid gives



at 130—140° the dilactone, m. p. 141°, and cyclohexane-1-acetone-1-acetic acid, m. p. 73° (semicarbazone, m. p. 185°) (I. RR'=[CH₂]₅), whilst cyclopentane-1-acetone-1-malonic acid gives at 140—150° the dilactone, m. p. 139°, and

cyclopentane-1-acetone-1-acetic acid, m. p. 53° (semicarbazone, m. p. 191°) (I, RR'=[CH₂]₄). These acetic acids were synthesised as follows for confirmation of their constitution. cyclohexane-1:1-diacetic anhydride gives by boiling with methyl alcohol the silver salt of methyl hydrogen cyclohexane-1:1-diacetate; the acid ester is converted by thionyl chloride into the chloride, which with zinc methyl iodide in cold benzene solution gives methyl cyclohexane-1-acetone-1-acetate, b. p. 152°/18 mm., d_4^{20} 1.0363, n_D^{20} 1.46748 (semicarbazone, m. p. 137°). When heated with alcoholic sodium ethoxide the keto-ester gives cyclohexanespirocyclohexane-3:5-dione, and with methyl-alcoholic aqueous potassium hydroxide, cyclohexane-1-acetone-1-acetic acid and small amounts of cyclohexane-1:1-diacetic acid. cyclopentane-1:1-diacetic acid is transformed into methyl hydrogen cyclopentane-1:1-diacetate (silver salt), and this, through the acid chloride by interaction with zinc methyl iodide, gives methyl cyclopentane-1-acetone-1-acetate, b. p. 130°/12 mm., d_4^{17} 1.0386, n_D^{17} 1.46021 (semicarbazone, m. p. 119°), from which either cyclopentanespirocyclohexane-3:5-dione or cyclopentane-1-acetone-1-acetic acid can be prepared. Acetyl chloride reacts with cyclohexane-1-acetone-1-acetic acid at the ordinary temperature and with cyclopentane-1-acetone-1-acetic acid at 100° to give the lactones, $\text{RR}'\text{C} \begin{array}{c} \text{CH}\cdot\text{CMe} \\ \text{CH}_2-\text{CO} \end{array} \text{O}$ (RR'=[CH₂]₅), b. p. 144°/17 mm., d_4^{19} 1.0533, n_D^{19} 1.4952, and (RR'=[CH₂]₄), b. p. 124°/14 mm., d_4^{19} 1.0573, n_D^{19} 1.49043, respectively. R. J. W. LE FÈVRE.

Constitution of isochondodendrine. III. F. FALTIS and K. ZWERINA [with A. B. G. ATTIA] (Ber., 1929, 62, [B], 1034—1041; cf. A., 1922, i, 569; 1923, 433).—The synthesis is described of certain acids required in connexion with the constitution of the tricarboxylic acid, C₁₇H₁₄O₉, derived from isochondodendrine. Opianic acid is transformed by an excess of bromine in water into bromo-opianic acid, m. p. 204°, converted by cautious treatment with hydroxylamine hydrochloride into the corresponding oxime anhydride, m. p. 220° (m. p. of bromohemipinimide), which with boiling water affords 6-bromohemipinic anhydride, m. p. 193°. The anhydride is not smoothly esterified by methyl alcohol and sulphuric acid, but is transformed by potassium hydroxide and methyl sulphate under defined conditions into methyl 6-bromohemipinate, m. p. 56—57°. Condensation of the bromo-ester with the potassium compound of methyl *p*-hydroxybenzoate in presence of copper powder and copper acetate at 150—170° yields methyl 5-*p*-carbomethoxyphenoxy-5:6-dimethoxybenzene-1:2-dicarboxylate, m. p. 108—109° [corresponding tricarboxylic acid, m. p. 242° (decomp.)], not identical with the product of the degradation of isochondodendrine. Similarly, the potassium derivative of methyl *m*-hydroxybenzoate and methyl bromohemipinate afford methyl 3-*m*-carbomethoxyphenoxy-5:6-dimethoxybenzene-1:2-dicarboxylate, m. p. 111—112° [corresponding acid, m. p. 185° (decomp.) when rapidly heated]. During the methoxyl determinations with the *p*- and *m*-esters, carbon dioxide is also lost and acids, C₁₄H₁₀O₇, m. p. 250° (decomp.) and 248° (decomp.),

are produced. Treatment of the *p*-acid with molten potassium hydroxide yields *p*-hydroxybenzoic acid, the expected hydroxyquinolcarboxylic acid undergoing total decomposition. *m*-Hydroxybenzoic acid is derived similarly from the *m*-acid. H. WREN.

4:5-Dimethoxyhemimellitic acid. F. FALTIS and F. KLOBER (Ber., 1929, 62, [B], 1041—1045).—Diazohemipinic acid is very cautiously neutralised with 0.2*N*-potassium hydroxide and the solution is added to potassium cuprocyanide at 60—70°; the crude nitrile thus obtained is converted by hydrochloric acid into 4:5-dimethoxyhemimellitic acid, m. p. 160—162° (decomp.) after softening at 156° when very rapidly heated (the m. p. depends greatly on the rate of heating owing to the conversion of the acid into the anhydro-acid); the calcium salt has 3H₂O. At 120—130° the acid passes into the anhydro-acid,

CO₂H·C₆H₂(OMe)₂ < $\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}$ > O, m. p. 179—180°. Methyl

4:5-dimethoxyhemimellitate, from the acid and diazomethane, has m. p. 86—87°. The acid is converted by heating at 300—320° and subsequent treatment with ethylamine into *m*-hemipinethylimide.

H. WREN.

Different behaviour of some bile acids in the classical colour reactions. L. CUNY (Compt. rend. Soc. Biol., 1928, 99, 613—615; Chem. Zentr., 1928, ii, 1700).—Pettenkofer's reaction with sucrose and sulphuric acid depends on the presence of glycolic, taurocholic, or cholalic acid; deoxycholic and other complex bile acids react differently.

A. A. ELDRIDGE.

Derivatives of methyl 2:2-dimethylcyclopentan-3-one-1-carboxylate. C. S. GIBSON, K. V. HARIHARAN, and J. L. SIMONSEN (J. Indian Inst. Sci., 1928, 11, A, 215—220).—See A., 1928, 173.

Thiophthalic acids. I. G. C. CHAKRAVARTI (J. Indian Inst. Sci., 1928, 11, A, 221—225).—See A., 1928, 1241.

Pyrolysis of benzaldehyde and of benzyl benzoate. C. D. HURD and C. W. BENNETT (J. Amer. Chem. Soc., 1929, 51, 1197—1201).—After being heated for 2 hrs. in a sealed tube at (a) 300—310°, (b) 350—370°, benzaldehyde is changed to the extent of (a) 5—12%, (b) 30%, mainly into benzyl benzoate and a trace of benzoic acid (cf. Lachman, A., 1924, i, 649). Benzene is also formed in (b), but no toluene or benzyl ether. These changes are analogous to the pyrolysis of hydrobenzamide and of dibenzylidene-*o*-phenylenediamine (cf. Hinsberg, A., 1896, i, 536; Bahrmann, A., 1883, 799). Benzyl benzoate at 350° gives mainly benzoic anhydride, toluene, and benzaldehyde, the last two probably arising from the decomposition of benzyl ether. Benzaldehyde, passed slowly through a pyrex tube at 680—690°, undergoes 66% decomposition, giving mainly benzene and carbon monoxide with small quantities of diphenyl, 1:4-diphenylbenzene, regarded by Peytral (A., 1921, i, 166) as anthracene, hydrogen, and carbon dioxide.

H. E. F. NOTTON.

Conjugated unsaturated compounds. VIII. R. KUHN and A. WINTERSTEIN (Helv. Chim. Acta, 1929, 12, 493—498).—Condensation of benzaldehyde

with crotonaldehyde in presence of aqueous-alcoholic sodium hydroxide gives 10% of cinnamylideneacetaldehyde, b. p. 160—162°/12 mm.: subsequent condensation of this with succinic and dihydromuconic acids affords pure conjugated unsaturated hydrocarbons (A., 1928, 281). Treatment of α,γ-diphenylhexatriene with sodium-potassium alloy in dry ether yields a 1:4-additive product, since decomposition with moist nitrogen affords α,δ-dibenzylbutadiene; with carbon dioxide an acid, decomp. 170° with elimination of carbon dioxide, is produced. Decomposition of the reaction product from lithium and α,γ-diphenylhexatriene gives an oily acid. α,θ-Diphenyloctatetraene reacts only slowly with lithium.

Nyctanthin (Perkin, J.C.S., 1912, 101, 1538; Hill, *ibid.*, 1907, 91, 1501) is identical with α-crocetin (A., 1928, 869).

H. BURTON.

***p*-Methoxycinnamaldehyde and *p*-methoxycinnamylideneacetaldehyde.** D. VORLANDER and K. GIESELER (J. pr. Chem., 1929, [ii], 121, 237—246).

—Condensation of anisaldehyde with acetaldehyde in presence of aqueous methyl-alcoholic sodium hydroxide (cf. Scholtz and Wiedemann, A., 1903, i, 436) gives *p*-methoxycinnamaldehyde (I), m. p. 58° [phenylhydrazone, m. p. 138° (corr.); hydrzone, m. p. 210—212° and 231° (corr.); here and wherever two m. p. are recorded it is indicated that the substance exhibits enantiotropic crystalline-liquid properties (cf. Vorlander and Gahren, A., 1907, ii, 441; Walter, A., 1926, 17)]. Condensation products of I with the following amines are described: aniline, m. p. 125° (corr.); *p*-toluidine, m. p. 126° and 138° (corr.) from alcohol, 122° and 129° (corr.) from benzene; *p*-chloroaniline, m. p. 133° and 147° (corr.); *p*-aminophenol, m. p. 196°; *p*-anisidine, m. p. 167° and 180° (corr.); *p*-phenetidine, m. p. 146° and 181° (corr.); *p*-aminoazobenzene, m. p. 168° (corr.) and about 240° with darkening; *p*-aminobenzoic acid, m. p. 200—202°; ethyl *p*-aminobenzoate, m. p. 97° and 129° (corr.); ethyl *p*-aminocinnamate, m. p. 134° and 188° (corr.); and β-naphthylamine, m. p. 171°. Condensation of I with acetone gives *p*-methoxycinnamylidene-, m. p. 108°, and di-*p*-methoxycinnamylidene-acetone, m. p. 168° and 183° (corr.) [octabromide, m. p. 163° (decomp.)]. Di-*p*-methoxycinnamylidene-cyclopentanone, m. p. 237° (corr.), and -cyclohexanone, m. p. 201° and 212°, are obtained by effecting condensation of I and the ketones in presence of methyl-alcoholic sodium hydroxide solution, whilst *p*-methoxycinnamylidene-*p*-hydroxyacetophenone, m. p. 169°, -*p*-methoxyacetophenone, m. p. 112°, and -*p*-acetoxyacetophenone, m. p. 134°, are prepared using hydrogen chloride as the condensing agent. Condensation of I with acetaldehyde in presence of aqueous-alcoholic sodium hydroxide below 10° gives a small amount of impure *p*-methoxycinnamylideneacetaldehyde (II) [phenylhydrazone, m. p. 173° and 184° (decomp.; corr.)], oxidised by ammoniacal silver oxide to *p*-methoxycinnamylideneacetic acid, m. p. 176° and 216—218° (corr.). Condensation products from II and the following amines are described: aniline, m. p. 125° and 135° (corr.); *p*-toluidine, m. p. 133° and 180° (corr.); *p*-anisidine, m. p. 192° and 218—220° (corr.); *p*-phenetidine, m. p. 167° and 217° (corr.); *p*-amino-

azobenzene, m. p. 174° (corr.), and β -naphthylamine, m. p. 162° and 200° (corr.). As by-products in the preparation of II there are obtained partly hydrogenated aldehydes and some β -*p*-methoxyphenylpropylideneacetic acid, m. p. 136—138°, oxidised by potassium permanganate to oxalic and β -*p*-methoxyphenylpropionic acids. These substances appear to be formed during the vacuum distillation of the reaction mixture of I and acetaldehyde. H. BURTON.

Electrolytic reduction of aldehydes. V. Cinnamaldehyde. VI. Complete reduction of the carbonyl group. G. SHIMA.—See this vol., 521.

Aldehydophenolphthalein dyes. R. N. SEN and K. C. KAR.—See B., 1929, 350.

Synthesis of cyclic compounds. V. Catalytic and thermal decomposition of some normal dibasic acids. Ease of formation of simple carbon rings. A. I. VOGEL (J.C.S., 1929, 721—733).—From comparative experiments on the preparation of suberone in which suberic acid was heated with different mixtures of iron filings and baryta it is concluded that, in this reaction, an intermediate iron salt is formed at lower temperatures and undergoes decomposition into the corresponding ketone at higher temperatures. If less iron than that required for formation of the ferrous salt be present, then variable quantities of *n*-heptoic acid are also formed. The use of baryta facilitates formation of the intermediate iron salt, lowers the decomposition temperature, and thus gives a purer product.

Application of the optimum conditions employed for suberic acid to glutaric, adipic, pimelic, and azelaic acids gave <1%, 51%, 56%, and 10% of cyclic ketone respectively. Sebacic acid gave only methyl octyl ketone. The results differ quantitatively more from those obtained using thorium salts than from those with calcium salts.

A discussion of methods for comparing ease of formation of simple carbon rings shows that there must be (1) a main reaction involving the formation of the cyclic compound, and (2) an alternative side reaction giving an open-chain product. Accordingly in the present work slow thermal distillation of the normal dibasic acids has been utilised. Glutaric acid yields only *n*-butyric acid; adipic and pimelic acids give 80%, and 32%, respectively, of cyclopentanone and cyclohexanone. Suberic, azelaic, and sebacic acids give mainly *n*-heptoic, *n*-octoic, and *n*-nonoic acids, respectively, and but little ketone in each case. It follows that, in particular, the cyclopentane ring is formed more readily than the cyclohexane ring. The results obtained are compared with the theoretical probabilities of formation of an *n*-membered ring (cf. Wojnicz-Sianozeneki, A., 1922, i, 330 and with the conclusions reached from calculations based on other physical measurements and considerations.

R. J. W. LE FEVRE.

Di-*p*-tolylketen. H. GILMAN and C. E. ADAMS (Rec. trav. chim., 1929, 48, 464—465).—Oxidation of 4:4'-dimethylbenzylmenohydrazone with mercuric oxide cf. Curtius and Kaserer, A., 1911, i, 324, affords the corresponding azo-derivative, which when heated at 80—90° in a vacuum yields di-*p*-tolylketen. This is decomposed by water and alcohol to di-*p*-

tolylacetic acid and its ethyl ester, respectively. It furnishes a quinoline compound, which when treated with di-*p*-tolyl ketone affords tetra-*p*-tolylethylene (cf. Gilman and Flick, this vol. 688). H. BURTON.

Radical nature of dark-coloured, dimeric diarylketens. W. LANGENBECK (Ber., 1929, 62, [B], 962—963; cf. Langenbeck and Langenbeck, A., 1928, 762; Wittig and von Lupin, *ibid.*, 1233).—Anisilic acid is converted when heated into a dark, bluish-green, molten mass which becomes colourless when cold. The solution in toluene is yellow at the ordinary temperature, becomes green at 50—80° and greenish-blue at the b. p. At 80°, the solution shows marked deviation from Beer's law, so that the presence of a radical is established. H. WREN.

o-Nitroacetophenone. W. O. KERMACK and J. F. SMITH (J.C.S., 1929, 814—815).—Satisfactory yields of *o*-nitroacetophenone may be obtained from ethyl *o*-nitrobenzoylacetate provided that the acetyl group is removed before hydrolysis of the ester group takes place. Thus, by boiling an alcoholic solution of ethyl *o*-nitrobenzoylacetate to which 10% by weight of sulphuric acid has been added the acetyl group is removed as ethyl acetate; the acetate and the bulk of the alcohol are distilled off and the residue is refluxed for an hour. The yield of redistilled *o*-nitroacetophenone exceeds 75%.

R. J. W. LE FEVRE.

9-Benzhydrylanthrone and isodianthranyl. E. DE B. BARNETT and N. F. GOODWAY (J.C.S., 1929, 813—814).—Treatment of anthrone with benzhydryl chloride in potassium hydroxide solution gave benzhydrylanthrone, m. p. 188—189° (acetate, m. p. 234—235°, lit. 228—229°), reduction of which by zinc dust and boiling acetic and hydrochloric acids gave a yellow isodianthranyl (accompanied by some diphenylmethane), m. p. 312° (decomp. 305°), probably identical with that of Schlenk (A., 1928, 1031) and different from that of Barnett and Matthews (J.C.S., 1923, 123, 380).

R. J. W. LE FEVRE.

Preparation of semicarbazones in pyridine solution. I. V. HOPPER (J. Roy. Tech. Coll. Glasgow, 1929, 2, [1], 52—56).—A generally applicable method of preparing semicarbazones is to allow semicarbazide hydrochloride to react with an aldehyde or a ketone in aqueous pyridine solution, the pyridine acting both as a solvent and as a base to combine with the liberated hydrochloric acid. Under these conditions benzil gives the monosemicarbazone at the ordinary temperature and diphenyloxytriazine at 100° but no disemicarbazone. Acetophenone-5-benzylsemicarbazone, CPhMe·N·NH·CO·NH·CH₂·Ph, m. p. 128°, has been prepared by this method. A. R. POWELL.

Stereochemistry of the phenyl styryl ketones; ethylenic isomerism and polymorphism of the phenyl α -bromo- β -alkoxystyryl ketones. C. DUFRAISSE and A. GILLET (Ann. Chim., 1929, [x], 11, 5—21).—When the methylacetal of bromodibenzoylmethane, Bz·CHBr·CPh(OMe)₂, is heated above 150° a mixture, m. p. about 58°, is obtained of two isomeric phenyl α -bromo- β -methoxystyryl ketones, which are distinguished by their different crystalline forms. Seeding under aseptic conditions gave an isomeride A,

m. p. 101—102°; the other isomeride is dimorphous, the two forms B_α , m. p. 64—65°, and B_β , m. p. 71—72°, differing in their crystalline form and solubility in light petroleum, b. p. 80—85°, and in ethyl alcohol. A is partly converted into B by heat. Under the influence of light in neutral or slightly acid solution A is completely converted into B , but in an alkaline medium B passes completely into A . Bromodibenzoylmethane is formed from A in the presence of strong acids, particularly under the influence of light. Phenyl α -bromo- β -ethoxystyryl ketone, similarly prepared, was separated into three forms, m. p. 65°, 73°, and 76°, respectively. Phenyl α -bromo- β -propoxystyryl ketone was isolated in one form, m. p. 50—51° (lit. 49°). A. I. VOGEL.

Synthesis of acetosyringone. F. MAUTHNER (J. pr. Chem., 1929, [ii], 121, 255—258).—2 : 6-Dimethoxyphenyl acetate is isomerised by treatment with finely-divided aluminium chloride in nitrobenzene solution at 2—3° to 4-hydroxy-3 : 5-dimethoxyacetophenone, m. p. 122—123° (cf. Bradley and Robinson, A., 1928, 894) (p-nitrophenylhydrazones, m. p. 189—190°). Methylation of this with methyl iodide and methyl-alcoholic potassium hydroxide solution gives 3 : 4 : 5-trimethoxyacetophenone (trimethylgallacetophenone). H. BURTON.

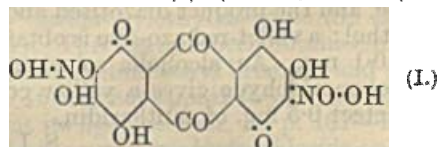
Chalkones [related to hyssopin]. R. L. SHRINER and E. C. KLEIDERER (J. Amer. Chem. Soc., 1929, 51, 1267—1270).—2 : 4 : 6-Trihydroxyacetophenone, m. p. 213—214°, from phloroglucinol and acetyl chloride in nitrobenzene in presence of aluminium chloride, gives with piperonal and alcoholic potassium hydroxide yellow 2 : 4 : 6-trihydroxyphenyl 3 : 4-methylenedioxyethyl ketone (I), decomp. 300—310° (triacetate, m. p. 218—220°). 2 : 4 : 6-Trihydroxybenzaldehyde and acetopiperone (Mauthner, A., 1927, 972) give similarly 3 : 4-methylenedioxyphenyl 2 : 4 : 6-trihydroxyethyl ketone (II), decomp. 265—270° (triacetate, m. p. 205—206°). The chalkone, decomp. 262—263° (triacetate, m. p. 196—197°), from hyssopin is probably identical with II, and not with I as stated by Oesterle (A., 1922, i, 849). H. E. F. NOTTON.

Syntheses of polyhydroxy-chalkones, -hydrochalkones, and -flavanones. IV. Synthesis of 5 : 7-dihydroxy-3' : 4'-dimethoxyflavanone and constitution of eriodictyol and homoeriodictyol. V. Synthesis of eriodictyol and homoeriodictyol. J. SHINODA and S. SATO (J. Pharm. Soc. Japan, 1929, 49, No. 563, 5—6, 7—9).—IV. Phloroglucinol condensed with 3 : 4-dimethoxycinnamoyl chloride in presence of aluminium chloride and nitrobenzene yields 5 : 7-dihydroxy-3' : 4'-dimethoxyflavanone, m. p. 200° (oxime, m. p. 252°), converted by diazomethane into 5-hydroxy-7 : 3' : 4'-trimethoxyflavanone (I), m. p. 136° (acetyl derivative, m. p. 155°). Hesperetin (this vol., 189), eriodictyol (II) (tetra-acetyl derivative, m. p. 137°), and homoeriodictyol (III) (triacetyl derivative, m. p. 115—116°; oxime, m. p. 224°), are all converted by diazomethane into I. Prolonged acetylation of I, II, and III gives acetyl derivatives, m. p. 160°, 196—197°, and 163—164°, respectively (cf. Power and Tutin, J.C.S., 1907, 91, 887; Mossler, A., 1907, ii, 291), which are probably substituted phenyl styryl ketones.

V. Phloroglucinol and 3 : 4-dicarbethoxyoxycinnamoyl chloride (Fischer and Oetker, A., 1914, i, 143) condense in presence of aluminium chloride, yielding eriodictyol (5 : 7 : 3' : 4'-tetrahydroxyflavanone), m. p. 267°, and a substance $[(OH)_2 \cdot C_6H_3 \cdot CH : CH \cdot CO]_2 C_6H(OH)_3$, m. p. 267°. Carbethoxyvanillin reacts with malonic acid in presence of pyridine and a small amount of piperidine, forming 3-methoxy-4-carbethoxyoxycinnamic acid, m. p. 180°, the acid chloride of which condenses with phloroglucinol, yielding homoeriodictyol (5 : 7 : 4'-trihydroxy-3'-methoxyflavanone), m. p. 224—225°, together with a substance, m. p. 233°. H. BURTON.

Polyiodoanthraquinones. A. ECKERT and M. KLINGER (J. pr. Chem., 1929, [ii], 121, 281—288).—When tetraiodobenzoylbenzoic acid (I) (Hofmann, A., 1916, i, 143) is heated rapidly to 190—200° with 10 parts of concentrated sulphuric acid some iodine is eliminated, but 1 : 2 : 3 : 4-tetraiodoanthraquinone, decomp. about 476°, was isolated from the reaction mixture. With fuming sulphuric acid at 100°, reaction occurs but no anthraquinone derivative is formed. Treatment of I with aluminium chloride at 150—175° affords a small amount of a di-iodoanthraquinone, m. p. 290—292°. Treatment of anthraquinone with iodine in presence of fuming sulphuric acid (70% SO_3) at 140—180° gives a mixture of tri-iodo-, m. p. 277°, penta-iodo-, decomp. 368°, and tetra-iodo-anthraquinones, not melted at 500° (main product). This last compound, probably the 1 : 4 : 5 : 8-derivative, is relatively stable. It resists nitration, does not react with aniline, yields a halogen-free, uncrystallisable substance when boiled with potassium methoxide, and when heated with a mixture of potassium acetate and acetic acid gives anthraquinone. Anthraquinone is also obtained by treatment with zinc dust and ammonia. H. BURTON.

Oxidising nitration and quinonenitronic acids. G. HELLER, E. MERTZ, and A. SILLER (Ber., 1929, 62, [B], 928—937).—1 : 2 : 5 : 6-Tetrahydroxyanthraquinone is converted by 100% nitric acid in glacial acetic acid into 3 : 7-dinitro-1 : 2 : 5 : 6-tetrahydroxyanthraquinone, which gradually darkens above 225° but does not melt below 300° (pyridine salt). It is reduced by sodium sulphide in aqueous alkaline solution or by stannous chloride and hydrochloric acid in glacial acetic acid suspension to 3 : 7-diamino-1 : 2 : 5 : 6-tetrahydroxyanthraquinone, which does not show a characteristic m. p. (sodium salt; acetyl derivative, $C_{28}H_{22}O_{12}N_2$, not molten below 300°). Concentrated sulphuric and fuming nitric acids transform 1 : 2 : 5 : 6-tetrahydroxyanthraquinone into 1 : 2 : 5 : 6-tetrahydroxyanthraquinone-4 : 3 : 8 : 7-diquinonenitronic acid (I) (also +2AcOH), decomp.

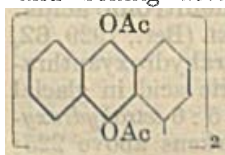


about 265° after softening (sodium salt, $C_{14}H_4O_{12}N_2Na_2$; phenylhydrazine salt, not molten below 290°; hydroxylamine salt). The quinonenitronic acid is also obtained by the action of nitrous fumes on

1 : 2 : 5 : 6-tetrahydroxyanthraquinone or by nitration of 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone in sulphuric acid. It is isomerised by dilute sulphuric acid to 3 : 7-dinitro-1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone, decomp. about 290° (accompanied by a substance, m. p. 225°), whereas the reverse transformation is effected in the presence of alkali or under the influence of pure nitric acid in presence of glacial acetic acid. A yellow variety of the nitronic acid is produced by the action of an excess of nitric acid on the form described above. Reduction of the nitronic acid is not effected by sulphurous acid or hydrogen sulphide, which induce isomerisation. Sodium sulphide converts the acid in alkaline solution into 1 : 2 : 5 : 6-tetrahydroxyanthraquinone-4 : 3, 8 : 7-diquinoxime (or 3 : 7-dinitroso-1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone), not molten below 300° (pyridine salt, m. p. 224°). 3 : 7-Diamino-1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone (sodium salt) is prepared by alkaline reduction of the corresponding dinitro-compound or of the nitronic acid; it is also obtained by catalytic reduction of the nitronic acid (after isomerisation) in presence of palladised barium sulphate.

1 : 2 : 7 : 8-Tetrahydroxyanthraquinone, with glacial acetic and 100% nitric acid, affords 3 : 6-dinitro-1 : 2 : 7 : 8-tetrahydroxyanthraquinone, m. p. 295—296° (decomp.), whereas with sulphuric and nitric (*d* 1.52) acids it gives 1 : 2 : 7 : 8-tetrahydroxyanthraquinone-4 : 3, 5 : 6-diquinoxime (also +2AcOH), decomp. about 246°. The last-named compound is isomerised by dilute sulphuric acid to 3 : 6-dinitro-1 : 2 : 4 : 5 : 7 : 8-hexahydroxyanthraquinone, decomp. 285°. H. WREN.

Reduction products of 1 : 1'-dianthraquinonyl. A. ECKERT (J. pr. Chem., 1929, [ii], 121, 273—277).—Reduction of 1 : 1'-dianthraquinonyl with zinc dust and boiling acetic anhydride gives a tetra-acetyl-1 : 1'-dianthrahydroquinonyl (annexed formula). The ready conversion of dianthrahydroquinonyl into mesobenzdianthrone, by elimination of 2 mols. of water, indicates that this last compound reacts as a hydroxyanthrone. Reduction of dianthraquinonyl with sodium hyposulphite affords helianthrone.



Manufacture of condensation products [from benzanthrone and naphthols]. I. G. FARBEN-IND. A.-G.—See B., 1929, 350.

Reactions of cantharidin. H. W. VAN URK (Pharm. Weekblad, 1929, 66, 313—317).—The material is evaporated on the water-bath with 50% nitric acid, the nitro-compound reduced with stannous chloride, and the product diazotised and coupled with β -naphthol; a violet-red azo-dye is obtained with as little as 0.1 mg. An alcoholic solution of *p*-dimethylaminobenzaldehyde gives a yellow coloration, which will detect 0.5 mg. of cantharidin.

S. I. LEVY.

Beet-saponin. K. REHORST (Z. Ver. deut. Zucker-Ind., 1929, 79, 155—175).—Purified beet-saponin was completely hydrolysed by treatment with successive quantities of 0.5—2% sulphuric acid at

temperatures rising from 96° to 147°. The *d*-glycuronic acid was separated as the barium salt and further identified by preparation of the lactone and saccharic acid. The saponin, repeatedly crystallised from alcohol and dried at 105—110°, had m. p. 301—306°, $[\alpha]_D +78.82^\circ$. Analysis, neutralisation equivalent, and mol. wt. indicated the formula $C_{31}H_{48}O_9$; this was confirmed by similar determinations on the acetyl derivative and by the proportion in the original saponin. Preparations several years old, which had originally given elementary analyses agreeing with this formula, were now found to give results suggesting the addition of water or oxygen. Distillation of saponin with zinc dust yielded a mixture of sesquiterpenes. Dehydrogenation by selenium gave a product from which two sesquiterpenes, cadalene and eudalene, and a substance, $C_{30}H_{20}O$ or $C_{30}H_{18}O$, were isolated. It is concluded that beet-saponin has the formula $C_{37}H_{56}O_9$, and that the saponin portion of its molecule contains two reduced naphthalene groups. F. E. DAX.

Natural and synthetic rubber. I. Destructive distillation of natural rubber. T. MIDDLEY, jun., and A. L. HENLE (J. Amer. Chem. Soc., 1929, 51, 1215—1226; cf. Ipatiev, A., 1897, i, 233; Harries, A., 1903, i, 189, 642; Bouchardat, A., 1875, 1259; Staudinger, A., 1926, 841).—Distillation of pale crêpe rubber at atmospheric pressure (*a*) alone, and (*b*) in presence of magnesium (10%), which increases the proportion of aromatic products, gives an oil (*A*) from which, in addition to a substantial amount of polymerised material, the following fractions were obtained: γ -methyl- Δ^2 -butene [% of *A*: (*a*) 0.04, (*b*) 0.2]; β -methyl- Δ^2 -butene [(*a*) 0.04, (*b*) 0.2]; isoprene [(*a*) and (*b*) 10.0]; β -methyl- Δ^2 -butene [(*a*) 0.04, (*b*) 0.2]; α β -methylpentene [(*a*) 0.06, (*b*) 0.3], b. p. 59—60°, *d* 0.730, *n* 1.4117 (*d*²⁰ and *n*²⁰ in all cases), hydrogenated to β -methylpentane; γ -methyl- Δ^2 -pentene [(*a*) 0.03, (*b*) 0.15]; an impure diene [(*a*) 0.03, (*b*) 0.15], b. p. 76—79°, *d* 0.742, *n* 1.4346, hydrogenated to γ -methyl- Δ^2 -pentene, possibly γ -methyl- Δ^2 -pentadiene; benzene [(*a*) 0.005, (*b*) 0.1]; an impure (?) γ -methylhexene [(*a*) 0.03, (*b*) 0.15], b. p. 93—95°, *d* 0.744, *n* 1.422, hydrogenated to a (?) γ -methylhexane, b. p. 92—95°, *d* 0.723, *n* 1.4032, which contains methylcyclohexane; Δ^3 - [(*a*) 0.01, (*b*) 0.1], Δ^2 -, and Δ^1 - [(*a*) 0.1, (*b*) 1.0], -tetrahydrotoluenes; an impure β -methylheptene [(*a*) 0.02, (*b*) 0.1], b. p. 109—110°, *d* 0.783, *n* 1.4413, hydrogenated to pure isooctane; toluene [(*a*) 0.05, (*b*) 1.0]; fractions, b. p. 121—122° and b. p. 124—125° [(*a*) 0.04, (*b*) 0.2], hydrogenated to impure isooctane, probably mainly mixtures of β -methylheptenes; a dihydro-*m*-xylene [(*a*) 0.1, (*b*) 1.01], b. p. 129—130°, *d* 0.795, *n* 1.4451, probably the Δ^{13} -isomeride; *m*- [(*a*) 0.05, (*b*) 1.0], but no *o*- or *p*-xylenes; Δ^1 - or Δ^3 -*p*-ethyltetrahydrotoluene [(*a*) 0.08, (*b*) 0.8], b. p. 144—145°, *d* 0.813, *n* 1.4529; a dicyclic terpene [(*a*) 0.04, (*b*) 0.8], b. p. 158—159°, *d* 0.834, *n* 1.4665, possibly isomeric with thujene, and hydrogenated to a product, b. p. 158—161°, *d* 0.813, *n* 1.4498, apparently identical with thujane; *p*-ethyltoluene [(*a*) 0.04, (*b*) 0.8]; a monocyclic substance, $C_{10}H_{18}$, b. p. 162—163°, *d* 0.828, *n* 1.46, obtained only in presence of magnesium and

hydrogenated to a compound, $C_{10}H_{10}$, b. p. 162—164°, d 0.791, n 1.4407; a product, b. p. 162—163°, d 0.8105, n 1.456, obtained in absence of magnesium, probably a mixture of dimethyloctadienes, and, finally, dipentene [(a) and (b) 20.0]. Myrcene, a terpene, b. p. 168—169°, and dimethylbutadiene were not detected. The carbon skeletons of all the above products except benzene are derivable from fragments of Staudinger's formula for rubber. The proportions in which they occur throw light on the relative ease of scission of the linkings in the rubber molecule and on the laws governing the transformation of the primary scission products into stable molecules.

H. E. F. NOTTON.

Action of alcoholic hydrochloric acid on diphenylmethyltetrahydropyrone. H. RYAN and J. J. LENNON (Sci. Proc. Roy. Dubl. Soc., 1928, 19, 121—124; cf. A., 1925, i, 1282).—Treatment of 2:6-diphenyl-3-methylpyran (I) with dry alcoholic hydrogen chloride at 15° affords a product from which 3:4-diphenyl-2-methyl- Δ^3 -cyclopentenone (II) has been isolated (cf. Japp and Maitland, J.C.S., 1904, 85, 1488). The conversion, with benzaldehyde and alcoholic hydrochloric acid, of (I) into 3:4-diphenyl-2-benzylidene-5-methyl- Δ^3 -cyclopentenone (III) recorded by Ryan and Devine (A., 1916, i, 654) therefore proceeds by way of II. An account of the direct conversion of γ -benzylidenemethyl ethyl ketone into III with benzaldehyde in concentrated alcoholic hydrochloric acid solution is given, and an improved preparation of I is described.

C. W. SHOPPEE.

Synthesis of 5:7:2':4'-tetrahydroxyflavone and of 7:2':4':6'-tetrahydroxyflavone. N. M. CULLINANE, J. ALGAR, and H. RYAN (Sci. Proc. Roy. Dubl. Soc., 1928, 19, 77—83).—Phloracetophenone 1:6-dimethyl ether condenses with methyl 2:4-dimethoxybenzoate in presence of sodium at 150—160° to give 2-hydroxy-4:6:2':4'-tetramethoxybenzoylacetophenone (I), m. p. 151°, converted by brief treatment with hydriodic acid (d 1.7) into 5:7:2':4'-tetramethoxyflavone, m. p. 186°. Demethylation by hydriodic acid (d 1.94) affords 5:7:2':4'-tetrahydroxyflavone, darkens at 270°, chars at 300°. This substance closely resembles natural lotoflavin and is also obtained directly from I under similar conditions. Condensation of phloracetophenone 2:4:6-trimethyl ether with methyl 2:4-dimethoxybenzoate gives 2:4:6:2':4'-pentamethoxybenzoylacetophenone (II), m. p. 153° (copper derivative), converted by hydriodic acid (d 1.7) into 7:2':4':6'-tetramethoxyflavone, m. p. 171°, demethylated by hydriodic acid (d 1.94) to 7:2':4':6'-tetrahydroxyflavone, m. p. 240° (decomp.) (acetyl derivative, m. p. 230°), which is also obtained directly from II under similar conditions.

C. W. SHOPPEE.

Naphthophenoxanthones. A. PIERONI (Atti R. Accad. Lincei, 1929, [vi], 9, 420—424).—The general reactions of formation of xanthones serve for the preparation of $\beta\beta$ - and $\beta\alpha$ -naphthophenoxanthones but not for that of the $\alpha\beta$ -isomeride, possibly owing to the readiness with which the α -carboxyl is eliminated. This compound, m. p. 173°, may, however, be obtained by heating 1-benzoyl- β -naphthol with aluminium chloride for 2 hrs. at 150°.

T. H. PORR.

Difurylethylene. P. F. BRUINS (J. Amer. Chem. Soc., 1929, 51, 1270—1271).—Polythiofurfuraldehyde (Lintner, Z. ges. Brauw., 1910, 15, 189), precipitated by acid as a rubber-like mass from 3% aqueous furfuraldehyde saturated with hydrogen sulphide, is converted by distillation at 95—135°/10—15 mm., into 18% of the theoretical of *s*-di-2-furylethylene, m. p. 100°.

H. E. F. NOTTON.

Constitution of carthamin. II. (Miss) C. KURODA (Proc. Imp. Acad. Tokyo, 1929, 5, 82—85; see this vol., 430).—By heating carthamin with dilute phosphoric acid and extracting with ether, yellow, crystalline carthamidin, $C_{11}H_{12}O_6 \cdot H_2O$, m. p. 218°, was obtained, accompanied by isocarthamidin, m. p. 238°. From these were prepared α -, β -, and γ -acetylcarthamidins, m. p. 158°, 143°, and 179°, respectively, and acetylisocarthamidin, m. p. 180°. From a comparison of the colour (and other) reactions of these compounds with those of naringenin and phloretin it was deduced that probably isocarthamin is 1:3:4:4'-tetrahydroxychalkone-4-glucoside, the quinonoid form of this being carthamin; carthamidin is 1:3:4:4'-tetrahydroxyflavanone and isocarthamidin 1:2:3:4'-tetrahydroxyflavanone.

B. W. ANDERSON.

Constitution of carthamidin. III. (Miss) C. KURODA (Proc. Imp. Acad. Tokyo, 1929, 5, 86).—Methylation of β -acetylcarthamidin by Freudenberg's method gave a substance identical with 2:3:4:6:4'-pentamethoxychalkone, m. p. 112°, as proved by an independent synthesis of the latter, thus confirming the formulæ suggested (preceding abstract).

B. W. ANDERSON.

Pyrrolines from γ -chloropropyl- and cyclopropyl ketimines. J. B. CLOKE (J. Amer. Chem. Soc., 1929, 51, 1174—1187).—Magnesium phenyl bromide and γ -chlorobutyronitrile in ether give the bromomagnesium derivative of phenyl- γ -chloropropylketimine, which is decomposed by ice and ammonium chloride to the impure ketimine. This gives an impure hydrochloride, m. p. 85—88°, which is rapidly hydrolysed by water at 0° to phenyl γ -chloropropyl ketone, b. p. 130—133°/4 mm. (decomp.) (semicarbazone, m. p. 136—137°), and when heated rearranges to 2-phenylpyrroline hydrochloride. This is also formed in small yield from phenyl γ -chloropropyl ketone and alcoholic ammonia at the ordinary temperature. Phenylcyclopropylketimine (Bary, A., 1923, i, 226) (hydrochloride, m. p. 104—105°, with immediate isomerisation) changes rapidly at 200°, or, in presence of a trace of hydrochloride, at lower temperatures, giving mainly 2-phenylpyrroline. This appears to be a general reaction for cyclopropyl and cyclobutyl ketones. Similarly, magnesium ethyl bromide and γ -chlorobutyronitrile give 2-ethylpyrroline, previously described as cyclopropylethylketimine (de Booseré, A., 1923, i, 311). This has now been obtained in an impure state from magnesium ethyl bromide and cyanocyclopropane. It does not appear to yield 2-ethylpyrroline at 185°, but its hydrochloride, m. p. 101—103°, passes at 130° into the pyrroline hydrochloride and is readily hydrolysed by water to cyclopropyl ethyl ketone. Contrary to the statement of de Booseré, 2-ethylpyrroline does not yield with alkali cyclopropyl ethyl ketone.

H. E. F. NOTTON.

Substituted aromatic aldehydes in Hantzsch's pyridine condensation. I. Methoxy-, chloro-, and hydroxy-benzaldehydes. L. E. HINKEL and W. R. MADEL (J.C.S., 1929, 750—754).—In all cases the introduction of a substituent into benzaldehyde lowers the yield of dihydropyridine obtained compared with that obtained from benzaldehyde itself. Apart from the observed general depressant effect the results are not in agreement with the theory of alternate polarities, but appear to correspond with the depressant effects of substituents on the affinity of benzaldehyde for hydrogen cyanide (Lapworth and Manske, A., 1928, 1245). The abnormal behaviour of salicylaldehyde is attributed to co-ordination between the hydroxyl and the aldehyde group, whereby the typical properties of each radical are modified.

The following derivatives of ethyl 4-phenyl-2:6-dimethylpyridine-3:5-dicarboxylate are described (the substituent being in the phenyl group in each case): *p*-, *o*-, and *m*-methoxy-, m. p. 50°, 65°, and 82°, respectively; *p*-, *o*-, and *m*-chloro-, m. p. 68°, 62°, and 53°, respectively; also the 1:4-dihydro-derivatives of these, m. p. 159°, 151°, 120°, 149°, 132°, and 142°, respectively, and of the 4'-*p*- and 4'-*m*-hydroxyphenyl compounds, m. p. 227° and 202°, respectively. With the exception of derivatives of the hydroxy-aldehydes, the oxidation of the dihydropyridines proceeded normally and in no case was any elimination of phenyl observed.

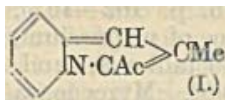
R. J. W. LE FÈVRE.

2:6-Dibromo- and 2:6-dichloro-pyridine-4-carboxylic acids and some derivatives. W. H. LEVELT and J. P. WIBAUT (Rec. trav. chim., 1929, 48, 466—473).—Crude 2:6-dihydroxypyridine-4-carboxylic acid (I) (Behrmann and Hofmann, A., 1885, 138) is converted by phosphoryl chloride at 200° into a mixture of 2:6-dichloropyridine-4-carboxylic acid (II), m. p. 208—209° after previous sintering [acid chloride (III), b. p. 243—246°/760 mm., m. p. 25—27°; amide, m. p. 207—208° (lit. 200°)], and 2:6-dichloro-4-cyanopyridine, m. p. 95.5—96.5° (derived from the admixed amide of I). Hydrolysis of this with 30% hydrochloric acid gives II. Treatment of I with phosphoryl bromide at 170° yields 2:6-dibromopyridine-4-carboxylic acid (IV), m. p. 184—185° [acid chloride (V), b. p. 160°/21 mm., m. p. 9—11°; amide, m. p. 202—204°], together with 2:6-dibromo-4-cyanopyridine, m. p. 139—140°. Thermal decomposition of the silver salt of IV affords 2:6-dibromopyridine, m. p. 118—119°, also formed in small amount, together with unchanged material, by the action of hydrogen on V in presence of xylene and a palladium-barium sulphate catalyst. Similar treatment of III with hydrogen furnishes a small amount of 2:6-dichloropyridine together with unchanged material.

H. BURTON.

Picolide of M. Scholtz and acetyl derivatives of indolizine and 2-methylindolizine. A. E. TSCHITSCHIBABIN and F. N. STEPANOV (Ber., 1929, 62, [B], 1068—1075).—2-Methylindolizine, prepared by the condensation of 2-methylpyridine with chloroacetone and distillation of the product with steam in the presence of sodium hydrogen carbonate, is converted by anhydrous sodium acetate and boiling

acetic anhydride into 1-acetyl-2-methylindolizine (I), b. p. 159—160°/7 mm., m. p. 83°, in which the ketonic group cannot be detected by phenylhydrazine or hydroxylamine under the



usual conditions. It does not react normally with Grignard reagents, yielding with magnesium ethyl bromide a compound, b. p. 95°/9 mm., m. p. 59—60°, with the composition of methylethylindolizine (also obtained by reduction of the acetyl compound with aluminium amalgam). The acetyl compound is converted by acetic anhydride at 230—240° into 1:3-diacetyl-2-methylindolizine, m. p. 123°, in which the presence of only one ketonic group is readily established [monophenylhydrazone, m. p. 210° (decomp.)]; it is converted by 25% sulphuric acid into 2-methylindolizine. 1-Acetylindolizine, b. p. 148—149°/9.5 mm., prepared according to Scholtz (A., 1912, i, 385, 648; 1913, i, 514), is converted by acetic anhydride at 220—230° into picolide, m. p. 176°. The complete analogy in the properties of the acetyl derivatives of methylindolizine, acetylindolizine, and picolide leads to the conclusion that the last-named compound is 1:3-diacetylindolizine. H. WREN.

Indoline and 2-methyl-4:5:6:7-tetrahydroindole. G. PLANCHER (Ber., 1929, 62, [B], 1088—1089).—*o*-Dihydroindole (cf. Ferber, this vol., 308) has been isolated previously by the author (A., 1905, i, 611). 2-Methyl-4:5:6:7-tetrahydroindole (cf. von Braun, A., 1924, i, 545) has been obtained by Plancher and Zambonini from ethyl acetoacetate and 2-chlorocyclohexanone and hydrolysis followed by distillation with lime of the product. H. WREN.

Additive reaction of indolenines. III. Ketonic fission of acetoacetic esters. H. LEUCHS, A. HELLER, and A. HOFFMANN (Ber., 1929, 62, [B], 871—881; cf. A., 1925, i, 1281; 1928, 528).—Ethyl α -dibenzylacetoacetate, m. p. 57°, undergoes acid fission when treated with alkali, whereas it is converted by a mixture of glacial acetic acid and hydriodic acid (*d* 1.7) at 115° into *as*-dibenzylacetone, b. p. 186°/10 mm., 190—192°/15 mm., in 80% yield; dibenzylacetic acid does not appear to be formed. The semicarbazone, m. p. 153—154°, *oxime*, m. p. 75—76°, and unstable phenylhydrazone, m. p. 86—87°, of the ketone are described. The crude phenylhydrazone is converted by zinc chloride in anhydrous alcohol at 100—120° into the non-crystalline 2-methyl-3:3-dibenzylindolenine [picrate, m. p. 180—181° (decomp.); hydrochloride, m. p. 180—182°]. The free base is transformed by acetic anhydride and sodium acetate at 100° into *N*-acetyl-3:3-dibenzyl-2-methyleneindoline, m. p. 96—97°, not affected by methyl alcohol at 100° or by aqueous ammonia or alkali. Similarly, with benzoic anhydride and sodium benzoate the base affords *N*-benzoyl-3:3-dibenzyl-2-methyleneindoline, m. p. 164°, which behaves similarly to the acetyl compound.

Phenyl isopropyl ketone, from benzene and isobutyl chloride, is converted by successive treatment with phenylhydrazine and zinc chloride into non-crystalline 2-phenyl-3:3-dimethylindolenine (picrate, m. p. 158—160°), which does not add acetic anhydride. With benzoyl chloride and sodium carbonate the base

affords 1-benzoyl-2-phenyl-3 : 3-dimethylindolin-2-ol, m. p. 138° after softening. The methiodide of the base, m. p. 203°, is converted by silver carbonate in the presence of alcohol into 2-phenyl-1 : 3 : 3-trimethylindolin-2-ol, m. p. 107—108°. 2-Phenyl-3 : 3-dimethylindoline, m. p. 93°, its hydrochloride, m. p. 193—194°, nitrate, m. p. 187° (decomp.), and acetyl derivative, m. p. 82—83°, are described. Methyl iodide in methyl alcohol at 100° converts 2-phenyl-3 : 3-dimethylindoline into a substance, $C_{17}H_{19}N$, m. p. 88°, and 2-phenyl-1 : 3 : 3-trimethylindoline methiodide.

3 : 3-Dimethylindolenine, $(C_{10}H_{11}N)_3$, is transformed by acetic anhydride and sodium acetate at 100° into 0 : 1-diacetyl-3 : 3-dimethylindolin-2-ol, m. p. 60—61°, converted by boiling methyl alcohol into 1-acetyl-2-methoxy-3 : 3-dimethylindoline and by boiling 90% acetic acid into 1-acetyl-3 : 3-dimethylindolin-2-ol, m. p. 117—118°. Methyl-alcoholic ammonia at 100° converts the diacetyl derivative into 2-amino-1-acetyl-3 : 3-dimethylindoline, m. p. 78° (picrate, m. p. 159—161°). 0 : 1-Dibenzoyl-3 : 3-dimethylindolin-2-ol, m. p. 147—148°, 1-benzoyl-2-methoxy-3 : 3-dimethylindoline, m. p. 71—72°, 1-benzoyl-3 : 3-dimethylindolin-2-ol, m. p. 202—204°, and 2-amino-1-benzoyl-3 : 3-dimethylindoline, m. p. 115—117° (picrate, m. p. 191—194° after softening), are described. The indolenine, $(C_{10}H_{11}N)_3$, could not be caused to add phthalic anhydride or phenylhydrazine. H. WREN.

5 : 8-Dihydroxy- β -anthrapyridinequinone. H. RAUDNITZ [with G. LAUBE] (Ber., 1929, 62, [B], 938—939).—Comparison of the absorption spectra of β - and α -anthrapyridinequinones shows that the maxima of the bands lie more towards the red end with the β - than with the α -compound. Treatment of cinchomeronic anhydride and quinol with a mixture of sodium and aluminium chlorides at 180—200° affords 5 : 8-dihydroxy- β -anthrapyridinequinone, m. p. 211° (sodium salt). 5 : 8-Dihydroxy-6 : 7-benzo- β -anthrapyridinequinone, m. p. 343° (sodium salt), is derived similarly from 1 : 4-dihydroxynaphthalene. H. WREN.

Diphenyl derivatives of the Kaufler type, and the formation of dibenzocdiazines. R. J. W. LE FÈVRE (J.C.S., 1929, 733—738).—The malonyl-benzidine of Remfry (*ibid.*, 1911, 99, 610) is shown to contain a free amino-group, since it furnishes a salicylidene derivative, m. p. 298—300°, and a sulphate; it is therefore probably 4-amino-4'-malonylamidodiphenyl. The carbonyl- and thiocarbonyl-dianisidines of Starke (A., 1899, i, 589) yield salicylidene derivatives as yellow, insoluble powders; the former substance is best prepared by heating 1 mol. of *o*-tolidine with 2 mols. of carbamide, and can also be obtained by mixing solutions of *o*-tolidine hydrochloride and potassium cyanate; it has therefore the structure I ($R = NH_2$, $X = O$), and the thio-compound has the analogous structure (with $X = S$). The oxalybenzidine of Taussig (A., 1904, i, 663) does not react with salicylaldehyde and analysis indicates that it is 4 : 4'-diethyl-

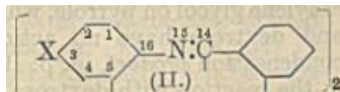
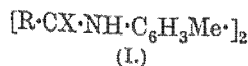
preparation of cycloformazyl methyl ketone (Wedekind, A., 1898, i, 454) proved unsuccessful.

2 : 2'-Diaminodiphenyl (disalicylidene derivative, m. p. 153—154°; NN'-thiocarbonyl derivative, m. p. 243°), obtained by a modification of the method of Ullmann and Bielecki (A., 1901, i, 586), condenses with phenanthraquinone in acetic acid at 100° to yield 13 : 14-(*oo'*-diphenylene)dibenzocd-12 : 15-diazine, m. p. 268—269° (II : $X = H$), and with chloro-2 : 4-dinitrobenzene to give 2 : 2'-di-(2'' : 4''-dinitrophenylamino)diphenyl, m. p. 177—178°, together with N-2' : 4'-dinitrophenylcarbazole, m. p. 216—217°. Repetition of the preparation of di-*m*-nitrodi-*o*-aminodiphenyl (cf. Tauber, A., 1892, i, 480) yields a product which is probably a mixture of 5 : 5', 4 : 4', and 4 : 5'-dinitro-derivatives together with a little of 3 : 3'- and 3 : 5'-compounds; attempts to obtain dinitro-octadiazines from it were unsuccessful, as was also condensation of 2 : 2'-diaminodiphenyl with benzil-3 : 3'-disulphonic acid (cf. Kafka, A., 1891, i, 720). Definite compounds could not be isolated from the interaction of 2 : 2'-diaminodiphenyl with ethyl malonate, ethyl phthalate, or ethyl oxalate. 2 : 2'-Diacetamidodiphenyl, obtained by the process described by Brady and McHugh (J.C.S., 1923, 123, 2047) for benzidine, is converted by bromine in acetic acid at 90—100° into 5 : 5'-dibromo-2 : 2'-diacetamidodiphenyl, m. p. 266—267°, hydrolysed by sodium hydroxide to 5 : 5'-dibromo-2 : 2'-diaminodiphenyl, m. p. 140—141° (disalicylidene derivative, m. p. 263—265°), which condenses with phenanthraquinone to yield 3 : 8-dibromo-13 : 14-(*oo'*-diphenylene)dibenzocd-12 : 15-diazine (II : $X = Br$), m. p. above 280°. By contrast, 4 : 4'-dibromo-2 : 2'-diaminodiphenyl, m. p. 192—194° (disalicylidene derivative, m. p. 210—211°), obtained by reducing 4 : 4'-dibromo-2 : 2'-dinitrodiphenyl (Ullmann and Bielecki, *loc. cit.*) with iron and water at 100°, does not yield an octadiazine under similar conditions. The following esters, prepared by heating the appropriate hydroxy-compound with diphenic anhydride at 160°, are described: benzyl hydrogen diphenate, m. p. 112—113°; α -naphthyl hydrogen diphenate, m. p. 202—203°, and β -naphthyl hydrogen diphenate, m. p. 178—179°. C. W. SHOPPEE.

$\alpha\alpha'$ -Dipyrryl-pentadione and -butadione. T. N. GODNEV and N. A. NARYSCHKIN (J. pr. Chem., 1929, [ii], 121, 369—373).—By the action of magnesium pyrryl iodide on ethyl succinate is obtained *s*-dipyrrylethane (2 : 2'-dipyrrylglyoxal) (Oddo and Dainotti, A., 1912, i, 721) together with a substance to which the annexed formula is assigned. Similarly, with ethyl glutarate is obtained $\alpha\gamma$ -dipyrrylpropane ($\alpha\gamma$ -dipyrryl- $\alpha\gamma$ -diketopropane), m. p. 125°, together with an amorphous substance, but with ethyl malonate only amorphous products could be obtained.

J. W. BAKER.

Pyrimidines. CV. Test for thymine and 5-methylcytosine in presence of uracil and cytosine. H. H. HARKINS and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 1237—1242).—1 Mg. of thymine (prepared by an improved method) or



oxamido-3 : 3'-dimethyldiphenyl (I ; $R = CO_2Et$, $X = O$) (cf. A., 1928, 283). Attempted repetition of the

5-methyleytosine is detected by the formation of acetylcarbinol when its aqueous solution is treated with bromine, boiled to remove excess, and distilled with barium hydroxide (cf. Baudisch, A., 1918, ii, 412; 1925, i, 1100). Uracil and cytosine do not give acetylcarbinol, but are converted into the highly characteristic barium dialurate (A., 1907, ii, 826).

H. E. F. NOTTON.

Pyrimidines. CVI. Leuco-bases of dyes containing pyrimidine rings. T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 1274—1276).—2-Thio-4-aldehydothymine (A., 1916, i, 756) and dimethyl-aniline in presence of zinc chloride at 100° give pp'-tetramethyldiaminodiphenyl-2-thio-4-thyminylmethane, m. p. 212—214°. 2-Ethylthiol-4-aldehydothymine gives similarly pp'-tetramethyldiaminodiphenyl-2-ethylthiol-4-thyminylmethane, m. p. 218—219°, and 4-aldehydothymine gives pp'-tetramethyldiaminodiphenyl-4-thyminylmethane, m. p. 197—198°. These are oxidised in acid solution to dyes analogous to malachite-green, which are of interest as bactericides.

H. E. F. NOTTON.

Action of o-phenylenediamines on dihydroxy-tartaric acid. F. D. CHATTAWAY and W. G. HUMPHREY (J.C.S., 1929, 645—651; cf. A., 1894, i, 624).—Interaction of sodium dihydroxytartrate and o-phenylenediamine in aqueous solution at 90° for 0.5 hr., followed by addition of 1 mol. of hydrochloric acid affords quinoxaline-2:3-dicarboxy-o-phenylenediamide (I), m. p. 184° (decomp.), readily soluble in sodium hydroxide solution and precipitated unchanged, and decomposing on attempted acetylation or benzoylation; I dissolves in hot dilute hydrochloric acid (1:50), but on cooling the o-phenylenediamine salt (II) of quinoxaline-2:3-dicarboxylic acid, m. p. 186° (decomp.), separates, whilst if hot concentrated hydrochloric acid (1:1) is employed quinoxaline-2:3-dicarboxylic acid (III), m. p. 190° (decomp.) [dihydrate (loses 2H₂O at 110°); ethyl ester, m. p. 83°; ammonium salt, m. p. 220—230° (decomp.)], is obtained on cooling; III condenses readily with o-phenylenediamine in aqueous or in alcoholic solution to yield II. When treated with acetic anhydride, III affords quinoxaline-2:3-dicarboxylic anhydride, m. p. 250—260° (decomp.), converted by treatment with dry ammonia in benzene suspension into the ammonium salt of quinoxaline-2:3-dicarboxylic acid, which by acidification yields quinoxaline-2:3-dicarboxylic acid, m. p. 190—195° (decomp.) (compound + 1AcOH), with conversion into quinoxalinedicarboxylimide, m. p. 260° (decomp.) [acetyl derivative, m. p. 220° (decomp.)]. When heated above its m. p. III decomposes and gives a 10% yield of quinoxaline, m. p. 27°, b. p. 225—226° [tetrachloroiodide, m. p. 125—130° (decomp.)]; the yield may be increased to 30% by using the ammonium salt of III at 220—240°. Oxidation of III with 2% potassium permanganate at 100° affords dipotassium dihydrogen pyrazinetetracarboxylate, converted by 20% hydrochloric acid into pyrazinetetracarboxylic acid, m. p. 205° (decomp.) (dihydrate; tetraethyl ester, m. p. 104°).

p-Chloro-o-phenylenediamine reacts with sodium dihydroxytartrate in a similar manner to yield the following compounds, which exhibit reactions analogous to those above: 6-chloroquinoxaline-

2:3-dicarboxy-p-chloro-o-phenylenediamide, m. p. 207° (decomp.); p-chlorophenylenediamine salt of 6-chloroquinoxaline-2:3-dicarboxylic acid, m. p. 205° (decomp.); 6-chloroquinoxaline-2:3-dicarboxylic acid, m. p. 175° (decomp.) [dihydrate (loses 2H₂O at 110°); anhydride, m. p. 235—240° (decomp.)]; ethyl hydrogen ester, m. p. 159°; ethyl ester, m. p. 60°; ammonium salt, m. p. 215—225° (decomp.)], which at 190° passes into 6-chloroquinoxaline, m. p. 60° (yield 20%); an improved yield is obtained by employing the ammonium salt.

p-Bromo-o-phenylenediamine and sodium dihydroxytartrate yield a corresponding series of compounds: 6-bromoquinoxaline-2:3-dicarboxy-p-bromo-o-phenylenediamide, m. p. 198° (decomp.); p-bromophenylenediamine salt of 6-bromoquinoxaline-2:3-dicarboxylic acid, m. p. 199° (decomp.); 6-bromoquinoxaline-2:3-dicarboxylic acid, m. p. 172° (decomp.) [dihydrate (loses 2H₂O at 110°); anhydride, m. p. 235—245° (decomp.)]; ethyl hydrogen ester, m. p. 161°; ethyl ester, b. p. 69°; ammonium salt, m. p. 235—240° (decomp.)]; 6-bromoquinoxaline, m. p. 56°.

Both 6-chloro- and 6-bromo-quinoxaline-2:3-dicarboxylic acids yield pyrazinetetracarboxylic acid when oxidised with 2% potassium permanganate at 100°.

C. W. SHOPPEE.

Acridine. IV. Formation of diacridyl derivatives from N-methylacridone. K. LEHMSTEDT and H. HUNDERTMARK (Ber., 1929, 62, [B], 1065—1067; cf. this vol., 454).—10-Methylacridine is reduced by zinc dust in boiling glacial acetic acid to 10:10'-dimethyl-5:5'-diacridine, $\text{NMe} \langle \text{C}_6\text{H}_4 \rangle \text{C:}$, converted by hot dilute nitric acid into dimethyldiacridylum nitrate. Treatment of the salt with sodium hydroxide precipitates the carbinol base, $\left[\text{NMe} \langle \text{C}_6\text{H}_4 \rangle \text{C(OH)} \right]_2$, m. p. above 300°, which, with potassium iodide, affords 10:10'-dimethyldiacridylum iodide (cf. Decker and Dunant, A., 1909, i, 433). The course of the action assumed by the latter authors thus receives confirmation (cf. Ehrlich and Benda, A., 1913, i, 904). Diacridyl (Decker and Dunant, loc. cit.) is conveniently prepared from o-chloroacridine and copper powder at 140°.

H. WREN.

Manufacture of pharmaceutical products [quinazolines]. I. G. FARBENIND. A.-G.—See B., 1929, 377.

Polymerisation of pyrrole. A. K. PLISOV (Ukraine Chem. J., 1928, 3[Sci.], 471—475, 477—480).—Tripyrrole is formed by the action at 100° of aqueous ethylene oxide on pyrrole. The catalytic agent is glycol formed from ethylene oxide during the reaction, since anhydrous ethylene oxide or water alone has no polymerising action. Aqueous trimethyl-ethylene oxide has a similar, although feebler reaction.

Glycerol has a more intense polymerising action than ethylene glycol on pyrrole, whilst mannitol, erythritol, and dextrose have no action in this respect. A condensation product, m. p. 190°, is, however, formed in the reaction with dextrose. A resinous product is obtained in the reaction between pyrrole and acetaldehyde.

R. TRUSZKOWSKI.

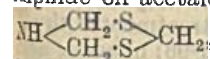
Stability of diazonium salts of the triazole series. J. REILLY and D. MADDEN (J.C.S., 1929, 815—816).—The velocity of decomposition of triazole diazonium salts has been measured; the reaction is more rapid than in the pyrazole and pyrazolone series, and does not follow the unimolecular law. Substitution of alkyl groups in the 3 position confers increased stability in the sequence *isobutyl* > *Pr*^β > *Et* > *Me* > *H*, whilst the nature of the anion and the amount of acid present also influence the decomposition velocity; thus the nitrates are more stable than the chlorides. The following are described: 5-amino-3-ethyl-1:2:4-triazole, m. p. 152° (nitrate, m. p. 167°); 3-ethyl-1:2:4-triazole-5-azo-β-naphthylamine, m. p. 259°, β-naphthol, m. p. 180—181°, and -acetylacetone, m. p. 236°; 5-diazo-3-ethyl-1:2:4-triazole chloroaurate; 5-amino-3-isobutyl-1:2:4-triazole nitrate, m. p. 171°.

C. W. SHOFFEE.

1:3:4-Ox Diazines. IV. J. VAN ALPHEN (Rec. trav. chim., 1929, 48, 417—421).—Chloroacetyl chloride reacts with benzoylhydrazine in benzene solution, forming β-benzoyl-α-chloroacetylhydrazine, m. p. 165°, which when treated with potassium carbonate in acetone yields Δ²-5-keto-2-phenyl-1:3:4-oxdiazine, m. p. 161°. Diphenylchloroacetyl chloride (1 mol.) and benzoylhydrazine (3 mols.) give β-benzoyl-α-(β-benzoylhydrazino)diphenylacetylhydrazine, m. p. 217°, but with 1.35 mols. of the hydrazine, Δ²-5-keto-2:6:6-triphenyl-1:3:4-oxdiazine, m. p. 185°, is obtained. β-Cinnamoyl-α-chloroacetylhydrazine, m. p. 185°, furnishes Δ²-5-keto-2-styryl-1:3:4-oxdiazine, m. p. about 190° after sintering at 174°. The 2-phenyl derivative is hydrolysed by 10% aqueous-alcoholic sulphuric acid to hydrazine, whilst the other oxdiazines are unaffected. The presence of two phenyl groups in positions 2 and 4 of the oxdiazine ring is necessary to prevent fission (cf. this vol., 334).

H. BURTON.

1:3-Dithio-5-azine (formothialdine). T. G. LEVI (Atti R. Accad. Lincei, 1929, [vi], 9, 424—427; cf. A., 1924, i, 964).—2:4:6-Trimethyl-1:3-dithio-5-azine (2:4:6-trimethylthioformaldine) may be readily prepared by the action of ammonium sulphide on acetaldehyde. Similarly, thioformaldine,



formed, together with trithioformaldehyde, by treating aqueous formaldehyde with sulphur or preferably with ammonium hydrogen sulphide. Thioformaldine, which may also be obtained by saturating an ammoniacal solution of trioxymethylene with hydrogen sulphide, gives silver sulphide when treated with aqueous silver nitrate, and is decomposed by hot concentrated hydrochloric acid, yielding trithioformaldehyde, formaldehyde, and ammonium chloride.

T. H. POPE.

Caffeino-salicylic acid; a molecular compound. N. SCHOORL (Pharm. Weekblad, 1929, 66, 317—358).—Following the preparation of the acid from molecular proportions of caffeine and salicylic acid (Schoorl and Regenbogen, *ibid.*, 1924, 34) the sodium salt $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{C}_7\text{H}_5\text{O}_3\text{Na}\cdot 5\text{H}_2\text{O}$ has been prepared by dissolving the theoretical quantities of caffeine and sodium salicylate in hot water, and allowing to

crystallise. The salt loses its water of crystallisation slowly on the water-bath or in a vacuum.

S. I. LEVY.

Carnegine. E. SPATH [in part with J. PASSEL] (Ber., 1929, 62, [B], 1021—1024; cf. Heyl, this vol., 201).—*N*-Acetylhomoveratrylamine is converted by phosphoric oxide in toluene into 6:7-dimethoxy-1-methyl-3:4-dihydroisoquinoline, transformed by methyl iodide at 100° into the corresponding methiodide, m. p. 176—178° (vac.) [trihydrate, m. p. 100—102°]. Reduction of the hydrate with tin and hydrochloric acid affords 5:6-dimethoxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline, as a colourless, viscous oil, b. p. 170° (bath temp.)/1 mm., in which the position of the methoxyl groups is established by the formation of *m*-hemipinic acid on oxidation. The identity of the synthetic base with carnegine is established by direct comparison of the hydrochlorides, m. p. 210—211°, picrate, m. p. 212—213° (decomp.), 2:4:6-trinitro-*m*-tolyl oxide, m. p. 169—170°, and methiodide, m. p. 210—211° (vac.).

H. WREN.

Alkaloids of Angostura bark. J. TROGER (Pharm. Zentr., 1929, 70, 213—222, 229—239, 245—252).—A critical survey of previous work.

S. COFFEY.

Synthesis of coptisine. E. SPATH and R. POSEGA (Ber., 1929, 62, [B], 1029—1033; cf. Kitasato, A., 1926, 1160).—Palmitine chloride is hydrolysed with fuming hydrochloric acid at 140° and the product is treated in an atmosphere of hydrogen with an excess of methylene iodide and alcoholic sodium ethoxide and then reduced with zinc dust in acid solution; small amounts of an amorphous, tertiary base, which does not contain tetrahydrocoptisine, are thus obtained; replacement of methylene iodide by methylene sulphate effects no improvement. Small amounts of tetrahydrocoptisine, m. p. 228—229° (vac.) (cf. *loc. cit.*), are obtained by heating tetrahydropalmitine with fuming hydrochloric acid and treatment of the product with methylene chloride and sodium methoxide under definite conditions. Protopine is converted by sodium amalgam into the corresponding carbinol base and thence by evaporation of the solution in hydrochloric acid into a quaternary salt from which tetrahydrocoptisine is derived by distillation in a high vacuum. Incidentally to their synthesis of protopine, Haworth and Perkin have prepared a base, m. p. 219°, of the constitution of tetrahydrocoptisine which they describe as 2:3:9:10-dimethylenedioxytetrahydropyroberberine.

H. WREN.

Microchemical reactions of physostigmine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 381—382).—The reactions with sodium salicylate and gold bromide are described; the former will detect 10 mg. at a dilution of 1:200 and the latter 5 mg. at a dilution of 1:500.

S. I. LEVY.

Acids obtained from brucine by oxidation with chromic acid. H. WIELAND and W. MUNSTER (Annalen, 1929, 469, 216—224).—Oxidation of brucine with chromic acid in dilute sulphuric acid solution first at 60—70° and then at 100° gives two monobasic acids, (a) $\text{C}_{17}\text{H}_{22}\text{O}_6\text{N}_2$ (+5H₂O), darkens at 250—280°, not melted at 345°, $[\alpha]_D^{25} +49.2^\circ$ in water (hydrochloride,

m. p. above 320° ; *hydrobromide*; *hydriodide*; *chloroplatinate*), and (b) $C_{16}H_{20}O_4N_2$ (+2 or $4H_2O$), m. p. 311° (decomp.) after darkening at 250° and sintering at 307° , $[\alpha]_D -116.3^{\circ}$ in water (*hydrobromide*, decomp. 286° ; *chloroplatinate*). This last substance is identical with the acid, $C_{16}H_{18}O_4N_2$, described by Hanssen (A., 1885, 276, 1146), and is formed by degradation of the benzene nucleus. The original double linking is unaffected.

H. BURTON.

Determination of brucine as silicotungstate and analysis of nux vomica. B. KLJATSKHINA and M. STRUGADSKI (Arch. Pharm., 1929, 267, 177—192).—Stuber and Kljatschkina (A., 1928, 532) showed that the composition of strychnine silicotungstate depended on the conditions of precipitation. It is now found that brucine silicotungstate is similarly of variable composition. When it is precipitated from neutral solution the molecular ratio of base to complex acid is as high as 4 : 1; this ratio falls with increase in the acid (hydrochloric or nitric, but not acetic) concentration of the solution, until in 20% hydrochloric acid it becomes 1.5 : 1. The ratio is also lowered when the solution contains salts of strong electrolytes or an excess of the precipitant, and it is further dependent on the temperature of precipitation. Precipitates with high ratio, as from neutral solution, are colloidal in nature. The precipitate, however, always has the same composition when the conditions of precipitation are the same. It is recommended that the precipitation be carried out at the ordinary temperature, in 1% hydrochloric acid, and that the exact amount of precipitant to use be determined by a preliminary series of titrations, in which the filtrates are tested for alkaloid or silicotungstic acid. The precipitate will then have the composition: 3.5 (brucine) $12WO_3 \cdot SiO_2 \cdot 2H_2O + 8H_2O$. Strychnine yields under the same conditions a precipitate of similar composition, so that the conversion factors (weight of ash : weight of alkaloid) become 0.4849 and 0.411, respectively. Brucine can be detected at a concentration of 1 in 160,000 and strychnine at a concentration of 1 in 220,000 by this method. Details are given for analysing nux vomica both gravimetrically and volumetrically.

W. A. SILVESTER.

Synthesis of *r*-corydaline. E. SPATH and E. KRUTA (Ber., 1929, 62, [B], 1024—1029).—Papaverine is converted by 40% aqueous formaldehyde at 125° into methylenepapaverine, m. p. 154 — 155° , hydrogenated in presence of palladised charcoal to methylpapaverine, m. p. 154° . Reduction of the last-named compound at a lead cathode gives *methyltetrahydro-papaverine*, $(C_{21}H_{27}O_4N)_2 \cdot H_2O$, m. p. 93 — 95° (decomp.) (also *anhydrous*); the corresponding *picrate* has m. p. 215 — 216° (vac., decomp.). Treatment of the bases with fuming hydrochloric acid at 150 — 155° causes complete hydrolysis of the methoxyl groups and production of the *hydrochloride*, $C_{17}H_{20}O_4NCl$, m. p. 238 — 240° (also *monohydrate*). This is condensed with formaldehyde and the free base so produced is treated in methyl alcohol with diazomethane. The mixture of methylated products gives 10% of *mesocorydaline* when crystallised from ether at 0° . Separation of the remaining material into its components could not be effected by fractional extraction

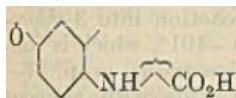
with hydrochloric acid, crystallisation, or by means of salts. Separation of tertiary bases of the type of tetrahydropalmatine from other bases is effected by treatment with alcoholic iodine, giving yellow quaternary iodides which are transformed into the more readily separable tetrahydro-compounds by zinc and acetic acid. Fractional precipitation of the acid solution of these bases by potassium bromide yields precipitates from which *r*-corydaline can be extracted in small amount.

H. WREN.

New strychnos alkaloid [vomicine]. I. H. WIELAND and G. OERTEL (Annalen, 1929, 469, 193—215).—A new alkaloid has been obtained as a by-product in the isolation of strychnine and is named *vomicine* (I), $C_{22}H_{24}O_4N_2$, m. p. 282° , $[\alpha]_D^{25} +80.4^{\circ}$ in alcohol [*monohydrochloride* (II), m. p. 245° (decomp.) after darkening and sintering at 210 — 215° ; *benzoyl derivative hydrochloride*, m. p. 182° after darkening at 173°]. When heated with 20% methyl-alcoholic potassium hydroxide solution in absence of oxygen, I yields *vomicinic acid* (III), $C_{22}H_{26}O_5N_2$, sinters at 164° with loss of 1 mol. of water, giving I; in presence of air an intense green solution is obtained which gives a characteristic permanganate coloration with oxidising agents. This acid yields a stable *hydrochloride* in the cold, but in the hot regenerates I, indicating formation of a lactam grouping. When II is treated with bromine water below 20° a perbromide is produced which decomposes into *bromovomicine* (IV), m. p. 306° with darkening; this is converted as above into *bromovomicinic acid*. Methyl iodide has no action on I at 150° , but converts III in alcoholic alkaline solution into a mixture of *N-methylvomicinic acid*, m. p. 254° (*hydrochloride*, m. p. above 320°), and *vomicinic acid betaine*, m. p. about 210° after sintering at 175° , decomp. 230° (*hydrochloride*). The methylated acid is unaffected by hot hydrochloric acid. With methyl sulphate I yields an additive compound (1 : 1) which when crystallised from water loses methyl alcohol forming a *methosulphate* $[I + MeSO_3H]$, m. p. 264° (decomp.); this gives the *hydriodide*, m. p. 260 — 270° (decomp.), of I with aqueous potassium iodide. Reduction of I with hydrogen in presence of platinum oxide and dilute acetic acid affords *dihydrovomicine*, m. p. 290° with darkening, whilst treatment with red phosphorus and hydriodic acid (d 1.96) in acetic acid solution yields *deoxyvomicine* (V), $C_{22}H_{24}O_3N_2$. The presence of a tertiary hydroxyl group is assumed to explain this last change. Catalytic reduction of IV gives *bromodihydrovomicine*, m. p. 280° , whilst V furnishes a mixture of two bases, $C_{22}H_{23}O_3N_2$, m. p. 213° [*methiodide*, m. p. 236° (decomp.)], and $C_{20}H_{20}O_2N$ (VI), m. p. 179° . The elimination of an oxygen atom during this last reduction indicates the presence of an oxide ring in I (cf. Fawcett, Perkin, and Robinson, this vol., 82). Fission of VI into the corresponding acid occurs only with concentrated alkali at 160° ; the acid is then reconverted into VI by short heating with hydrochloric acid. Treatment of VI with bromine in dilute hydrochloric acid gives a *monobromo-derivative*, m. p. 159° . Treatment of dihydrovomicine with red phosphorus, hydriodic and acetic acids yields *iododihydrodeoxyvomicine*, $C_{22}H_{25}O_3N_2I$, decomp. 242° , which when boiled with alcoholic potassium hydroxide

solution furnishes a halogen-free substance, and when treated with zinc dust and alcohol containing a small amount of acetic acid affords *dihydrodeoxyvomine*, m. p. 210°.

Oxidation of I with chromic anhydride in 4*N*-sulphuric acid solution at 70° gives an acid, $C_{16}H_{20}O_3N_2$, m. p. 304° (decomp.) after sintering and colouring at 285°; when oxidation is carried out first in the cold and then successively at 50—90°, two acids, $C_{17}H_{22}O_7N_2$ and $C_{17}H_{22}O_5N_2$, m. p. 262° (decomp.) and 312—314 (decomp.), respectively, are obtained. The annexed grouping is probably present in III and when oxidised gives a coloured quinonoid oxonium salt. H. BURTON.



Synthetical experiments on the aporphine alkaloids. V. Laurotetanine. Syntheses of 2:3:6:7- and 3:4:6:7-tetramethoxyaporphines. R. K. CALLOW, J. M. GULLAND, and R. D. HAWORTH (J.C.S., 1929, 658—670).—The constitution assigned by Gorter (A., 1921, i, 587) to the (supposed) dimethyl derivative of laurotetanine, *isoglaucine*, as 2:3:6:7-tetramethoxyaporphine (cf. Spath and Strauhl, also Barger and Silberschmidt, this vol., 80) has been shown to be incorrect by synthesis of this compound. As the result of a comprehensive study of the colour reactions of the aporphines, on which Gorter partly based his suggestion, the isomeric 3:4:6:7-tetramethoxy-base was also synthesised; neither substance resembles *isoglaucine*.

β -2:3-Dimethoxyphenylpropionamide, m. p. 98—99°, b. p. 233—235°/16 mm., obtained in 95% yield from the corresponding acid chloride and ammonia (cf. Haworth, A., 1927, 1088) or from methyl β -2:3-dimethoxyphenylpropionate, b. p. 166—176°/15 mm., and ammonia, was converted into β -2:3-dimethoxyphenylethylamine (I), b. p. 158—159°/25 mm., as described by Haworth (*loc. cit.*). 6-Nitro-3:4-dimethoxyphenylacetic acid, m. p. 206—207°, was obtained by nitrating 3:4-dimethoxyphenylacetic acid in glacial acetic acid, and also from 6-nitrohomoveratrole by way of 6-nitro-3:4-dimethoxyphenylpyruvic acid by a modification of the method of Oxford and Raper (A., 1927, 365), improved yields, 77% and 83%, respectively, being recorded for both stages of the process. Greatly enhanced reactivity is displayed by derivatives of 6-nitrohomoveratrole as compared with those of 2-nitrohomoveratrole (cf. A., 1928, 532); thus 6-nitro-3:4-dimethoxyphenylacetyl chloride is very unstable (cf. A., 1928, 781) and a mixture of 6-nitro-3:4-dimethoxyphenylacetic acid and I at 130° gives pure 6-nitrohomoveratrole in theoretical yield, whilst no reaction occurs between 2-nitro-3:4-dimethoxyphenylacetic acid and I below 175°. 6'-Nitro-3':4'-dimethoxyphenylaceto- β -2:3-dimethoxyphenylethylamide, m. p. 144.5—145.5°, obtained by addition of a chloroform solution of 6-nitro-3:4-dimethoxyphenylacetyl chloride to a mixture of a chloroform solution of I and a dilute solution of sodium hydroxide at 0°, was converted by phosphorus pentachloride in cold chloroform suspension into 6'-nitro-3:4':5:6-tetramethoxy-1-benzyl-3:4-dihydroisoquinoline, melting at 187.5—189.5° to a deep red liquid which became colourless on resolidification.

This base yielded a *methiodide*, which appears to be dimorphous (*red* and *yellow* forms, m. p. variable), and by reduction with zinc dust and hydrochloric acid, followed by treatment of the product with dry hydrogen chloride in chloroform-ether solution, afforded 6'-amino-3':4':5:6-tetramethoxy-1-benzyl-2-methyltetrahydroisoquinoline dihydrochloride, m. p. 233.5—235° (decomp.), diazotised in methyl-alcoholic sulphuric acid to yield dl-2:3:6:7-tetramethoxyaporphine, m. p. 115.5—116.5° [*methiodide*, m. p. 204—208°; *hydriodide*, m. p. 227.5—230.5° (decomp.)]. The base could not be resolved by means of *d*- and *l*-tartaric acids, and gave colour reactions with sulphuric acid, nitric acid, Mandelin's, Frohde's, and Erdmann's reagents which did not resemble those described by Gorter for *isoglaucine*.

2-Nitro-3:4-dimethoxyphenylacetyl chloride when condensed with I in cold dry benzene gave 2'-nitro-3':4'-dimethoxyphenylaceto- β -2:3-dimethoxyphenylethylamide, m. p. 95—96°, converted by phosphorus pentachloride in chloroform suspension into 2'-nitro-3':4':5:6-tetramethoxy-1-benzyl-3:4-dihydroisoquinoline, melting at 152—156° to a red liquid [*methiodide*, m. p. 183—184° (decomp.) (*compound* + *n*MeI, m. p. 110—116°)]. The *methiodide* of the base was reduced with zinc and hydrochloric acid to 2'-amino-3':4':5:6-tetramethoxy-1-benzyl-2-methyltetrahydroisoquinoline, m. p. 117.5—119.5°, which when diazotised in methyl-alcoholic sulphuric acid yielded dl-3:4:6:7-tetramethoxyaporphine, m. p. 131—132° (*hydriodide*, m. p. 257—262°). Resolution of the *dl*-base with *d*- and *l*-tartaric acids gave *d*-3:4:6:7-tetramethoxyaporphine hydrogen *d*-tartrate, $[\alpha]_D^{25} +84.9^\circ$, as the hygroscopic *dihydrate*, m. p. 174—185°, and *l*-3:4:6:7-tetramethoxyaporphine hydrogen *l*-tartrate, $[\alpha]_D^{25} -85.2^\circ$, as the *dihydrate*, m. p. 170—180°, from which *d*-3:4:6:7-tetramethoxyaporphine, m. p. 125—125.5°, $[\alpha]_D^{25} +168^\circ$, and *l*-3:4:6:7-tetramethoxyaporphine, m. p. 125.5—126°, $[\alpha]_D^{25} -167^\circ$ (*methiodide*, m. p. 208—210°), were obtained respectively.

The colour reactions of the aporphine alkaloids with Mandelin's, Erdmann's, and Frohde's reagents and with sulphuric acid and nitric acid are given in tabular form.

C. W. SHOPPEE.

Trypanocidal activity and chemical constitution. I. New sulphur derivatives of aromatic organic arsenicals. J. G. EVERETT (J.C.S., 1929, 670—679).—Thiocarbonyl compounds described below have been compared with the analogous carbonyl compounds for trypanocidal action; substitution of sulphur for oxygen causes no appreciable difference in toxicity or therapeutic activity (cf. A., 1926, 1173), and permanence of cure is uninfluenced except in those compounds containing arsenic in the 5-position of a 2-thiolbenzimidazole ring, which are outstandingly efficacious. *p*-Arsanilic acid boiled with alcoholic alkali and carbon disulphide affords *pp'*-dithiocarbaminophenylarsenic sesquisulphide (I), hydrolysed by boiling 25% sodium hydroxide to *diphenylthiocarbamide-pp'*-arsenic sesquisulphide (II); reduction of I by sodium hyposulphite at 55° yields *pp'*-dithiocarbiminoarsenobenzene (III), which is completely soluble in cold 5% sodium hydroxide solution, and by hydrolysis with this reagent affords

pp'-*arseno(diphenylthiocarbamide)* (IV), also obtained by reduction with sodium hyposulphite from II (62% yield) or III, and by simultaneous hydrolysis and reduction of I with sodium hydroxide and sodium hyposulphite at 90°, as an orange, amorphous solid insoluble in sodium hydroxide. By treatment with iodine IV gives a 42% yield of *diphenylthiocarbamide*-pp'-*diarsinic acid* (V) (calcium, magnesium, and barium salts), also prepared by iodine oxidation of II (yield 31%), or by treatment of *p*-arsanilic acid with thiocarbonyl chloride (yield 69%); V is reduced by sodium hyposulphite, regenerating IV (yield 71%), and is further oxidised by iodine in the presence of sodium hydrogen carbonate to give a 43% yield of *diphenylcarbamide*-pp'-*diarsinic acid* (calcium, magnesium, and barium salts), also obtained from *p*-arsanilic acid and carbonyl chloride. Conversion analogous to the change III \rightarrow IV also occurs among the non-arsenated compounds; thus phenylthiocarbimide is completely converted into thiocarbimide by boiling 20% sodium hydroxide (1 hr.).

1-*Thiobenzoxazolone-4-arsenic disulphide* (VI) is obtained in 64% yield from 3-amino-4-hydroxyphenylarsinic acid by treatment with carbon disulphide and alcoholic sodium hydroxide. It is readily soluble in dilute sodium cyanide solution, and is reduced by sodium hyposulphite to 4:4'-*arseno-(1-thiobenzoxazolone)* (VII), a yellow, amorphous powder readily soluble in dilute sodium cyanide. Both VI and VII are oxidised by iodine to 1-*thiobenzoxazolone-4-arsinic acid* (VIII) (magnesium salt), also obtained from 3-amino-4-hydroxyphenylarsinic acid and thiocarbonyl chloride (yield 78%), and reconverted into VII by sodium hyposulphite. The acid VIII reacts further with iodine in the presence of sodium hydrogen carbonate giving benzoxazolone-4-arsinic acid (yield 77%), also prepared from 3-amino-4-hydroxyphenylarsinic acid and carbonyl chloride (Fargher, J.C.S., 1919, 115, 991). Similarly, 3:4-diaminophenylarsinic acid affords 2-*thiolbenziminazole-5-arsenic disulphide* (yield 64%), reduced by sodium sulphite to 5:5'-*arseno-(2-thiolbenziminazole)* (IX) (72% yield); both these compounds by iodine oxidation give 2-*thiolbenziminazole-5-arsinic acid* (X) (calcium, magnesium, and barium salts), which is also obtained from 3:4-diaminophenylarsinic acid and thiocarbonyl chloride (yield 78%), and is reconverted by sodium hyposulphite into IX. Further oxidation of X with iodine and sodium hydrogen carbonate gives benziminazole-5-arsinic acid (yield 83%).

In order to compare the effects of oxygen and sulphur in analogous compounds, the following were prepared: pp'-*arseno(diphenylcarbamide)* by reduction of diphenylcarbamide-pp'-*diarsinic acid* with sodium hyposulphite; 2:3-dihydrobenziminazolone-5-arsinic acid (calcium, magnesium, and barium salts) (cf. Berthelm, A., 1911, i, 1055) giving 5:5'-*arseno-(2:3-dihydrobenziminazolone)* by reduction with sodium hyposulphite. C. W. SHOPPEE.

10-Chloro-5:10-dihydrophenarsazine and its derivatives. VII. Synthesis of the 1-methyl and 3-methyl homologues. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1929, 767—787).—Attempts to differentiate between the alternative formation of

1- or 3-substituted isomerides by ring closure of *m*-substituted diphenylamines with arsenious chloride, or of substituted diphenylamine-*o*-arsinic acids by reduction, has led to inconclusive results, and a series of apparent identities is described.

3-Amino-*p*-tolylarsinic acid, m. p. 184—185°, obtained by a slight modification of the method of Jacobs, Heidelberger, and Rolf (A., 1919, i, 50), is converted by the Sandmeyer reaction into 3-*chloro-p*-tolylarsinic acid (I), m. p. 189—191°, which is convertible into 3-*chloro-p*-tolylidichloroarsine, m. p. 27—29°, b. p. 166—167°/17 mm.; this with aqueous ammonia gives 3-*chloro-p*-tolylarsenious oxide, m. p. 277°, soluble in sodium hydroxide and reprecipitated by carbon dioxide (distinction from I). 3-Bromo-*p*-tolylarsinic acid (II), m. p. 208—210° (decomp.) [calcium, barium, mercurous, silver (soluble in ammonia), and mercuric salts], is similarly prepared and converted into 3-bromo-*p*-tolylidichloroarsine, m. p. 47—49°, b. p. 176—177°/14 mm., which with aqueous ammonia affords 3-bromo-*p*-tolylarsenious oxide, m. p. 266—268°, soluble in sodium hydroxide but insoluble in sodium carbonate. By oxidation with boiling alkaline potassium permanganate, I yields 2-*chloro-4-carboxyphenylarsinic acid*, m. p. above 310° [calcium, barium, mercurous, silver (soluble in ammonia), and mercuric salts]; 2-bromo-4-carboxyphenylarsinic acid, m. p. above 317°, similarly obtained from II, condenses readily with aniline giving 3-methyldiphenylamine-6-arsinic acid (III), m. p. 158—159° [sodium, potassium, ammonium, calcium, barium, magnesium, lead, mercurous, silver (soluble in ammonia), and mercuric salts], which is very easily reduced by sulphur dioxide to 10-*chloro-3-methyl-5:10-dihydrophenarsazine* obtained as a homogeneous product, m. p. 216—216.5°, oxidised with hydrogen peroxide or "chloramine-T" to 3-methylphenarsazinic acid, decomposing slightly at 316° [compound + 1AcOH; sodium salt: hydrochloride, m. p. 232—233° (decomp. turning emerald-green)]; the same hydrochloride appears to be obtained directly from III by boiling with excess of concentrated hydrochloric acid. When 3-methylphenarsazinic acid is reduced with sulphur dioxide in hydrobromic acid-alcoholic solution, 3-methyl-*o*:10-dihydrophenarsazine, m. p. 206—208°, is obtained.

3-Amino-*o*-tolylarsinic acid (IV), prepared according to the method of Jacobs, Heidelberger, and Rolf (*loc. cit.*), was accompanied by a substance, m. p. 11°, which was not identical with *m*-toluidine arsenate, m. p. 141—144°; IV (Sandmeyer reaction) furnishes 3-*chloro-o*-tolylarsinic acid, m. p. 236—239° (decomp.) (silver, mercurous salts), slowly reduced by sulphur dioxide in boiling hydrochloric acid solution to 3-*chloro-o*-tolylidichloroarsine, m. p. 37.5°, b. p. 156°/11 mm., which is converted by aqueous ammonia into 3-*chloro-o*-tolylarsenious oxide, melting at 234—237° to a turbid liquid which clears at 254°. 3-Bromo-*o*-tolylarsinic acid (V), melting below 260° with apparent conversion into an anhydride, m. p. above 306° (calcium, barium magnesium, lead, silver, and mercurous salts), is similarly obtained from IV, and is very slowly reduced by sulphur dioxide in boiling alcoholic hydrochloric acid to 3-bromo-*o*-tolylidichloroarsine, m. p. 25—27°, b. p. 170—171°/13 mm., which affords 3-bromo-*o*-tolylarsenious oxide, m. p. 214—219°, when

treated with aqueous ammonia. Condensation of V with aniline yields 3-methyldiphenylamine-2-arsinic acid (VI), m. p. 170—171° (decomp.) (ammonium, calcium, barium, magnesium, lead, mercurous, silver, and mercuric salts), somewhat difficultly reduced by sulphur dioxide to 10-chloro-1-methyl-5:10-dihydrophenarsazine, m. p. 216—216.5°, which is oxidised by alkaline potassium permanganate to 1-methylphenarsazinic acid, m. p. 316° (decomp.) [sodium salt; hydrochloride, m. p. 231—232° (decomp. turning emerald-green)]; the same hydrochloride was also obtained from VI by boiling with concentrated hydrochloric acid.

o-Bromophenylarsinic acid condenses with *m*-toluidine to yield 3-methyldiphenylamine-6'-arsinic acid (VII), m. p. 141—142° (sodium salt), reduced by sulphur dioxide in hot alcoholic hydrochloric acid solution to 1- and/or 3-methyl-10-chloro-5:10-dihydrophenarsazine, m. p. 216—217°, obtained as a homogeneous product identical with the reduction product of III; the substance is oxidised by hydrogen peroxide or "chloramine-T" to a product indistinguishable from synthesised 1-methyl- or 3-methyl-phenarsazinic acids. The action of concentrated hydrochloric acid on VII affords a hydrochloride, m. p. 232—233° (decomp. turning emerald-green), indistinguishable from the hydrochloride of either 1-methyl- or 3-methyl-phenarsazinic acid. Hot 50% sulphuric acid appears to convert VII into 3-methylphenarsazinic acid. Reduction of 1- and/or 3-methylphenarsazinic acid with sulphur dioxide in boiling alcoholic hydrobromic acid gives 1- and/or 3-methyl-10-bromo-5:10-dihydrophenarsazine, apparently identical (direct comparison and mixed m. p.) with the genuine 3-methyl compound. The solubilities of 10-chloro-1-methyl- and -3-methyl-5:10-dihydrophenarsazines in benzene are approximately the same, viz., about 0.3% at the ordinary temperature and about 3% at the b. p.

3-Nitro-*p*-tolylchloroarsine, m. p. 113°, may be obtained by sulphur dioxide reduction of 3-nitro-*p*-tolylarsinic acid. 3-Nitro-*o*-toluidine (cf. Gabriel and Thieme, A., 1919, i, 398) is converted by the method of Jacobs, Heidelberger, and Rolf (*loc. cit.*) into 3-nitro-*o*-tolylarsinic acid, m. p. above 300° (sodium hydrogen salt + 6H₂O, m. p. 97°), which by reduction with sulphur dioxide affords 3-nitro-*o*-tolylchloroarsine, m. p. 93°; the corresponding 3-nitro-*o*-tolyl-dibromoarsine, m. p. 116.5—117.5°, is obtained by reduction with hydrobromic acid (*d* 1.49) containing a trace of iodine. C. W. SHOPPEE.

Organic compounds of mercury. I. Synthesis of aromatic organomercury salts. A. N. NESMEJANOV. II. Preparation of symmetrical, aromatic, organomercury compounds. A. N. NESMEJANOV and E. J. KAHN (Ber., 1929, 62, [B], 1010—1018, 1018—1020).—The double salts of diazonium compounds and mercuric halides decompose in the presence of copper powder with formation of mercuric aryl halides. If substituents are present in the benzene nucleus, the best yields are obtained when they are most positive in character, whereas strongly negative substituents inhibit more or less completely the production of mercury derivatives. The results depend also on the nature of the solvent used. Acetone is generally most useful. The change proceeds

according to the equation $\text{PhN}_2\text{Cl} \cdot \text{HgCl}_2 + 2\text{Cu} = \text{HgPhCl} + \text{N}_2 + 2\text{CuCl}$. The diazonium double salts are prepared (I) by mixing a diazotised solution of the amine in hydrochloric acid with a solution of mercuric chloride in the same solvent, (II) by adding a large excess of sodium nitrite to mercuric chloride dissolved in hydrochloric acid and shaking the solution with the amine in ether, and (III) by diazotising the amine hydrochloride with amyl nitrite in alcohol containing hydrochloric acid and pouring the resulting solution into ethereal mercuric chloride. The double salts, mixed with the requisite amount of copper powder, are decomposed by agitation at the ordinary temperature with a suitable solvent, generally ether. The following mercury compounds are described: the phenyl iodide, m. p. 269°; the phenyl chloride, m. p. 258°, and the parent diazonium compound, $\text{PhN}_2\text{Cl} \cdot \text{HgCl}_2$; the *o*-tolyl chloride, m. p. 143°, and salt, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{Cl} \cdot \text{HgCl}_2$; the *p*-tolyl chloride, m. p. 238—239°, and salt, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{Cl} \cdot \text{HgCl}_2$, m. p. 107° (decomp.) when rapidly heated; the α -naphthyl chloride, m. p. 191, and salt, $\text{C}_{10}\text{H}_7\text{N}_2\text{Cl}_3\text{Hg}$, m. p. 120—121° (decomp.); the β -naphthyl chloride, m. p. 270°, and salt, $\text{C}_{10}\text{H}_7\text{N}_2\text{Cl}_3\text{Hg}$, m. p. 120—125° (decomp.); the *p*-hydroxyphenyl chloride, m. p. 226—227°, and salt, $\text{C}_6\text{H}_5\text{ON}_2\text{Cl}_3\text{Hg}$, m. p. 156°; the *o*-anisyl chloride, m. p. 180—181°, and salt, $\text{C}_7\text{H}_7\text{ON}_2\text{Cl}_3\text{Hg}$, m. p. 121.5°; the *p*-phenetyl chloride, m. p. 249—250°, and salt, $\text{C}_8\text{H}_9\text{ON}_2\text{Cl}_3\text{Hg}$, m. p. 109°; the *p*-chlorophenyl chloride, m. p. 240°, and salt, $\text{C}_6\text{H}_4\text{N}_2\text{Cl}_4\text{Hg}$, m. p. 124.5°; the *p*-bromophenyl chloride, m. p. 249.5°, and salt, $\text{C}_6\text{H}_4\text{N}_2\text{Cl}_3\text{BrHg}$, decomp. 119°; the *p*-iodophenyl chloride, m. p. 272.5°, and salt, $\text{C}_6\text{H}_4\text{N}_2\text{Cl}_3\text{IHg}$, m. p. 120—121.5° (decomp.); the 2:5-dichlorophenyl chloride, m. p. 208°, and salt, $\text{C}_6\text{H}_3\text{N}_2\text{Cl}_5\text{Hg}$, m. p. 147—148°. Methyl *o*-chloromercuribenzoate, m. p. 184—185°, and the diazonium salt, $\text{C}_6\text{H}_7\text{O}_2\text{N}_2\text{Cl}_3\text{Hg}$, m. p. 121°, are described. 2:4:6-Tribromoaniline gives a diazonium double compound, $\text{C}_6\text{H}_3\text{Cl}_3\text{Br}_3\text{N}_2\text{Hg}$, m. p. 146°, from which the mercury compound could not be obtained. Diazotised *p*-nitroaniline gives a double salt, $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_6\text{Cl}_4\text{Hg}$, m. p. 106—107°, converted by ethereal mercuric chloride into the compound, $\text{C}_6\text{H}_4\text{O}_2\text{N}_3\text{Cl}_3\text{Hg}$, m. p. 102—103°; either compound in ether yields minute amounts of mercury *p*-nitrophenyl chloride, m. p. 267—269°. Diazotised *p*-amino-benzoic acid affords the double salt, $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_4\text{Cl}_4\text{Hg}$, which does not yield a corresponding mercury compound.

II. The additive compounds of diazonium and mercuric chlorides, mixed with copper powder, are covered with cooled acetone or alcohol; when the first, energetic action has subsided, 25% aqueous ammonia is added and the mixture is preserved for 12—24 hrs. The change follows the course $2\text{ArN}_2\text{HgCl}_3 + 6\text{Cu} = \text{Ar}_2\text{Hg} + \text{Hg} + 6\text{CuCl} + 2\text{N}_2$. The following mercury compounds have been thus prepared in % yields shown in parentheses: diphenyl (65), m. p. 125°; di- α -naphthyl (53), m. p. 249°; di-*p*-tolyl (76), m. p. 243—244°; di-*p*-bromophenyl, m. p. 243—244°; di-*p*-iodophenyl (70), m. p. 270—272°; di-2:5-dichlorophenyl, (20), m. p. 237°; di-*o*-anisyl (60), m. p. 108°; di-*p*-nitrophenyl (10), decomp. 320°.

H. WREN.

Bases and mercurated anilines. F. C. WHITMORE, E. R. HANSON, and F. L. CARNAHAN (J. Amer. Chem. Soc., 1929, 51, 894—900).—Dialkylanilines are converted by mercuric acetate in aqueous alcohol into *p*-acetoxymercuri-derivatives. These yield in aqueous alcohol with calcium chloride and sodium bromide, respectively, *p*-chloromercuri- and *p*-bromomercuri-derivatives, and with sodium iodide (1 mol.) in cold acetone, *p*-iodomercuri-derivatives. Excess of sodium iodide yields the mercury tetra-alkyldiaminodiphenyls, which are also obtained with sodium thiosulphate. With potassium hydroxide (32 mols.) in boiling aqueous alcohol small amounts of the mercury diphenyls are again formed, together with dialkylaminophenylmercuric hydroxides and oxides, mercury and its oxides, and ethane hexamercarbide, but with sodium ethoxide or aqueous ammonia (cf. Pesci, A., 1898, i, 648) mercury diphenyls are not obtained. The following are described: *p*-Acetoxymercuri-derivatives of dimethyl-, m. p. 165°, diethyl-, m. p. 105°, di-*n*-propyl-, m. p. 99°, di-*n*-butyl-, m. p. 89—90°, methylethyl-, m. p. 92—93°, and benzylethyl-, m. p. 92—94°, -aniline, and the corresponding mercury tetra-alkyldiaminodiphenyls, m. p. 168°, 161°, 86°, 79—80°, 139—142°, and 128°; *p*-chloromercuri-derivatives of diethyl-, m. p. 164°, di-*n*-propyl-, m. p. 170—172°, di-*n*-butyl-, m. p. 162—163°, methylethyl-, m. p. 162—166°; and benzylethyl-, m. p. 150—151°, -aniline; *p*-bromomercuri-derivatives of aniline, m. p. 181°, diethyl-, m. p. 158°, di-*n*-propyl-, m. p. 165—167°, di-*n*-butyl-, m. p. 164—165°, methylethyl-, m. p. 154—155°, and benzylethyl-, m. p. 155°, -aniline; *p*-iodomercuri-derivatives of aniline, m. p. 165°, diethyl-, m. p. 120—121°, di-*n*-propyl-, m. p. 150°, di-*n*-butyl-, m. p. 151°, methylethyl-, m. p. 137—138°, and benzylethyl-, m. p. 132—134°, -aniline; the dialkylaminophenylmercuric hydroxides, from dimethyl-, m. p. 152—156°, methylethyl-, m. p. 192—199°, and benzylethyl-, m. p. 158—167°, -aniline, and oxides from dimethyl-, m. p. 180°, diethyl-, m. p. 210—219°, di-*n*-propyl-, m. p. 184—185°, and di-*n*-butyl-, m. p. 170°, -aniline.

H. E. F. NOTTON.

Organo-metallic compounds. I. New class of tin aryl compounds: tin phenyl trihalides. K. A. KOZESCHKOV (Ber., 1929, 62, [B], 996—999).—*Tin phenyl trichloride*, b. p. 142—143°/25 mm., is prepared in 80% yield by heating a mixture of 1 mol. of tin tetraphenyl with 3 mols. of tin tetrachloride for 1½—2 hrs. at 210—220°; at 190° for 1 hr. the yield of trichloride is diminished, whilst that of the dichloride is increased. The last-named compound, m. p. 42°, is formed almost quantitatively from tin tetraphenyl (1 mol.) and tin tetrachloride (1 mol.) at 220° and is converted by 1 mol. of tin tetrachloride at the same temperature into tin phenyl trichloride. In cold water, the trichloride dissolves without decomposition to a clear, acidic solution; it is partly hydrolysed by boiling water. Concentrated hydrochloric acid converts it into benzene and tin tetrachloride. Pyridine, ammonia, and other bases give the corresponding additive compounds. *Tin phenyl tribromide*, from the trichloride and hydrobromic acid (*d* 1.78), has b. p. 182—183°/29 mm. *Tin phenyl tri-iodide* appears to be formed as a heavy, unstable oil by the action of hydriodic acid on the bromide.

H. WREN.

Racemisation. VIII. Action of alkali on proteins; racemisation and hydrolysis. P. A. LEVENE and L. W. BASS (J. Biol. Chem., 1929, 82, 171—190).—The previous work on the action of alkali in varying concentrations on gelatin and caseinogen (A., 1928, 1043) has been repeated and extended to albumin, odestin, and fibrin. None of these proteins except gelatin exhibited the characteristic behaviour of diketopiperazines (*i.e.*, rapid racemisation by 0.1*N*. and rapid hydrolysis by 1.0*N*-alkali), but behaved rather as peptides; the apparent exception in the case of gelatin may be explained by the preponderance of laevorotatory amino-acids in this protein. The diketopiperazine theory of protein structure is further criticised on analytical grounds. In the light of experiments on simple peptides, the differences exhibited by different proteins in their rates of hydrolysis and of racemisation by alkali may be explained on the ground of differences in the nature of the constituent amino-acids and in the order in which they are combined.

C. R. HARRINGTON.

Characterisations of small quantities of proteins by Van Slyke's method. N. NARAYANA and M. SREENIVASAYA (J. Indian Inst. Sci., 1929, 12A, 37—40).—The protein is digested with 20% hydrochloric acid, the product, freed from acid, is made up to a definite volume, and portions are analysed for amide-nitrogen by alkali distillation, for melanin-nitrogen by isolation of melanin and micro-Kjeldahl determination, for hexone bases by precipitation with phosphotungstic acid, and for arginine by the action of arginase. The method is applicable to quantities of about 0.125 g. Analyses of caseinogen and gelatin are given as examples.

R. J. W. LE FÈVRE.

Determination of carbon and carbon dioxide. T. E. FRIEDEMANN and A. I. KENDALL (J. Biol. Chem., 1929, 82, 45—55).—Good results by the wet combustion method are obtainable only when the relative amount of water present is small. An apparatus is described in which organic material is oxidised with chromic acid in presence of a large excess of sulphuric and phosphoric acids, the carbon dioxide being swept by a stream of air into standard sodium hydroxide solution. The method gives practically quantitative results with compounds such as acetic acid and fats which are known to be oxidised only with difficulty.

C. R. HARRINGTON.

Analysis of thiazine eosinates. W. C. HOLMES (Stain Tech., 1929, 4, 49—52).—Moisture is determined by drying at 110°. The thiazine content is determined by dissolving 0.2 g. in 50 c.c. of glacial acetic acid, adding 100 c.c. of alcohol, heating to boiling, and titrating with *N*-titanous chloride in a current of carbon dioxide. The thiazine is thus reduced, whilst the eosin is unaffected. The disappearance of a bluish-green tint in the orange solution gives the end-point. The total dye content is determined by dissolving 0.2 g. in 100 c.c. of alcohol, adding 100 c.c. of water and 50 c.c. of 20% solution of sodium potassium tartrate, heating to boiling, and titrating as before. Under these conditions both the thiazine and the eosin are reduced. The disappearance of the pink tint gives the end-point.

H. W. DUDLEY.

Determination of tin in organic compounds. H. GILMAN and W. B. KING (*J. Amer. Chem. Soc.*, 1929, **51**, 1213—1215).—This extension of the method given for lead (A., 1928, 1041; cf. Krause and Becker, A., 1920, i, 340) is applicable to alkyl and aryl derivatives. Treatment in a large porcelain crucible with 4% bromine in carbon tetrachloride is followed by oxidation with graduated mixtures of sulphuric and nitric acids.

H. E. F. NOTTON.

Methods. IX. L. PINCUSSEN. Determination of halogens in organic substances. W. ROMAN (*Biochem. Z.*, 1929, **207**, 416—425).—A method is outlined for the determination of the iodine, bromine, and chlorine contents of organic substances. The substance is fused with potassium hydroxide and the iodide separated from the bromide and chloride by extraction with alcohol. The iodide is then oxidised

to iodate, potassium iodide added, and the iodine set free titrated with thiosulphate. The bromine liberated by oxidising the chloride-bromide mixture with hydrogen peroxide is extracted with chloroform and allowed to react with iodide, the equivalent amount of iodine being titrated. The chloride is then obtained by difference from the total halide of the bromide-chloride mixture.

P. W. CLUTTERBUCK.

Van Slyke's method [for the determination of amino-acids]. L. ROSENTHALER (*Biochem. Z.*, 1929, **207**, 298—301).—The amounts of nitrogen liberated from a number of nitrogenous substances (substituted amines, amides, hydrazines, semicarbazones, pyrazolones, etc.) by the action of nitrous acid for varying lengths of time are tabulated.

P. W. CLUTTERBUCK.

Biochemistry.

Resorption of carbon dioxide through the skin. S. HEDIGER (*Klin. Woch.*, 1928, **7**, 1553—1557; *Chem. Zentr.*, 1928, ii, 2263).—The resorption of carbon dioxide and the so-called respiration of the skin depend on a diffusion phenomenon.

A. A. ELDRIDGE.

Determination of blood volume in small animals. S. WENT and C. K. DRINKER (*Amer. J. Physiol.*, 1929, **88**, 468—478).—A method for the determination of blood volume after the injection of vital-red is detailed. Only 0.01 c.c. of heparinised blood is required.

B. A. EAGLES.

Rate of sinking of erythrocytes in relation to the Hofmeister ionic series. II. D. VON KLOBUSITZKY (*Biochem. Z.*, 1929, **207**, 80—90; cf. A., 1925, i, 710).—In hypertonic solutions anions alter the electric charge, viscosity, and density of blood-plasma and the volume and density of the erythrocytes according to the Hofmeister salt series. There is complete agreement between the effects on these properties and that on the rate of sinking of the erythrocytes, the most important and dominating factor being the alteration in the electric charge. The cations have only a slight influence on the charge and hence the effects they produce are irregular.

W. MCCARTNEY.

Hæmoglobin and its biological significance. J. BARCROFT (*Naturwiss.*, 1929, **17**, 261—269).—A lecture.

R. A. MORTON.

Iron in the lungs of mammals and the formation of melanin pigments. F. GRANEL and L. HEDON (*Compt. rend. Soc. Biol.*, 1928, **99**, 22—24; *Chem. Zentr.*, 1928, ii, 2039).—A study of the effect of the injection of hæmoglobin into guinea-pigs.

A. A. ELDRIDGE.

Blood pigments. IX. Linking between the protein and the prosthetic group in hæmoglobin. F. HAUROWITZ and H. WAELSCH (*Z. physiol. Chem.*, 1929, **182**, 82—96).—Globin prepared according to the method of Hill and Holden (A., 1927, 67), freed from salts by dialysis, contained 0.05% of an alcohol- or ether-soluble substance (sterol). When warmed to

47° the aqueous solution of the chloride-free dialysate became opalescent; in the presence of salt it coagulated at 47°. The isoelectric point measured by the cataphoresis method was p_H 7.0 in phosphate-buffered solution, 6.9—7.0 in cacodylic acid-sodium cacodylate solution. Dimethylmesohæmin dissolved in methyl alcohol yielded when treated with dialysed globin in the presence of ammonium sulphide first dimethylmeso-oxyhæmoglobin and then dimethylmesohæmoglobin. By the use of titanous tartrate in the Van Slyke gasometric apparatus the synthesised hæmoglobin has been shown to be able to form oxyhæmoglobin with molecular oxygen. The authors could not confirm the compound formation between globin and porphyrin observed by Hill and Holden (*loc. cit.*). Lipase after 24 hrs. caused no change in hæmoglobin which could be measured spectroscopically, whereas trypsin completely hydrolysed the protein portion. Whilst oxyhæmoglobin formed from hæmin and native globin coagulated at 47°, a specimen of the oxyhæmoglobin, from which the globin employed in the synthesis was prepared, coagulated at 63°.

C. C. N. VASS.

Normal bilirubin content in human sera. R. SIVÓ (*Folia Clin. Chim. Micros.*, 1928, **3**, 1—4; cf. Enriques and Sivó, A., 1926, 648).—In the great majority of normal cases the bilirubin content of human serum lies between 0.8 and 1.1 mg.-%, and cases showing more than 1.2 mg.-% are to be regarded as pathological, as also are some individual instances of values below 1.2.

T. H. POPE.

Determination of serum-proteins. Comparison of results obtained by the gravimetric method and determination of nitrogen and of refractive index. C. O. GUILLAUMIN, R. WAHL, and M. L. LAURENCIN (*Bull. Soc. Chim. biol.*, 1929, **11**, 387—399).—The refractometric method gives results varying to some extent with the proportion of globulin present in the serum. The best method is that of Howe (A., 1922, ii, 171) in which the nitrogen in the various fractions is determined.

E. BOYLAND.

Molybdc acid as a precipitant for blood-proteins. S. R. BENEDICT and E. B. NEWTON (J. Biol. Chem., 1929, 82, 5—10).—Molybdc acid may be utilised as a precipitant for blood-proteins under conditions closely analogous to those employed by Folin and Wu (A., 1919, ii, 308) in the case of tungstic acid. The use of molybdc acid is necessary in the determination of ergothioneine and is preferable in the determination of uric acid in blood.

C. R. HARRINGTON.

Occurrence and determination of ergothioneine in human blood. J. A. BEHRE and S. R. BENEDICT (J. Biol. Chem., 1929, 82, 11—15).—Blood is freed from protein with molybdc acid, an aliquot portion of the filtrate is treated with silver lactate, the uric acid is extracted from the precipitate with sodium chloride and hydrochloric acid, and the residue dissolved in sodium cyanide; the resulting solution is treated with the uric acid reagent (A., 1922, ii, 405) and sodium hydroxide, in presence of which the colour given by uric acid is only 1.4 times as great as that given by the same weight of ergothioneine. The colour is compared with that given by a known solution of ergothioneine similarly treated. The average concentration of ergothioneine in human blood is 7.5 mg. per 100 c.c. C. R. HARRINGTON.

"Protein-sugar" of the blood. E. J. BIGWOOD and A. WUILLOT (Compt. rend. Soc. Biol., 1928, 99, 352—356; Chem. Zentr., 1928, ii, 2034).—The difference in reducing power of blood-serum before and after acid hydrolysis is no proof of the presence of a "protein-sugar." A. A. ELDRIDGE.

Determination of true sugar in blood. E. S. WEST, F. H. SCHARLES, and V. L. PETERSON (J. Biol. Chem., 1929, 82, 137—153).—Blood is laked by dilution and treated with mercuric nitrate and the mixture shaken with excess of barium carbonate; the filtrate is freed from barium and mercury with sulphuric acid and hydrogen sulphide; or, better, the laked blood is treated with a solution of 30% mercuric sulphate in 10% sulphuric acid and shaken with barium carbonate, traces of barium and mercury being removed from the filtrate as above, or by treatment with sodium sulphate and zinc dust. Filtrates so prepared from human blood are apparently free from non-dextrose reducing substances, since their direct analysis with the reagent of Somogyi (A., 1927, 69, 1214) gave, except in one pathological case with a high non-protein-nitrogen concentration, figures for the sugar content in close agreement with those obtained by the yeast fermentation method of the latter author. Similar agreement by the two methods was obtained in various animal bloods, although discrepancies occurred with certain samples of pig's blood, which could not be accounted for by the presence of glutathione or of ergothioneine.

C. R. HARRINGTON.

Copper method of determining blood-sugar. O. FOLIN (J. Biol. Chem., 1929, 82, 83—93).—The author's recent method (A., 1926, 648) for the determination of blood-sugar is discussed and certain modifications are suggested. C. R. HARRINGTON.

Lactic acid content of the blood. M. HOCHREIN and R. MEIER (Deut. Arch. klin. Med., 1928, 161,

59—83; Chem. Zentr., 1929, ii, 2101).—Human blood normally contains 6—10 mg.-% of lactic acid; higher values are found after febrile conditions and in certain pathological conditions of the heart and liver. A. A. ELDRIDGE.

Calcium and inorganic phosphorus in the blood of rabbits. IV. Influence of light environment on normal rabbits. W. H. BROWN and M. HOWARD (J. Exp. Med., 1929, 49, 103—126).—The chemical equilibrium of the blood of rabbits, as indicated by the calcium and inorganic phosphorus content, is affected by exposure to neon light.

CHEMICAL ABSTRACTS.

Anticoagulant action of Witte's peptone. J. W. PICKERING (Proc. Roy. Soc., 1929, B, 104, 512—518).—Undisturbed plasma protects platelets against clumping and lysis. The principal influence of small amounts of peptone on blood freshly shed into paraffined vessels is the restraint of changes in the plasma. This reaction, by delaying the disintegration of platelets, assists in the inhibition of blood-clotting.

B. A. EAGLES.

Fats of Japanese birds. I. R. KOYAMA (J. Soc. Chem. Ind. Japan, 1928, 31, 292—296).—The fats obtained from Daurian tern (*Sterna longipennis*, Nordmann), Japanese snipe Mibuto (*Gallinago Mibuto*, Koyama), and Javan buzzard (*Butastur indicus*, Gmelin) have been studied. Males, females, chickens, and adults were examined separately. These fats had m. p. from 29.8° to 41.9°, d_{40}^{20} from 0.887 to 0.912, n_{40}^{20} from 1.464 to 1.471, saponification values from 179 to 196, acid values from 0.08 to 2.67, iodine values from 61 to 103, unsaponifiable matter from 0.53 to 7.94%, and insoluble bromine compounds from 1.88 to 31.08% (Br 52.51—71.53%). The fats of these birds contained some higher unsaturated fatty acids; the saturated fatty acids were apparently chiefly palmitic and stearic acids. The quantity of higher unsaturated fatty acids seemed to increase as the birds grew, and the properties of the fats varied during their breeding season. Y. NAGAI.

Silkworm chrysalis oil. E. DE'CONNO and A. QUARTO (Annali Chim. Appl., 1929, 19, 91—97).—In comparison with oil obtained from the normal chrysalises, that obtained from chrysalises which have been killed with chloropicrin shows little difference in physical and chemical characters, but increased proneness to turn rancid. The lecithum undergoes hydrolysis, stearic acid being liberated; this action of chloropicrin is analogous to that of snake-poison, which causes loss of an oleic residue by the lecithin. T. H. POPE.

Action of bromine on insect oils. J. T. DAVID (Compt. rend., 1929, 188, 1122—1124).—The high iodine values of the oils from the larvæ of certain *Lepidoptera* and *Coleoptera* are given. The action of bromine on these oils was found to give in some cases a small precipitate (2—6%), in others a larger amount (14%), and in some cases none. The presence of linolenic acid in the oil from *Colaspidema atra* was proved by the isolation of hexabromostearic acid after the treatment with bromine.

B. W. ANDERSON.

Transmicroscopic structure of living bodies.
III. Otoliths of *Rana esculenta*. S. FUNAOKA and S. TOYOTA (*Folia anat. Jap.*, 1928, 6, 323—325; *Chem. Zentr.*, 1928, ii, 2158).—The otoliths and the calcium salt in the lime sac consist of aragonite.

A. A. ELDRIDGE.

Colorimetric method of determining guanine : application to determination of nucleocytoplasmic ratios. T. B. ROBERTSON (*Austral. J. Exp. Biol.*, 1929, 6, 33—58).—The oxidation of guanine to guanidine with potassium permanganate and hydrochloric acid and the colorimetric determination of the latter is used as a basis for the determination of guanine. The reagent used comprises 5 c.c. each of 10% solutions of sodium nitroprusside, potassium ferricyanide, and sodium hydroxide, diluted to 60 c.c. with distilled water. Certain oxidation products of guanine depress the colour value obtained; this depression is removed by treatment with alkaline hydrogen peroxide. The application of the method to the determination of nucleic acid in animal tissues is described and the ratio nucleic acid-nitrogen to coagulable protein-nitrogen is suggested as a measure of nucleocytoplasmic ratios.

F. C. HAPFOLD.

Philothion. DE RAY-PAILHADE (*Bull. Soc. Chim. biol.*, 1929, 11, 308—311).—Philothion is a complex protein which evolves hydrogen sulphide at 100° and reduces sulphur to hydrogen sulphide at 30°.

E. BOYLAND.

Seasonal variation in iodine percentage and dry weight of thyroid glands of sheep in Australia. M. C. DAWBARN (*Austral. J. Exp. Biol.*, 1929, 6, 65—77).—A statistical examination of the results of determinations of dry weight and iodine content of 106 sheep's thyroid glands reveals a seasonal variation in the iodine percentage which is 25% less on the average in the early summer months than in the winter. The sex of the animal affects the dry weight but not the percentage iodine content of the thyroids.

F. C. HAPFOLD.

Carbohydrate of rabbit's skeletal muscle. H. HANDOVSKY and K. WESTPHAL (*Pflüger's Archiv*, 1928, 220, 399—409; *Chem. Zentr.*, 1928, ii, 2039).—Values are: total carbohydrate 509—568, glycogen 377—493, lower sugars 39—165 (30% reducing sugar), lactose 123—153 mg.-%.

A. A. ELDRIDGE.

Glycogen content of the liver. I. Determination of the glycogen and carbohydrate content of the liver. E. BURGHARD and H. PAFFRATH (*Z. Kinderheilk.*, 1927, 45, 68—77; *Chem. Zentr.*, 1928, ii, 174—2175).—On account of post-mortem decomposition of glycogen in muscle and liver it is recommended that the total carbohydrate content should be determined and the liver-glycogen calculated from this, the constant difference being 0.23.

A. A. ELDRIDGE.

Chemical examination of a mummy. A. TULLI (*Atti R. Accad. Lincei*, 1929, [vi], 9, 233—237).—Examination of a mummy from the Vatican Museum showed absence of nitre, arsenic, heavy metals, and bitumen. Probably natural balsams were used in the mummifying process.

T. H. POPE.

Regulation of respiration. XXVII. Effect on salivary secretion of varying carbon dioxide and

oxygen content of inspired air. N. B. EDDY (*Amer. J. Physiol.*, 1929, 88, 534—545).—The sub-maxillary gland of the dog was made to secrete at a constant rate by continuous intravenous administration of pilocarpine. Under these conditions, an increased carbon dioxide content of the inspired air produced an increased rate of secretion of saliva and decreased oxygen content a decreased rate of secretion.

B. A. EAGLES.

Regulation of respiration. XXVIII. Lymph acidity and lymph flow during administration of sodium hydrogen carbonate and carbon dioxide. XXIX. Lymph acidity and lymph flow during impaired oxidations produced by cyanide. R. GESELL (*Amer. J. Physiol.*, 1929, 88, 546—553, 554—561).—XXVIII. Intravenous injections of sodium hydrogen carbonate solution decreased the hydrogen-ion concentration of the lymph and blood. Administration of carbon dioxide increased the acidity of the lymph and blood.

XXIX. Cyanide markedly increased the flow of lymph.

B. A. EAGLES.

Mechanism of lymph-formation. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1929, [vi], 9, 243—249).—The differences in chemical constitution and chemico-physical properties between lymph and plasma are explainable in some degree on the assumption that, when the two liquids are separated by a membrane more readily permeable by electrolytes than by colloids, a membrane equilibrium either is established or tends to become established.

T. H. POPE.

Acid-base composition of gastric secretions. J. L. GAMBLE and M. A. McIVER (*J. Exp. Med.*, 1928, 48, 837—847).—A study of the secretion of isolated pouches constructed in the fundus and in the pyloric antrum of the cat's stomach.

CHEMICAL ABSTRACTS.

Acid-base composition of pancreatic juice and bile. J. L. GAMBLE and M. A. McIVER (*J. Exp. Med.*, 1928, 48, 849—857).—The concentration of fixed base in the pancreatic juice is approximately equal to that in the blood-plasma; the concentration of chlorine ion is 25—50% of the fixed base value. In bile as delivered by the liver the concentrations of fixed base and chlorine ion correspond with those in the blood-plasma, whilst in gall-bladder bile the concentration of fixed base is double that of hepatic duct bile and the chlorine ion has almost entirely disappeared.

CHEMICAL ABSTRACTS.

Physical decolorisation of bile. H. WIT (*Biochem. Z.*, 1929, 207, 141—145).—Of adsorbents which are in the form of powders animal charcoal is the best for decolorising bile; kaolin, talc, and kieselguhr are much less active. The efficiency of these powdered adsorbents is increased by the presence of acid and decreased by that of bile acids or of protein. It is chiefly on the electrochemical nature of the adsorbent that the removal of colouring matter depends, but the reaction of the bile also has an important influence on the process.

W. MCCARTNEY.

Iodine as a biogenic element. XVIII. Method of combination of iodine in milk. K. SCHARER and J. SCHWAIBOLD (*Biochem. Z.*, 1929, 207, 332—

340).—Under normal conditions only a small part of the iodine of milk is present as inorganic salts. It is mostly combined with organic substances of the serum. Feeding iodised protein alters the proportions a little, whilst administration of moderate amounts of alkali iodides causes a considerable increase in the inorganic fraction. By feeding di-iodostearic acid, the chief portion of the iodine carried over into the milk is iodised fatty acid or glyceride.

P. W. CLUTTERBUCK.

Composition of liquor folliculi. M. TESTA (Arch. Farm. sperim., 1929, 46, 174—176).—Analysis of two samples of liquor folliculi gave the following results in mg. per 100 g.: free cholesterol, 28.57, 30.07; cholesteryl esters, 27.96, 29.44; neutral fats, 13.46, 12.65; fatty acids, 36.90, 32.42; phosphatides, 34.90, 26.50. About 0.907% of the protein present is precipitable by alcohol but not coagulable by heat and appears to be a mucoid (cf. Testa and Tafuri, Boll. Soc. Biol. sperim., 1927, 2, 893). When isolated by the method used by Needham for the mucoid of hen's eggs (A., 1927, 787) and hydrolysed by means of 20% hydrochloric acid solution, it yields 9.192% of total, 0.392% of melaninic, 3.721% of basic, and 5.075% of amino-nitrogen, and when dissolved in a solution of potassium chloride and hydrochloric acid, it gives 16.49% of reducing substance calculated as dextrose.

T. H. PORE.

Composition of the body fluids of the goosfish (*Lophius piscatorius*). H. W. SMITH (J. Biol. Chem., 1929, 82, 71—75).—The goosfish differs from other teleosts in that its pericardial and perivisceral cavities contain considerable quantities of fluid; these fluids are slightly more alkaline than the blood-serum, but in other respects neither they nor the spinal fluid show marked difference in composition from the serum.

C. R. HARRINGTON.

Determination of organic acids in small amounts of urine and of the basic equivalents combined with the acids. F. MAINZER and A. JOFFE (Biochem. Z., 1929, 207, 167—176).—By means of a modification of the method of Van Slyke and Palmer (A., 1920, i, 459) the organic acids of urine can be determined in a volume of 10 c.c. A process for the titration of the bases combined (at the p_H of the urine) with these acids is also described. The extent of combination of the bases in urine shows no detectable dependence on the p_H .

W. MCCARTNEY.

Acetone and acetoacetic acid in urine. C. OTTO (Pharm. Ztg., 74, 499).—The ethylenediamine test gives with acetone a pale to deep violet colour and with acetoacetic acid an orange to brown colour. In the presence of both substances, the latter is masked by the former. Proof of the presence of acetoacetic acid depends on the sensitiveness of the Jack test, which is not given by acetone. Results obtained from the application of the tests show that the presence of small amounts of acetone in urine can be considered normal.

B. A. EAGLES.

Acetone and acetoacetic acid in urine. P. HORKHEIMER (Pharm. Ztg., 74, 499—500).—A reply to the criticisms of Otto (preceding abstract). In urines containing small amounts of acetone substances

a positive acetone test is due to acetoacetic acid rather than to acetone. Both the Lang and Legal test and the ethylenediamine test are more sensitive to acetoacetic acid than they are to acetone.

B. A. EAGLES.

Determination of laevulose in urine. C. I. KRUISHEER (Biochem. Z., 1929, 207, 441—446).—Laevulose can be determined in urine (after destruction of aldehyde sugars and urinary reducing substances by treatment with alkaline iodine) by determining the reducing power to Fehling's solution with an accuracy of 0.05%.

P. W. CLUTTERBUCK.

Colouring matters of urine. VII. Spectrometric determination of urobilin. M. WEISS (Biochem. Z., 1929, 207, 151—158).—By means of a method described previously (cf. this vol., 91) the urobilin content of urine, faeces, or bile can be quantitatively determined. A spectrometer and a urobilin solution of known concentration are employed. The amount of urobilin which can be determined in 1 day's urine is not less than 0.5 mg.

W. MCCARTNEY.

Upper limit of hydrogen-ion and hydrogen carbonate concentrations of urine. F. MAINZER (Biochem. Z., 1929, 207, 159—166).—Determinations made with urine from women to whom large amounts of hydrogen carbonate had been orally administered and with that from a dog into which sufficient sodium carbonate to produce alkali poisoning had been intravenously injected show that the p_H of urine cannot exceed 8.3. The amount of hydrogen carbonate excreted in the urine is simply related (at constant carbon dioxide tension) to the p_H . The maximum possible concentration of hydrogen carbonate in urine is 536 millimol.-%, but this concentration is influenced by other factors than the p_H .

W. MCCARTNEY.

Anæmia as an avitaminosis. O. STINER (Mitt. Lebensm. Hyg., 1928, 19, 79—84; Chem. Zentr., 1928, ii, 2261).

Metabolism in pernicious anæmia. H. L. ALT (Arch. Int. Med., 1929, 43, 488—503).—Patients with pernicious anæmia showed negative nitrogen balance. Positive nitrogen balances occurred shortly after treatment with liver extract was begun. The output of nitrogen decreased definitely about the time of the rise in the number of reticulocytes.

B. A. EAGLES.

Analysis of the liquid from a splenic cyst. S. GRILLON (J. Pharm. Chim., 1929, [viii], 9, 23—25).—See this vol., 342.

Diabetes insipidus. III. The diuretic substance. H. BOURQUIN (Amer. J. Physiol., 1929, 88, 519—528).—Experimental diabetes insipidus in dogs gives rise to a greatly increased amount of diuretic substance in the urine. This substance has also been demonstrated in extracts of the mammillary bodies and thalamus of the brains of normal animals.

B. A. EAGLES.

Microchemistry of the nervous system. II. Cerebral water, nitrogen, sulphur, and phosphorus in experimental traumatic encephalitis. R. M. MAY (Bull. Soc. Chim. biol., 1929, 11, 312—332).—On degeneration after trauma of the cerebra

hemisphere, the sulphur, nitrogen, and water contents of the nervous tissue increased, whilst the amount of total phosphorus decreased. The increased sulphur may be due to the increased oxidation in the degenerating cells, the nitrogen may be due to blood, whilst the decrease in phosphorus is probably caused by decomposition of phosphatides. E. BOYLAND.

Ehrmann's alcohol test for examining the gastric functions. P. INTROZZI (*Folia Clin. Chim. Micros.*, 1928, 3, 44—64).—This test possesses distinct practical advantages over others, the alcohol furnishing an adequate stimulus for developing the maximum secretory capacity of the gastric mucous membrane. The test renders possible the study of all the gastric functions, and, to some extent, of the mobility of the stomach itself. It serves also indirectly for the examination of the function of the liver (bile) and pancreas and of the effect of duodenal reflux in the stomach. Chemical, histological, and, since the alcohol administered is readily sterilised, bacteriological investigations are also possible with its help. T. H. POPE.

"Haff disease." G. LOCKEMANN (*Biochem. Z.*, 1929, 207, 194—216).—A previously unknown disease ("Haffkrankheit") which broke out in the Frische Haff region in 1924 was believed to have been caused by the presence of a volatile arsenic compound in the atmosphere. The belief is erroneous. The disease was probably caused by products of putrefaction derived from sewage and consumed by eels which were used as food. W. MCCARTNEY.

Lactic acid of the blood in hepatic disease. H. SCHUMACHER (*Klin. Woch.*, 1928, 7, 1733—1737; *Chem. Zentr.*, 1928, ii, 2161).—In severe hepatic disease the blood-lactic acid value is high, and falls only slowly after intravenous administration of sodium lactate. A. A. ELDRIDGE.

Hypertension and blood-sugar. E. WIECHMANN (*Deut. Arch. klin. Med.*, 1928, 61, 92—109; *Chem. Zentr.*, 1928, ii, 2161).

Variations of blood-sugar in disease. Effect of potassium iodide and thyroid preparations on the blood-sugar curve. O. HOLSTI (*Acta Med. Scand.*, 1927, 66, 443—446; *Chem. Zentr.*, 1928, ii, 2161).—In most acute diseases the blood-sugar level is higher than the normal; after administration of dextrose (10 g.) the curve falls more slowly than normally. In chronic diseases the relation is not simple. Potassium iodide has no influence on the blood-sugar level. Thyroid gland preparations raise the blood-sugar. A. A. ELDRIDGE.

Changes in the mineral constituents of the blood in experimental nephritis. Serum-potassium and -calcium. A. BOLLIGER and F. BREH (*Zentr. inn. Med.*, 1928, 49, 825—831; *Chem. Zentr.*, 1928, ii, 2161).—In interstitial nephritis caused by irradiation of the kidneys with X-rays, the blood-potassium and inorganic phosphate are increased, the alkali reserve is frequently markedly diminished, whilst the blood-calcium may be increased or decreased. A. A. ELDRIDGE.

Distribution of the globulin and albumin fractions in the blood and urine [of children] in

nephrosis. F. W. SCHULTZ and M. R. ZIEGLER (*Amer. J. Dis. Children*, 1928, 36, 756—763).—The total plasma-protein is decreased, and the cholesterol increased; the albumin:globulin ratio is lowered or inverted. During nephrosis the non-protein-nitrogen of the blood varies from 19.6 to 43.2 mg. per 100 c.c. The urine may contain fat and globulin as well as albumin, the concentration of the globulin eventually exceeding that of the albumin. CHEMICAL ABSTRACTS.

Chloride, sugar, and calcium content of the cerebrospinal fluid in children. A. V. NEALE and M. S. ESSLEMONT (*Arch. Dis. Childhood*, 1928, 3, 243—256).—A study of pathological conditions of the nervous system and of the meninges. CHEMICAL ABSTRACTS.

Porphyrin. A. A. H. VAN DEN BERGH and A. J. HYMAN (*Deut. med. Woch.*, 1928, 54, 1492—1494; *Chem. Zentr.*, 1928, ii, 2046).—In congenital porphyrinuria large quantities of porphyrin were detected in the urine and faeces, from which methyl esters differing in the absorption spectra from those of uro- and copro-porphyrin (Fischer) were isolated. Four carboxyl groups were present. Lead poisoning leads to the presence of porphyrin in the urine; porphyrin was never found in the serum but was present in considerable amount in the red blood-corpuscles. A. A. ELDRIDGE.

Metabolic changes in rickets. I. Phosphate metabolism in the musculature in experimental rickets in rats. H. HENTSCHEL and E. ZOELLER (*Z. Kinderheilk.*, 1927, 44, 146—162; *Chem. Zentr.*, 1928, ii, 2037).—In rachitic rats the synthetic phase of the lactacidogen metabolism in the musculature suffered injury, whilst the splitting-power for lactacidogen was conserved. Values for the total phosphoric acid content of the musculature varied around 0.812 g.-%. The inorganic phosphoric acid is chiefly reduced, and the organic fraction after 14 days. The former increased on irradiation. A. A. ELDRIDGE.

Metabolic changes in rickets. II. Carbohydrate metabolism. E. AYRER and H. HENTSCHEL (*Z. Kinderheilk.*, 1928, 45, 289—295; *Chem. Zentr.*, 1928, ii, 2037).—Large variations in the glycogen content of both normal and rachitic rats were observed. A. A. ELDRIDGE.

Behaviour of lactic acid in the blood. I. Typhoid and tuberculous infections. G. MARGRETH (*Folia Clin. Chim. Micros.*, 1928, 3, 5—43).—A review is given. In patients suffering from slowly-progressing phthisis and in good nutritional condition, the lactic acid content of the blood does not differ from the normal, even when there is a temperature rise. Where there is cachexia, values slightly higher than the normal are observed. High proportions of lactic acid were, however, found with two patients in which tubercular infection was developing rapidly. Slightly raised values, comparable with those accompanying pulmonary lesions, exist in cases of marked malnutrition. T. H. POPE.

Influence of high altitude on the catalase content of blood. A. I. ALEXEEFF (*Biochem. Z.*, 1929, 207, 28—38).—The catalase content of, and

amount of erythrocytes in, blood from tubercular patients resident in the plains at Tashkent decrease after two months' sojourn in the hills (at 1500 m.). The fall in the catalase content occurs rapidly and almost entirely in the first week after return from the hills, but the decrease in the amount of erythrocytes proceeds regularly during four months. In the blood of healthy persons the same changes take place except that a pronounced decrease both in catalase content and amount of erythrocytes occurs in the first two weeks after return. The curve of the colour index of the blood runs almost parallel with that showing the changes in the amount of erythrocytes.

W. MCCARTNEY.

Influence of cations on the fermenting power of tumour cells. I. A. LASNITZKI and O. ROSENTHAL (Biochem. Z., 1929, 207, 120—140).—The fermenting power of tissue from tumours decreases when the Ringer solution used as a medium in which fermentation takes place contains neither potassium nor calcium ions. The extent of the decrease, in the case of tumours from rats, is from 25 to 40%.

W. MCCARTNEY.

Non-consumption of vitamin-B by growing chicken sarcoma. W. NAKAHARA and E. SOMEKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 211—220).—The vitamin-B content of the liver of chickens fed on a diet lacking in vitamin-B is not reduced as the result of the inoculation of the bird with a rapidly growing Rous sarcoma no. 1. It therefore appears that the tumour may not require vitamin-B for its growth.

W. O. KERMACK.

Vital staining of normal and malignant cells. II. Staining of malignant tumours with trypan-blue. R. J. LUDFORD (Proc. Roy. Soc., 1929, B, 104, 493—511).—It is possible that most malignant cells fail to stain like their normal prototypes because their greater acidity prevents the flocculation of acid dyes.

B. A. EAGLES.

Calcium and phosphorus metabolism. V. Bone trabeculae as a readily available reserve supply of calcium. W. BAUER, J. C. AUB, and F. ALBRIGHT (J. Exp. Med., 1929, 49, 145—161).—Easily mobilisable calcium is not deposited in the shafts of adult animals, but in the trabeculae of bone. The shafts show a slow progressive exchange of inorganic salts.

CHEMICAL ABSTRACTS.

Ionic mobility as a factor in influencing the distribution of potassium in living matter. A. B. MACALLUM (Proc. Roy. Soc., 1929, B, 104, 440—458).—From solutions containing equimolecular quantities of potassium and sodium chlorides or potassium and lithium chlorides considerable quantities of potassium and very little of sodium or lithium are adsorbed by a naturally occurring quartz sand, the exact quantity of potassium adsorbed depending on the rate of percolation of the solution through the sand and on the quantity of sand used. With a solution containing 0.7614% of sodium chloride and 0.0381% of potassium chloride, the quantity of potassium adsorbed was about double that of the sodium adsorbed. It is suggested that the preferential adsorption of potassium depends on the higher ionic mobility of this ion which results in its reaching first

and so occupying the interfacial surfaces. The bearing of these results on the role of potassium in living cells is discussed.

W. O. KERMACK.

Ion content of mother and embryo. S. HAYASHI (Biochem. Z., 1929, 207, 432—436).—The potassium, calcium, magnesium, and phosphorus contents of the liver, heart, and bones of female rats on a sufficient diet are carefully preserved during the period of growth of the embryo, the ratio of K/Ca for liver increasing slightly (at the most by 10%) and for heart decreasing slightly owing to increase in calcium. The bones preserve the calcium and magnesium contents absolutely. The ratio Ca/Mg for pregnant is somewhat less than for normal animals. The potassium and magnesium contents of the embryo scarcely change after the twelfth day, the values being rather higher in the earlier stages. The calcium and phosphorus contents increase with the formation of bone and attain the highest values just before birth.

P. W. CLUTTERBUCK.

Metabolism following anoxaemia. I. Oxygen consumption and blood-lactates after exercise. E. G. MARTIN, J. FIELD, and V. E. HALL (Amer. J. Physiol., 1929, 88, 407—419).—In dogs under certain conditions of exercise, the excess oxygen consumption following exercise is not determined by the amount of lactate disappearing from the body.

B. A. EAGLES.

Lactic acid metabolism in athletics. I. SNAPPER and A. GRUNBAUM (Deut. med. Woch., 1928, 54, 1494—1495; Chem. Zentr., 1928, ii, 2263).—Football does not usually lead to marked increase of blood-lactic acid; on warm days the urinary excretion of lactic acid does not exceed 60 mg., but on cold days it may reach 290 mg. Excretion of lactic acid through the skin may amount to 1.1—2.5 g.

A. A. ELDRIDGE.

Muscle contraction. II. Distribution of phosphorus in frog muscle during delayed relaxation. H. H. DIXON, H. A. DAVENPORT, and S. W. RANSON (J. Biol. Chem., 1929, 82, 61—70).—The gastrocnemii of frogs which had received intraperitoneal injections of hypertonic solutions of various substances showed an increase of 500% in the relaxation time over that of muscles from normal animals and a distribution of phosphorus similar to that found in fatigued muscles. The effect is ascribed to dehydration.

C. R. HARRINGTON.

Purine metabolism of muscle, and the parent substance of muscle-ammonia. J. K. PARNAS (Klin. Woch., 1928, 7, 1423—1424; Chem. Zentr., 1928, ii, 2038).—The chief purine base of (frog's) muscle is adenine, present probably as the nucleotide. Processes which lead to elimination of ammonia convert the adenine into hypoxanthine. Hypoxanthine and inosic acid are related to adenine and adenine nucleotide as is lactic acid to glycogen. Conversion of adenine nucleotide into inosic acid is the source of traumatic ammonia formation in muscle.

A. A. ELDRIDGE.

Possible origin of uric acid. L. BERNARD (Compt. rend. Soc. Biol., 1928, 99, 314—315; Chem. Zentr., 1928, ii, 2166).—The following scheme is

suggested: (i) $\text{COMe}\cdot\text{CHO} + 2\text{NH}_3 + \text{H}\cdot\text{CHO} \longrightarrow \text{CMe}\cdot\text{NH}\cdot\text{CH} + 3\text{H}_2\text{O}$; (ii) $\text{CO}(\text{NH}_2)_2 + \text{C}_4\text{H}_6\text{N}_2 + 5\text{O} \longrightarrow \text{C}_5\text{H}_4\text{O}_3\text{N}_3 + 3\text{H}_2\text{O}$. A. A. ELDRIDGE.

Nucleoprotamine and its components in animal metabolism. H. HENSCHER (Z. Biol., 1929, 88, 594—603).—The effect of the ingestion by dogs of clupeine sulphate, nucleic acid, and clupeine nucleinate (in the form of dried fish sperm) has been determined on the nitrogen, uric acid, and phosphoric acid output in the urine and the nitrogen and phosphoric acid output in the faeces.

W. O. KERMAK.

Amino-acid catabolism. III. Fate of ω -hydroxy-derivatives of propionic, butyric, valeric, and hexoic acids in the phloridzinised dog. R. C. CORLEY and C. S. MARVEL (J. Biol. Chem., 1929, 82, 77—82).—Extra dextrose is excreted by the phloridzinised dog following administration of γ -hydroxybutyric acid, but not of hydracrylic, δ -hydroxyvaleric, or ϵ -hydroxyhexoic acids; since ornithine, but not lysine, gives rise to extra dextrose formation in the phloridzinised animal, further evidence is thus afforded for the view (A., 1926, 1171) that catabolism of the diamino-acids proceeds through the stages of the ω -amino- and ω -hydroxy-acids with one carbon atom less.

C. R. HARRINGTON.

Derivative of dextrose concerned in the oxidation-reduction equilibrium of cells. R. WURMSER and J. GELOSO (Compt. rend., 1929, 188, 1186—1188).—Dextrose in alkaline solution under vaseline generates a substance (probably a dienolic form, the time required varying with temperature and p_{H} value) which is rapidly oxidised either by dehydrogenation in the presence of methylene-blue as an acceptor or by molecular oxygen, and which is regenerated on keeping. Electrometric titration shows that this solution has an oxidation-reduction potential similar to that in the interior of living cells and a mechanism of the regulation of intracellular potential based on the presence of this intermediate substance (derived from glucosides) is suggested.

J. W. BAKER.

Carbohydrate metabolism of the normal, phloridzinised and diabetic viviperfused stomach. R. K. S. LIM, T. G. NI, H. NECHELES, and H. C. CHANG (Chinese J. Physiol., 1929, 3, 123—155).—In a non-secreting dog's stomach subjected to viviperfusion according to the authors' method (cf. Ni and Lim, A., 1928, 442) the uptake of dextrose is reduced when phloridzin is administered or insulin is deficient. Under these conditions stimulation of secretion by histamine results in no increase but sometimes in a decrease in the uptake of dextrose, whereas an increase frequently occurs in the case of a non-phloridzinised stomach supplied with insulin. Neither the presence of phloridzin nor the deficiency of insulin affects the uptake of oxygen, and this is increased when secretion is stimulated. It is concluded that some substance other than carbohydrate is probably oxidised during secretion.

W. O. KERMAK.

Changes of metabolism during irradiation. L. PINOUSSEN. Fat content of organs. E.

ZUCKERSTEIN (Biochem. Z., 1929, 207, 426—431).—During irradiation the fat content of the serum of guinea-pigs increases considerably but the cholesterol content is scarcely affected; the fat content of the heart decreases considerably with and without the presence of eosin as sensitiser, whereas the cholesterol content without sensitiser decreases slightly but with sensitiser increases considerably; the fat content of the liver decreases considerably without and to an even greater extent with sensitiser, whilst the cholesterol content is slightly increased; in the kidney a small decrease of fat and increase of cholesterol is obtained, whilst in muscle the fat content is decreased and the cholesterol content is unchanged.

P. W. CLUTTERBUCK.

Cholesterol. IV. Relation of ovaries and testes to cholesterol metabolism. F. S. RANGLES and A. KNUDSON (J. Biol. Chem., 1929, 82, 57—59).—Removal of the ovaries or testes from rats has no effect on the cholesterol content of the blood.

C. R. HARRINGTON.

Role of phospholipins of intestinal mucosa in fat absorption. Phospholipins of liver and muscle. R. G. SINCLAIR (J. Biol. Chem., 1929, 82, 117—136).—The composition, but not the total amount, of the phospholipins of the intestinal mucosa is influenced by changes in the nature of the fat of the diet; such changes are without effect on the composition or total amount of the phospholipins of plain or striated muscle. It is thought that the phospholipins of the intestinal mucosa represent an intermediate stage in the re-synthesis of neutral fat from the absorbed fatty acids.

C. R. HARRINGTON.

Effect of gestation and lactation on the growth and composition of swine. D. J. GRISWOLD, P. F. TROWBRIDGE, A. G. HOGAN, and L. D. HATCH (Missouri Agric. Exp. Sta. Res. Bull., 1928, No. 114, 6 pp.).—The ash of pre-natal and new-born pigs contains more sodium, chlorine, and sulphur, and less magnesium, potassium, and silicon than that of older animals. The percentage of iron is low and constant. The ash at all ages contains about 75% $\text{CaH}_4(\text{PO}_4)_2$. Results of experiments on digestion are recorded.

CHEMICAL ABSTRACTS.

Action of chalybeate waters on metabolism. M. KOCHMANN and H. SEEL (Deut. med. Woch., 1928, 54, 1321—1322; Chem. Zentr., 1928, ii, 2263).—Ferrous hydrogen carbonate in a natural water had a favourable action on the metabolism of young growing rats, possibly owing to an increase of plasma-iron.

A. A. ELDRIDGE.

Relationship between chemical constitution and physiological action. E. MANELI (Boll. Chim. farm., 1929, 58, 299—308, 351—356, 399—402).

Aluminium toxicity. F. T. McLEAN and B. E. GILBERT (Plant Physiol., 1928, 3, 293—302).—Low concentrations ($3\text{--}13$ in 10^6) of aluminium are stimulating, and higher concentrations toxic, to plants. Aluminium in combination with organic acids (citric, tartaric) is toxic at low acidities (p_{H} 6.5). Non-dialysable aluminium is toxic when placed in contact with the roots of barley. At equivalent concentration, phosphate prevents toxic action by aluminium compounds.

CHEMICAL ABSTRACTS.

Relation of arsenicals to the glutathione content of animal tissues. H. BROWN and J. A. KOLMER (J. Pharm. Exp. Ther., 1929, 35, 417—424).—The reduced glutathione content of the blood and various organs of rats, rabbits, guinea-pigs, and dogs has been determined. No relation appears to exist between the susceptibility of the animal species to salvarsan poisoning and the content of its organs in reduced glutathione. The administration of numerous therapeutic doses of salvarsan or neosalvarsan to rabbits is without significant effect on the reduced glutathione content of its organs but a single very large dose brings about a decrease.

W. O. KERMACK.

Pharmacological significance of reactions between arsenious acid and thiol compounds. R. LABES (Arch. exp. Path. Pharm., 1929, 141, 148—160).—The toxic effect of injected arsenious acid on mice is greatly delayed if cysteine is administered at the same time. Mixture of solutions of these two compounds results in the rapid precipitation of a compound containing 1 mol. of arsenious acid and 3 mols. of cysteine, the solubility of which is less than 8×10^{-12} . It is suggested that the delayed toxic effect is due to the catabolism of the cysteine portion of the compound in the animal body. The influence of cysteine on the tone of smooth muscle preparations is compared with that of adrenaline; both reduce the muscle tone of frog-stomach preparations, but with the former there is frequently a marked increase in the excitability of the preparation. With the rabbit's uterus there is a differentiation in action; cysteine again reduces muscle tone, adrenaline increases it.

F. C. HAPFOLD.

Action of rubidium on the serum. A. H. ROFFO and H. DE GIORGI (Bol. Inst. Med. exp., 1926, No. 14, 14 pp.; Chem. Zentr., 1928, ii, 2259).—Intravenous administration of rubidium chloride or sulphate to guinea-pigs or man causes a slight diminution of the p_H and surface tension of the blood. Apparently the colloid equilibrium in the serum is altered.

A. A. ELDRIDGE.

Absorption and excretion of magnesium. W. F. TAYLOR and J. E. WINTER (J. Pharm. Exp. Ther., 1929, 35, 435—439).—In rabbits, light and deep narcosis occur when the blood-magnesium level exceeds 7—11 and 18—21 mg. per 100 c.c., respectively. In the dog even light narcosis is not produced when the blood-magnesium level is 10.44 mg. per 100 c.c. In dog and man approximately 7.5—11% Mg ingested as magnesium chloride is excreted in the urine. The temperature of dogs with fever is reduced approximately 1° for each rise of 2 mg. in the blood-magnesium content.

W. O. KERMACK.

Distribution of mercury in the organism and its elimination after injection of "salyrgan." J. MÜLLER (Arch. exp. Path. Pharm., 1929, 141, 1—18).—After intravenous injection of "salyrgan" into dogs the highest concentrations of mercury are found in the bile and the wall of the gall bladder followed by the adrenals and then the kidneys and large intestine. Most of the other organs contain small quantities of mercury. Both in man and in animals after salyrgan injection elimination of the

mercury takes place chiefly in the urine and only to a small extent in the faeces and is practically complete within 24 hrs.

W. O. KERMACK.

Pharmacology and toxicology of some new organo-mercury compounds. S. J. COHEN (J. Pharm. exp. Ther., 1929, 35, 343—350).—The sodium or potassium salts of methyl-, ethyl-, and butyl-mercurithioglycollic acids, which are strongly bactericidal towards the tubercle bacillus, are also highly toxic to animals, causing paralysis of the hind-limbs.

W. O. KERMACK.

[Biological] action of certain metals. K. WALTNER (Arch. exp. Path. Pharm., 1929, 141, 123—128).—The effect has been determined of the administration to animals in their food of considerable quantities of metallic magnesium, nickel, cobalt, copper, zinc, molybdenum, cadmium, tin, tungsten, and bismuth, particularly on growth, bone formation, fertility, and serum-phosphorus.

W. O. KERMACK.

Colloidal metals and glycolysis. A. FRANCAVIGLIA (Arch. Farm. sperim., 1929, 46, 201—206).—Incubation of blood containing colloidal silver causes a marked increase in the proportion of combined sugar, the silver either accelerating the action of the enzyme which determines glucoprotein synthesis or retarding that of the enzyme effecting true glycolysis. A similar mechanism is suggested for the action of colloidal metals *in vivo*.

T. H. POPE.

Pharmacology of stabilised colloidal lead sulphide. A. CHISTONI and E. MILANESI (Arch. Farm. sperim., 1929, 46, 147—173).—Colloidal lead sulphide, when prepared as a suspensoid in presence of a denatured protein, which acts as a protecting colloid, is far more stable than any colloidal lead preparation previously described. This colloid is rapidly absorbed even by subcutaneous tissue and, in consequence of its ready oxidisability, easily undergoes further transformations; it is eliminated by the intestine and kidney like other lead salts. The minimum fatal dose is 0.016 g. per kg. body-weight (rabbit). The changes produced in the different organs by the colloid are described.

T. H. POPE.

Chemistry and therapeutic action of dextrose. F. FISCHER (Münch. med. Woch., 1928, 75, 1541—1544; Chem. Zentr., 1928, ii, 2260).—A discussion.

A. A. ELDRIDGE.

Action of decamethylenediguanidine (synthalin) on the blood-sugar of normal and depancreatized dogs. F. RATHERY, R. KOURILSKY, and S. GIBERT (Compt. rend. Soc. Biol., 1928, 99, 282—284, 284—287; Chem. Zentr., 1928, ii, 2034).—Small doses of synthalin cause glycosuria in the depancreatized dog. Its action on the normal dog is variable.

A. A. ELDRIDGE.

Nephropathogenic action of cystine. G. J. COX, C. V. SMYTHE, and C. F. FISHBACK (J. Biol. Chem., 1929, 82, 95—103).—Young rats develop an acute nephrosis when kept on synthetic diets containing 0.3% or more of free cystine; restoration to normal diet usually results in recovery, and some spontaneous recoveries occur even when the cystine diet is continued.

C. R. HARRINGTON.

Cellular toxicity of gaseous and volatile poisons. S. LALLEMAND (J. Pharm. Chim., 1929, [viii], 9, 380—390).—Hen's eggs were placed in an atmosphere of the gas for varying periods of time, then exposed to room air for 24 hrs. and incubated for 48 hrs., and the development of the embryo was noted. Hydrogen, nitrogen, oxygen, and carbon dioxide are non-toxic. Embryonic development is slightly retarded by nitrous oxide. Hydrogen chloride, sulphur dioxide, and chlorine are more toxic. Exposure to ammonia or hydrogen sulphide for 3 min. prevents development of the embryo. B. A. EAGLES.

Use and elimination of water-soluble camphor derivatives. M. PROHON (J. Pharm. Chim., 1929, [viii], 9, 369—371).—The taking of sodium camphor-sulphonate does not lead to an increased excretion of conjugated glycuronates, as is the case after the ingestion of camphor. B. A. EAGLES.

Promoting action of saponin on resorption and the action of cholesterol. L. KOFLER and R. FISCHER (Arch. exp. Path. Pharm., 1929, 141, 105—115).—Various types of saponin very strongly increase the rate of absorption of curare from the intestine of the frog, the quantities required being less than one hundredth of the toxic dose. When the saponin is combined with cholesterol, this action, like most of its other biological activities, is largely or entirely inhibited, but the mere presence of cholesterol as distinct from combination is not sufficient to cause this inhibition. W. O. KERMACK.

Determination of the potency of digitalis: (A) Pigeon-emesis. P. J. HANZLIK. **(B) Results with the pigeon-emesis method of estimating the probable therapeutic dose of digitalis.** P. J. HANZLIK and A. B. STOCKTON (J. Pharm. Exp. Ther., 1929, 35, 363—391, 393—407).—(A) Digitalis preparations may be conveniently assayed by determining the minimum dose necessary to produce vomiting in pigeons. (B) From observations on human subjects it is found that the therapeutic dose for man can be satisfactorily determined from assay by the pigeon-emesis method. W. O. KERMACK.

Pharmacological action of some tertiary amines related to ephedrine. F. R. CURTIS (J. Pharm. Exp. Ther., 1929, 35, 321—332).—Tertiary amines of the type $\text{CHPh}(\text{OH})\cdot\text{CHMe}\cdot\text{NMeR}$, in which $\text{R}=\text{Me}$, Et , $(\text{CH}_2)_2\text{OH}$, Pr^α , Pr^β , or Bu , as well as the amine $\text{CHPh}(\text{OH})\cdot\text{CHMe}\cdot\text{NEt}_2$, possess little power to raise the blood-pressure of a pithed cat, but on the isolated uterus they produce contraction and act more strongly than ephedrine itself ($\text{R}=\text{H}$). The compounds containing $\text{R}=\text{Me}$ and Et and also the diethyl compound dilate the bronchi of a cat as efficiently as does ephedrine, and this property associated with their small action on the blood-pressure may render them capable of clinical application. W. O. KERMACK.

Phytopharmacological examination of adrenaline and ephedrine. D. I. MACHT (J. Amer. Pharm. Assoc., 1929, 18, 335—337).—Adrenaline is much more toxic to living seedlings of *Lupinus albus* than is ephedrine. This method enables the activity

of different samples of adrenaline to be evaluated and distinguishes them from ephedrine.

E. H. SHARPLES.
Antipyretic action and toxicity of combinations of magnesium with phenylcinchoninic acid. H. G. BARBOUR and J. E. WINTER (J. Pharm. Exp. Ther., 1929, 35, 425—434).—The antipyretic action of phenylcinchoninic acid on dogs or rabbits with fever is increased by the simultaneous administration of salts of magnesium. W. O. KERMACK.

Antitoxic properties of calcium in respect of sparteine sulphate. P. L. VIOLE and A. GIBERTON (Compt. rend., 1929, 188, 1181—1182; cf. this vol., 348).—Subcutaneous or intracardiac injections of an isotonic solution of calcium chloride (4 g. calcium/litre) into a guinea-pig have an antitoxic effect on a simultaneous injection of a lethal dose (0.01 g./100 g. body-weight) of sparteine sulphate, the animal usually surviving indefinitely. A similar effect (survival for 4 days) is produced by frequent injections of calcium prior to the injection of sparteine sulphate. Similar experiments using diphtheria toxin, however, give negative results, showing that the antitoxic effect is specific to certain poisons. J. W. BAKER.

[Respiratory enzymes.] O. WARBURG (Biochem. Z., 1929, 207, 494—495).—A criticism of Keilin's paper (this vol., 470). P. W. CLUTTERBUCK.

Malt amylase. V. Determination of the power of amylase to convert starch into dextrins and sugars and a comparison of the two reactions. T. SABALITSCHKA and R. WEIDLICH (Biochem. Z., 1929, 207, 476—493).—A method is described for the determination colorimetrically of the velocity of dextrin formation and breakdown during the hydrolysis of starch by amylase. The dextrination constant so obtained permits the comparison of the dextrin-forming and hydrolysing actions of different amylases. The ratio of the dextrination constant to the saccharification constant (obtained simultaneously by iodometric determination of the maltose formed) in seven experiments with different amounts of amylase gave a quotient of 1.12 ± 0.14 .

P. W. CLUTTERBUCK.
Takadiastase. Inactivation and reactivation; importance of these processes in the therapeutic use of the enzyme. E. OHLSSON and T. SWAETICHIN (Bull. Soc. Chim. biol., 1929, 11, 333—386).—Takadiastase loses its power to hydrolyse starch in acid or alkaline solution (below p_H 2.0 or above p_H 11.5), but on neutralisation the activity slowly returns. The enzyme has maximum stability between p_H 5 and 9. Reactivation in neutral solution (p_H 6—7) is generally almost complete in an hour, but both inactivation and reactivation are delayed by the presence of starch and accelerated by phosphate. Takadiastase acts between p_H 2.5 and 8.0 with an optimum zone between p_H 4.5 and 6.5. Inactivation experiments indicate that takadiastase is a simple dextrinase. Although takadiastase is inactivated in the acid of the stomach it is slightly more effective than malt diastase, and under normal conditions the enzyme will become reactivated in the intestine. It is suggested that the reversible activation is due to a change in dispersion of the enzyme. E. BOYLAND.

Enzymes and light. XIV. L. PINCUSSEN. Effect of temperature on the action of light. T. OYA (Biochem. Z., 1927, 207, 410—415).—Comparison of the theoretical amounts with the amounts of maltose actually formed by the action of taka-diastase on starch at varying temperature and p_H and after the enzyme had been irradiated or heated shows that the mechanism of the injury brought about by light and by heat is different. Diastase solutions after injury by irradiation can be reactivated by addition of a small amount of unirradiated solution, but reactivation does not occur when the enzyme is injured by heat. P. W. CLUTTERBUCK.

Specificity and mechanism of action of the sugar-hydrolysing enzymes. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1929, 79, 115—154).—From a detailed review of recent work it is concluded that there is no evidence for the existence of specific disaccharases. The hydrolyses described can be referred to the action of glucosidases (cf. Oppenheimer, A., 1923, i, 495). These exhibit structural specificity, e.g., glucosidases, galactosidases, stereo-specificity as regards the glucoside carbon atom, e.g., α - and β -glucosidases, and ring-specificity depending on the oxygen linking in the hexose molecule, e.g., n - and h -fructosidases. Conclusions as to specificity based on the inhibiting effect of added hexoses are unsound, since the effects of impurities are obscure.

F. E. DAY.

Action of invertase: free water, viscosity, and rate of reaction. H. COLIN and A. CHAUDUN (Bull. Soc. Chim. biol., 1929, 11, 258—267).—With low concentrations of sucrose the rate of hydrolysis varies logarithmically with the concentration of sugar, but high concentrations reduce the rate of hydrolysis. Additions of gelatin or of agar, which increase the viscosity, produce proportional decreases in the rate of hydrolysis, although a mixture of agar and gelatin seemed to have less effect on the hydrolysis than either agar or gelatin alone. Solutions of sucrose and of mixtures of sucrose and lactose having equal viscosities are hydrolysed at the same rate, but the addition of glycerol affected the hydrolysis more than the viscosity. The rate of hydrolysis of concentrated sucrose solutions cannot be completely explained either by viscosity or by retention of water.

E. BOYLAND.

Fermentation of lactic acid by the tissues of warm-blooded animals. I. Conditions for obtaining "extra" fermentation with liver tissue. O. ROSENTHAL (Biochem. Z., 1929, 207, 263—297; cf. A., 1928, 916).—The amount of fermentation with glandular tissue depends on whether the tissue is asphyxiated immediately after removal from the organ or some time subsequently, the fermentation being 50—150% higher after aërobiosis for 1 hr. at 37.5°. This extra fermentation with liver tissue is due to fermentation of lactic acid, some carbohydrate specific to the cell being the substrate. Extra fermentation never occurs with tissues of starving rats nor with foetal livers. Nourishment of the animal is one condition for obtaining extra fermentation. The maximal effect is obtained with an aerobic period of 15 min., and body temperature is

also necessary. Extra fermentation is not obtained when, during the aerobic period, potassium- and calcium-free Ringer's solution is used as medium. Replacement of Ringer's solution by fresh serum does not affect the intensity of fermentation.

P. W. CLUTTERBUCK.

Isolation of methylglyoxal in lactic acid fermentation. C. NEUBERG and M. KOBEL (Biochem. Z., 1929, 207, 232—262).—From the dried sterile material extracted by alcohol-ether from cultures of *B. Delbrücki* water (or 1% sodium chloride solution) extracts an enzyme, "glycolase," which produces methylglyoxal from magnesium hexosediphosphate. The yields of this substance are the higher the greater is the concentration of the substrate and in some cases are equivalent to 100% of the hexose decomposed. Very little co-enzyme is present in the aqueous extracts. The residue from them only gives methylglyoxal with high concentrations of hexosediphosphate, and with low concentrations converts it quantitatively into lactic acid. The methylglyoxal is isolated as the bisdinitrophenylhydrazone and also as the dioxime. Glycolase is found also in animal tissues and in higher plants and may be expected to occur wherever glyoxalase is found. W. MCCARTNEY.

Dehydrogenation of malic acid. II. A. HAHN, W. HAARMANN, and E. FISCHBACH (Z. Biol., 1929, 88, 587—593).—A mixture of frog-muscle pulp, methylene-blue, and malic acid containing semicarbazide was incubated at 38° and the deproteinised filtrate evaporated to dryness. The residue was treated with 50% sulphuric acid at 50° to decompose the oxalacetic acid semicarbazide, and the pyruvic acid formed was finally isolated as the phenylhydrazone. The quantity of phenylhydrazone obtained was greater than when no malic acid was present, the pyruvic acid in the latter case being formed from lactic acid as the result of the treatment. The above result confirms the view that oxalacetic acid is the first product formed from malic acid during dehydrogenation by muscle pulp in presence of methylene-blue (cf. A., 1928, 1281).

W. O. KERMAK.

Barley-malt catalase. II and III. M. O. CHARMANDARJAN (Biochem. Z., 1929, 207, 462—471, 472—475).—II. The amount of hydrogen peroxide decomposed by malt extract varies with the volume of fluid and the concentration of peroxide. Addition of toluene increases slightly the amount of decomposition. Prolonged exposure to water decreases the decomposing power.

III. Malt on keeping loses its power to decompose peroxide, more quickly in ground than in whole grain, more quickly in air than in carbon dioxide, and very quickly over sulphuric acid in a desiccator.

P. W. CLUTTERBUCK.

Peroxidase nature of "active" iron. H. UCKO (Klin. Woch., 1928, 7, 1515—1517; Chem. Zentr., 1928, ii, 2155).—The effect of vegetable and animal peroxidases and iron compounds on peroxide systems (hydrogen peroxide and benzidine, pyrogallol, and potassium iodide) has been studied. Aqueous and alcoholic benzidine solutions give with most iron compounds, and with compounds of other heavy metals,

a bluish-green product; there is a group of complex iron compounds which, in acid solution, like true peroxidases and oxyhæmoglobin, give a positive reaction. The catalytic oxidation of pyrogallol to purpurogallin by hydrogen peroxide is effected by peroxidase, oxyhæmoglobin, complex iron salts, and copper ions; ferric and ferrous ions give a violet compound which rapidly becomes brown. The reaction between potassium iodide and hydrogen peroxide is not catalysed by the "active" iron compounds or by other complex iron salts, whilst ferric and ferrous ions have a certain stoichiometric effect. Thus for testing peroxidase activity the effect on potassium iodide and hydrogen peroxide, as well as on the benzidine reaction, must be examined.

A. A. ELDRIDGE.

Activation of pancreatic lipases in serum by leucylglycylglycine. Modification of Rona's test. A. ROSEN (Klin. Woch., 1928, 7, 1693—1694; Chem. Zentr., 1928, ii, 2155).—The presence of active lipase in the serum after treatment with atoxyl is a proof of the transition of pancreas lipase into the blood, since atoxyl is toxic to the serum lipases. Pancreatic lipases are strongly activated by leucylglycylglycine.

A. A. ELDRIDGE.

Molecular constitution and accessibility to enzymes. Effect of various substances on the velocity of hydrolyses by pancreatic lipase. D. R. P. MURRAY (Biochem. J., 1929, 23, 292—308).—Ketones and aldehydes produce an inhibition of the velocity of hydrolysis out of proportion to that produced by the chemically related compounds investigated. This power is lost by the ketone when converted into its oximes. Secondary alcohols also produce an inhibition which may be due to reversal of hydrolysis. The former inhibition is due to the specific affinity between the carbonyl group and the active centre of the enzyme and to the consequent influence on the normal adsorption of esters preparatory to their hydrolysis by the enzyme.

S. S. ZILVA.

Disaggregating action of pepsin. M. FRANKEL (Biochem. Z., 1929, 207, 53—65).—The optical rotatory powers of gelatin solutions containing pepsin and the amounts of amino-nitrogen present in them remain practically unchanged at temperatures from 10° to 37° during the period of induction before hydrolytic action sets in. It follows that the pepsin has no disaggregating effect during this interval.

W. MCCARTNEY.

Relationship between chemical properties of a series of pepsin preparations and their activity towards different proteins. J. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1929, 182, 1—7).—A series of pepsin preparations, the activities of which were determined by the method outlined (A., 1928, 1282), showed relatively corresponding proteo-elastic action on caseinogen, edestin, gelatin, egg-white, and myosin.

C. C. N. VASS.

Relation of structure to rate of hydrolysis of peptides. V. Enzymic hydrolysis of dipeptides. P. A. LEVENE, R. E. STEIGER, and L. W. BASS. VI. **Hydrolysis of dipeptides by alkali.** P. A. LEVENE, W. BASS, and R. E. STEIGER (J. Biol. Chem., 1929,

82, 155—166, 167—170).—V. The results of earlier experiments (this vol., 301) together with those now recorded show that dipeptides of which one component is the enantiomorph of the naturally occurring amino-acid, and those in which the free amino- or carboxyl group is attached to a tertiary carbon atom, are not attacked by crepsin; those in which one component is a *dl*-amino-acid are hydrolysed to the extent of 50%. As in the case of acid hydrolysis, the intrinsic dissociation constants of the groups involved play a part in determining the velocity of the reaction. *Glycyl- α -aminoisobutyric acid* was obtained by conversion of α -aminoisobutyric acid into the *chloroacetyl* derivative, followed by treatment of the latter with ammonia. *l-Phenylglycine*, $[\alpha]_D^{25}$ —111.7° in water, was treated with bromoacetyl bromide, and the product, with ammonia, yielded *glycyl-l-phenylglycine*, $[\alpha]_D^{25}$ —173.9° in water. *Glycyl-dl-phenylmethylglycine* was prepared similarly.

VI. The rate of hydrolysis of dipeptides by alkali bears no relationship to the intrinsic dissociation constants of the groups involved in the peptide linking, and is possibly determined by the dissociation constants of the enolic forms of the peptides. As in the cases of acid and creptic hydrolysis, those peptides in which the free acidic or basic group is attached to a tertiary carbon atom show the greatest resistance.

C. R. HARRINGTON.

Specificity of animal proteases. XVI. Dipeptidase and polypeptidase from the mucous membrane of the intestine. E. WALDSCHMIDT-LEITZ, A. K. BALLS, and J. WALDSCHMIDT-GRASER (Ber., 1929, 62, [B], 956—962; cf. A., 1928, 1401).—The separation of the mixture of peptidases into di- and poly-peptidase, which cannot be effected by aluminium hydroxide C_3 , is relatively easily brought about by ferric hydroxide. The bulk of the poly-peptidase remains in the mother-liquor from the adsorption and is obtained free from dipeptidase after three treatments. The dipeptidase is concentrated in the adsorbates, from which it is obtained by elution with alkali phosphate in poor yield. It is less stable than the polypeptidase, particularly in acid solution.

H. WREN.

Arginase. VII. Ureotelic character of the nitrogen metabolism of Chelonia. A. CLEMENTI (Atti R. Accad. Lincei, 1929, [vi], 9, 505—509).—Like that of *Bufo*, the urine of *Testudo graeca* and *Emys europaea* contains uric acid in proportions almost too small to be determined. In the summer, the urine of these two animals contains about 0.5 part of urea per 1000, which is approximately the same as in the urine of *Bufo* at the same period. Contrary to what is observed with uricotelic animals (birds), oral administration of ammonia to *Testudo* and *Emys* produces marked increase in the urea content *per diem* and per 1000 of the urine, so that the nitrogen metabolism of the Chelonia is not uricotelic, as with other reptiles and with birds, but ureotelic.

T. H. POPE.

Isoelectric point of crystalline urease. J. B. SUMNER and D. B. HAND (J. Amer. Chem. Soc., 1929, 51, 1255—1260; cf. A., 1928, 329, 1401).—In phosphate, phthalate, and acetate buffers of

p_H 7—5.5, crystalline urease migrates towards the anode, but in more acid solutions no electrophoresis occurs. Urease is precipitated by (a) 0.02*M*-phthalate ion, (b) 0.008*M*-lead ion in acetate buffer, precipitation beginning at p_H (a) 5.3, (b) 4.7, and being complete at p_H (a) 4.6, (b) 5.6. Precipitation causes no separation of urease from protein and, near the isoelectric point, very little loss of activity. Mercuric and cupric ions precipitate urease over a much wider range and almost completely inactivate it. It is soluble in excess of phosphate, acetate, and hydrogen carbonate buffers at all p_H values, but in very dilute solutions the isoelectric point is given by a precipitation maximum at p_H 5.0—5.1. The solubility relations of crystalline urease are those of a typical globulin. It is active on both sides of the isoelectric point.

H. E. F. NOTTON.

Kinetics of the formation of acetaldehyde in alcoholic fermentation with dried yeast. B. KISCH and J. LEIBOWITZ (Biochem. Z., 1929, 207, 384—394).—Under optimal conditions (concentration of sulphate 2—5%, and of sugar 1—3%) the amount of aldehyde formed is almost a linear function of the time, the linear course of the aldehyde-time curve being unaffected by changes of temperature over the optimal zone, 31—38°.

P. W. CLUTTERBUCK.

Alcoholic fermentation. XIX. Fermentative bacteria in maceration juice. S. KOSTYTSHEV and O. SCHULGINA (Z. physiol. Chem., 1929, 182, 50—56).—Cell-free fermentation is not yet established. Invisible forms of fermentative bacteria play an important part in the processes occurring in maceration juices. Intensive fermentation in the presence of powerful stimulants can be brought about by a very small quantity of living cells contained in a large quantity of dead yeast-cells.

C. C. N. VASS.

Production of starch in moulds (*Penicillium*, Link); its relation to acid production. T. CHRZASZCZ and D. TIUKOV (Biochem. Z., 1929, 207, 39—52).—The formation of starch-like substances in moulds is a normal process requiring special conditions for particular species of moulds. These species form two groups: starch producers, which are older evolutionary forms and produce less organic acid than the others; and acid producers. The acid and the starch-like substances play the part of reserve materials. The production of starch-like substances by those moulds which normally accumulate other materials is an atavistic phenomenon. Normally, the starches, in varying amounts, are deposited in layers in the mould, but their nature and localisation are dependent on external conditions and on the species of the mould.

W. MCCARTNEY.

Coloration of *Aspergillus niger* grown on fatty media. C. PONTILLON (Compt. rend., 1929, 188, 1184—1185).—By cultivation on media both with and without fatty constituents prepared in different ways it is shown that the yellow pigment sometimes observed in the cultures of *A. niger* (Roussv, *ibid.*, 1909, 149, 482; 1911, 151, 884) is due, not to the presence of fats, but to the disturbance of the equilibrium composition of the media by

the removal of various salts consequent on filtration after prolonged boiling.

J. W. BAKER.

Conversion of acetic acid by *Mucor stolonifer* into succinic and fumaric acids and a method of separation and quantitative determination of these acids. W. S. BUTKEVITSON and M. W. FEDOROV (Biochem. Z., 1929, 207, 302—318).—Fumaric acid does not accumulate when *Mucor stolonifer* is grown on solutions of succinic, malic, lactic, or tartaric acid in presence of calcium carbonate, but is formed in considerable amounts when the organism is grown on solutions of glycerol under the same conditions. Acetic acid in presence of calcium carbonate is converted into succinic and fumaric acids, 15—30% being so converted. In these experiments the succinic acid constitutes 80—90% of the mixed acids, whereas in experiments with sugar it formed only 10% of the mixture.

P. W. CLUTTERBUCK.

Metabolism of *Ustilina vulgaris*, L. H. WUNSCHENDORFF and C. KILLIAN (Compt. rend., 1929, 188, 1124—1126).—Cultures of *U. vulgaris* were maintained at 25° in a medium containing 1% of peptone. After 3 weeks the medium answered faintly or not at all to the biuret reaction. The amount of ammonia evolved is dependent on the surface area of the fungus and not on its dry weight. However, a constant ratio exists between the amount of nitrogen fixed by the fungus and its weight; this ratio is not maintained when the concentration of peptone in the medium is lowered or raised. As the weight of the fungus increases, the acidity of the medium decreases.

B. W. ANDERSON.

Oxidases of wood-destroying moulds. I. W. BAVENDAMM (Z. Pflanzenkrankh., 1928, 38, 257—276; Chem. Zentr., 1928, ii, 2154—2155).—For the plate method for the detection of oxidases the use of tannin or gallic acid is preferred.

A. A. ELDRIDGE.

Three new species of sulphur-oxidising bacteria. Y. EMOTO (Proc. Imp. Acad. Tokyo, 1929, 5, 148—151).

C. C. N. VASS.

Metabolism of *Bacillus tetani*. II. Bases of the culture medium. H. SIEVERS and E. MÜLLER (Z. Biol., 1929, 88, 553—560).—From culture media on which tetanus bacilli have been grown, the following compounds have been isolated after removal of the ether-soluble constituents: hypoxanthine, ammonia, histidine, carnitine, γ -butyrobetaine, β -homobetaine, and methylamine.

W. O. KERMACK.

Tetanus toxin, ricin, and some alkaloids and their detoxication. J. SCHUBERT (Z. Immunitäts., 1928, 57, 261—284; Chem. Zentr., 1928, ii, 2259).—*In vitro*, tetanus toxin is detoxicated by tyrosine, cholesterol, or ethereal alcoholic extracts of human bone marrow, cod-liver oil, octoic or oleic acid, certain vegetable oils, and solutions of cocaine, morphine, and "heroin." Ricin poisoning is prevented by previous treatment of the poison with cholesterol or "heroin." Aconitine is not detoxicated by alkaloids.

A. A. ELDRIDGE.

Relationship between the physical properties of chemical substances and their action on

micro-organisms. T. SABALITSCHKA (Arch. Pharm., 1929, 267, 272—290).—The antiseptic and germicidal properties of various phenolic substances are connected with their adsorptive powers.

S. COFFEY.

Germicidal and hæmolytic action of α -bromo-soaps. A. H. EGGERTH (J. Exp. Med., 1929, 49, 53—62).—The soaps of the α -bromo-fatty acids are (except for *Bacillus typhosus*) usually more germicidal than the unsubstituted soaps and are most active when the reaction is acid. The germicidal and hæmolytic action at first increases rapidly with increasing mol. wt. and then diminishes.

CHEMICAL ABSTRACTS.

Mercuric oxycyanide compounds of organic acids and their sterilising action on *Gonococcus*. H. TAKAKA (Bull. Osaka Inst. Ind. Res., 1928, 4, 1—8).—The compound $\text{HgC}_4\text{H}_4\text{O}_6 \cdot \text{Hg}(\text{CN})_2 \cdot \text{H}_2\text{O}$ (from tartaric acid and $\text{HgO} \cdot 3\text{Hg}(\text{CN})_2$ in 90% alcohol) has an immediate sterilising effect on *Gonococcus* at a dilution of 1 in 5×10^4 . The corresponding salicylate ($+2\text{EtOH}$) and citrate were also prepared.

CHEMICAL ABSTRACTS.

Adrenaline content of the suprarenal capsule in the hen embryo. M. OKUDA (Endocrinol., 1928, 12, 342—348).—Adrenaline appears at about the eighth day; a close relation with tyrosine and with the chromic reaction in the cells is indicated.

CHEMICAL ABSTRACTS.

Effect of pituitary extract and adrenaline on ketonuria and liver-glycogen. J. H. BURN and H. W. LING (Quart. J. Pharm., 1929, 2, 1—16).—Injections of pituitary extract into rats fed on butter fat cause an inhibition of the output of acetone substances; with adrenaline a seemingly inhibitory as well as the augmentor effect observed by Anderson and Anderson (A., 1928, 90) is recorded. During the spring there is a steady rise in the glycogen content of the liver as also observed in the winter (*ibid.*, 925) which bears no relationship to the ketonuria. Injections of pituitary extract during the first 5 days of the fat diet reduce the liver-glycogen to a negligible quantity, whilst administration of adrenaline causes the rise in the liver-glycogen to occur more slowly.

C. C. N. VASS.

Oxytocin and vasopressin. Examination of separated principles of pituitary (posterior lobe) extract. J. H. BURN (Quart. J. Pharm., 1928, 1, 509—512).—The antidiuretic activity of oxytocin and vasopressin has been tested on man. Oxytocin is devoid of activity; vasopressin has an activity which is equal, per unit pressor activity, to that of a sample of pituitrin. The power of pituitrin to inhibit the hypoglycæmic effect of insulin is possessed by vasopressin but not by oxytocin.

F. C. HAPFOLD.

Oxytocic, pressor, and antidiuretic activities of commercial samples of pituitary extract. U. G. BIJLSMA, J. H. BURN, and J. H. GADDUM (Quart. J. Pharm., 1928, 1, 493—508).—Four commercial preparations of pituitary extract have been tested independently by the authors and compared with the international standard for oxytocic and pressor power. A new method of testing the antidiuretic power on the human is described; this

factor has been measured in the unanæsthetised dog. The antidiuretic activity is due neither to the pressor nor to the oxytocic principle, consequently the test for any one of these three active principles does not provide an index of the concentration of either of the others in a commercial extract.

F. C. HAPFOLD.

Use of rabbits in insulin assay. K. CULHANE (Quart. J. Pharm., 1928, 1, 517—533).—Marks' "cross test" used on ten or more selected rabbits in an insulin assay gives an error of less than 5%. The variability of response to insulin is affected by weight and season, heavier animals give a higher percentage reduction than light ones and all are more sensitive in summer. Rabbits used in cross tests have been grouped according to the accuracy of the results to which they have contributed; certain rabbits are consequently designated as unsuitable for insulin testing.

F. C. HAPFOLD.

Activation of insulin by yeast juice. E. GLASER and G. HALPERN (Biochem. Z., 1929, 207, 377—383).—Yeast juice after boiling for 8 hrs. does not, on injection, cause a decrease in blood-sugar, but if allowed to remain with insulin in solution at p_{H} 7.8 and then injected, it increases the effect of the insulin. It is suggested that a portion of the insulin, present in an inactive form, is activated.

P. W. CLUTTERBUCK.

Pancreatic hormone and mineral metabolism. II. Influence of the pancreatic hormone on the blood constituents. S. TAKEUCHI (Tohoku J. Exp. Med., 1928, 11, 327—343).—With normal dogs the pancreatic hormone causes a decrease in blood-sugar, inorganic phosphorus, potassium, and calcium, and tends to increase the chlorine and serum-albumin, whilst the sodium and magnesium are unchanged. In dogs with pancreatic diabetes, in addition to the above changes the sodium, but not the magnesium, tends to increase.

CHEMICAL ABSTRACTS.

Effect of insulin and thyroxine on autolysis in liver. A. SIMON and P. WEINER (Biochem. Z., 1929, 207, 319—331).—After administration of large doses of insulin to starving and normal cats, liver autolysis at p_{H} 6.04—6.24 proceeds more slowly than with the liver of normal cats. The inhibitory action of insulin and of thyroxine on autolysis is not obtained in experiments *in vitro*.

P. W. CLUTTERBUCK.

Method of action of the thyroid hormone. R. WEIL and M. LANDSBERG (Biochem. Z., 1929, 207, 186—193).—Thyroxine, in concentrations as low as 1 in 4×10^5 , quantitatively promotes the autolysis of tissue at neutral reaction. The effects of the hormone on metabolism are explained on a physico-chemical basis.

W. MCCARTNEY.

Lipoid-soluble and -insoluble forms of the ovarian hormone. E. GLIMM and F. WADEHN (Biochem. Z., 1929, 207, 361—367).—Ether-soluble and -insoluble œstrus-producing substances occur in urine, the former in predominating amount. The former is converted into a form insoluble in ether by heating in alkaline solution and this on heating with hydrochloric acid is partly reconverted into an ether-soluble substance.

P. W. CLUTTERBUCK.

Vitamin content of meadow and pasture grass. A. SCHEUNERT (Biochem. Z., 1929, 207, 447—457).—In experiments with rats, the vitamin-A and -B contents of the second crop of nine different kinds of mowing and pasture grasses are investigated. The differences in vitamin-A and -B content were small, but whereas pasture grass contained less vitamin-A than mowing grass no difference in vitamin-B content was detected. The grasses had a high vitamin-A and a low vitamin-B content. P. W. CLUTTERBUCK.

Vitamin-A. I. Vitamin-A-choleic acid. T. SHIMIZU and T. HATAKEYAMA (Z. physiol. Chem., 1929, 182, 57—71).—The view that vitamin-A (bio-sterin) is related to both sterol and the bile acids has led to the adoption of the choleic acid method of Wieland and Sorge (A., 1916, i, 710) in order to prepare a water-soluble vitamin-A compound. Vitamin-A, from egg-yolk, dissolved in 100 parts of alcohol was treated with four to five times its weight of deoxycholic acid and evaporated to dryness on a water-bath. The residue was extracted with warm alcohol and water added until the fluorescence disappeared. On keeping, vitamin-A-choleic acid (gallosterin) crystallised as yellow needles which were freed from excess of vitamin-A and cholesterol by repeated extraction with dry ether or chloroform and were recrystallised from aqueous alcohol; m. p. 179°. Gallosterin is insoluble in chloroform or ether, but readily soluble in acetone or alcohol. Titration with 0.01N-sodium hydroxide gave equivalent weight 468 [$(C_{24}H_{40}O_4)_5 \cdot C_{27}H_{44}O_2 \cdot 2H_2O$ requires 476], $[\alpha]_D^{25} +45^\circ$. Treatment of gallosterin with ten times its weight of xylene under reflux in an atmosphere of carbon dioxide under reduced pressure for 1 hr. caused a precipitation of xylenecholeic acid, m. p. 183°, the vitamin remaining in solution. Removal of the xylene under diminished pressure in carbon dioxide gave a residue from which after treatment with a little alcohol the vitamin crystallised as needles. Distillation of gallosterin in a high vacuum in nitrogen at 200—260° removed the vitamin, which was crystallised from alcohol, m. p. 187°. Palladium-hydrogen reduction of gallosterin corresponded with four atoms of hydrogen; its iodine value was 20.2 (95% of theory). Mice fed on vitamin-A-free diet to which gallosterin was added showed normal growth; without gallosterin, avitaminosis set in which disappeared on adding gallosterin. Whilst deoxycholic acid showed no difference when added to a normal diet, when added to a vitamin-A-free diet the animals died within four to six days. C. C. N. VASS.

Detection of vitamin-A. H. STEUDEL (Biochem. Z., 1929, 207, 437—440).—The author claims the isolation of a substance which gives no blue colour reaction with antimony chloride but contains sufficient vitamin-A, as shown by feeding experiments, to maintain young rats in normal growth.

P. W. CLUTTERBUCK.

The Rosenheim-Drummond colour tests of vitamin-A in cod-liver oil. E. C. TOWLE and E. C. MERRILL (J. Amer. Pharm. Assoc., 1929, 18, 357—359).—In the antimony chloride test for vitamin-A according to the method of Carr and Price, the development of the blue colour and its change to red

are positively influenced by the temperature of the reaction mixture. At 10° or below, the rate of change is about one twentieth of that at 25° and a definite working temperature should be specified. The addition of small quantities of alcohol tends to accelerate the reaction and the change from blue to red, and the presence of varying amounts of water influences the reaction in a very uncertain manner. The development of the red coloration may be associated with an oxidation process.

E. H. SHARPLES.

Chemistry of fat-soluble vitamins in cod-liver oil. A. L. BACHARACH and E. L. SMITH (Quart. J. Pharm., 1928, 1, 539—545).—Zucker's claim to have separated vitamins-A and -D is confirmed. Vitamin-D is present in cod-liver oil mainly in a form soluble in ethyl alcohol, in which vitamin-A is insoluble; it is rendered soluble by saponification without affecting its vitamin or chromogen activities.

F. C. HAPFOLD.

Vitamin-A in the liver. E. LAQUEUR, L. K. WOLFF, and E. DENGEMANSE (Deut. med. Woch., 1928, 54, 1495—1497; Chem. Zentr., 1928, ii, 2035—2036).—As determined colorimetrically, the vitamin-A content of liver-oils of different origin varies between 34 and 187 (biological) units. Human liver contains 0—160 units per g. Animal liver contained 30—50 units in autumn, and 10—20 units in winter and spring.

A. A. ELDRIDGE.

Vitamin colour reactions. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1929, 11, 294—307).—The colour reaction of Jendrassik (A., 1923, ii, 892) for vitamin-B, although given by phenols, is much more sensitive to vitamin-B than to phenols. It is suggested that determination of oxidation-reduction potential and the colour reactions given by many reagents would be useful in the determination of vitamins.

E. BOYLAND.

Fundamental role of the alimentary equilibrium in the utilisation of lactose. (MME.) L. RANDOIN and R. LECOQ (Compt. rend., 1929, 188, 1188—1190; cf. A., 1928, 92).—Pigeons fed on a balanced artificial diet containing 66% of lactose to which varying daily doses of brewer's yeast have been added all develop polyneuritis, the yeast not having any retarding effect on the development of this condition. Death occurred after 18—30 days. Similar results are obtained when hydrolysed lactose, or an artificial mixture of 33% of dextrose and 33% of galactose, was used in place of lactose. On giving an artificial diet of composition analogous to that of cow's milk, but deficient in vitamins-B, polyneuritis develops and death occurs after 35—50 days, but in this case addition of large daily doses (0.5 g.) of brewer's yeast prolongs life for 150 days. Thus modification of the composition of the diet enables a better utilisation of lactose by the pigeon, but such utilisation is not entirely conditioned by the presence of sufficient vitamins-B but by a very rigid alimentary equilibrium. J. W. BAKER.

Formation of vitamin-B by *B. vulgatus* (Flügge) Migula. M. SCHIEBLICH (Biochem. Z., 1929, 207, 458—461).—The formation of vitamin-B by *B. vulgatus* is demonstrated by growing the

organism on a medium devoid of the vitamin and feeding the resulting material to young rats.

P. W. CLUTTERBUCK.

Vitamin-C content of fresh and frozen winter cow's milk. W. SALECK (Milchwirt. Forsch., 1928, 6, 464—486; Chem. Zentr., 1928, ii, 2301).—The vitamin-C content of cow's milk is diminished only slightly by freezing for 3 days. A. A. ELDRIDGE.

Antirachitic principle of irradiated food. A. HOTTINGER (Z. Kinderheilk., 1927, 43, 8—23; Chem. Zentr., 1928, ii, 2036).—Cholesterol, olive oil, cholesteryl oleate, and bile salts have no antirachitic action, but after irradiation with ultra-violet light all except bile salts are antirachitic. Active cholesterol preparations gradually lose their activity, the loss with olive oil being less rapid. Cholesterol is inactivated by heating at 150—200°, and partly at 100—120°. Irradiation for several hours inactivates active olive oil or cholesterol. A. A. ELDRIDGE.

Influence of changes in body-weight of the test rats on the accuracy of the assay of vitamin-D by means of the line test. K. H. COWARD and M. R. CAMDEN (Quart. J. Pharm., 1929, 2, 44—47).—Rats fed on a rachitogenic diet showed at the best only slight evidence of healing due to a more or less temporary loss of weight (cf. Bills, Honeywell, and MacNair, A., 1928, 332). C. C. N. VASS.

Chemical reaction for antirachitic vitamin. W. STOELTZNER (Münch. med. Woch., 1928, 75, 1584; Chem. Zentr., 1928, ii, 2036).—Addition of phosphorus pentoxide to the oil containing antirachitic vitamin produces a reddish-brown coloration, gradually darkening, finally becoming almost black.

A. A. ELDRIDGE.

Irradiation of ergosterol: action of quartz [lamp] ultra-violet rays and of soft X-rays. R. DELAPLACE and G. REBIERE (Compt. rend., 1929, 188, 1169—1172).—The absorption of an alcoholic solution of ergosterol irradiated by the quartz lamp showed an absorption maximum and minimum during the first minutes of irradiation. After about 7—10 min. it attained its maximum (vitamin-D) activity, though 40 min. exposure was required for the full production of the absorption band attributed to this vitamin. Analogous results were obtained with soft X-rays. J. GRANT.

Absorption spectrum of vitamin-D. R. B. BOURDILLON, C. FISCHMANN, R. G. C. JENKINS, and T. A. WEBSTER (Proc. Roy. Soc., 1929, B, 104, 561—583).—The action of ultra-violet radiation on ergosterol has been studied by comparing the absorption spectra and antirachitic activity of the products formed. It is concluded that three substances are produced in succession of which the first shows an absorption band similar to that of ergosterol (maximum 280 μ) but more than twice as intense. Evidence is given showing that this substance is probably vitamin-D. The second product, which is formed by further irradiation of the first, shows a strong absorption band with maximum at 240 μ and has no antirachitic activity. The third substance is formed by further irradiation of the second, and shows neither antirachitic activity nor marked absorption. B. A. EAGLES.

Origin of chlorophyll and its relation to blood pigments. K. NOACK and W. KIESSLING (Z. physiol. Chem., 1929, 182, 13—49).—Protochlorophyll was obtained as a dark green non-crystalline powder, m. p. 80—129°, by extraction of the inner skin of cucumber seeds, after removal of fat, with 80% acetone and precipitation with light petroleum. It has not yet been obtained pure. The absorption spectra agree with those found by Monteverde and Labimenko (A., 1912, ii, 800) and differ from that of chlorophyll in diminished absorption in the red, a displacement towards the violet, and a more intense green band. It is more basic than chlorophyll. Acid treatment of its ethereal solution yields the magnesium-free pigment protophæophytin, precipitated by light petroleum as a dark green, non-crystalline substance which could not be purified. Protophæophytin on treatment with the Grignard reagent yields a magnesium-containing pigment the spectrum of which is identical with that of protochlorophyll. Comparison of the absorption spectra of protophæophytin and phylloerythrin obtained from the bile of animals shows a complete agreement in the intensities of the series, whilst the single bands of the latter were removed 50—70 Å. towards the violet. The magnesium Grignard reagent yields with phylloerythrin a pigment the absorption spectrum of which shows an analogous agreement with that of protochlorophyll. Treatment of phylloerythrin in isopropyl alcohol with a minimal quantity of aqueous potassium hydroxide at 25° gives a substance containing a free carboxyl group the absorption spectrum of which is fundamentally the same as that of blood-protoporphyrin. The free carboxylic acid is extremely labile, reverting to a less acid substance the spectrum of which is of the same type as that of phylloerythrin. When boiled with methyl-alcoholic hydrogen chloride it yields an alkali-insoluble anhydrous compound. Light converts the free carboxylic acid and its methyl ester into a chlorophyll-green substance with the characteristic red band of chlorophyll (670—653 μ). Hydrolysis of protophæophytin with methyl-alcoholic potassium hydroxide yields an alkali-insoluble compound spectroscopically identical with the anhydrous compound derived from the carboxylic acid obtained from phylloerythrin. Hydrolysis of protophæophytin with methyl-alcoholic hydrogen chloride yields a pigment which crystallises in brownish-red plates or olive-green prisms and having a spectrum identical with that of the carboxylic acid from phylloerythrin. A pigment having the same spectrum may also be obtained by alkaline hydrolysis of protophæophytin. Chlorophyll in isopropyl-alcoholic solution on treatment with iron powder and hydrochloric acid yields, on subsequent extraction with ether and treatment with hydrochloric acid, on addition of light petroleum a dark red powder the absorption spectrum of which agrees with that of natural protophæophytin. Reduction of chlorophyll in glacial acetic acid by hydrogen iodide and red phosphorus gives an olive-green substance almost identical spectroscopically with phylloerythrin. Natural and synthetic protophæophytin have the same ester characteristics as chlorophyll, hence the absence of the well-defined crystalline property found in phylloerythrin. It has

not been possible to confirm the analogy between chlorophyll and protochlorophyll by the separation of the latter into the *a* and *b* forms. Hydrolysis of synthetic protophaeophytin with methyl-alcoholic potassium hydroxide yields a free carboxylic acid the absorption spectrum of which is identical with that of the acid derived from phylloerythrin.

C. C. N. VASS.

Chlorophyll content and rate of photosynthesis. R. EMERSON (Proc. Nat. Acad. Sci., 1929, 15, 281—284).—An internal factor, the chlorophyll content, affecting the rate of photosynthesis, was controlled in *Chlorella vulgaris*, and the rate of photosynthesis was determined at high light intensity and plotted against relative chlorophyll concentration, and also for two different values of the latter, as a function of the temperature. It is shown that the rate of photosynthesis is a function of the chlorophyll content, and is the same function of the temperature, independent of the chlorophyll concentration. The inhibition of photosynthesis by hydrocyanic acid is discussed.

N. M. BLIGH.

Absorption of carbon dioxide by roots and its utilisation in chlorophyllous photosynthesis. (SIGNA.) M. BERGAMASCHI (Atti R. Accad. Lincei, 1929, [vi], 9, 238—242).—Maize and other plants grown in an atmosphere free from carbon dioxide form starch in their leaves from carbon dioxide absorbed by the roots from either the soil or the nutrient solution in which they are grown, and, since the plants contain a greater quantity of carbon than the original seeds, the contention that the organic material is formed solely at the expense of carbon dioxide of respiration is refuted.

T. H. POPE.

Growth of the tomato as correlated with organic nitrogen and carbohydrates in roots, stems, and leaves. G. T. NIGHTINGALE, L. G. SCHERMERHORN, and W. R. ROBBINS (N. J. Agric. Exp. Sta. Bull., 1928, No. 401, 1—38).—The roots contain little carbohydrate, but much protein-nitrogen. In vigorously growing plants the assimilated nitrogen is high in the stem, but the protein-nitrogen is low except at or near the growing point. Sucrose, starch, and dextrin do not in general accumulate unless the reducing sugar is high. Petioles and veins correspond with stems as regards carbohydrates and nitrate-free nitrogen. In general, proteose, basic-, amino-, amide-, and ammonia-nitrogen increase during darkness, but in the upper stems the proteose, protein, and basic nitrogen decreased, whilst the amino-, amide-, and ammonia-nitrogen increased. On return to light, carbohydrates and protein increased, and all forms of nitrate-free soluble nitrogen decreased.

CHEMICAL ABSTRACTS.

Behaviour of the olive under the influence of uranium radiations and of the ionisation of the air. L. PETRI (Atti R. Accad. Lincei, 1929, [vi], 9, 188—189).—The stimulating effect produced on the growth of the olive by ionised air is completely annulled by radiations emitted by green uranium oxide when these exceed a certain limiting intensity. Plants thus treated stopped growing entirely when cold weather set in, whereas the control plants con-

tinued to grow, even at temperatures between 5° and 15°; the functional activity of the former, indicated by the quantity of water used up, was only about one half of that of the controls.

T. H. POPE.

Influence of the nitrate-ion concentration of nutrient solutions on the growth of summer wheat. M. A. J. GORDEWAAGEN (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 135—150).—Nitrate-ion concentrations were used which it may be assumed occur in the soil solution. Solutions of sodium nitrate were employed, but as the sodium-ion concentration alters with the nitrate-ion concentration, experiments were made in such a way that the effect of the former could be judged separately. As a general result of the experiments it is shown that good growth of wheat plants is possible with nutrient solutions having widely divergent nitrate content. The maximum nitrogen concentration for good growth is between 182 and 238 parts per million. The lowest concentration permitting fairly good growth lies below 5 parts per million.

A. J. MEE.

Nutrition of higher plants with ammonia. D. PRANISCHNIKOV (Biochem. Z., 1929, 207, 341—349).—In neutral reaction ammonia, and in acid reaction nitrate, is the better source of nitrogen. Optimal development can be obtained by administration of either ammonia or nitrate by suitably adjusting either the p_{H} or the content of cation associated with ammonium in the nutritive mixture.

P. W. CLUTTERBUCK.

Nitrogen metabolism of forest soil. D. FEHER (Biochem. Z., 1929, 207, 350—360).—Tables and curves show the changes of total nitrogen, nitrate-nitrogen, and humus contents, of the protozoal and bacterial counts, of the p_{H} , and air- and ground-temperatures of the soil of three types of pine wood during a period of 12 months. The total nitrogen content is maximal in June and July, rapidly decreasing in autumn, and is minimal in September. The nitrate-nitrogen follows a similar course, but the maximal values are obtained in April and May. The bacterial count is also maximal in the spring and summer months. There does not appear to be the same causal connexion between the changes in number of nitrifying and fixing organisms and the changes of nitrate- and total nitrogen as was observed between the bacterial count and carbon dioxide production (A., 1928, 558, 1406; B., 1928, 381), the chief factor being the intensity of the activity of the organisms rather than their number.

P. W. CLUTTERBUCK.

Nucleo-cytoplasmic ratio in plant tissues. F. E. HUELIN (Austral. J. Exp. Biol., 1929, 6, 59—63).—Nucleo-cytoplasmic ratios have been determined for young wheat plants by the method of Robertson (this vol., 715). The ratio diminishes rapidly with age at a comparatively early stage of growth.

F. C. HAPFOLD.

Effects of the waxy gene in maize on fat metabolism. F. A. ABEGG (J. Agric. Res., 1929, 38, 183—193).—The differences in acid value and saponification value of the ether-soluble oils from non-waxy and waxy maize grains are shown to be due to the

high acid value and saponification value of the fat from the endosperm tissue in the waxy gene.

E. A. LUNT.

Isolation of methyl alcohol from tobacco smoke. C. NEUBERG and M. KOBEL (Biochem. Z., 1929, 206, 240—244).—The presence of methyl alcohol in tobacco smoke was demonstrated by the isolation of the pure substance in a yield of 0.24% on tobacco.

J. H. BIRKINSHAW.

Microanalytical tobacco determinations. II. Determinations of nicotine in fresh green tobacco. J. BODNAR and V. L. NAGY (Biochem. Z., 1929, 206, 410—415).—Drying of the fresh green leaves at 95—97° caused no loss in nicotine content. The dried leaves after powdering are extracted with a mixture of ether and light petroleum under faintly alkaline conditions. The extract is freed from ammonia by means of a current of air, an equal volume of water added, and a known amount of 0.01N-hydrochloric acid. The excess of hydrochloric acid is determined by titration with 0.01N-sodium hydroxide, using methyl-red as indicator. One c.c. of 0.01N-hydrochloric acid corresponds with 1.62 mg. of nicotine. This method compares favourably with the gravimetric method of Rasmussen (A., 1916, ii, 359).

C. C. N. VASS.

[Non-]occurrence of fatty acids with an uneven number of carbon atoms in natural fats, oils, and waxes. I. Oil from *Datura stramonium*. L. P. E. VERKADE and J. COOPS, jun. (Biochem. Z., 1929, 206, 468—481).—Fractionation of the methyl esters of the saturated fatty acids obtained from the oil of *D. stramonium*, and a comparison of their m. p. with those of the m.-p. diagram of a mixture of methyl palmitate and methyl stearate, show the so-called margaric or daturic acid to be a mixture of palmitic and stearic acids in the ratio 5:1. Pure methyl stearate has m. p. 38.70°, methyl palmitate 29.70°. X-Ray analysis shows that the spectrum of the methyl ester of the supposed heptadecic acid is identical with the spectrum of a synthetic mixture of methyl palmitate and stearate having the same m. p.

C. C. N. VASS.

Seeds of *Monarda punctata*. A. A. HARWOOD (J. Amer. Pharm. Assoc., 1929, 18, 228—231).—Light petroleum extraction of the seeds (3.6% water, 7.5% ash) of *M. punctata* gave 20.5—25.2% of oil having d_{25}^{25} 0.9100 and saponif. value 173.3. Ether extraction gave 29.7% of oil having d_{25}^{25} 0.9217, n_D^{25} 1.4840, saponif. value 206 and 207.8, iodine value 207.

E. H. SHARPLES.

Ether-soluble substances of cabbage-leaf cytoplasm. V. Isolation of *n*-nonacosane and *n*-tetradecyl ketone. H. J. CHANNON and A. C. CHIBNALL (Biochem. J., 1928, 23, 168—175).—These compounds are precipitated in the so-called phosphatide fraction obtained by the addition of cold acetone to the ethereal extract of cabbage leaf (A., 1927, 1227). They were removed from this fraction by extraction with boiling acetone. The paraffin was obtained by crystallising the lower-boiling fractions of the mixture from alcoholic benzene. The ketone, m. p. 80.5—81°, was separated by taking advantage of the greater solubility of the ketoxime in a mixture

of light petroleum and acetone. The number of carbon atoms and the purity of the paraffin were determined by X-ray analysis. The ketone gave the same m. p. when mixed with the synthetic compound, but a depressed m. p. when mixed with synthetic palmitone. *Di-n-tetradecyl ketone* was synthesised by Kipping's method (J.C.S., 1890, 57, 980) for the preparation of palmitone. *Palmityl myristyl ketone*, m. p. 74—74.5°, was synthesised as follows. *Ethyl α -dodecyl-acetoacetate* was prepared by treating dodecyl iodide with alcoholic sodium and ethyl acetoacetate and extracting with ether. It was then treated in dry ether with sodium and palmityl chloride and the resulting *ethyl α -dodecylpalmitylacetoacetate* was saponified with potassium hydroxide. The palmityl myristyl ketone was finally extracted with ether and precipitated with acetone from the ethereal solution.

S. S. ZILVA.

Ether-soluble substances of cabbage-leaf cytoplasm. VI. Summary and general conclusions. A. C. CHIBNALL and H. J. CHANNON (Biochem. J., 1929, 23, 176—184).—A summary and discussion of results previously obtained (cf. A., 1927, 386, 799, 1227). The chlorophyll content of the acetone-ether fraction of one of the batches was 9.3%, the carotin 0.86%, and the xanthophyll 0.62%. The chemical character of the unsaturated fraction of the unsaponifiable fraction which consists of sterols and unidentified products, probably alcohols and hydrocarbons, is described.

S. S. ZILVA.

Nature of the pectic substances of flax. F. W. NORRIS (Biochem. J., 1929, 23, 195—198).—Pectic substances were prepared from flax by Clayton, Norris, and Schryver's method (A., 1922, i, 206). The ash content, and furfuraldehyde and carbon dioxide produced on hydrolysis with 12% hydrochloric acid were determined for each product and in the case of the soluble pectin methoxyl groups were also determined. The results obtained are in accordance with expectations based on the ring formula of Nanji, Paton, and Ling (J.S.C.I., 1925, 44, 253r) and do not support Henderson's simpler galactose-tetragalacturonic acid formula (A., 1928, 1119).

S. S. ZILVA.

Sarmentocymarin and sarmentogenin. W. A. JACOBS and M. HEIDELBERGER (J. Biol. Chem., 1929, 81, 765—779).—By the usual direct methods of extraction *Strophanthus sarmentosus* seeds yielded small amounts of *sarmentocymarin*, $C_{30}H_{46}O_8 \cdot 2H_2O$, m. p. 130°, $[\alpha]_D^{25}$ -12.5° in methyl alcohol; further larger amounts of the same compound, together with dextrose, were obtained by digestion of the crude residual glucosides with an enzyme prepared from the seeds. When hydrolysed with hydrochloric acid the compound yielded *sarmentogenin*, $C_{23}H_{34}O_5$, m. p. 265—266°, $[\alpha]_D^{25}$ +21.5° in 95% alcohol, forming, when crystallised from pyridine, a compound, $C_{23}H_{35}O_5 \cdot C_5H_5N$, m. p. 258°; *sarmentogenin* gave a *dibenzoate*, m. p. 281°, $[\alpha]_D^{25}$ +14°, and, with hydrogen and platinum, yielded *dihydrosarmentogenin*, $C_{23}H_{36}O_5 \cdot EtOH$, m. p. 142°; when oxidised with chromic acid it gave *sarmentogenone*, $C_{23}H_{32}O_5$, m. p. 226° (*semicarbazone*, m. p. 200°). With methyl-alcoholic potassium hydroxide, *sarmentogenin* gave *isosarmentogenin*,

$C_{23}H_{34}O_6$, EtOH, m. p. 248° (dibenzoate, m. p. 297°), which, when treated with sodium hydroxide, yielded the lactone acid, isosarmentogenic acid, $C_{23}H_{34}O_6$, m. p. 212° (methyl ester, m. p. 274°). Sarmentogenin is thus isomeric with periplogenin and gitoxigenin and shares with these the general chemical characteristics of the strophanthidin series. It is probably identical with the "strophanthidin" described by Kohn and Kulisch (A., 1898, i, 329).

C. R. HARRINGTON.

Two phloroglucinol drugs. W. PEYER and W. LIEBISCH (Pharm. Zentr., 1929, 70, 197—200).—Phloroglucinol has been detected in the drugs obtained from *Albizia anthelminthica* and *Combretum rambaultii*; the first contains 8.2% of saponin and the second 2.25% of saponin and considerable quantities of a tannin.

W. O. KERMACK.

Occurrence of euxanthone in heart-wood of *Platonia insignis*, Mart ("Geelhart" or "Pakoeli"). D. B. SPOELSTRA and M. J. VAN ROYEN (Rec. trav. chim., 1929, 48, 370—371).—Extraction of 2 kg. of the wood with benzene gave 1.3% of euxanthone, m. p. 239° (acetyl derivative, m. p. 185°; bromo-derivative, m. p. 278°). Further extraction of the wood with alcohol yielded a dark-coloured, brittle residue, m. p. 205—225° (decomp.), completely soluble in alkali, but insoluble in water. No definite product was isolated by fusion with potassium hydroxide or distillation with zinc dust.

H. BURTON.

Proteins of the avocado (*Persea americana*, Mill). D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1929, 81, 533—539).—The finely-divided fruit was extracted with 10% sodium chloride solution; when the extract was heated to 68° there was obtained a globulin in a yield of 0.44% of the original fruit; the same protein could be obtained by treating the extract with ammonium sulphate to 67% saturation, or by acidifying to p_H 3.9 with acetic acid. The residue left after extraction with sodium chloride was boiled with 60% alcoholic 0.1N-sodium hydroxide and the filtrate acidified with acetic acid; this yielded a second protein. A third protein was obtained by dilution of the mother-liquor with water. Figures are given for the nitrogen distribution of the various proteins.

C. R. HARRINGTON.

Similarity between physico-chemical and biological reactions. C. P. SIDERIS (Plant Physiol., 1928, 3, 79—83).—The isoelectric points of two proteins, A and B, isolated from the stem of the pineapple, are, respectively, p_H 6.4 and 4.8. Various organisms were unable to grow in the protein-A at the isoelectric point.

CHEMICAL ABSTRACTS.

Modification of f.-p. determinations for small quantities of biological fluids. E. FROMM and T. LEIPERT (Biochem. Z., 1929, 206, 314—318).—Details of the method and apparatus used to determine f. p. and the depression of m. p. in 3 c.c. of a fluid by means of an ordinary thermometer graduated in hundredths of a degree are given.

C. C. N. VASS.

Determination of cysteine, cystine, and their derivatives in tissues and biological fluids. Y.

OKUDA (J. Dept. Agric. Kyushu, 1929, 2, 133—148).—The proteins of biological tissues or fluids are coagulated by means of a solution of sulphosalicylic acid and the cysteine in the filtrate is determined by titration with a standard iodate solution containing iodide. Cystine is similarly determined after reduction to cysteine. For precipitation of proteins, sulphosalicylic acid possesses advantages over trichloroacetic acid, since in presence of the latter acid the iodine titration is untrustworthy.

W. O. KERMACK.

Purification of picric acid. S. R. BENEDICT (J. Biol. Chem., 1929, 82, 1—3).—Picric acid, for the purpose of the colorimetric determination of creatinine, is best purified by crystallisation from glacial acetic acid, or by solution in sodium carbonate, separation of the sodium salt, and decomposition of the latter with dilute hydrochloric acid.

C. R. HARRINGTON.

Ergosterol-digtonin complex. H. PENAU and Z. HARDY (J. Pharm. Chim., 1929, [viii], 9, 145—151, and Bull. Soc. Chim. biol., 1929, 11, 437—442).—The influence of time, temperature, and the presence of water on the formation of ergosterol-digtonide from alcoholic solutions of its constituents has been studied. The following procedure for its preparation is described. Ten c.c. of a 0.175% solution of ergosterol in 99% alcohol are introduced into a dried and weighed centrifuge tube; 9 c.c. of a 1% solution digtonin in 99% alcohol are added, and then 2 c.c. of water. The mixture is shaken and kept for 18 hrs. at about 18°, then centrifuged for 15 min. and the supernatant liquor decanted. The solid is stirred with 3 c.c. of a mixture of acetone 73 c.c., water 18 c.c., and alcohol 9 c.c., the stirrer washed with 1 c.c. of the same mixture and, after centrifuging and decanting the supernatant wash-liquor, the tube and contents are dried for 18—24 hrs. over phosphorus pentoxide. 1 G. of the ergosterol-digtonide complex is equivalent to 250 mg. of ergosterol.

E. H. SHARPLES.

Micro-determination of phosphorus in tissue. Y. NAITO (J. Biochem. Japan, 1928, 9, 45—69).—The method depends on the production of a precipitate of ammonium phosphomolybdate of definite composition when a phosphate solution containing ammonium nitrate is treated at 80° with ammonium molybdate at a definite acidity; the compound is then decomposed by sodium hydroxide, and the residual alkali titrated. Accurate results can be obtained with 0.03 mg. of phosphorus. The tissue, containing 0.1—0.005 mg. of phosphorus, is digested with 3 c.c. of 20% sulphuric acid, the digestion being completed with nitric acid or redistilled hydrogen peroxide; 3 c.c. of ammonium nitrate solution (30 g. in 100 c.c.) are added, and water to 9 c.c. At 80°, 1 c.c. of 10% ammonium molybdate solution is added, and the precipitate, after being kept overnight, is washed with 20% alcohol and decomposed with 0.04N-sodium hydroxide.

CHEMICAL ABSTRACTS.

Determination of halogens in organic substances. W. ROMAN.—See this vol., 713.

Van Slyke's method. L. ROSENTHALER.—See this vol., 713.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1929.

General, Physical, and Inorganic Chemistry.

Amplifier for comparison of spectra. S. PINA DE RUBIES (Anal. Fis. Quím., 1929, 27, 48—56).—A method whereby the spectrum of a mineral may be projected simultaneously with those of its constituent elements is described. H. F. GILLBE.

Theory of coupling-widening of spectral lines. J. HOLTSMARK (Z. Physik, 1929, 54, 761—763).—From considerations of quantum mechanics the width of a spectral line is proportional to the square root of the density of the oscillators or resonators. The recently published work of Waibel on the caesium principal series (this vol., 479) in which the square root law was found to be obeyed in all cases is shown to be in error as far as calculation of the width of lines is concerned. After correction the results agree with those of the present author. The small coupling width of emission lines found by Hasche, Póányi, and Vogt (A., 1927, 396) is explained by the small coupling of the emitting resonators. A. J. MEE.

Emission lines in the spectrum of the solar corona. V. ZESSEVITSCH and V. NIKONOV (Nature, 1929, 123, 909—910).

Light-emission from atoms. D. G. BOURGIN and E. E. LIBMAN (Ann. Physik, 1929, [v], 1, 1096—1098).—A criticism of the work of Kleiber (this vol., 2).

R. A. MORTON.

Physical criticism of Schrödinger's theory of light emission. I. Intensity relation in the effect of electric fields on spectral lines. II. Amount and frequency of optical energy. III. Fundamental difficulties. J. STARK (Ann. Physik, 1929, [v], 1, 1009—1024, 1025—1034, 1035—1040).—I. It has been stated (cf. Foster and Chalk, A., 1928, 687; this vol., 616) that the relative intensities of Stark components in hydrogen agree within experimental error with the new calculations by Schrödinger. Under precisely defined conditions, the *pa*-component $\pm\frac{1}{2}$ of the hydrogen line H_α is considerably more intense than the *pa*-component ± 3 . It is shown that the intensity ratios for the outer components of H_α , H_β , and H_γ obtained under the influence of electric fields are by no means constants characteristic of the hydrogen atom, since the values can vary over wide depending on the conditions of experiment. Considerable deviations from the Schrödinger values are obtained, and it is stated that the theory has not been confirmed.

II. For many reasons it is necessary to retain the idea of a strict correspondence between the amount of energy emitted and the frequency of the light, the

relationship being definitely based on experience. Schrödinger's theory involves the breaking up of the elementary optical energy into any number of other frequencies, a view which cannot satisfactorily be reconciled with experience. Attempts to solve the difficulty are unconvincing.

III. Schrödinger's theory is based on the assumption that a stationary state can be regarded as determined by characteristic vibrations of an electric charge distributed continuously over the space-field of the atom. Thus the electron of the hydrogen atom must have its mass distributed over the whole space of the atomic field (diameter of the order 5×10^{-9} cm.). The space occupied by the electrical charge of a free electron is very much smaller, and the idea of an "attenuated" electron is open to objection from the physical point of view. Schrödinger bases the equation for the stationary vibration state on the calculation of light emission from the damping of hypothetical oscillations, instead of an equation for the vibration state, which, in consequence of the damping by emission, shows a time change with respect to amplitude and energy. R. A. MORTON.

Spectrum of H_α . The bands analogous to the parhelium line spectrum. II, III, IV. O. W. RICHARDSON and P. M. DAVIDSON (Proc. Roy. Soc., 1929, A, 123, 466—488; 124, 50—68, 69—88; cf. this vol., 616).—II. The system with *P* strong, *R* weak ($3^1A \rightarrow 2^1S$) is described. This system has no *Q* branches and the lines do not show the Zeeman effect, with the exception of $21420.70(3) = R(1)1' \rightarrow 2''$. This appears to be a genuine abnormality. The same type of alternation of intensity is met with as in the other systems. The initial rotational levels present a curious oscillation in the second term difference both with *m* and *n'*. The three systems $3^1A \rightarrow 2^1S(P > R)$, $3^1B \rightarrow 2^1S(Q)$, and $3^1C \rightarrow 2^1S(R > P)$ are compared. Five systems coming from electronic levels with principal quantum number 4, denoted by $4^1A \rightarrow 2^1S$, $4^1B \rightarrow 2^1S$, $4^1C \rightarrow 2^1S$, $4^1X \rightarrow 2^1S$, and $4^1E \rightarrow 2^1S$, are described. Apart from some perturbations, these bands which come from $4'$ electronic levels all show the alternation in intensity which is so marked for all the other bands in this spectrum. The weight ratio of alternate states is found to be 3 to 1, as with the other systems, and the transitions are also governed by the same rules. The following values have been calculated: for neutral H_α , the ionisation potential is 15.381 volts, and the heat of dissociation is 4.465 ± 0.04 volts; for

the hydrogen molecule ion, H_2^+ , the heat of dissociation is 2.50 volts, the vibration frequency at zero amplitude (ω_0) = 2280 wave numbers, and $x\omega_0 = 60$. These values are in excellent agreement with Burran's computations based on the wave mechanics (K. Danske Vid. selsk., Math-fys., 1927, 7, 14).

III. Descriptions are given of a number of band systems having *P* and *R* branches in which there is not so much disparity between the strengths of the two sets of branches as in the systems previously described. In these systems the rotational energy levels are remarkably close together compared with those of the bands previously described, the differences of the intervals increasing with *m*. A full account is given of the way in which the data for the rotational energy interval tables are obtained.

IV. Descriptions are given of the system $1^0 \rightarrow 2^1S(v_e = 22814)$, the progression $1^0Q = 2^1S(v_e = 21843)$, the progression starting from 4142.801 Å., and the progression 4097.433 Å. L. L. BIRCUMSHAW.

Para- and ortho-hydrogen. K. F. BONHOEFFER and P. HARTECK (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 103—108).—A more detailed account of work previously reported (cf. this vol., 479).

R. A. MORTON.

Band systems in the molecular spectrum of hydrogen. I. Singlet system. II. Triplet system. W. FINKELNBURG and R. MECKE (Z. Physik, 1929, 54, 198—214, 597—631).—I. A discussion of the new measurements on the hydrogen band spectrum by Finkelburg (this vol., 118), Gale, Monk, and Lee. Four band systems containing 383 lines are distinguished.

II. 825 lines in 60 bands have been classified and shown to belong to the triplet system of the hydrogen molecule. Nuclear vibration quantum numbers and moments of inertia can be derived for the terms 2^3S , 3^3P , and 3^3D . All the bands have the 2^3S -term as their common final term and, since this is also the initial term of the ultra-violet Lyman bands, the latter would appear to be given by the combination $1^1S - 2^3S$. The Balmer bands (α -, β -, γ -, δ -bands), described by Richardson as a triplet system, are shown to be singlet. Since most of the strongest lines of the spectrum have now been classified, such groups as H_2^+ and H_3 can play only a minor part in the emission (cf. this vol., 624).

E. B. ROBERTSON.

Parahydrogen. K. F. BONHOEFFER and P. HARTECK (Naturwiss., 1929, 17, 321—322).—Parahydrogen melts and vaporises at lower temperatures than ordinary hydrogen. On the basis of *m. p.* 13.95° Abs., and *b. p.* 20.39° for ordinary hydrogen, parahydrogen shows pressures of 57.0 and 787 mm. as against 53.9 and 760 mm., whilst at 760 mm. the *b. p.* of parahydrogen is 20.26° Abs. The difference between the two forms arises from the smaller (0.65%) heat of vaporisation of the parahydrogen.

The α -system of the many-lined spectrum, emitted by normal hydrogen, has been compared with that from parahydrogen and striking intensity changes are observed.

R. A. MORTON.

Variation of intensities in helium spectrum with pressure and electron velocity. (FRL.) M. G.

PETERI and W. ELENBAAS (Z. Physik, 1929, 54, 92—98).—The relative intensities of the following helium lines have been measured, using Ilford special rapid panchromatic plates: (a) excited in a Geissler tube of 2.18 mm.² cross section by 1000 volts D.C., pressure 6.9 mm.; (b) excited in field-free space by electrons of known velocity, 60 volts, pressure 0.045 mm.: 6678, 5876, 5048, 5016, 4922, 4713, 4472, 4438, 4388, 4169, 4144, 4121, 4026, 3965, 3889 Å. It is found in all cases that at the lower pressure the lines are stronger. R. W. LUNT.

Variation of the intensities in the helium spectrum with the velocity of the exciting electrons. J. H. LEES and H. W. B. SKINNER (Nature, 1929, 123, 836).—For high exciting velocities the triplets vanish in intensity compared with the singlets, whilst for low exciting velocities the singlets are weak compared with the triplets. Further, whilst the light of the triplets is confined closely to the electron beam, the light from the singlets tends to spread away from it. A. A. ELDRIDGE.

Intensity measurements in the helium spectrum. D. BURGER (Z. Physik, 1929, 54, 643—655).—The intensity relationship for 56 helium lines has been measured, using a quartz spectrograph and Moll microphotometer. Only one line (3889 Å.) of the principal triplet series was included, but many lines of other series. The decrease of intensity appears to be greater in the principal singlet series than in the subordinate series; in all cases it is approximately equal to that found by Bongers (Diss., Utrecht, 1927) for the Balmer series. The ratio intensity/ v^4 for corresponding lines of the singlet and triplet systems of the subordinate series has been determined in many cases. For the lower terms it is found to be greater, and for higher terms less, than the expected value of 1:3. E. B. ROBERTSON.

New regularities in the band spectrum of helium. II. G. H. DIEKE, S. IMANISHI, and T. TAKAMINE (Z. Physik, 1929, 54, 826—843; cf. A., 1928, 677, 1295).—A series of new helium bands is investigated. They are mainly below 4500 Å. in wave-length. Those specially considered are the band complex $2p-2d$, at λ 440 m μ ; the bands of wave-length 378 m μ and 611 m μ , and the complex band λ 416 m μ . A. J. MEE.

Polarisation in the case of neon electron collision emission and the neon canal-ray emission. W. HANLE and B. QUARDER (Z. Physik, 1929, 54, 819—825).—An arrangement of apparatus is described for the polarisation of the emission due to electron collisions in neon at low pressures, and of the emission of the slow neon canal rays. Most of the lines showed partial polarisation, partly parallel with and partly perpendicular to the electron beam. As for mercury, with increasing velocity of the colliding electrons there was a decrease in the degree of polarisation. The optimum for most lines lies in the neighbourhood of 20—25 volts. The results are compared with those found for mercury, and show an agreement between analogous lines. The canal rays also show partial polarisation. The effect of a weak magnetic field on

the lines is also investigated. The mercury triplet lines, 5460.7, 4358.3, and 4046.6 Å., were weakened.

A. J. MEE.

Series in the krypton arc spectrum. W. GREMMER (Z. Physik, 1929, 54, 215—226).—The arc spectrum of krypton has been photographed and measured. Series have been found which correspond with the *sp* combination, using Paschen's notation, and the krypton spectrum has been shown to be of similar structure to those of neon and argon. 4s- and 9p-series of the 10p-term have been worked out, and these explain many lines of the spectrum.

E. B. ROBERTSON.

Spectroscopic method for the proof of the existence of unstable intermediate products in activated gases, and its application to active hydrogen, nitrogen, and oxygen. Z. BAY and W. STEINER (Z. physikal. Chem., 1929, B, 3, 149—161).—The method depends on the production of an emission spectrum from the activated gas by using high-frequency discharges with external electrodes, or electrodeless ring discharges. A method involving emission spectra is better than one using absorption spectra, because it is much more sensitive. The method can be used for the identification of intermediate products, and to follow the concentration changes of an intermediate product. The method is applied to active hydrogen, in which case the intermediate product is atomic hydrogen. The spectra of active nitrogen and oxygen obtained by this method were also investigated. Arc lines of nitrogen were shown to be present in the spectrum of the activated gas.

A. J. MEE.

Electrodeless ring discharge with undamped excitation. H. STEINHAUSER (Z. Physik, 1929, 54, 788—797).—The conductivity and relative sparking potentials of air, oxygen, nitrogen, carbon dioxide, hydrogen, helium, neon, and argon were determined over a pressure range of 0—16 mm. by the electrodeless discharge method. The apparatus and method are described. A direct measurement of the sparking potential cannot be obtained by this means, but it is possible to find relative sparking potentials by finding the smallest current in the exciting coil that will bring about sparking. Curves are drawn for each gas showing (a) relative conductivity and (b) sparking current against pressure. It was found that the minimum sparking current coincided with the maximum value of the conductivity. For the "base" gases the sparking potential is reached at a lower pressure and has a greater value than in the case of the rare gases. The curves for both types of gas show maxima or minima, but in the case of the rare gases the maxima are not so sharp and extend over a wider pressure range. The effect of the life period of electron is discussed. The life period of the electrons in the rare gases is longer than in the "base" gases, and this fact plays an important part in causing the difference between damped and undamped excitation.

A. J. MEE.

Spectrum of doubly-ionised chlorine. K. MAJUMDAR and S. C. DEB (Indian J. Physics, 1929, 3, 445—450).—An extension of the work of Bowen (cf. A., 1928, 210). Thirty additional lines are classified,

and are attributed to the transition $2M_0(M_3 \leftarrow N_2 \leftarrow N_3)$.

N. M. BLIGH.

Spectra of As III and Sb III. P. PATTABHIRAMIAH and A. S. RAO (Indian J. Physics, 1929, 3, 437—444; cf. Rao and Narayan, A., 1928, 929).—Tables are given showing the relativity doublet law variations and a comparison of the term values in gallium-like and indium-like atoms. Forty-one lines of As III and 25 lines of Sb III are tabulated and classified; other combinations involving the characteristic difference 722 in arsenic and 1668 in antimony are also given.

N. M. BLIGH.

Arc spectrum of silicon. A. FOWLER (Proc. Roy. Soc., 1929, A, 123, 422—439).—The arc spectrum of silicon has been investigated with the vacuum grating spectrograph, the arc being passed in nitrogen at atmospheric pressure in order to extend the observations as far as possible to short wave-lengths and to minimise the introduction of lines of Si II. A catalogue of lines from 11231 to 1600 Å. is given, including many previously unrecorded lines in the Schumann region. Most of the deeper terms predicted by the Heisenberg-Hund theory have been identified, and several series of more than two members are available for the determination of term values. The term $3p^3P_0$, representing the lowest normal state of the Si I atom, is assigned the value 65765, representing an ionisation potential of 8.12 volts. Comparison is made between the triplets of Si I and P II, and except for the $3p^1$ terms, which are relatively much greater in P II than in Si I, the general expected similarity is found.

L. L. BIRCUMSHAW.

Titanium band spectrum. A. CHRISTY (Nature, 1929, 123, 873—874).—Twenty bands, extending from 7990 to 6270 Å., have been assigned to a new resonance system. The frequencies of the heads of the new system are given by the expression: $14172.2, 14105.8, 14030.8, +(862.5n' - 3.84n'^2) - (1003.8n'' - 4.61n''^2)$.

A. A. ELDRIDGE.

Analysis of the arc and spark spectra of yttrium (Y I and Y II). W. F. MEGGERS and H. N. RUSSELL (Bur. Stand. J. Res., 1929, 2, 733—769).—The available data for the arc and spark spectra of yttrium, including wave-length measurements, intensities, temperature classes, and Zeeman effects, have been collected and analysed. In the spectrum of doubly-ionised yttrium, Y III, the number of lines is relatively small, but they are characterised by an enormous difference in intensity between arc and spark lines. The series limit corresponds with an ionisation potential of 20.4 volts for the Y^{++} atom. The spectrum of singly-ionised yttrium, Y II, shows a larger number of lines, which can be divided roughly into two classes. The strongest lines are formed by combinations of low energy states with the next higher or middle set. The second class is very much enhanced in passing from arc to spark. In the arc they are faint, but in the spark they are inclined to be hazy. This fact suggests that these high terms correspond with higher electron orbits and are therefore especially susceptible to Stark and pressure effects. The Y II spectrum parallels that of Sc II. A term table is given. The ionisation potential of singly-ionised yttrium is 12.3 volts. A term table is also given for the spectrum

of neutral yttrium, the ionisation potential being in this case 6.5 volts. The analyses given are supported by measurements of the Zeeman effect. All details of the three spectra are in agreement with Hund's correlation of spectral terms with electron configurations. The presence of yttrium in the sun is discussed. The evidence for the existence of both neutral and ionised yttrium is conclusive, but the two sets of lines behave very differently. It is shown that this behaviour is what would be expected of an element of moderate abundance and easy ionisation.

A. J. MEE.

Length of the spectral lines of a spark in relation to the concentration of the element. A. OCCHIALINI (*Atti R. Accad. Lincei*, 1929, [vii], 9, 573—577).—With increasing resistance in the circuit the length of lines produced in a nickel or lead-tin spark decreases, the decrease being rather greater in the latter than in the former case. With alloys containing between 0 and 8% Sn, the length of the tin line at 5800 Å. increases rapidly, the increase being more rapid the greater the capacity of the circuit. With alloys containing between 10 and 100% Pb the length of the lead line 5609 Å. increases approximately linearly with the lead content, the increase becoming less rapid the greater is the resistance of the circuit.

F. G. TRYHORN.

Intensity of spectral lines. W. HANLE (*Z. Physik*, 1929, 54, 852—855).—It is usually assumed that the intensity ratio of spectral lines belonging to one term is constant. This is the case if the total radiation is considered, but if the collisions in one direction only are taken into account this ceases to be true. The intensities of two mercury lines, of wave-lengths 3663 Å. ($2^3P_2-3^1D_2$) and 3132 Å. ($2^3P_1-3^1D_2$) were compared parallel and perpendicular to the direction of electron collision, and it was shown that the intensity of the 3163 Å. line compared with that of the 3125 Å. line was 10% stronger parallel to the radiation than perpendicular to it. The same was found with the 5461 Å. mercury line. The mathematics of the problem is given for the ideal case of a rectilinear electron stream.

A. J. MEE.

Excitation function of the mercury resonance line λ 2537 Å. W. HANLE (*Z. Physik*, 1929, 54, 848—851).—Apparatus for the determination of the excitation function of the ultra-violet resonance line of mercury λ 2537 Å. is described. The light measurements were made with a photo-cell. The intensity of the line for excitation by electron collisions is found in relationship to the velocity of the exciting electrons. The sharing function increases linearly at first, reaching a maximum at a potential about 1.5 volts greater than the excitation potential, after which it falls. The results obtained agree within the experimental error with those of Bricout (*A.*, 1927, 1125) using a different method.

A. J. MEE.

Zeeman effect in the spectrum of ionised neon (Ne II). C. J. BAKKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, 32, 515—522).—The observed g values arising from the 3s and 3p electrons are compared with those calculated from Landé's formula; those of the 3s electron are normal, whilst certain anomalous values of the 3p electron correspond with

analogous terms in the A (II) spectrum which exhibit abnormal g values.

H. F. GILLBE.

Second order Stark effect for H_γ. H. R. VON TRAUBENBERG and R. GEBAUER (*Z. Physik*, 1929, 54, 307—320).—The second order Stark effect for the fine components of H_γ has been determined by Stark's method, using fields up to 702,500 volts/cm. The components σ 0, σ 3, σ 10, σ 13, σ 15, and π 18 are found to undergo a slight shift, which is proportional to the square of the field strength, towards the red. In no case do the results agree with Epstein's calculations based on the Bohr theory (*Ann. Physik*, 1916, [iv], 51, 184), but those for the middle component agree exactly with Schrodinger's theory. The higher components show systematic discrepancies from Schrodinger's theory, but the discrepancies decrease for lower pressures, so that they may be due to collisions.

E. B. ROBERTSON.

Theories of the continuous X-spectrum and of the Compton effect. E. SEVIN (*Compt. rend.*, 1929, 188, 1245—1246; cf. this vol., 483).—A comment on Decombe's deductions (this vol., 615).

J. GRANT.

Change in resonance lines through multiple Compton effect. W. ORTHMANN (*Z. Physik*, 1929, 54, 767—778).—Mathematical.

A. J. MEE.

Possible existence of important exceptions to the selection principle relative to the total quantum number. N-spectrum of thorium. J. THIBAUD (*Compt. rend.*, 1929, 188, 1394—1396).—Bohr and Coster's values of the energy of the N -levels obtained by extrapolation of high-frequency spectrographic measurements give results for the electronic transitions $N_{IV}-N_V$ and N_V-N_{VI-VII} in agreement with Thibaud and Soltan's experimental values (*A.*, 1927, 1000) for the abnormal N -doublets of tantalum and tungsten, a difference of 1—3% being found for platinum and gold. Idei's values (this vol., 630) give closer agreement. Examination of the spectra of silver, palladium, bismuth, and thorium indicates that these levels alone among the outer levels are likely to violate the selection principle.

J. GRANT.

Spectral relations between certain iso-electronic systems and sequences. II. Sc I, Ti II, V III, Cr IV, and Mn V. H. E. WHITE (*Physical Rev.*, 1929, [ii], 33, 672—683).—Previous work (cf. *A.*, 1927, 601; this vol., 3) is extended to include the spectra of V III, Cr IV, and Mn V, which closely resemble those of Sc I and Ti II, extrapolation from the known data of which have led to the identification of terms arising from the electron configurations $3d^3$, $3d^24s$, $3d^24p$, and $3d^24d$. The term values are tabulated for the three elements in each case. The Moseley diagram and the irregular doublet law are used to determine the positions of doublet and quadruplet levels and the location of the radiated frequencies. The respective ionisation potentials are approximately 29.6, 50.4, and 75.7 volts.

N. M. BLIGH.

Perturbations in molecules and the theory of predissociation and diffuse spectra. O. K. RICE (*Physical Rev.*, 1929, [ii], 33, 748—759).—When the discrete vibration rotation absorption bands con-

nected with transitions to a final electronic state of a molecule overlap the continuous region for the transitions to another final state, some of the discrete bands may be diffuse, and the rotation lines broad. Using the methods of wave mechanics the width of the line is calculated directly in terms of the perturbation matrices. The total absorption over the width of the line is also found. N. M. BLIGH.

Space charge sheaths in positive-ray analysis. R. W. GURNEY and P. M. MORSE (Physical Rev., 1929, [ii], **33**, 789—799).—It is shown that in the ionising chambers used for the positive-ray analysis of ionisation products a positive ion sheath is formed, and concentrates the applied field near the slit. The sheath thickness varies with the applied voltage, the electron current, and the pressure, and by making these variations the relative proportions of secondary and primary ions reaching the analyser collector can be changed. Curves are given for the sheath thickness and for the various ionic currents through the slit for several conditions in the chamber.

N. M. BLIGH.

Ionisation by collision in a uniform electric field. M. J. DRUXVESTEYN (Z. Physik, 1928, **52**, 197—202).—Expressions are derived for the probability of ionisation by electron collisions in a gas under a uniform electric field; these may be used to derive the energy loss in "elastic" collisions when the electron density is accurately known.

R. W. LUNT.

Ionisation of potassium vapour. R. W. DITCHBURN and F. L. ARNOT (Proc. Roy. Soc., 1929, **A**, **123**, 516—536).—Experiments are described on the ionisation of potassium vapour by which it is possible to measure the m/e ratio for the ions produced. The apparatus employed is similar to that used by Smyth (A., 1924, ii, 85), and the ions are produced by three methods: (1) by photo-ionisation, (2) by electron impact, and (3) by the attachment of K^+ ions from a Kunsman filament (cf. A., 1926, 218). The results are expressed by curves showing the ion current for different magnetic fields. The curve obtained with photo-ions is identical with that obtained with the Kunsman filament, except that it is slightly broader; the only ion present is K^+ . Important differences are found between the results for slow and fast electrons, probably due to the fact that the K_2^+ ion formed by the impact of 120-volt electrons is more highly excited than the K_2^+ ion formed by the impact of 35-volt electrons. With ions formed by attachment definitely stable and unstable K_2^+ ions are found. Estimates are given of the probabilities of ionisation by electron impact, of the formation of K^+ , and of the attachment of K^+ to K . The lives of the unstable compounds are shown to be of the order of 10^{-6} sec. The results are considered in connexion with the band spectra of the alkali-metal molecules and other optical data. It is assumed that all the transitions of the K_2 and molecules are such that the moment of inertia increases and the heat of dissociation decreases on excitation.

L. L. BIRCUMSHAW.

Latent carriers of electricity in the gaseous discharge. S. A. RATNER (Proc. Nat. Acad. Sci.,

1929, **15**, 318—323).—An investigation of the large ionisation currents observed inside the electrodes during some experiments on the discharge of electricity through gases, using special large hollow electrodes, is described. It is concluded that these currents are due to metastable atoms diffusing into the ionisation chamber and being present at a concentration higher than 10^{-5} . The investigation throws some light on the phenomena observed behind a perforated cathode.

N. M. BLIGH.

Increase of the sparking potential of a gas mixture by irradiation. F. M. PENNING (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 341—343).—See this vol., 114.

Method for determination of critical potentials and its application to mercury vapour. V. PAVLOV and (FRL.) N. SUEVA (Z. Physik, 1929, **54**, 236—245).—It is shown that the relative number of slowly moving electrons in an electron beam traversing a dilute gas will exhibit maxima whenever the accelerating potential slightly exceeds a critical potential. The relative number of slowly moving electrons is given by the ratio $(I_V - I_{V+4V})/I_V$, where I_V is the electron current corresponding with a potential V at a given gas pressure. The smaller is the value of ΔV the more closely may maxima be detected; a value of 0.2 volt was chosen for the experiments in mercury vapour. In addition to the following critical potentials below the first resonance potential: 0.45, 0.65, 0.95, 1.20, 1.40, 1.65, 1.80, 2.00, 2.25, 2.60, 2.85, 3.10, 3.45, 3.6, 3.85, 4.15, and 4.40 volts, new critical potentials were observed at 5.25, 5.75, 6.05, 6.30, 7.10, 7.45, and 8.05 volts for which no corresponding spectral lines are known. R. W. LUNT.

Theory of the photo-electric effect. P. AUGER (Compt. rend., 1929, **188**, 1287—1289).—Sommerfeld's formula expressing the probability of expulsion of a photo-electron in terms of the direction and speed of departure and the velocity of light ("Atombau und Spectrallinien," 1929) is in agreement with experimental results.

J. GRANT.

Longitudinal distribution of photo-electrons. A. CARRELLI (Nature, 1929, **123**, 836—837).

Variation of the photo-electric effect with temperature and determination of the long wavelength limit for tungsten. A. H. WARNER (Physical Rev., 1929, [ii], **33**, 815—818).—The photo-electric current is plotted against temperature up to 1140° Abs. for carefully outgassed tungsten. A marked increase in sensitivity was found from 800° to 1000° Abs. The long wave-limit was found to be 2570 ± 50 Å., and was independent of temperature.

N. M. BLIGH.

Release of photo-electrons by X-rays from metallic reflectors at angles bordering on total reflexion. W. EHRENBERG and F. JENTZSCH (Z. Physik, 1929, **54**, 227—235).—At total reflexion of X-rays from metallic mirrors, the number of photo-electrons emitted will be a minimum, thus furnishing a method of determination of the angle of total reflexion. Curves obtained from measurements on mirrors of steel, silver, and gold are given.

G. E. WENTWORTH.

Greatest speed of photo-electric electrons in the selective sensitivity range of potassium. H. TEICHMANN (Ann. Physik, 1929, [v], 1, 1069—1095).—The Einstein equation $eV = h(\nu - \nu_0)$ fixes the maximal velocity of the liberated electron. It is now shown that for the mercury lines 436, 405, 365.5, 313, 302, and 280 μ , i.e., over the region of selectivity, the greatest speeds observed agree well with the theoretical values. A method whereby gas-free electrodes can be obtained by volatilisation of metal in a high vacuum is described. R. A. MORTON.

Hydrogen ions as the reason for the occurrence of photo-electric spectral selectivity of potassium. R. FLEISCHER (Physikal. Z., 1929, 30, 320—322).—Three different methods of sensitising potassium photo-electric cells indicate that potassium vapour plays an essential part in effecting the increased sensitivity. The vapour pressure of potassium at the ordinary temperature is insufficiently large for the effect to be realised. As a result of this treatment combination between potassium and the hydrogen present occurs readily, but it is not clear whether neutral hydrogen or H^+ ions are responsible. The work of Suhrmann (cf. A., 1928, 1068) is therefore indecisive. R. A. MORTON.

Photo-electric effect with aluminium and its amalgams. A. SMITS and H. GERDING (Physikal. Z., 1929, 30, 322—325).—Measurements of the photo-electric effect with active and passive iron are open to criticism on the ground that adsorbed gases are present. Little progress seems possible in elucidating the physical difference between the active and passive states by photo-electric studies of iron. Aluminium and its amalgams present far less difficulty. It is found that an amalgam containing 0.26 at.-% Hg shows a photo-electric effect four or five times as great as that of pure aluminium. Even the threshold wave-length is altered. From this it is concluded that a change in the inner state of the aluminium has occurred. Earlier work on the influence of small quantities of mercury on the electromotive behaviour of aluminium yielded similar results. The work is interpreted to mean that passive aluminium is not in inner equilibrium, but is instead in a disturbed state deficient in ions and electrons. Traces of mercury set up the condition of inner equilibrium in the metal and the change involves an increase in the number of ions and electrons. This implies the observed increase in photo-electric effect.

R. A. MORTON.

Emission of positive ions from metals. H. B. WAHLIN (Nature, 1929, 123, 912).—When heated, copper, iron, nickel, and platinum give alkali ions only, whilst tungsten, molybdenum, and tantalum give ions of at. wt. in agreement with that of the emitting metal. A. A. ELDRIDGE.

Statistics of photons. I. I. PLACINTEANU (Ann. Sci. Univ. Jassy, 1929, 15, 359—362).—Mathematical.

Test for polarisation of electron waves by reflexion. C. J. DAVISSON and L. H. GERMER (Physical Rev., 1929, [ii], 33, 760—772; cf. A., 1928, 683, 1173).—Measurements were made of the intensity of an electron beam twice reflected from nickel crystal

faces at bombarding potentials from 10 to 200 volts. Within this range five selectively reflected beams were observed and tested for polarisation by measuring the current received by a collector. No variation of the current is observed with variations of the planes of incidence of the two reflexions. It is concluded that electron waves are not polarised by reflexion (cf. Darwin, A., 1928, 1300). N. M. BLIGH.

Determination of the charge of positive thermions from measurements of shot effect. N. H. WILLIAMS and W. S. HUXFORD (Physical Rev., 1929, [ii], 33, 773—788).—The shot effect consists in fluctuations, which can be calculated on probability theory, taking place in the electron stream set up when electrons evaporating from a hot metal surface are attracted to a positively-charged electrode. A potassium-iron oxide mixture source of positive ions was used to investigate the shot effect of a space current of positive ions. Results indicate that the discharge may be properly controlled and temperature limited currents obtained, giving a value for the K^+ ion equal in magnitude to the electron charge.

N. M. BLIGH.

Effect of external fields on the polarisation of the light in hydrogen canal rays. I. WALTERSTEIN (Physical Rev., 1929, [ii], 33, 800—814).—It is found that the application of electric or magnetic fields to a canal ray in a high vacuum causes a periodic variation of the polarisation along the length of the beam. Curves showing polarisation ratio against the length of the canal ray are given for fields of varying intensities and parallel and perpendicular to the beam and to the line of vision. In some cases strong fields increase the number of changes in the polarisation in the length observed, and in other cases increase only the amplitude of the variation. N. M. BLIGH.

Isotope of oxygen of mass 17 in the earth's atmosphere. W. F. GIAUQUE and H. L. JOHNSTON (Nature, 1929, 123, 831).—Of 34 lines observed by Dieke and Babcock (unpublished), 27 are due to the alternate rotation levels of $O^{16}O^{18}$. Other lines are considered to originate from the molecule $O^{16}O^{17}$. Measurements of band spectra are regarded as being more trustworthy than those with the mass spectrograph. The maximum abundance of the $O^{16}O^{17}$ molecule is estimated to be 1 in 10^4 .

A. A. ELDRIDGE.

Isotope of oxygen, mass 18. Interpretation of the atmospheric absorption bands. W. F. GIAUQUE and H. L. JOHNSTON (J. Amer. Chem. Soc., 1929, 51, 1436—1441).—The weak band in the atmospheric absorption bands for oxygen (cf. Mulliken, A., 1928, 1165) originates from oxygen molecules each consisting of an atom of mass 16 combined with an atom of mass 18. S. K. TWEEDY.

At. wt. of phosphorus. M. RITCHIE (Nature, 1929, 123, 838).—Determinations of the density and compressibility of phosphine give 30.97(9) and 30.98(2) for the at. wt. of phosphorus. A. A. ELDRIDGE.

Quantum mechanics of radioactive change. J. KUDAR (Z. Physik, 1929, 54, 297—299).—A continuation of a previous paper (*ibid.*, 53, 61) on the mathematical aspect of radioactivity.

G. E. WENTWORTH.

Energy changes in nuclear collisions. W. KUHN (*Z. Physik*, 1929, 52, 151—157).—Energy changes associated with collisions between rapid α -particles and atomic nuclei are discussed with reference to the possible changes which may take place in atoms in fixed stars. R. W. LUNT.

Actinium problem. G. ELSÉN (*Z. anorg. Chem.*, 1929, 180, 304—320).—An historical survey is given of the problem of the genesis of the actinium family of elements. All the known facts support the view that the actinium series is derived from a radioactive isotope of uranium, actino-uranium, which must have at. wt. >238 . O. J. WALKER.

Production of disintegration H -rays under the action of the α -radiation of polonium. C. PAVLOVSKI (*Compt. rend.*, 1929, 188, 1248—1250).— H -rays produced by disintegration of aluminium were demonstrated by the scintillation method and shown to be produced by α -radiation of polonium having a range of 3.9 or 2.4 cm. In general the results agree with those of Rutherford, who used α -rays of 4.9 cm. range. The maximum range of the $H_{\alpha 1}$ particles is 48.2 cm. J. GRANT.

Disintegration of aluminium. C. PAVLOVSKI (*Compt. rend.*, 1929, 188, 1334—1336; cf. preceding abstract).—Extrapolation of the curve relating the path of the α -particles with the maximum path of the $H_{\alpha 1}$ -particles they expel, shows that the lower limit of the former is 1 cm. (cf. Schmidt, A., 1927, 494). Bothe's formula (A., 1928, 1302) for the maximum path of an H -particle which holds for nitrogen was not confirmed for aluminium, and it is inferred that the disintegration of the latter involves a more complicated mechanism. The curve relating the path of the α -particles and the relative number of H -particles indicates that the number of $H_{\alpha 1}$ -particles increases rapidly for high-speed α -particles, but is in disagreement with the theoretical results of Gamow (this vol., 234). J. GRANT.

Rate of decay of polonium at different points in the U.S.S.R. L. N. BOGOJAVLENSKY (*Nature*, 1929, 123, 872).—The half-value period of polonium, kept for about 5 months in each of 18 Russian towns, varied between 125.6 days (Tiflis) and 181.6 days (Krasnodar), whilst the same specimens, after being kept for 5 months at Leningrad, gave values between 137.2 and 139.5 days. The phenomenon supports Perrin's assumption of the existence of an external source of radiant energy which produces the radioactive decay of atoms. The greatest deviations occur places with disturbed tectonics.

A. A. ELDRIDGE.

New fast β -radiation. D. SKOBELZYN (*Z. Physik*, 1929, 54, 686—702).—Six hundred Wilson chamber photographs of β -particles subjected to a magnetic field of 1500 gauss showed 32 almost straight tracks. Their length, slight curvature, and spatial distribution suggest identity with electrons scattered by the cosmic radiation. The Klein-Nishina relation is preferred to that of Dirac and Gordon for interpretation of absorption measurements, although predicted energy values no longer fit with "packing" values. Some of

the observed tracks are multiple. The method of absorption measurements is discussed.

A. B. D. CASSIE.

Emanation method as an aid to chemical and physico-chemical investigations. O. HAHN (*Naturwiss.*, 1929, 17, 295—296).—A summary.

R. A. MORTON.

Electrical detection of single corpuscular rays. G. ORTNER and G. STETTER (*Z. Physik*, 1929, 54, 449—476).—The detection of corpuscular rays by means of thermionic valves is discussed. The essential details are a detector of high impedance and low grid current, a linear amplifier, and a thread galvanometer. The arrangement was used to examine the α -particles from radium-C. W. E. DOWNEY.

Absorption of high-frequency radiation. E. C. STONER (*Phil. Mag.*, 1929, [vii], 7, 841—858).—The results of Ellis and Wooster (A., 1925, ii, 923; 1927, 606) on the β -rays and the heating effect of the γ -rays have been used in the determination of the intensities of the γ -rays of radium-B and -C. On the basis of these results it is shown that the number of impulses observed by Kovarik (A., 1924, ii, 447) is greater than the number of γ -ray quanta emitted by the disintegrating atoms. The results of Ahmad (A., 1924, ii, 440, 582; 1925, ii, 923) on the absorption of γ -rays are used to deduce γ -ray absorption coefficients and the values so obtained agree closely with those calculated from the formula of Klein and Nishina. Some apparently anomalous results of Ahmad are attributed to secondary scattering effects. The most penetrating cosmic radiation observed by Millikan and Cameron, having an absorption coefficient of 0.04 m^{-1} , has a wave-length, calculated from the Klein-Nishina formula, corresponding with the electron-proton annihilation wave-length. A. E. MITCHELL.

Existence of radioactive recoil ions of high mobility. L. L. LOEB and L. B. LOEB (*Proc. Nat. Acad. Sci.*, 1929, 15, 305—310).—From experiments made using a Rutherford alternating-current method it is concluded that the existence of Erikson's high-mobility radioactive recoil ions formed from recoil atoms of radium, thorium, and actinium emanations is very doubtful, and at present unconfirmed.

N. M. BLIGH.

Hydrogen-ion wave function. V. GUILLEMIN, jun., and C. ZENER (*Proc. Nat. Acad. Sci.*, 1929, 15, 314—318).—Mathematical.

N. M. BLIGH.

Why no hydrogen nuclei are emitted in radioactive changes. A. VON GROSSE (*Z. Physik*, 1929, 54, 764—766).—Mathematical. Using Einstein's relativity relationship and Aston's curve (packing fractions plotted against at. wt.) it is shown that in consequence of the large packing fraction of the hydrogen nucleus it would be possible for it to be emitted only if there were a large absorption of energy.

A. J. MEE.

Penetration of polonium into lead. (Mlle.) E. MONTEL (*J. Phys. Radium*, 1929, [vi], 10, 78—80).—When a drop of a slightly acid solution containing a little polonium was placed on a thin lead plate, pressed down on a photographic plate, the polonium penetrated the lead. By using lead plates containing large crystals it is concluded, from the shape of the

image, that the active material traverses the plate by passing between the crystals, the acid assisting by chemical action. J. L. BUCHAN.

Fine structure of the magnetic spectrum of the α -rays from thorium-C. S. ROSENBLUM (Compt. rend., 1929, 188, 1401—1403).—The Danysz focalisation method for the study of β -spectra has been applied to α -rays from thorium-C. Two very intense and almost coincident rays and two feeble isolated rays were observed in the magnetic spectrum for a field of 36,000 gauss. The results were independent of the nature and position of the radioactive source, of the degree of vacuum (0.1—0.001 mm.), and of the size of the slit. The velocities of the rays (thorium-C as unity) were 1.003, 0.975, and 0.961 for the weaker intense ray and for the two feeble rays, respectively. J. GRANT.

Action of metastable atoms of helium on a metal surface. M. L. E. OLIPHANT (Proc. Roy. Soc., 1929, A, 124, 228—242).—An apparatus is described for producing an intense beam of metastable helium atoms by the impact of positive ions at glancing incidence on the walls of a gas-free platinum canal. The excited ions are able to set free large numbers of electrons by collision with a metal target, by a process analogous to a collision of the second kind. By applying varying retarding potentials between the collecting cylinder and the target, the velocity distribution of the electrons has been investigated. Measurements with molybdenum, nickel, and magnesium targets indicate that the total number of electrons set free does not vary much with the surface, suggesting that every metastable atom gives rise to an electron. A fraction of the metastable atoms can be reflected from a metal surface, the amount of reflexion varying markedly with the gas condition of the surface and with the velocity of the original positive ions. Experiments are described which supply direct proof of the production of metastable atoms by glancing impact of positive ions on a metal surface. Some sputtering of the target is produced by the impact of the fast-moving neutral atoms, the kinetic energy of which is of the same order as that of the original beam of positive ions. L. L. BIRCUMSHAW.

Reflexion of ultra-violet rays from metallic surfaces in relation of their microstructures. H. KOTÔ (Mem. Coll. Sci. Kyoto, 1929, 12, 81—96).—The intensity of reflexion for λ 3650 in the ultra-violet was determined for the following series of alloys: copper-silver, cadmium-bismuth, zinc-cadmium, copper-nickel, and magnesium-zinc. The intensity curves appear to be related to the equilibrium diagrams. There is a minimum in the intensity curve at a eutectic, except in the case of copper-silver; a maximum at a composition corresponding closely with a compound; and a break or maximum at the limit of solid solubility. These results are similar to those obtained by Chikashige (A., 1926, 896) using visible radiation. C. J. SMITHELLS.

Electronic theory of the ether and of light. A. VÉRONNET (Compt. rend., 1929, 188, 1380—1381).

Experimental test of the Maxwell velocity distribution law for electrons liberated from a

glow cathode. A. DEMSKI (Physikal. Z., 1929, 30, 291—314).—Previous attempts to calculate the temperature of a glowing filament on the basis of the Maxwell velocity distribution law for liberated electrons have given discordant results, the values being mostly too high. The discrepancies have now been largely accounted for. The validity of the Maxwell law has been confirmed by using an alternating-current interrupter, although the condition of dynamic equilibrium required theoretically was not fulfilled. This method is not suitable for the measurement of temperature; the best method involves the use of a heated equipotential cathode without magnetic field. R. A. MORTON.

Perturbation theory in quantum mechanics. II. A. H. WILSON (Proc. Roy. Soc., 1929, A, 124, 176—188).—An extension of the theory previously developed (this vol., 363) to systems possessing both discrete and continuous spectra. The perturbation equations are derived in a somewhat more general form than has previously been given, those due to Born, Dirac (A., 1926, 1078), and Oppenheimer (A., 1928, 216) being particular cases obtained by different divisions of the Hamiltonian H into the parts H_0 , H_1 , $H_2(t)$. The necessary existence theorems are proved, and the validity of the perturbation theory is considered. L. L. BIRCUMSHAW.

Relativistic theory of an atom with many electrons. J. A. GAUNT (Proc. Roy. Soc., 1929, A, 124, 163—176).—Mathematical. The ordinary classification of multiplets and the selection and summation rules are derived from Dirac's relativistic equation, and it is shown that the selection rules are rigorous if there are no external fields, and that the rule " $\Delta\Sigma k$ is odd" is also rigorous, even in a uniform magnetic field. A practical consequence of this is that the O^{++} lines of nebular spectra, if correctly identified, can occur only in electric or non-uniform magnetic fields, since they have $\Delta\Sigma k=0$. The classification of multiplets is discussed from the point of view of wave mechanics, spin effects being treated as small perturbations. The azimuthal quantum number l is defined, and the values of j appropriate to a multiplet of given l are deduced. The summation rule for the intensities in a multiplet is proved to a first approximation. L. L. BIRCUMSHAW.

Fall of a heavy gas in a light gas. Stability of ozone in the higher atmosphere. Y. ROCARD (Compt. rend., 1929, 188, 1336—1338).—A formula for the rate of fall of a globular mass of heavy gas in a lighter gas based on the kinetic theory has been deduced in terms of the mol. wt. of the gases, the radii of their molecules, Avogadro's number, and the gas equation constants. For ozone in nitrogen or hydrogen the rates of fall are 22 and 17 m./day, respectively. The conditions governing the stability of the layer of atmospheric ozone are discussed in the light of these results. J. GRANT.

Possible synthesis of elements in stars. R. D'E. ATKINSON and F. G. HOUTERMANS (Z. Physik, 1929, 54, 656—665).— α -Particles and protons have, according to Gamow, a calculable chance of entering any nucleus. Thermal velocities within a star are such that α -particles are unlikely to enter any

nucleus, but protons may enter the lighter nuclei. The chance of formation, within a nucleus, of α -particles from protons is comparatively great. Energy due to packing may thus appear, and a new nucleus be formed. Synthesis of heavier nuclei presents more difficulties, but the Compton effect or spontaneous disintegration of light unstable nuclei may give velocities high enough for this possibility.

A. B. D. CASSIE.

Synthesis of elements. II. G. I. POKROVSKI (Z. Physik, 1929, 54, 724—730).—An electron and a positively-charged nucleus may combine with a loss of mass the equivalent energy of which is radiated. This electron-proton system recoils with kinetic energy calculable in terms of the mass lost. When this kinetic energy is great enough two such systems of like charge, possessed of magnetic doublets, may approach so closely that magnetic forces bind them together. The magnetic moment is assumed, and the critical loss of mass required for binding, calculated for the lighter elements. Calculations agree favourably with Aston's results. The radius of the sphere in interstellar space effectively radiating this "packing" energy to the earth is determined from Millikan and Cameron's results.

A. B. D. CASSIE.

First- and second-order equations of the quantum theory. H. T. FLINT (Proc. Roy. Soc., 1929, A, 124, 143—150).—A solution is suggested for two difficulties raised by Dirac's treatment of the quantum theory of the electron (A., 1928, 344), and the nature of the invariance to be associated with the first-order equations is indicated. The phenomena are assumed to be five-dimensional, and are described by the introduction of two tensors containing an antisymmetric and a symmetric component. This procedure is, however, unsatisfactory from the point of view of the theory of physical unity.

L. L. BIRCUMSHAW.

Translation of Dirac's theory of the electron into ordinary notation. E. MADELUNG (Z. Physik, 1929, 54, 303—306).—Mathematical. Dirac's theory is contained in a set of ordinary vector equations, which are established. The operational method is not required for solution of the central field problem. The equations established and Maxwell's have a surprising resemblance, which may lead to a better understanding of the interaction of matter and the electromagnetic field.

A. B. D. CASSIE.

Tensor form of the wave-mechanics equation for an electron. H. MANDEL (Z. Physik, 1929, 54, 567—570).—Mathematical.

W. E. DOWNEY.

Gravitation and the electron. H. WEYL (Proc. Acad. Sci., 1929, 15, 323—334).—Mathematical.

The translation of Dirac's theory of the electron into general relativity is considered. N. M. BUGH.

Possible geometrical explanation of the relativistic quantum theory. V. FOCK and D. IVANENKO (Z. Physik, 1929, 54, 798—802).—Mathematical. A geometrical explanation is given to Dirac's relationship.

A. J. MEE.

Constitution of the solar atmosphere and identification of boron in the spots. S. B.

NICHOLSON and N. G. PERRAKIS (J. Phys. Radium, 1929, [vi], 10, 49—51).—Although the elements composing the atmosphere of the sun are chiefly those with low ionisation potentials, there are two exceptions: helium, with a high ionisation potential is present, but boron, the ionisation potential of which is low, is apparently absent. An examination of the band spectrum of sun spots, however, has shown the presence of 28 lines which have been identified with those of the spectrum of boron. J. L. BUCHAN.

Quantum-mechanical dispersion formula of normal atomic hydrogen. F. REICHE (Z. Physik, 1929, 53, 168—191).—Mathematical.

G. E. WENTWORTH.

New band system of carbon monoxide ($3^1S \rightarrow 2^1P$); the Angstrom band system. R. C. JOHNSON and R. K. ASUNDI (Proc. Roy. Soc., 1929, A, 123, 560—574; cf. Jasse, A., 1926, 452; Birge, A., 1927, 184).—Details are given of a new band system of carbon monoxide corresponding with the transition $3^1S \rightarrow 2^1P$. Four bands have been observed, (0,0), (0,1), (0,2), and (0,3), with heads at 3680.05, 3893.19, 4125.02, and 4380.18 Å. The fine structure analysis of the (0,1), (0,2), and (0,3) bands has been determined, and it is found that the combination data obtained from this analysis fully supports the evidence that this system and the Angstrom system have a common final state 2^1P . The bands each have three branches of the *P*, *Q*, and *R* type, and are precisely similar to the Angstrom bands in structure. The nature of the electronic transition is confirmed by the fact that the lines $R(\frac{1}{2})$ and $Q(\frac{1}{2})$ are not observed. New experimental data are found in the case of the (0,0), (1,0), (0,4), and (0,5) Angstrom bands, and the combination data derived from these and from the new system, together with Hulthén's data (A., 1923, ii, 670), have been used to evaluate the constants of the 3^1S , 2^1S , and 2^1P levels of the CO molecule. An examination of the vibrational levels of the 2^1P state indicates that the perturbed level is $n''=1$ and not $n''=0$, as given by Birge (*loc. cit.*).

L. L. BIRCUMSHAW.

Frequencies characteristic of the carbonate group. C. SCHAEFER (Z. Physik, 1929, 54, 676—678).—A criticism of Herzfeld's article ("Handbuch der Experimental-physik, VII"), particularly of the suggested harmonic relation between the double bands near 7μ and 14μ .

A. B. D. CASSIE.

Quantum analysis of the blue-green bands of titanium oxide. A. CHRISTY (Physical Rev., 1929, [ii], 33, 701—729; cf. A., 1928, 1304).—The spectrum of the titanium bands is made up of a system in the blue-green and one in the yellow-red, both degrading to the red. The frequencies of all the heads in the blue-green region, and the frequencies of the lines and their combination differences for the (0,0), (0,1), and (1,0) bands are tabulated. Each band is composed of three *R* and three *P* branches. The combination principle is verified for about 90 lines, and quantum numbers are assigned. The moments of inertia of the TiO molecule are found to be 56.72×10^{-40} and 51.89×10^{-40} gm.cm.² for the initial and final states, and the initial and final state nuclear separations 1.693×10^{-8} and 1.619×10^{-8} cm., respectively. The

triplet separation of the lines, although irregular, indicates a transition between two triplet levels, and is assumed to be $^3P-^3P$; j is found to be half integral.

N. M. BLIGH.

Assignment of quantum numbers for electrons in molecules. III. Diatomic hydrides. R. S. MULLIKEN (Physical Rev., 1929, [ii], 33, 730—747; cf. this vol., 116; Hund, *ibid.*, 117).—A systematic survey is made of existing band spectrum data on energy levels of diatomic hydrides, and these data are interpreted in terms of theory. Quantum number assignments and multiplet separations are tabulated. Hund's new notation is explained and adopted. The formation of MH type molecules and the effects of the H on the M atom are discussed. Data are advanced as evidence that molecular stability is a matter of promotion energy rather than of valency linkings (Lewis and London). A simple explanation is given of observed multiplet widths in ^2II and ^3II states.

N. M. BLIGH.

Absorption of ultra-violet light by some purine derivatives and allied substances. L. MARCHLEWSKI and J. WIERZUCHOWSKA (Bull. Acad. Polonaise, 1929, A, 65—79).—In aqueous solution guanine (in presence of sodium hydroxide) gives two absorption bands with maxima at 2460 and 2744 Å.; adenine sulphate, one band with maximum at 2606 Å.; uric acid, two bands. Allantoin, alloxan, alloxanthin, parabanic acid, and carbamide exhibit no selective absorption; barbituric acid gives one band with maximum at 2566 Å. but does not follow Beer's law. Diethylbarbituric acid shows no selective absorption but conforms to Beer's law.

A. I. VOGEL.

Absorption of light by some organic substances. L. MARCHLEWSKI and O. WYROBEK (Bull. Acad. Polonaise, 1929, A, 93—110).—The absorption spectra of solutions of some organic substances have been measured; all follow Beer's law. Pyridine in water gives three bands with maxima at 2620, 2570, and 2510 Å.; quinoline, four bands with maxima at 3135, 3060, 3000, and 2780 Å.; phenylacetic acid, three bands with maxima at 2645, 2580, and 2530 Å.; phenylglycollic and benzilic acids give absorption spectra similar to phenylacetic acid; menthone, two bands with maxima at 2890 and 2530 Å.; menthol, no absorption band; benzil, one band with maximum at 2590 Å.; tribromophenol, one band with maximum at 2690 Å., and benzyl alcohol, one band with maximum at 2570 Å.

A. I. VOGEL.

Absorption of ultra-violet light by the methyl- α -glucosides. L. MARCHLEWSKI and J. MAYER (Bull. Acad. Polonaise, 1929, A, 111—118).—Pure α - and β -methyl- α -glucosides do not cause selective absorption of light in the ultra-violet.

A. I. VOGEL.

Intensities of the mercury hydride bands. W. KAPUSCINSKI and J. E. EYMERS (Z. Physik, 1929, 54, 246—256).—The intensity distribution in nine of the mercury hydride bands has been investigated under various conditions of discharge. The results are discussed with reference to the theory of Hill and Van Vleck (A., 1928, 1076) and appear to deviate from it, in that the higher rotation states are too strongly

represented. The heads of six of the bands have been measured, and an extension of Hulthén's tables (A., 1925, ii, 470; 1928, 1075) is given.

E. B. ROBERTSON.

Intensity of γ -bands of nitric oxide. B. POGANY and R. SCHMID (Z. Physik, 1929, 54, 779—787; cf. A., 1928, 930).—The nitric oxide γ -bands in the emission from the nitrogen afterglow were photographed and their intensities determined. Using the method due to Hill and Van Vleck, the so-called effective temperature of the emission from the light sources used (vacuum arc and copper arc) was found.

A. J. MEE.

Infra-red spectra of some halogen compounds. G. B. BONINO (Z. Physik, 1929, 54, 803—805).—In work by Pringsheim and Rosen on the Raman effect in organic liquids (A., 1928, 1307) it is shown that there is poor agreement between the wave-lengths of the infra-red bands and the Raman lines for compounds containing the C-H linking. It is now shown that if stricter methods are used the agreement is good for acetylene tetrachloride and dichloride, being even better in the latter case than in the former.

A. J. MEE.

Absorption bands in spectra of fixed stars. R. WILDT (Z. Physik, 1929, 54, 856—879).—By investigating the band spectra of stars the existence of certain molecules in stellar atmospheres can be proved. The spectra of oxides, carbon compounds, and hydrides are especially considered. The stability of chemical compounds in stellar atmospheres can be investigated also by the Nernst reaction isochore, and application is made of this method.

A. J. MEE.

Fine structure of diffused rays at critical opalescence, with reference to the Cabannes-Daure effect. A. BOGROS and Y. ROCARD (J. Phys. Radium, 1929, [vi], 10, 72—77).—An apparatus is described for studying the fine structure of the diffused light produced by a mixture of water and phenol in the state of critical opalescence. Evidence of the Cabannes-Daure effect, the increase of the wave-length on diffusion, was observed. An explanation for this is advanced, and the probable cause of the Cabannes-Daure effect is discussed.

J. L. BUCHAN.

Molecular spectrum of ammonia. II. Double band at 10 μ . E. F. BARKER (Physical Rev., 1929, [ii], 33, 684—691; cf. Robertson and Fox, A., 1928, 1073; Stinchcomb and Barker, this vol., 488).—By means of a specially ruled grating the fine structure details of the ammonia absorption band from 8 to 14 μ was studied. Two narrow zero branches appear at 10.3 and 10.7 μ , with each of which is associated a positive and negative branch consisting of 10 or 12 lines. The double character is shown to be a consequence of the close proximity of the two equilibrium positions for the nitrogen atom, one on each side of the plane formed by the hydrogen atoms. The structure of the vibration-rotation band at 1.9 μ is discussed and the total intensities are tabulated.

N. M. BLIGH.

Pure rotation spectrum of ammonia. R. M. BADGER and C. H. CARTWRIGHT (Physical Rev., 1929, [ii], 33, 692—700).—Improved experimental means

for the study of absorption spectra in the extreme infra-red are described and applied to the study of the polyatomic molecule ammonia in the region 55—130 μ . Six lines were observed; they belong to a pure rotation spectrum and are attributed to changes in the rotation energy of the molecule about an axis normal to the line of symmetry, j increasing by unity for the transitions. Results are shown to be in agreement with the predictions of wave mechanics. The moment of inertia of the molecule about the above axis is estimated as 2.77×10^{-40} g.cm.²

N. M. BLIGH.

Studies in photographic sensitivity. V. Effects of heat on the absorption spectrum and photo-electric conductivity of silver bromide, and their relation to the photographic action. O. MASAKI (Mem. Coll. Sci. Kyoto, 1929, 12, 127—134; cf. B., 1929, 377).—The effect of temperature between 30° and 100° on the absorption spectra and photo-electric conductivities of silver halides was examined. The long-wave limit of absorption for silver bromide was shifted towards the red 1.1 Å./1° rise in temperature, and similar results were obtained with silver chloride and iodide. The photo-electric conductivity of silver bromide decreased with rise in temperature, and the maximum shifted towards the red by about 1.4 Å./1°. It was previously observed that the sensitivity of certain photographic plates was increased and the maximum sensitivity shifted towards the red by rise in temperature, and a connexion between these phenomena is suggested.

C. J. SMITHELLS.

Photoluminescence of liquids. S. J. VAVILOV and L. A. TUMMERMANN (Z. Physik, 1929, 54, 270—276).—A study has been made of the blue luminescence obtained by ultra-violet irradiation, from a mercury-quartz lamp, of a number of colourless liquids, including organic compounds and solutions of mineral acids. The spectra for the same frequency of stimulation (400—560 m μ) are very similar. Other phenomena such as the extinction of the fluorescence, its polarisation and colour change with different irradiation have been investigated. It is concluded that the phenomenon discovered by Venkateswaran and Karl (this vol., 241) is another case of fluorescence.

G. E. WENTWORTH.

Duration of the phosphorescence of the I₂, K₂, Na₂, and Na resonance emission. H. H. HUFFELD (Z. Physik, 1929, 54, 484—497).—Gaviola's fluorometer (A., 1927, 712) was used to measure the duration of the phosphorescence of the iodine, potassium, and sodium band resonance emission as well as that of the D-line of sodium. For I₂, $t = 1.10 \cdot 10^{-8} \pm 1.10 \cdot 10^{-9}$ sec.; for K₂, $t = 8 \times 10^{-9} \pm 1.5 \times 10^{-9}$ sec.; for Na₂, $t = 7.5 \times 10^{-9} \pm 1.5 \times 10^{-9}$ sec.; for sodium D-line, $t = 1.2 \times 10^{-8} \pm 0.3 \times 10^{-8}$ sec.

W. E. DOWNEY.

Polarisation phenomena in the gradual excitation of the fluorescence of mercury vapour. W. HANLE and E. F. RICHTER (Z. Physik, 1929, 54, 811—818).—The fluorescence of mercury vapour for the gradual excitation of the 2537 and 4047 Å. lines in particular was investigated. Nitrogen was added, a pressure of 1.5 mm. being used. The polarisation effects and intensity displacement of the 5461, 4358,

and 4047 Å. lines are described and explained. The polarisation of the 4047 Å. line should be complete theoretically. This is not so in practice, the difference being ascribed to the effect of fine structure.

A. J. MEE.

Raman effect in alkali halides. C. SCHAEFER (Z. Physik, 1929, 54, 153—154).—A preliminary note stating that, as in the case of rock salt, no emission of the characteristic infra-frequency can be detected with lithium or sodium fluorides, and suggesting a possible theoretical basis for this. R. W. LUNT.

Raman effect in potassium carbonate solution. M. LEONTOVITSCH (Z. Physik, 1929, 54, 155—157).—Using exposures of 90 hrs., a satellite to the radiated lines 3126, 3132 Å. has been observed. This corresponds with an infra-red frequency, $\lambda = 9.26 \mu$, and thus lies close to the frequency characteristic of calcite, $\lambda = 9.13 \mu$. This frequency is therefore attributed to the CO₂ group.

R. W. LUNT.

Raman effect by helium excitation. R. W. WOOD (Phil. Mag., 1929, [vii], 7, 858—868).—The method of using a mercury arc for the excitation of Raman lines previously described (A., 1928, 1306) has been improved so that cooling is effected by only a small quantity of absorbing medium. The mercury arc method of excitation is unsatisfactory in that it is incapable of providing truly monochromatic exciting radiation. This defect is not present when radiation from a helium discharge tube is used in conjunction with a filter of nickel oxide glass which transmits the 3888 Å. line to almost its full intensity and the lines at 3965 and 4025 Å., with such feeble intensity as to give no Raman lines. The arrangement of the helium tube is described together with the method of preparing a standard scale from which the wavelengths of the infra-red absorption bands corresponding with the Raman lines can be read directly. The helium excitation apparatus has been used satisfactorily with liquids of b. p. 40°.

A. E. MITCHELL.

Raman effect. A. PETRIKALN and J. HOCHBERG (Z. physikal. Chem., 1929, B, 3, 217—228).—The Raman spectra of bromobenzene and pyridine resemble those of benzene and of chlorobenzene. The replacement of CH in the benzene nucleus by N does not alter the type of spectrum. With naphthalene the structure of the spectrum is quite different. Nitromethane gives a spectrum characteristic of methane derivatives, but with acetonitrile a different type of spectrum is obtained. The spectra of all the above substances have a Raman line characteristic of the C-H linking. This line is replaced by a strongly diffuse doublet in the Raman spectra of hexane and cyclohexane, which are closely similar to one another. The carbon disulphide spectrum shows only two lines. Diphenylmethane (in methyl alcohol) gave a very intense continuous spectrum, but no lines, and triphenylmethane (in ether) gave a few broad bands but also no lines. The corresponding infra-red bands have also been calculated from the observed frequency difference of the Raman lines. O. J. WALKER.

Raman spectra of solutions of some ionised substances. R. G. DICKINSON and R. T. DILLON (Proc. Nat. Acad. Sci., 1929, 15, 334—337).—Since

there is a close agreement between the strongest lines of the Raman spectra of calcite and sodium nitrate solutions, and in order to obtain further comparable data the spectrum of the radiation scattered by solutions containing the ions CO_3 , ClO_3 , BrO_3 , IO_3 , SO_3 , HCO_3 , SO_4 , and ClO_4 was photographed. The assignment of exciting lines to shifted lines and the magnitudes of the frequency shifts with their estimated relative prominence are tabulated. The strong lines show a regularity, the magnitudes of the frequency changes are uninfluenced by the nature of the positive ion, and the frequency change corresponding with the strong line decreases with increase in atomic number of the central atom of the negative ion.

N. M. BLIGH.

Raman effect in crystals. H. NISI (Proc. Imp. Acad. Tokyo, 1929, 5, 127—129).—The Raman spectra of quartz, topaz, and calcite have been determined. No Raman lines were found with fluor spar, contrary to the results of Landsberg and Mandelstam. The results for calcite confirm those of Wood, with the exception of a Raman line corresponding with an infra-red absorption band at 6.96μ . For topaz the mean differences between the exciting Hg lines and the Raman lines were 911 and 260 wave-numbers, corresponding with infra-red absorption bands at 11.0 and 38.5μ , respectively.

F. G. TRYHORN.

Change of the dielectric constant of a highly rarefied gas by means of electrons. L. BERGMANN and W. DURING (Ann. Physik, 1929, [v], 1, 1041—1068).—The change in the dielectric constant of a highly rarefied gas in the presence of electrons has been measured by the second method of Drude. As the electron density increases the dielectric constant steadily decreases. The absolute values for the constant agree with theoretical requirements, as also does the course of the dispersion. R. A. MORTON.

Dielectric constant of some ionised gases. H. GUTTON (Compt. rend., 1929, 188, 1235—1237; cf. this vol., 228).—It is shown that the dielectric constant (K) of a gas may be obtained from the ionisation currents of the gases constituting the dielectrics of two condensers in series, one containing the ionised gas under test, and the other a gas of known properties (air). The equation $K-1+[0.278 \times 10^{10}N/(35.5 \times 10^{10}N^{3/4}-\omega^2)]$ enables the number of electrons/c.c. of ionised gas (N) corresponding with resonance to be calculated for any pulsation ω . For $\lambda=248.7 \text{ cm.}$, $N=1.9 \times 10^8$.

J. GRANT.

Dielectric constants of some metallic vapours. F. KRÜGER and F. MASKE (Physikal. Z., 1929, 30, 314—320).—The dielectric constant of mercury vapour at 312° and 10 cm. pressure is $\epsilon=1.000622$. At this pressure $\epsilon-1$ is proportional to the density; at the normal density at 0° , ϵ is calculated to be 1.0101. On the basis of the simple Maxwell relation $\epsilon=n^2$ (n =refractive index) the value 1.00373 is obtained as against 1.0101. The lack of agreement makes it necessary to consider the rôle of characteristic frequencies of the kind postulated by the Ketteler-Helmholtz dispersion formula. Accepting Cuthbertson's dispersion data and using $\lambda=2537 \text{ Å.}$ for an ultra-violet frequency it becomes necessary to assume

the existence of selective absorption near 0.9μ , and in view of uncertainties in the data, the band is placed as somewhere between 1 and 2μ . If the value for the dielectric constant at a density 13.55 is calculated by extrapolation on the basis of the Clausius-Mosotti formula $(\epsilon-1)(\epsilon+2)/d=\text{constant}$ the dielectric constant for liquid mercury becomes a negative quantity. Similarly, the introduction of the refractive index at λ_∞ leads to a negative value, from which it is concluded that the extrapolation cannot be justified.

The dielectric constant of potassium vapour at 500° and 1 cm. of mercury is 1.00092 , i.e., 1.19 ± 0.04 at 0° and atmospheric pressure. From the dispersion data, $n^2=1.00252$, the discrepancy again pointing to the operation of infra-red frequencies. The dielectric constant of rubidium vapour was also studied, but the results were less satisfactory. R. A. MORTON.

Mol. vol. of organic groups in complex salts.

I. Volume of *o*-phenylenediamine in its compounds with metallic salts. W. HIEBER and K. RIES (Z. anorg. Chem., 1929, 180, 225—234).—The densities of a series of compounds of *o*-phenylenediamine with the halides of cadmium, nickel, cobalt, and zinc, and with the sulphates of cobalt, nickel, copper, zinc, and cadmium have been determined at 25° , and the corresponding mol. vol. calculated. From these values the mol. vol. of *o*-phenylenediamine in each of these compounds is obtained and compared with that in the uncombined state. The mol. vol. of *o*-phenylenediamine is in general greater in its compounds and increases in the order chloride, bromide, iodide, but it depends also on the number of molecules of *o*-phenylenediamine present in the compound and on the temperature. The regularities found by Biltz (A., 1928, 697) for the mol. vol. of ammonia in its compounds with metallic salts do not apply in the case of the diamine. O. J. WALKER.

Dispersion of double refraction in quartz. T. H. HAVELOCK (Proc. Roy. Soc., 1929, A, 124, 46—49).—The constant C in the relation for a uniaxial crystal, $(n_1^2-1)^{-1}-(n_2^2-1)^{-1}=C$, where n_1 is the ordinary and n_2 the extraordinary index (cf. *ibid.*, 1907, A, 80, 28), has been recalculated for quartz for wave-lengths from 1852 to $21,719 \text{ Å.}$, using the experimental data of Gifford (*ibid.*, 1902, A, 70, 329) from 1852 to 7950 Å. , and of Carvallo from 8320 to $21,719 \text{ Å.}$ The mean value of C over the range 3961—8320 Å. is 0.014416, with a definite fall to about 0.01422 at the two extremes of the scale. Using this value of C in conjunction with the dispersion formula for the ordinary index proposed by Coode-Adams (A., 1928, 220), the calculated values of the double refraction are found to be in excellent agreement with the experimental values obtained by Harris (Phil. Mag., 1929, [vii], 7, 80) and by Gifford (*loc. cit.*). There is some indication that Harris's values for the short wave-lengths may be somewhat low.

L. L. BIRCUMSHAW.

The $\tan \delta$ law of paramagnetic rotation of the plane of polarisation. W. SCHÜTZ (Z. Physik, 1929, 54, 731—735).—Mathematical.

Organic dipole-molecules with singly- and doubly-linked oxygen. K. L. WOLF (Z. physikal.

Chem., 1929, B, 3, 128—138).—The part played by singly- and doubly-linked oxygen in determining the dipole moments of organic compounds is discussed. The assumption is made that singly-bound oxygen makes an angle of about 110° with the normal valency linking in the rest of the compound. It is shown that this assumption leads to correct values for the dipole moments of certain classes of compounds containing the hydroxyl or methoxyl groups. It also removes many difficulties previously experienced in calculating the dipole moments of benzene substitution products, and contradictions in the signs of the group moments disappear. Two possible linkings for the oxygen in the carbonyl group are discussed. In order to settle which occurs it is necessary to obtain experimentally the dipole moment of a cyclic saturated ketone. The results of experiments on the ultra-violet absorptions of *cyclohexanone* and *menthone* are used for this purpose. The value obtained for the dipole moment is about 2.75×10^{-18} , which is the same as for an aliphatic ketone. This is the result which would be expected if the oxygen of the carbonyl group were bound to the carbon by an ordinary double linking. The structure of the carboxyl group is also discussed. The relatively strong acid character of the hydroxyl group in the fatty acids is due to the effect of the carbonyl dipole on the hydroxyl group.

A. J. MEE.

Expression for natural rotation [of light] corresponding with that for molecular refraction. K. L. WOLF and H. VOLKMANN (Z. physikal. Chem., 1929, B, 3, 139—148).—The expression obtained by Gans based on Born's theory, which has the same significance for natural rotation as the expression for specific refraction has for refraction is discussed. The formula is confirmed by the experiments of Wetterfors on bromocamphor in acetone (A., 1922, ii, 247). In order to test the Born-Gans theory on a somewhat wider basis, new determinations of the rotation, refractive indices, and densities of solutions of limonene in different solvents and for different concentrations were made. They provide a further confirmation of the theory. Deviations may be ascribed to the effect of the dipole moment of the solution and to molecular association, a fact which is confirmed by experiments on menthone and carvone and their solutions. In this connexion the dipole moment of menthone was determined and found to be 2.77×10^{-18} , whilst for limonene, in consequence of the small size of its moment, only the upper limit, 0.5×10^{-18} , could be determined. The ultra-violet absorption curves of a $0.14M$ -solution of menthone in hexane and absolute methyl alcohol are given.

A. J. MEE.

Use of a magnetic field in the measurement of the forces tending to orient an anisotropic liquid a thin, homogeneous layer. V. FREDERICKSZ and V. ZOLINA (Amer. Electrochem. Soc., May 1929. Advance copy, 11 pp.).—The forces which cause the orientation of the "drops" of an anisotropic liquid in the form of a homogeneous layer have been investigated by balancing them against magnetic forces. It is concluded that the magnitude of the orienting forces depends only on the nature and condition of

the anisotropic liquid itself and is independent of the kind of glass on which the liquid rests and of the method of cleaning the glass surface, provided that cleaning is done carefully. For phenetole and anisaldazine the orienting force is found to vary as the reciprocal of the eighth power of the thickness of the liquid layer for magnetic fields between 4000 and 9000 gauss. Rise of temperature produces a small but definite decrease in the orienting force.

H. J. T. ELLINGHAM.

Chemical and optical properties of the reactive organic groups. A. DADIEU (Z. Elektrochem., 1929, 35, 283—291).—A discussion on the relationships which subsist in various series of organic compounds between properties, such as dissociation constants, absorption spectra, and variations in reactivity and chemical constitution.

H. T. S. BRITTON.

Kerr effect in viscous liquids due to radio-frequency oscillating field. S. C. SIKKAR (Indian J. Physics, 1929, 3, 409—424).—The Kerr effect is reviewed theoretically and the method for its study in octyl, nonyl, and undecyl alcohols fully described. A restoration of light between crossed Nicols, differing entirely from the Kerr effect, was observed, and was most marked in the region of frequencies in which there is strong electric absorption, the liquid becoming translucent. The Kerr effect in undecyl alcohol became too small to be observed for an oscillating field of wave-length 114 cm., showing the existence of a time of relaxation lying between 10^{-8} and 10^{-9} sec.

N. M. BLYTH.

Texture of drawn magnesium and zinc wire. E. SCHMID and G. WASSERMANN (Naturwiss., 1929, 17, 312—314).—With metals showing the face-centred cubic lattice, the central zone of the drawn wire shows the ordinary fibre structure. For the hexagonal metals magnesium and zinc the former exhibits a (centred or homogeneous) ring fibre structure, whilst zinc shows a spiral or double-cone fibre texture. The portions near the edge of the wire show simple conical structure in all cases.

R. A. MORTON.

Improvement (by heat treatment) of an aluminium alloy in respect of X-ray structure. [FRL.] VON GOLER and [FRL.] G. SACHS (Naturwiss., 1929, 17, 309—312).—An aluminium alloy containing 5% of copper has been studied in relation to physical properties, extension, etc., and parallel determinations of lattice constants have been made after heat treatment for definite times at various temperatures. The lattice constants show no change until the heat treatment has brought about a very considerable improvement in respect of cohesion. The lattice constant of the supersaturated mixed crystals after heat treatment is the same as that of the quenched alloy, indicating that the copper is completely "built into" the lattice.

R. A. MORTON.

Plasticity. Deformation at low temperatures. M. PÓLANYI and E. SCHMID (Naturwiss., 1929, 17, 301—304).—Three kinds of plasticity are differentiated. Athermic plasticity occurs in crystals, e.g., uncrystalline zinc and cadmium. The materials begin to give way under a tension 10^{-3} times the theoretical value, and a fall of temperature from

300° to 20° Abs. causes only a 1:1.8 increase in the effective tension. It would appear that at the absolute zero such crystals would undergo plastic deformation under conditions not very different from those obtaining at the ordinary temperature. The extension curves for cadmium at 83° and 20° almost coincide, showing that the process of recovery is absent at these temperatures and the curve ceases to depend appreciably on temperature. Thermal plasticity, conditioned by heat motion, appears in amorphous substances like glass, pitch, and shellac. Deformation occurs under relatively small loads, the effect being a flow in the sense that an increase in the rate of deformation requires a considerable increase in the load. The effect depends greatly on temperature, and at absolute zero the plasticity might be expected to disappear, so that in the absence of cracks the theoretical cohesion of 10^2 – 10^3 kg./mm.² should be observed. R. A. MORTON.

Striking phenomenon with laminated mica crystals. H. W. ALBU and H. ZOCHER (Naturwiss., 1929, 17, 299–301).—Certain forms of mica in which the succession of laminae result in almost total reflexion of direct rays, transmit quite freely with oblique incidence within an apparently quite small angular region. The emergent light is practically completely polarised. Viewed through a microscope the transmission is confined to a bright ring when the incident light is convergent. Mica is suggested as a "dark field filter" in microscopy.

R. A. MORTON.

Refractivity of gaseous compounds. G. W. BRINDLEY (Phil. Mag., 1929, [vii], 7, 891–897).—The apparently simple relationships between the refractivities of a number of gaseous compounds previously discussed (this vol., 380) are examined further. The following numerical relationships are shown to hold with fair accuracy for any given wavelength $(\mu-1)_{\text{HCl}}=4/7(\mu-1)_{\text{Cl}_2}$, $(\mu-1)_{\text{CCl}_4}=16/7(\mu-1)_{\text{Cl}_2}$, $(\mu-1)_{\text{HBr}}=13/25(\mu-1)_{\text{Br}_2}$, and $(\mu-1)_{\text{CS}_2}=4/3(\mu-1)_{\text{S}_8}$. It is pointed out that the ratios obtaining are either the ratios or multiples of the ratios of the numbers of *M* electrons in the molecules and it is shown that this is in general conformity with both the quantum and the electronic theories of dispersion. The difference between $(\mu-1)_{\text{HCl}}/(\mu-1)_{\text{Cl}_2}$ and $(\mu-1)_{\text{HBr}}/(\mu-1)_{\text{Br}_2}$ is discussed and it is considered to be due to light absorption by bromine in the visible region of the spectrum. A. E. MITCHELL.

Quantum theory of gases and solutions. N. BARBULESCU (Bul. Soc. Stiinte Cluj, 1928, 4, 62–74; Chem. Zentr., 1928, ii, 2334).—The theory rests on the supposition that the translatory motion of molecules in the gaseous and liquid states is a vibratory movement of extremely small frequency. The mechanism of the increase of kinetic energy by absorption of heat radiation becomes a simple resonance phenomenon. A. A. ELDRIDGE.

Theoretical electronic explanation of organic compounds, especially benzene. M. ULMANN (Z. Elektrochem., 1929, 35, 268–274).—Theoretical.

H. T. S. BRITTON.

Experimental test of the quantum theoretical dispersion formula. II. R. LADENBURG (Natur-

wiss., 1929, 17, 296–299; cf. *ibid.*, 1926, 14, 1208).—A review (cf. A., 1926, 994; 1928, 577, 1172).

R. A. MORTON.

Liquid interference. H. MARK (Z. Physik, 1929, 54, 505–510).—Theoretical.

W. E. DOWNEY.

Co-ordination numbers. F. I. G. RAWLINS (Trans. Faraday Soc., 1929, 25, 283–285).—The quantity *C.N.* or the number of atoms or ions of a certain kind surrounding another atom at equal distances in the crystal lattice, and the inter-nuclear distance are discussed in relation to passage from crystalline to gaseous state, and some theoretical suggestions are made. The quantity *C.N.* is also found to be intimately associated with the degree of complexity of the infra-red spectra of crystals (cf. Tolsdorf, A., 1928, 565).

N. M. BUGH.

Electronic theory of valency. VII. Etch figures of sylvine. T. M. LOWRY and M. A. VERNON (Trans. Faraday Soc., 1929, 25, 286–291).—The possibility of a fine structure was investigated by etching sylvine crystals with a strong solution of potassium chloride. No evidence contrary or additional to that furnished by X-rays was obtained. The formation of ice is considered to be a polymerisation rather than an ionisation process. A network of single linkings is postulated also in the case of quartz and the anions of certain oxygenated crystalline salts.

N. M. BUGH.

Deflexion method for molecular beams. I. I. RABI (Z. Physik, 1929, 54, 190–197).—A modified form of molecular beam apparatus is described in which the deflexion produced in the stream is proportional to the strength of the magnetic field (and not as in earlier forms to the inhomogeneity), thereby greatly simplifying the technique. R. W. LUNT.

Experimental method for the measurement of molecular streams. H. MEYER (Z. Physik, 1928, 52, 235–248).—Experiments are described in which the momentum of gas molecules escaping through a narrow orifice is conveyed to a suspended quartz fibre system carrying a mirror. The deflexion of this system gives a measure of the momentum of the molecules and therefore of the number of molecules escaping through the orifice. R. W. LUNT.

Effective binding forces in polyatomic molecules. F. EBEL and E. BRETSCHER (Helv. Chim. Acta, 1929, 12, 443–449; cf. A., 1928, 485).—Two apparently opposed views regarding the nature of interatomic linkings are discussed: (1) that the magnitude of the force between two atoms in a molecule is a fundamental quantity characteristic of the particular atoms, and (2) that the force between two atoms depends on the constitution of the molecule, so that, for example, the magnitude of the C–C linking differs in ethane and in hexaphenylethane. Evidence for the latter view is obtained from an examination of the energy required to remove the sulphur atom in carbonyl sulphide. The values of the C–O and C–S linkings are 199.2 and 131.7 kg.-cals., respectively, when calculated by Fajans' method from the heats of formation of carbon dioxide and of carbon disulphide. From the heat of combustion

of carbonyl sulphide it can be shown that only 76.9 kg.-cals are required to remove the sulphur atom from that compound. The strength of the C-S linking in carbonyl sulphide is, therefore, apparently about half what it is in the disulphide. Similarly, the removal of a chlorine atom from carbonyl chloride requires only about half the amount of energy calculated for the C-Cl linking. The two views can, however, be reconciled. It is assumed that there is a spontaneous and periodic rearrangement of the interatomic forces in a molecule, so that the energy distribution in the molecule is continuously fluctuating between limiting states. The Fajans values of the atomic linkings represent the average distribution of the internal energy of the molecule, but in chemical reactions it is the extreme values of the binding forces which are effective.

O. J. WALKER.

Mutual dependence of binding forces between atoms. F. EBEL and E. BRETSCHER (Helv. Chim. Acta, 1929, 12, 450—463).—According to the views put forward by the authors (cf. preceding abstract), the magnitude of the binding force between two atoms A and B should depend on the nature of any other atoms which are joined to A. A case in which this view can be tested experimentally is that of the P-O linking in the oxyfluoride and oxychloride of phosphorus. The value of this linking is 63.3 and 70.6 kg.-cals. in the oxychloride and oxyfluoride, respectively, as calculated from the heats of formation of these compounds from the corresponding phosphorus trihalide and oxygen. The replacement of chlorine by fluorine atoms therefore brings about a strengthening of the P-O linking, and not a loosening as would be expected from the older theories of organic chemistry. The heat of the reaction $\text{PF}_3 + 0.5\text{O}_2 = \text{POF}_3$ was measured and found to be 70.6 ± 1.0 kg.-cal., starting with the reactants in the gaseous state. A special form of gas calorimeter is described.

O. J. WALKER.

Relation between the influence of the elements on the polymorphism of iron and their place in the periodic system. F. WEVER (Naturwiss., 1929, 17, 304—309).—A definite periodic relation has been detected between the influence of an element on the polymorphic transformations of iron (from face-centred to body-centred cubic lattices) and its position in the periodic system. Similar relationships are probable for the properties of homogeneous mixed crystal series.

R. A. MORTON.

Experimental determination of surface tension by the method of traction of discs. J. E. VER-SCHAFFELT (Bull. Acad. roy. Belg., 1928, [v], 14, 663—665).—A simplified process is described for calculating the results of determinations of surface tension (by measuring the force required to withdraw a disc from the liquid) from the formula given previously (*ibid.*, 530), by a method of successive approximation.

F. L. USEER.

Surface tension of sodium. F. E. POINDEXTER and (Miss) M. KERNAGHAN (Physical Rev., 1929, [ii], 33, 837—843).—Accurate experiments on molten sodium in a high vacuum, using a modified flat drop method gave values, corrected by Worthington's formula, of 206.4 and 199.5 dynes/cm. at 100° and

250°, respectively, for the surface tension of sodium. The molecules in liquid sodium are concluded to be polyatomic.

N. M. BLIGH.

Emission of soft X-rays by different elements at high voltages. O. W. RICHARDSON and F. S. ROBERTSON (Proc. Roy. Soc., 1929, A., 124, 188—196).—By means of the apparatus previously described (A., 1927, 804), an investigation has been made of the efficiency of 14 elements as emitters of soft X-rays at exciting voltages of about 2000, 4000, and 6000. Curves are plotted showing the relation of the ratio i_p/i_t to the atomic number, and are found to be of similar type to those previously obtained at lower voltages. Molybdenum maintains its position as the most efficient element over the whole range from 300 to 6000 volts. There is a remarkable change in the group of elements from chromium to copper; whereas at 300 volts chromium is the most and copper the least efficient of these elements, at the higher voltages this position is reversed. Similarly, in the middle of the fifth and sixth long periods, gold is much less efficient than platinum at low voltages, but at 6000 volts actually exceeds platinum. An indication of the same state of affairs is found for silver and palladium. Curves are also shown in which the values of i_p/i_t are plotted against the exciting voltage for each of the elements tested, and their individual peculiarities are discussed.

L. L. BIRCUMSHAW.

Absorption due to scattering of cathode rays. W. BOTHE (Z. Physik, 1929, 54, 161—178).—It is shown that the theory of multiple scattering suffices to account for the observed directional distribution of the scattering of an electron beam. In the case of aluminium the theory leads to an absorption coefficient in good agreement with the value found experimentally.

G. E. WENTWORTH.

Continuous spectrum X-rays from thin targets. W. W. NICHOLAS (Bur. Stand. J. Res., 1929, 2, 837—870).—The high-frequency limit of the continuous spectrum from an infinitely thin target consists of a finite discontinuity. The energy distributions on a frequency scale are approximately horizontal, for gold and for aluminium, when $\psi = 40^\circ$, 90° , and 140° , where ψ is the angle between measured X-rays and cathode stream. The intensities for these values of ψ are approximately 3:2:1, respectively. The bearings of these results on various theories of X-ray production are discussed and a structure for the moving electron is proposed which explains classically X-ray continuous spectrum phenomena.

W. E. DOWNEY.

New integrating photometer for X-ray crystal reflexions, etc. W. T. ASTBURY (Proc. Roy. Soc., 1929, A., 123, 575—602).—The development of the new principle in photometry recently described (A., 1927, 912) had led to the design of an integrating photometer which is found by experiment to give correct measurements of the total intensity in X-ray crystal reflexions, and also seems capable of adaptation to the measurement of the integrated intensity of other types of radiation. The method uses a carbon print of a negative instead of the negative itself, and α -rays. By using the "stopping power" for

α -rays of a carbon tissue positive, ionisation is produced in an α -ray electroscope in direct proportion to the original X-ray intensity which formed the negative. Experimental tests of the integrating properties of the new instrument show that when a uniform radioactive deposit is covered with successive thicknesses of uniform carbon tissue, then, provided that the angle of emergence of the α -rays from the tissue does not exceed a certain limiting value defined by the "stop" in the base of the electroscope, the increase in ionisation recorded by the electroscope is directly proportional to the increase in X-ray intensity as represented by the thickness of the tissue. The applicability of the photometer to the measurement of the integrated intensity of any radiation the photographic density curve of which is approximately exponential is discussed, and it is shown how the instrument may be used for the measurement of α -, β -, and γ -rays, and also of visible light.

L. L. BIRCUMSHAW.

Determination of particle size by means of X-rays. R. BRILL (Z. Krist., 1928, 68, 387; Chem. Zentr., 1928, ii, 2620).—The methods of Scherrer and of Laue are discussed; calculation of particle size by the former method fails only for large particles, and for weakly absorbing substances. Preparations of iron of varying origin and treatment usually give fairly concordant values.

A. A. ELDRIDGE.

X-Ray evidence for intermolecular forces in liquids. J. A. PRINS (Nature, 1929, 123, 908—909).—Whilst the principal halo of water lies at a diffraction angle corresponding with a spacing of about 3 Å., at the inner side of this halo the intensity is rather strong and approximately constant until an angle corresponding with a spacing of about 17 Å. is reached, when it diminishes rapidly and for still smaller angles approaches a limiting value. It appears that in the immediate neighbourhood of every molecule the mean density must be greater than at greater distances, indicating, in a dynamical sense, a "tendency to association" on account of the nature of the attractive intermolecular forces. Scattering inside the principal halo is observed also with liquids which are not usually regarded as "associating."

A. A. ELDRIDGE.

X-Ray pattern of metallic crystals. G. B. DEODHAR (Nature, 1929, 123, 909).—Experiments with metal foils kept for about 20 yrs. at the ordinary temperature indicate that for silver and gold the lattice is the same, and is of the same magnitude, that these metals do not recover from the effects of the process by which the leaves are made (cf. Nishikawa and Asahara, Physical Rev., 1920), and that a thin metal leaf is to be regarded as an assemblage of metallic crystals.

A. A. ELDRIDGE.

Intensity of total scattering of X-rays. I. WALLER and D. R. HARTREE (Proc. Roy. Soc., 1929, A, 124, 119—142).—Theoretical. Starting from Waller's general scattering formula (Z. Physik, 1928, 51, 213), an expression is deduced for the total scattering of the atoms in a gas; it is approximately valid if the frequency of the incident radiation is essentially higher than the K-absorption frequency of the atoms. This is first applied to the special case of the scattering by helium atoms, and it is then shown how approxi-

ate wave functions of required symmetry properties can be formed for an atom containing several electrons. The formula for the total scattering is evaluated for the case of argon and found to be in satisfactory agreement with Barrett's experimental results (A., 1928, 939).

L. L. BIRCUMSHAW.

Spectroscopic measurements of M absorption levels for the elements uranium to tungsten. E. LINDBERG (Z. Physik, 1929, 54, 632—642).—The absorption edges $M\ v$, $M\ iv$, and $M\ iii$ have been determined for uranium, thorium, bismuth, lead, mercury, gold, platinum, and tungsten. Absorbing layers were metal deposits on aluminium foil, 0.5 μ thick, or a powder of the element or its compound suspended in a celluloid film. The absorption levels $M\ v$, $M\ iv$, and $M\ iii$, determined from previously known $L\ iii$ levels and L and M emission lines, are compared with those directly observed; a systematic deviation is noted. N levels are deduced from the M absorption and emission spectra.

A. B. D. CASSIE.

X-Ray examination of highly-polymerised organic substances. E. OTT (Helv. Chim. Acta, 1929, 12, 330—331).—A reply to the criticisms of Mie and Hengstenberg and of Staudinger and Signer (this vol., 49) of the author's previous paper (A., 1928, 465). The assumption that the elementary cell in highly-polymerised polyoxymethylene compounds contains one molecule is supported by X-ray as well as osmotic experiments.

O. J. WALKER.

Diffraction of cathode rays by powdered crystals. T. MUTO and T. YAMAGUTI (Proc. Imp. Acad. Tokyo, 1929, 5, 122—124).—Celluloid and mica films were unsuccessfully tried as supports for powders for cathode-ray analysis. The effect produced by diffraction by the supporting film was superposed on that due to the substance with consequent blurring. Satisfactory results were obtained by using as a support a slice 40—50 μ in thickness of the pith of *Tetrapanax papyrifer*, K. Koch. Microscopic examination showed that on this support the particles of the substance under examination adhered to the fibres. The most satisfactory support was strands of spider's web stretched on a metal frame, and dusted with the substance to be examined. The results for graphite and magnesium oxide obtained by cathode-ray diffraction using such a support agreed closely with the X-ray measurements of these substances.

F. G. TRYHORN.

Influence of temperature on the X-ray liquid haloes. V. I. VAIDYANATHAN (Indian J. Physics, 1929, 3, 391—398).—The X-ray diffraction haloes were studied at two temperatures of the order 30 and 140° for camphene, mesitylene, acetic acid, butyric acid, and ethyl alcohol, and the results were interpreted theoretically. These liquids, with the exception of camphene, show two haloes. With rise of temperature increase in the scattering at small angles was found, a contraction of the haloes and an increase in their diffuseness, a tendency for the separation between the inner and outer haloes to be effaced and for the inner one to become diffuse more quickly than the outer one. These effects are especially marked in the case of the last-mentioned three liquids, which

are associated at ordinary and dissociated at higher temperatures.

N. M. BLIGH.

Classical derivation of the Compton effect. C. V. RAMAN (Indian J. Physics, 1929, 3, 357—369).—By using an atomic model in which the electrons are regarded as a gas distributed in a spherical enclosure surrounding the nucleus, it is shown that a combination of statistical mechanics and classical wave theory leads directly to a quantitative theory of the Compton effect and an explanation of the known experimental facts.

N. M. BLIGH.

Fine structure absorption edges of metals and metalloids in the X-ray region. B. RAY and P. C. MAHANTI (Z. Physik, 1929, 54, 534—536).—The fine structure absorption edges of vanadium, chlorine, and sulphur in the X-ray region are discussed on the hypothesis of the existence of free electrons in metals.

W. E. DOWNEY.

X-Ray analysis of the system chromium-nitrogen. Constitution of ferrochromium containing nitrogen. R. BLIX (Z. physikal. Chem., 1929, B, 3, 229—239).—X-Ray investigations by the powder method of preparations of chromium containing nitrogen in varying proportions, obtained by passing ammonia over chromium heated to 800°, show the existence of two intermediate phases. The first phase is homogeneous within a fairly wide interval of concentration round about 33 at.-% N, which corresponds with the formula Cr_2N . The chromium atoms are arranged in a hexagonal lattice with densest spherical packing, the nitrogen atoms probably being distributed at random in the hollow spaces of the lattice. The lattice constants increase with the nitrogen content from $a_1=2.747$ and $a_2=4.439$ Å. to the values 2.770 and 4.474 Å., respectively, the axial ratio remaining constant at 1.616. The second phase corresponds with the compound CrN and has the NaCl structure ($a=4.140$ Å.; $d_{\text{calc.}}=6.1$, $d_{\text{obs.}}=5.9$). X-Ray examination of a ferrochromium alloy (60.3% Cr, 2.4% N, 0.7% Mn, 2% Si, and 0.21% C) indicates that the nitrogen is present mainly as the hexagonal Cr-N phase.

O. J. WALKER.

Refractive indices and anomalous dispersion of soft X-rays in platinum, silver, calcite, and glass. E. DERSHEM (Physical Rev., 1929, [ii], 33, 659—671).—The refractive indices of several substances for homogeneous X-rays obtained by reflexion from a gypsum crystal were measured by the total reflexion method for the wave-length range 0.8—9.15 Å. Dispersion curves obtained by plotting $\delta=1-u$ against λ are given, and anomalous dispersion as shown by depressions in the curves is discussed in detail for each substance. The results fully reveal for the first time the type of anomalous dispersion occurring in the region of the K, L, and M absorption discontinuities. The form of the curve was independent of the sample used, but values of δ varied with film thickness and surface conditions.

N. M. BLIGH.

Compton modified line structure and its relation to the electron theory of solid bodies.

W. M. DU MOND (Physical Rev., 1929, [ii], 33, 643—658; cf. this vol., 123).—The structure of the

Compton line obtained with a special tube for a scattering angle of nearly 180° with a metallic beryllium scatterer is shown. Experimental line structure curves obtained by a photo-micrometric analysis of the spectra, and a general method of computing and normalising line structure curves are given. The relation between Compton line structure and electron velocity distribution according to various alternative assumptions is discussed. The evidence is in favour of the new wave-mechanical atom model and the new Sommerfeld theory of distribution of metallic electron velocities and of the degenerate gas state.

N. M. BLIGH.

Crystal structure and chemical constitution. V. M. GOLDSCHMIDT (Trans. Faraday Soc., 1929, 25, 253—283).—A lecture.

N. M. BLIGH.

Chemical combination as an electrostatic phenomenon. V. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 210—216).—The stability of various types of crystal lattice for simple compounds is discussed on the basis of the work of Goldschmidt (A., 1927, 611).

S. I. LEVY.

Crystal structure of lithium chloride monohydrate. S. B. HENDRICKS (Z. Krist., 1927, 66, 297—302; Chem. Zentr., 1928, ii, 2621).—The unit cell, probably containing 1 mol., is tetragonal; d_{001} 3.88, d_{100} 3.81 Å.

A. A. ELDRIDGE.

Calcium carbide lattice. C. HERMANN (Z. Krist., 1927, 66, 314—316; Chem. Zentr., 1928, ii, 2621—2622).—A lattice somewhat like the pyrite type is suggested.

A. A. ELDRIDGE.

Structural relationships between pyroxene and amphibolite. B. GOSSNER (Zentr. Min. Geol., 1928, A, 340—341; Chem. Zentr., 1928, ii, 2341).—Comparison of the lattice constants indicates an isomorphism which is not exhibited in the external crystal morphology.

A. A. ELDRIDGE.

Crystal habit of calcite from the minerogenetic point of view. G. KALB (Zentr. Min. Geol., 1928, A, 337—339; Chem. Zentr., 1928, ii, 2341).

Crystal structure of potassium chloroplatinate. F. J. EWING and L. PAULING (Z. Krist., 1928, 68, 223—230; Chem. Zentr., 1928, ii, 2432—2433).—Potassium chloroplatinate has d_{100} 9.73 Å.; μ 0.24 ± 0.005 Å., and possesses the structure of potassium chlorostannate.

A. A. ELDRIDGE.

Crystal structure of ethylammonium chlorostannate. R. W. G. WYCKOFF (Z. Krist., 1928, 68, 231—238; Chem. Zentr., 1928, ii, 2433).—Ethylammonium chlorostannate and chloroplatinate have, respectively, a_0 7.24, 7.13 Å., c_0 8.41, 8.53 Å. Parameters for the chlorine ions in the chlorostannate are u 0.16, v 0.17. The structure is the pyrochroite arrangement.

A. A. ELDRIDGE.

Lattice constants of various fahl ores. F. MACHATSCHKI (Z. Krist., 1928, 68, 204—222; Chem. Zentr., 1928, ii, 2448).—All fahl ores are hexakis-tetrahedral, space-group T_d^2 . The size of the unit cell varies about a 10.30 Å. according to the composition. Variations etc. are considered.

A. A. ELDRIDGE.

Structure of analcime. I. Space-group. J. W. GRUNER (Z. Krist., 1928, 68, 363—378; Chem. Zentr., 1928, ii, 2545).—The unit cell (cubic) has a 13.539 Å., and contains 16 mols. The lattice is body-centred; space-group probably O_h^h .

A. A. ELDRIDGE.

Fine structure of brookite and the physical behaviour and changes of state of three natural forms of titanium dioxide. A. SCHRODER (Z. Krist., 1928, 67, 485—542; Chem. Zentr., 1928, ii, 2230).—The unit cell of brookite has a 9.136±0.020, b 5.439±0.010, c 5.153±0.030 Å.; the unit cell contains 8 mols. of TiO_2 . A very slow change into rutile is postulated, and a study has been made of the effect of temperature on the physical properties of brookite. Dispersion and dilatation curves were obtained for anatase and rutile. Nigrin, which is also obtained by heating rutile at 700°, is not a new modification.

A. A. ELDRIDGE.

Simple method of obtaining a single crystal of zinc with approximately any desired orientation of its principal axis. S. ITO (Mem. Coll. Sci. Kyoto, 1929, 12, 97—105).—A method of preparing single crystal sheets of zinc about 9×7×0.15 cm. is described. A zinc sheet is supported in a thick asbestos box and heated until just molten. A small single crystal of known orientation is then placed in contact with one end of the sheet and the rate of cooling from this end is so controlled that a single crystal develops, the principal axis of which has the same orientation as that of the nucleus crystal. The orientation about the principal axis cannot be predetermined by this method.

C. J. SMITHELLS.

Principles determining the structure of complex ionic crystals. L. PAULING (J. Amer. Chem. Soc., 1929, 51, 1010—1026).—The following five fundamental principles are enunciated which govern the structure of crystals containing only small cations (valency= z) with relatively large electric charges, and having crystal radii not exceeding about 0.8 Å., the anions being large, univalent, or bivalent, and not too highly deformable. (I) A co-ordinated polyhedron of anions is formed about each cation, the cation-anion distance being determined by the radius sum and the co-ordination number (v) of the cation by the radius ratio (r). The minimum values of r are: tetrahedron, $v=4$, $r=0.225$; octahedron, $v=6$, $r=0.414$; cube, $v=8$, $r=0.732$. (II) In a stable co-ordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valency linkings ($s,=z/v$) reaching to it from the cations at the centres of the polyhedra of which it forms a corner. All crystals which have been investigated conform to this principle. (III) Shared edges, and particularly shared faces, decrease the stability of a co-ordinated structure; the effect is large for cations with large z and small v , and is especially large when r approaches the lower limit of stability of the polyhedron. (IV) In a crystal containing different cations those with large z and small v tend not to share polyhedron elements with each other. (V) The number of essentially different kinds of constituents in a crystal tends to be small. A method of estimating any distortion which may

occur in crystals is also given. The principles are used to predict the structures of cyanite, andalusite, and sillimanite. The principles require that no stable basic silicates of bivalent metals exist, and that in aluminium silicates of alkali metals there should be at least one aluminium ion for every alkali ion. The structures of aluminium silicates of bivalent metals which are simplest from the co-ordination point of view are shown to correspond with the formulæ $R^{II}_3Al_2Si_3O_{12}$ and $R^{II}_3Al_2Si_6O_{18}$, which include the garnets and beryl. S. K. TWEEDY.

Determination of parameters in crystal structure by means of Fourier series. W. L. BRAGG (Proc. Roy. Soc., 1929, A, 123, 537—559).—Previous work on the Fourier representation of the results of X-ray analysis is discussed (cf. Allison and Duane, A., 1925, ii, 930; Havighurst, A., 1926, 995). In Havighurst's calculations, although a triple Fourier series in x, y, z is used, the density is calculated only for a series of points along a chosen line in a crystal. The present paper describes more extensive evaluations of the series, in that the density is calculated for values of two variables. The values of $F(hkl)$ are measured for all crystal directions round a given zone; e.g., if the zone is the a axis, the values of $F(0kl)$ are used. A Fourier series is formed in which these values appear as coefficients, the variables being the co-ordinates y and z . Values of y and z are taken at convenient intervals and the Fourier series is summed for every pair of co-ordinates. The result is a table of figures indicating the distribution of scattering matter in the unit cell, as projected on the face (100). This is done for the a, b , and c axes as zones in turn, leading to projections of the unit cell on the (100), (010), and (001) faces. The projections enable the atomic parameters to be measured and the number of electrons in each atom to be counted. The series is applied to the crystal diopside, $(CaMgSiO_3)_2$, which has already been analysed by another method (Warren and Bragg, Z. Krist., 1928, 69, 167), and the two sets of 14 parameters, found by the two methods, agree to within 0.5%. The numbers of atomic electrons in the projections are approximately: Ca 16.5, Mg 12.5, Si 11.5, O 8.5—9. The oxygen does not appear to be an ion O^{2-} with 10 electrons. The groups of F values used for any projection may be conveniently described as the "weights" attached to a network of points on a central section of Ewald's reciprocal lattice (Z. Krist., 1921, 56, 129).

L. L. BIRCUMSHAW.

Crystal structure of gallium. F. M. JÄGER, P. TERPSTRA, and H. G. K. WESTENBRINK (Z. Krist., 1927, 66, 195—216; Chem. Zentr., 1928, ii, 2620).—Gallium, m. p. 30.2°, on rapid crystallisation gives bipyramidal crystals; on slow growth they tend to be tabular. Crystals obtained from the super-cooled liquid were ditetragonal-bipyramidal, $a:c=1.16753$. The space-group is probably D_{2d}^6 ; the smallest separation of two gallium atoms is 2.56 Å.

A. A. ELDRIDGE.

Crystal lattice of Fe_4N . R. BRILL (Z. Krist., 1928, 68, 379—384; Chem. Zentr., 1928, ii, 2621).—An iron catalyst used for the synthesis of ammonia and containing 5% N was cubic, with lattice constant

3.80 Å. The presence of the compound Fe_4N with 1 mol. in the unit cell is postulated.

A. A. ELDRIDGE.

X-Ray study of the binary systems of iron with phosphorus, arsenic, antimony, and bismuth. G. HÄGG (Z. Krist., 1928, 68, 470—472; Chem. Zentr., 1928, ii, 2620—2621).—The compound Fe_3P is tetragonal (sub-group of C_4^2), body-centred, with 8 mols. in the unit cell. The symmetry of Fe_3P is a sub-group of D_{6h} . FeAs has a rhombic unit cell. The system iron-antimony forms mixed crystals between 63.5 and 65.5% Sb. FeSb_2 is rhombic; the unit cell contains 2 mols.; space-group apparently V^2 .

A. A. ELDRIDGE.

Atomic distances in mixed crystals of gold and copper. A. E. VAN ARKEL and J. BASART (Z. Krist., 1928, 68, 475—476; Chem. Zentr., 1928, ii, 2621).—Values for a complete series, the members varying by 10 at.-%, are tabulated. The differences are proportional to the fifth power of the mixture ratio.

A. A. ELDRIDGE.

Arrangement of minute crystals in electrolytically deposited bismuth and antimony. I, II. H. HIRATA (Elec. Rev. Japan, 1928, 16, 651—656, 761—767).—Small current densities and low electrolyte concentrations favour regular arrangement of the minute crystals of bismuth. The orientation of the crystals when arranged in fibres or in single pointed crystals was examined.

CHEMICAL ABSTRACTS.

Crystal form of boleite. B. GOSSNER (Amer. Min., 1928, 13, 580—582).—Boleite is cubic, a 15.6 Å., with 32 mols. in the unit cell.

CHEMICAL ABSTRACTS.

Atomic spacing in gypsum. S. VON FRIESEN (Z. Physik, 1929, 54, 679—685).—Precision measurements of the grating constant for gypsum show this to be independent of the specimen.

A. B. D. CASSIE.

Structure of boracite. J. W. GRUNER (Amer. J. Sci., 1929, [v], 17, 453—460).—The unit cell of boracite is a base-centred orthorhombic prism, $a_0=b_0=16.97$ Å., $c_0=12.00$ Å.: there are eight molecules to the unit cell. The probable formula is $\text{Mg}_6\text{Cl}_2\text{B}_{14}\text{O}_{26}$. The space-group is either C_2^2 or C_2^3 , the former being the more probable.

C. W. GIBBY.

Crystalline hydrated aluminium hydroxide of von Bonsdorff. II. R. FRICKE (Z. anorg. Chem., 1929, 179, 287—292; cf. A., 1928, 1199).—The relatively slight differences existing between the X-ray diagrams of bayerite- α and bayerite- β indicate that the latter resembles hydrargillite to a greater extent than does the former.

H. F. GILLBE.

New determination of the lattice constants of CsCl , and BaF_2 . E. BROCH, I. OFTEDAL, and A. PABST (Z. physikal. Chem., 1929, B, 3, 209—214).—The lattice constants of carefully purified samples of the above substances were determined by the powder method, using magnesium oxide and silver as reference substances. The following mean values of a were obtained: KF 5.333, CsCl 4.113, and BaF_2 6.184 Å. The corresponding values of d_{obs} are 2.5283, 3.9905, and 4.8943, and of d_{calc} 2.5053 \pm 0.0005, 3.988 \pm 0.004, and 4.893 \pm 0.009.

O. J. WALKER.

Crystal structure of strontium. A. J. KING (Proc. Nat. Acad. Sci., 1929, 15, 337—338).—A more accurate determination by means of powder spectrograms (cf. Simon and Vohsen, A., 1928, 694) confirmed a face-centred cubic structure and gave the values 6.075 \pm 0.004 Å. for the unit cube edge, 4.295 Å. for the distance between strontium atoms and d_{calc} 2.58.

N. M. BLIGH.

Atomic arrangement in the silicates. W. L. BRAGG (Trans. Faraday Soc., 1929, 25, 291—314).—A general survey of the structures of silicates analysed by X-ray methods is given. Data are examined and a structure is illustrated for the following minerals: beryl, phenacite, olivine, monticellite, norbergite, chondrodite, humite, clinohumite, zircon, topaz, staurolite, cyanite, sillimanite, mullite, andalusite, and diopside, as well as for the garnet series. A method of determining the position of atoms by means of a two-dimensional Fourier series is illustrated and compared with a method based on calculated and observed strengths of diffraction. The nature of the SiO_4 group and the general features of silicate structures are summarised.

N. M. BLIGH.

Structure of the AX_4 group. A. M. TAYLOR (Trans. Faraday Soc., 1929, 25, 314—316).—Measurements of the infra-red spectra of some substances of the AX_4 type are tabulated, and it is shown that generally two vibration frequencies are present. Their bearing on inter-atomic forces and the relations between atoms in a chemical radical is discussed. Evidence indicates that the atoms of the group are linked by semi-polar linkings. Shared electrons appear to be more effective in screening the oxygen atoms than in screening the central atom.

N. M. BLIGH.

Fine structure of feldspars. E. SCHIEBOLD (Trans. Faraday Soc., 1929, 25, 316—320).—X-Ray crystal analysis indicates that the feldspars have similar crystalline structures. Crystallographic data for various feldspars are tabulated, and the monoclinic feldspars are referred to a four-fold primary base-centred unit from which is deduced a double primary unit into which the corresponding unit of the triclinic feldspars would pass by a simple deformation. The structures, effects of replacements of different metallic atoms, and pseudocubic character of the substances are discussed in detail. An attempt is made to deduce details of the atomic arrangements in feldspars from radiograms.

N. M. BLIGH.

Constitution and structure of ultramarine. F. M. JAEGER (Trans. Faraday Soc., 1929, 25, 320—345).—The general preparation and characteristics of the ultramarines or sodium aluminosilicates are described. Some substituents are replaceable, as in the case of the permutites, and investigations are described of their relations with certain natural minerals such as sodalite, hauyene, and nosean, analogous to the permutites. The results of the substitution of silver in silver ultramarine by the alkali metals are tabulated and plotted; tables of powder-spectrogram and rotation-spectrogram data are given for a number of ultramarines and related compounds, and deductions therefrom on the structure of the substances are made and discussed in detail.

The causes of their colours is also considered. It is concluded that data are not yet sufficient for the structure problem to be finally settled and that much analytical work on substitution compounds is necessary.

N. M. BLIGH.

X-Ray diffraction in liquid alloys of sodium and potassium. K. BANERJEE (Indian J. Physics, 1929, 3, 399—408).—The X-ray diffraction haloes produced by alloys of varying compositions were studied, and interpreted with the help of the theory of X-ray diffraction in liquids and aqueous solutions. The effect is found to be additive as regards that due to the liquid compound Na_2K and that due to the excess of either metal dissolved in this compound. The halo for Na_2K indicates that the atoms of this compound are placed at the apices of a triangle.

N. M. BLIGH.

Corrosion of a crystal of dolomite by an active isotropic liquid. L. ROYER (Compt. rend., 1929, 188, 1303—1305).—According to the author's deductions (this vol., 631) the corrosion of a dolomite crystal by an inactive organic liquid is in accord with the existence of the elements of symmetry Λ^3C only. Active organic acids, however, produce effects indicating a ternary Λ^3 axis as the only element of symmetry and characterise the crystal as a ternary tetartohedral. It is concluded that although the true symmetry of dolomite is ternary parahemihedral, it may assume a tetartohedral form in an active medium.

J. GRANT.

Mechanical model of an asymmetric carbon atom. H. G. TANNER (J. Physical Chem., 1929, 33, 755—759).—A description is given of the construction and functioning of a mechanical model of an asymmetric carbon atom, the analogy being based on the postulate that electro-dynamical asymmetry of the four valency linkings of the carbon atom is responsible for optical activity. Rotational polarisation can be imitated with the model as well as preferential transmission of one of two species of circularly polarised waves.

L. S. THEOBALD.

Crystal structure of solid methane. J. C. McLENNAN and W. G. PLUMMER (Phil. Mag., 1929, [vii], 7, 761—764).—The crystal structure of solid methane at temperatures between -190° and -255° has been examined by the X-ray powder method. The results indicate the occurrence of a face-centred cube of edge 6.35 \AA , having 4 mols. per unit cell. The space-group of the carbon atoms is either T^2 or T_d^2 . There is no evidence of the occurrence of a pyramidal structure.

A. E. MITCHELL.

Hydrocarbon model. A. MULLER (Trans. Faraday Soc., 1929, 25, 347—348).—A model is constructed for the hydrocarbon $\text{C}_{25}\text{H}_{60}$ previously examined (cf. A., 1928, 1176).

N. M. BLIGH.

Structure of the carbon chain in hydrocarbons C_nH_{2n} . J. HENGSTENBERG (Z. Krist., 1928, 67, 583—594; Chem. Zentr., 1928, ii, 2221).—Pentatriacontane has a 7.43 , b (perpendicular) 4.97 \AA ; d 0.942 , whence the unit cell contains 2 mols. The CH_2 group in the C direction occupies 1.27 \AA . Paraffins of high mol. wt. yield diagrams due to a simple CH_2 -lattice. Assuming rhombic symmetry, the space-group is probably V_h^{16} . Zig-zag chains, in

which the carbon atoms are 1.52 \AA . apart, are postulated.

A. A. ELDRIDGE.

X-Ray evidence on the structure of the benzene nucleus. (Mrs.) K. LONSDALE (Trans. Faraday Soc., 1929, 25, 352—366).—An historical survey of X-ray work on carbon, benzene, and benzene derivatives is given. A number of questions on the structure and size of the benzene nucleus and of its component atoms are listed, and it is shown that some of these have been partly or wholly answered by means of a complete crystalline analysis of hexamethylbenzene (cf. this vol., 17). The fate of the fourth valency linking and the relationship of the aromatic to the aliphatic carbon atom are discussed in the light of recent theoretical X-ray work.

N. M. BLIGH.

Structure of the benzene ring in hexamethylbenzene. (Miss) K. LONSDALE (Proc. Roy. Soc., 1929, A, 123, 494—515).—One of the chief difficulties encountered hitherto in the study of the benzene nucleus has been that the unit cell of the various crystalline derivatives examined invariably contained more than one molecule, and so far no aromatic substance has had a simple enough structure for the positions of the separate atoms to be found without any previous hypotheses as to the shape or size of the molecule. Hexamethylbenzene, however, avoids this difficulty; the unit cell is triclinic and contains one molecule only. The prisms have been examined by the ionisation spectrometer using a Coolidge tube with a molybdenum anticathode. The dimensions of the cell are $a=9.010$, $b=8.926$, $c=5.344 \text{ \AA}$; $\alpha=44^\circ 27'$, $\beta=116^\circ 43'$, $\gamma=119^\circ 34'$; $a:b:c=1.0095:1:0.5987$. The space-group is either C_1^1 or C_1^1 , the molecule being either asymmetrical or centro-symmetrical; probably the latter, on analogy with benzene, hexachlorobenzene, and hexabromobenzene. The crystal is easily deformed by slipping about any of the crystallographic axes. The structure factors have been calculated for a large number of planes from the observed intensities and are found to obey the following rules: (1) the factors in the $[001]$ zone repeat themselves closely throughout the series of planes $(100) \rightarrow (010)$, $(010) \rightarrow (110)$, and $(110) \rightarrow (100)$. This clearly indicates a hexagonal arrangement of atoms in the $[001]$ zone. (2) The factors are almost independent of the last index l , which shows that the carbon atoms at least must all lie within 0.1 \AA . of the (001) cleavage plane. It is deduced from the relative values of the factors that a unique structure can be assigned to the molecule, which exists in the crystal as a separate entity and has a hexagonal form. Thus the X-ray evidence supplies a definite proof that the chemist's conception of the benzene ring is a true representation of the facts. The puckered or "diamond" type of ring and the more compact model proposed by Morse (A., 1928, 222) are shown to be wholly inadmissible. Only a plane ring can account both qualitatively and quantitatively for the hexagonal structure of the $[001]$ zone, for the lack of dependence on l , and for the relative values of the structure factors observed for (001) and a large number of other planes. The diameter of the aromatic carbon atom is $1.42 \pm 0.03 \text{ \AA}$, i.e., the ring is similar

in structure and in dimensions to that occurring in graphite. Three of the valencies of the aromatic carbon atom are co-planar, the ring itself and all the side-chain carbon atoms lying in one plane. The methyl group does not scatter like a single atom, but in scattering power is heavily weighted at the end nearer to the benzene ring. L. L. BIRCUMSHAW.

Crystal class of pentaerythritol. E. ERNST (Z. Krist., 1928, 68, 139—151; Chem. Zentr., 1928, ii, 2221).—The class has not yet been determined, despite detailed morphological and optical investigations. A. A. ELDRIDGE.

Lauric acid. R. BRILL and K. H. MEYER (Z. Krist., 1928, 67, 570—582; Chem. Zentr., 1928, ii, 2221).—The unit cell, in which a 9.76 and b 4.98 Å. are at a right angle; d 27.5 Å.; $\sin \beta$ 0.750, whence the c axis is 36.9 Å., contains four molecules, since $d=1.020$. The space-group is C_{2h}^2 . A spiral structure of the chain is not possible; the crystal contains bi-molecules with the like ends one against another. A. A. ELDRIDGE.

Long spacings of fatty acids. S. H. PIPER (Trans. Faraday Soc., 1929, 25, 348—351).—Although the method is of limited scope, an X-ray investigation of long-chain compounds can be made by measuring the spacings and intensities of reflexion from a set of widely-spaced planes which are characteristic of the length of the chain. Some equimolar mixtures of acids having odd and even numbers of carbon atoms give photographs similar to those from pure acids, and sometimes have the spacings of pure acids. These mixtures both in spacings and m. p. show alterations resembling those of the pure odd and even acids.

N. M. BLIGH.

Nature of dextrin, gelatin, and sodium oleate solutions as revealed by X-ray diffraction. P. KRISHNAMURTI (Indian J. Physics, 1929, 3, 307—329).—An extension of previous work (cf. this vol., 236) to colloidal solutions. Dextrin and gelatin gave patterns similar to those of the sugars, and in dilute solutions both gave rise to gaseous scattering from which the mol. wts. were calculated as approximately 600 and 3000, respectively. Sodium oleate showed a separate ring just below the water ring, of approximately the same size as for the powder, explained as due to large groups of molecules. The powder patterns of gelatin and starch also showed at very small angles a fairly intense ring not previously observed.

N. M. BLIGH.

X-Ray diffraction in liquid mixtures. P. KRISHNAMURTI (Indian J. Physics, 1929, 3, 331—355; cf. preceding abstract).—The pattern for a mixture was, in general, found not to be a superposition of those due to its components. For phenol, trimethylcarbinol, and piperidine the rings due to the two components exist separately in the mixture pattern; for glycerol, ethyl alcohol, and lactic acid only one ring is observed, the water ring having contracted and the liquid ring expanded. For pyridine solutions the pyridine ring has expanded slightly, the water ring being unchanged. Butyric acid solutions gave only one broad ring. The last two liquids thus form a transition between the previous two groups, the difference between which is

suggested as being due to the difference in the attractive forces between similar and dissimilar molecules in the mixtures. In the case of non-aqueous systems, a mixture of methyl salicylate and o-nitrobenzaldehyde gave a pattern almost the same as that for either liquid, results being similar for aniline and cyclohexane. In the case of cyclohexane and methyl salicylate a different pattern was given for the mixture. N. M. BLIGH.

X-Ray diffraction in liquids of the terpene series. V. I. VAIDYANATHAN (Indian J. Physics, 1929, 3, 371—389).—Using $\text{CuK}\alpha$ radiations, the haloes of 21 liquids were examined, and the results explained on the assumption that the X-ray diffraction peaks in liquids occur at wave-lengths corresponding with the mean molecular distances between them. In some cases a less distinct inner halo was observed. The molecular diameters obtained were, for the long-chain olefinic terpenes, geraniol, linalol, rhodinol, citral, and citronellal 4.95 Å.; for terpineol, 5.08 Å.; for menthone, carvone, and thujone, 5.35 Å.; for the cyclic $\text{C}_{10}\text{H}_{16}$ terpenes, terpinene, *d*-limonene, *d*(*l*)-limonene, *d*- α -phellandrene, sylvestrene, camphene, and *d*- and *l*-pinene, values increasing from 5.44 to 6.02 Å.; for the sesquiterpenes, cadinene, inene, caryophyllene, and cedrene, 7 Å., approximately. The last four showed an exterior diffuse halo. The values were in general found to increase gradually and to be approximately constant in each class. Densities were calculated. N. M. BLIGH.

Magnetostriction and the phenomena of the Curie point. R. H. FOWLER and P. KAPITZA (Proc. Roy. Soc., 1929, A, 124, 1—15).—Magnetostriction must be related to the change of length at the Curie point in exactly the same way as Weiss's thermomagnetic effects are related to the change of specific heat at the Curie point. From a revision of Heisenberg's calculation of the partition function for a magnetised crystal (A., 1928, 1300), and a theoretical examination of the size of the crystal as a function of the magnetisation, it is shown that the phenomena of the Curie point and magnetostriction will both fit satisfactorily into Heisenberg's theory. An explanation is suggested for the origin of these changes of sign. L. L. BIRCUMSHAW.

Role of conductivity electrons in ferromagnetism. J. DORFMAN and R. JAANUS (Z. Physik, 1929, 54, 277—288).—An investigation is made (cf. this vol., 127) of the position of the elementary magnet in the case of metallic nickel. It may be either the electron bound to the positive ion of the metal or the "free" conductivity electron. At the Curie point the jump of the specific heat of the conductivity electron is only slightly greater than the corresponding change, per atom, of the metal. Hence the electron bound to the positive metallic ion plays no important part in ferromagnetic processes, the seat of the elementary magnet being the conductivity electron.

G. E. WENTWORTH.

Role of conductivity electrons in ferromagnetism. J. DORFMAN and I. KIKOIN (Z. Physik, 1929, 54, 289—296; cf. preceding abstract).—The fact that the conductivity electron plays the part of the

elementary magnet in ferromagnetic processes has led to the possibility of calculation of the magnetic spin moment of the conductivity electron, which is found, within an accuracy of 5%, to be a Bohr magneton. G. E. WENTWORTH.

Hall effect in very intense magnetic fields. A. MAZZARI (Nuovo Cim., 1928, 5, 215—223; Chem. Zentr., 1928, ii, 2226—2227).

Paramagnetic susceptibility of quinquevalent vanadium ion. N. PERRAKIS (Amer. Electrochem. Soc., May, 1929. Advance copy, 5 pp.).—The paramagnetic susceptibilities of ammonium and sodium vanadates and of two forms of vanadium pentoxide are independent of temperature over the range 17—77°. To the molar susceptibilities of these compounds estimated corrections for the diamagnetism of the rest of the molecule are applied, and the mean value of 44×10^{-6} is obtained for the susceptibility of the quinquevalent vanadium ion. The difference between this value and data for metallic vanadium obtained by Honda and by Owen is discussed.

H. J. T. ELLINGHAM.

Magnetic moment of the complex ions of the iron group. P. WEISS (Amer. Electrochem. Soc., May, 1929. Advance copy, 4 pp.).—The magnetic moments of the simple ions of the iron group, with minor exceptions, depend only on the number of electrons in the ion, in accordance with Kossel's displacement law, but for complex ions containing these metals the magnetic moment is either equal to that of the normal ion of the same valency or to that of a normal ion the effective atomic number of which is greater by 4 units. The significance of this relation is discussed.

H. J. T. ELLINGHAM.

Two Curie points, ferromagnetic and paramagnetic. R. FORRER (Compt. rend., 1929, 188, 1242—1244).—A study of the thermal variation of an almost rectangular hysteresis cycle of nickel shows that the two Curie points determine two different coexistent regions, a hysteresis region extending to the paramagnetic Curie point, and a region of spontaneous orientation below the ferromagnetic point. The former point is always higher than the latter by about 15—40°. Ferromagnetism can exist only below both points, whilst paramagnetism is limited solely by the upper.

J. GRANT.

Magnetic properties of iron sesquioxide and some ferrites above their Curie point; conservation of the paramagnetism constant in these compounds. (MILLER.) A. SERRES (Compt. rend., 1929, 188, 1239—1241).—The mean value of 28.17×10^{-6} /g. (error 0.3%) was obtained for the susceptibility of iron at 700—750° from measurements on pure ferrous and ferric oxide, and the fact that this value falls between the extreme values obtained by other workers for γ -iron indicates that the paramagnetism of the latter is conserved in combination. The reciprocal of the susceptibility of magnesium, copper, lead, and nickel ferrites corrected for the paramagnetism of the sesquioxide ($\chi 1573 \times 10^{-6}$) is a linear function of temperature up to 750°, but slight changes in direction of the lines in all cases except that of lead confirm the hypothesis of the superposition of a

constant and variable paramagnetic constant (cf. Forestier and Chaudron, A., 1927, 11).

J. GRANT.

Ferromagnetic properties of ferrites. (MILLER.) S. VEIL (Compt. rend., 1929, 188, 1293—1294).—The author's experiments (this vol., 248) on the precipitation of a ferric salt by sodium hydroxide in the presence of a bivalent salt of the same anion have been extended to copper, and the same results obtained in the cold. If, however, the hydroxides were suspended in warm water they changed from para- to ferro-magnetic, although when iron was replaced by nickel or cobalt the differences between the relative coefficients of magnetisation of the calcined precipitates prepared in the cold and in the warm were far less marked.

J. GRANT.

Variation of the piezo-electric constant of quartz with temperature. A. ANDREY, V. FREEDERICKSZ, and I. KAZARNITSKY (Z. Physik, 1929, 54, 477—483).—The piezo-electric modulus, d_{11} , of quartz between 15° and 500° has been measured by the method of electrical oscillations. The modulus, d_{11} , depends only slightly on temperature, a result which is at variance with that obtained by the electrostatic method. Piezo-electric oscillations have been observed up to 575°.

W. E. DOWNEY.

Atomic theory of ferro-magnetism. N. AKULOV (Z. Physik, 1929, 54, 582—587).—Theoretical.

W. E. DOWNEY.

Electromagnetic theory of Maxwell-Lorentz and the molecular diffusion of light. J. CABANNES and Y. ROCARD (J. Phys. Radium, 1929, [vi], 10, 52—71).—Theoretical. A study of the undulatory and quantum theories of light with special reference to the Raman effect.

J. L. BUCHAN.

Magnetostriction in bismuth. E. VAN ATREL (Bull. Acad. roy. Belg., 1928, [v], 15, 148—149).—A claim for priority against Schulze (cf. A., 1928, 1314).

F. L. USHER.

Law of magnetisation of solid crystals. Resolution of the Faraday effect into two effects of different origin. Diamagnetic and paramagnetic rotation of the plane of polarisation. J. BECQUEREL and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 536—549).—Measurements have been made at very low temperatures (about 2° Abs.) of the variation of the magnetic rotatory power with intensity of the field. The law governing the relationship between rotation and field intensity, which below about 4.2° Abs. is no longer linear, is independent of the wave-length, and its significance for molecular physics is discussed.

H. F. GILBE.

Coercivity and mechanical hardness. A. KUSSMANN and B. SCHARNOW (Z. Physik, 1929, 54, 1—15).—Experiments are described to show that, in a number of alloys of the metals iron and nickel with aluminium, copper, and chromium, no simple relationship can be traced between coercivity and mechanical hardness.

R. W. LUNT.

Theory of the plasticity of metals. H. SHÖJI (Bull. Inst. Phys. Chem. Res., Japan, 1929, 8, 180—186).—In a previous paper the plasticity, P ,

of a metal was shown to be represented by $P - (1/w_0)(dv/dw)$, where dv/dw is the final velocity of elongation per unit length, caused by a load w_0 exceeding the elastic limit. It is now proposed that dv/dw and w_0 represent two different constants of plasticity, and the values of plasticity for a number of metals are recalculated using the previous data.

C. J. SMITHELLS.

Dehydration of benzene. J. J. MANLEY (Nature, 1929, 123, 907).—Determinations of the refractivity of benzene in the presence of phosphorus pentoxide during about 6 months were plotted against the time; the resulting curve consists of two distinct smooth portions having different directional values. It is concluded that the first limb represents the rate of removal of mechanically admixed water, whilst the second measures the rate of withdrawal of water in actual combination with benzene. It thus appears that benzene forms one or more hydrates, a view which is supported by the observation that the specific volume of benzene in the presence of phosphorus pentoxide depends on the temperature to which the benzene has been exposed immediately before the determination is carried out. Within certain limits of temperature the drying power of anhydrous benzene is greater than that of phosphorus pentoxide.

A. A. ELDRIDGE.

Physical properties of platinum. A. T. GRIGORIEV (Z. anorg. Chem., 1929, 178, 213—218).—See A., 1928, 941.

Determination of mol. wts. in the vapour state from vapour-pressure and evaporation data. E. W. WASHBURN (U.S. Bur. Stand. Res. Pap., 1929, No. 53).—The determination of the vapour pressure of a substance by measuring the amount required to saturate, by aspiration, a known volume of an indifferent gas, is chiefly open to error in the measurement of the gas volumes, quantities which have large temperature coefficients. By using a reference substance of known mol. wt. the measurement of these gas volumes is eliminated. The possible errors due to pressure, temperature, and saturation measurements are considered.

F. J. WILKINS.

Electrical conductance method for determining liquefaction temperatures of solids. E. W. WASHBURN and E. R. SMITH (Bur. Stand. J. Res., 1929, 2, 787—791).—When a solid or mixture of solids behaves as an electrical insulator below its m. p., but conducts as soon as the liquid phase appears, it will be easy to determine this temperature by noting where the change in conductance occurs. The method will be especially useful where only a small quantity of the substance is available, and will be trustworthy where other methods fail. The apparatus and method used are described. The eutectic temperatures of several substances were found. The transition temperature of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4$ was found to be 32.33° (usually accepted value, 32.384°), and of

$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$, 19.51° (usually accepted value, 19.525°).

A. J. MEE.

Temperature-conductivity curves of solid salts. II. Halides of potassium and thallium. T. E. PHIPPS and E. G. PARTRIDGE (J. Amer. Chem.

Soc., 1929, 51, 1331—1345).—The conductivities, κ , of solid potassium and thallium halides have been investigated. $\log \kappa$ is a linear function of $1/T$, although for the potassium salts the graph is two intersecting straight lines (cf. Phipps and others, A., 1926, 231). The graph for thallous iodide is also two straight lines, relatively slightly inclined, owing to a change of crystal form. In polar lattices only the positive ion conducts at lower temperatures; both ions conduct at high temperatures (cf. A., 1928, 1192). The "heats of liberation," H , of the ions are calculated from the graphs; they represent the minimum energy an ion must possess in order to be able to partake in the conduction process. H for the potassium ion exceeds that for the sodium ion in the same halide salt; the values for thallium are smaller than those for sodium except in the iodide. In the sodium and potassium halides, H appears to be proportional to the m. p. of the salts.

S. K. TWEEDY.

Table of electrochemical equivalents. G. A. ROUSH (Amer. Electrochem. Soc., May, 1929. Advance copy, 11 pp.).—Electrochemical equivalents of the elements calculated on the basis of the 1929 at. wts. and expressed in mg. per coulomb, g. per amp.-hr., lb. per amp.-hr., and the corresponding reciprocals, are tabulated. H. J. T. ELLINGHAM.

Experiments on the conductivity of ionic crystals. Effect of tempering, treatment with water, and plasticising. F. QUITTNER and A. SMEKAL (Z. physikal. Chem., 1929, B, 3, 162—165).—The results of experiments on the conductivity of ionic crystals are summarised and discussed. The dependence of conductivity phenomena on the loose structure of the crystal is shown. The effect of heating the crystals at 400° , and then cooling, is described; conductivity is increased by this treatment. By treating the crystals with water, there is still an effect on the conductivity even after they have been carefully dried. The inner structure of the crystal must therefore be altered by this treatment. Experiments on the plastic deformation of crystals were first carried out with natural sylvine. The resulting effect on the conductivity can be ascribed to changes in the structure of the crystal, a fact which can be verified independently by coloration experiments with the radiation from radium.

A. J. MEE.

Intensity gauge for supersonic radiation in liquids. W. T. RICHARDS (Proc. Nat. Acad. Sci., 1929, 15, 310—314).—High-frequency sound waves of high intensity have been applied to chemical phenomena (cf. Richards and Loomis, A., 1928, 141). The difficulties of absolute intensity measurements are discussed, and a gauge of the ear-trumpet type which is capable of giving reproducible values is described.

N. M. BLIGH.

Transmissibility of thin metal foils for long-wave infra-red radiation, and their electrical conductivity. H. MURMANN (Z. Physik, 1929, 54, 741—760).—A formula for the transmissibility of plane parallel metallic plates for long-wave infra-red radiation is derived from Maxwell's theory. According to this formula the transmissibility should

be independent of the wave-length and dependent only on the product of the thickness and electrical conductivity of the foil. Experiments were carried out to test this. The transmissibilities relative to a plain celluloid sheet in the spectral range $6.7\text{--}108\ \mu$ were determined. It is shown that in agreement with the theory the transmissibility is independent of wave-length. In order to test its dependence on thickness and electrical conductivity the resistances of the foils were determined. The transmissibility was found to be dependent on the product of thickness and electrical conductivity. For antimony and silver, two modifications with different conductivities were shown to exist.

A. J. MEE.

Results of the wave-mechanics calculation of the temperature relationship of the electrical resistance of pure metals. G. BORELIUS (Z. Physik, 1929, 54, 806—810).—By applying work on X-rays to the scattering of de Broglie waves, formulae for the effect of temperature on the resistance of pure metals have been derived by Houston (A., 1928, 695), Frenkel and Mirolubov (A., 1928, 933), and Bloch (this vol., 247). Without entering very far into the theory and underlying assumptions, a critical examination of these formulae is made. None agrees entirely with the experimental results. The best equation put forward to connect temperature with the resistance of pure metals was the empirical formula of Gruneisen (Physikal. Z., 1918, 19, 282). For low temperatures this gives the resistances proportional to T^4 , where T is the absolute temperature. Houston gives the resistance proportional to T^2 , and Frenkel and Mirolubov, and Bloch give it proportional to T^3 . Actually Gruneisen's formula deviates from the truth at lowest temperatures. A. J. MEE.

Optical characters of copper halides. M. HAASE (Z. Krist., 1928, 68, 82—86; Chem. Zentr., 1928, ii, 2329).—The refractive indices of cuprous chloride, bromide, and iodide between 535 and $700\ \mu$ have been measured, and the molecular volumes and molecular refractions for the D-line determined. Values increase regularly from chloride to iodide.

A. A. ELDRIDGE.

Optical properties of some salts of gluconic acid. G. L. KEENAN and S. M. WEISBERG (J. Physical Chem., 1929, 33, 791—794).—Optical data for the gluconates of ammonium, potassium, sodium, barium, and lead, and for the gluconic γ -lactone are recorded together with the interference figures and values of $2E$. The double refraction is strong, except in the case of the lead salt, which is only moderate.

L. S. THEOBALD.

B. p. of magnesium, calcium, strontium, barium, and lithium. H. HARTMANN and R. SCHNEIDER (Z. anorg. Chem., 1929, 180, 275—283; cf. Ruff and Hartmann, A., 1924, ii, 481).—The b. p. of the above metals have been determined at various pressures by direct measurement of the temperature of the condensing metallic vapour. From the temperature-pressure diagram the following values are obtained for the b. p. at 760 mm.: magnesium $1380 \pm 5^\circ$, calcium $1712 \pm 5^\circ$, strontium $1639 \pm 5^\circ$, barium $1810 \pm 10^\circ$, and lithium $1609 \pm 5^\circ$. From

these values the heat of evaporation, conventional chemical constant, Trouton's constant, and critical temperature are calculated. The irregular sequence of the b. p. in the alkaline earth-metal series corresponds with the irregular variations of the crystal structure of these metals. O. J. WALKER.

[Specific heats of] solid elements. W.

(Z. anorg. Chem., 1929, 180, 284—286).—The entropy at the ordinary temperature (S) and the specific heat (s) of solid elements satisfy the relationship $Ss = k$, where k is about 5. Since a similar relationship, $SL = k'$, holds for the heat of evaporation per g. (L), the expression $(L/s) = \text{constant}$ can be derived.

O. J. WALKER.

Thermochemical studies in the acetylene series. P. LANDRIEU and F. BAYLOCC (Bull. Soc. chim., 1929, [iv], 45, 217—225; cf. A., 1914, ii, 30).—The heats of combustion of *n*-amylacetylene and *n*-hexylacetylene have been determined by improved methods (A., 1923, ii, 535; 1925, 427) with the object of obtaining an accurate value for the heat of saturation of the acetylenic linking. The following constants are given: *n*-amylacetylene, b. p. $99\text{--}100^\circ/763\ \text{mm.}$, m. p. $-81\text{ to }-80^\circ$, $d_4^{20} 0.7505$, $n_D^{20} 1.4086$; *n*-hexylacetylene, b. p. $124\text{--}125^\circ/763\ \text{mm.}$, m. p. $-80\text{ to }-79^\circ$, $d_4^{20} 0.7667$, $d_4^{20} 0.7470$, $n_D^{20} 1.4172$. Although the pressure of oxygen in the bomb sometimes reached $45\ \text{kg./cm.}^2$, combustion was never complete, and a correction was applied for the residual carbon (less than 2 mg.). The molecular heats of combustion at constant volume (Q_v) and constant pressure (Q_p) are: *n*-amylacetylene, $Q_v 1092\ \text{kg.-cals.}$, $Q_p 1093.5\ \text{kg.-cals.}$; *n*-hexylacetylene, $Q_v 1243.5\ \text{kg.-cals.}$, $Q_p 1245.5\ \text{kg.-cals.}$ The heats of saturation, obtained by using the accepted data for *n*-heptane and *n*-octane, are respectively $58.8\ \text{kg.-cals.}$ and $58.7\ \text{kg.-cals.}$ F. L. USHER.

M. p. of palladium. C. O. FAIRCHILD, W. H. HOOVER, and M. F. PETERS (Bur. Stand. J. Res., 1929, 2, 931—962).—The m. p. of palladium has been determined by measuring with an optical pyrometer the ratio of brightness of the red light ($\lambda = 6258\ \text{\AA.}$) emitted by black bodies at the m. p. of palladium and gold, respectively. The crucible method was shown to be more trustworthy than the wire method. The result obtained by the crucible method, when substituted in Wien's or Planck's equation, gives the m. p. of palladium as 1556.6° with an uncertainty of 1° . In the computations C_2 was taken as $1.432\ \text{cm. deg.}$ and the m. p. of gold as 1063° . The average of this result and those of six previous determinations is $1553^\circ \pm 0.7^\circ$. The uncertainty in C_2 is estimated as 0.002 , and in the m. p. of gold as 0.5° ; it is concluded that the uncertainty in the value of the m. p. of palladium on the centigrade thermodynamic scale is approximately 2° . If 1063° is the m. p. of gold, the m. p. of palladium is 1553° .

W. E. DOWNEY.

Entropy of gases in irreversible processes. D. ENSKOG (Z. Physik, 1929, 54, 498—504).—Mathematical.

W. E. DOWNEY.

Coefficient of cubical expansion of liquids and critical temperature. V. N. THATTE (Phil. Mag.,

1929, [vii], 7, 887—891).—In the application of van der Waals' equation to the liquid state it is assumed that the term a/v^2 is large compared with the external pressure p , i.e., $a/v^2 \simeq RT/(v-b)$. It is also assumed that the ratio of the volume of the liquid occupied by the molecules to the total volume of the liquid is practically constant for liquids under the ordinary temperatures and pressures; hence, taking $1/R$ as proportional to the critical temperature T_c , the coefficient of cubical expansion of the liquid $C = 1/(kT_c - 2T)$. k has been found from the known values of C and T_c for a number of liquids to be 2.5. The equation is similar to that deduced by Davies (A., 1912, ii, 426) from Mathias's law and Guldberg's density calculations, but the results obtained from it are in closer agreement with the accepted values.

A. E. MITCHELL.

Vaporisation under the influence of an electric field. E. H. GREIBACH (Physical Rev., 1929, [ii], 33, 844—850).—The effect of a non-uniform electric field on the vaporisation of a solid is shown to consist in a minute increase in the heat of vaporisation and a decrease in the rate of evaporation. In the case of a metal filament, expressions are obtained for the density of the saturated vapour, the increase of heat of vaporisation, and the ratio of apparent to normal rate of evaporation. Comparison of the last result with experimental data is inconclusive.

N. M. BLIGH.

Heat of decomposition of azoimide. W. A. ROTH and F. MÜLLER (Ber., 1929, 62, [B], 1188—1194).—Attempts are described to deduce the heat of decomposition of homogeneous liquid azoimide by subtracting from the heats of combustion of phenyl azide and ethyl azidoacetate the "heat values" of the inset groups C_6H_5 and CH_3CO_2Et . The minimal value of 67 kg.-cal. is thus obtained, whereas 53 kg.-cal. is calculated from Berthelot's observations for dilute solution. Ethyl azidoacetate burns quantitatively and the heat of combustion is independent of the age (4511—4512 g.-cal./g.), whereas phenyl azide almost always yields a certain amount of soot and its heat of combustion diminishes with age so regularly that the value for the fresh material can be calculated by extrapolation. The heat of formation of phenyl azide is about 70 kg.-cal. more negative than that of benzene, whereas that of ethyl azidoacetate is about 77 kg.-cal. smaller than that of ethyl acetate.

The production of unusually large quantities of nitric acid during the combustion of azido- and diazo-compounds is discussed from the point of view of energy. A primary elimination of $2N_2$ from 2 mols. of azido-compound would liberate more than twice as much heat as is required for the fission of the quantity of nitrogen and oxygen into atoms from which the observed excess of nitric acid could be produced.

H. WREN.

Thermal expansion of tantalum. P. HIDNERT (Bur. Stand. J. Res., 1929, 2, 887—896).—Three samples of worked and annealed tantalum have been examined over the range -198° and $+500^\circ$. Worked tantalum was found to expand to practically the same degree as annealed tantalum. Between 20° and 500° the

expansion may be expressed by the equation $L_t = L_0[1 - (6.59t + 0.00008t^2)10^{-6}]$. The coefficient increases slightly with rise of temperature.

W. E. DOWNEY.

Heat capacity of hydrogen iodide from 15° Abs. to its b. p. and its heat of vaporisation. Entropy from spectroscopic data. W. F. GIAUQUE and R. WIEBE (J. Amer. Chem. Soc., 1929, 51, 1441—1449).—Experiments previously described (A., 1928, 228, 1083) are repeated with hydrogen iodide. As in the case of hydrogen bromide, two regions of high heat capacity occur in the solid state, apparently due to internal molecular transitions. The molal heat of fusion is 686.3 g.-cal. at the m. p. (222.31° Abs.) and that of evaporation, 4724 g.-cal. at the b. p. (237.75° Abs.). The "observed" molal entropy at the b. p. is 47.8 g.-cal./ 1° , in agreement with the value calculated from spectroscopic data.

S. K. TWEEDY.

Critical temperature measurements on carbon dioxide in small capillaries. H. T. KENNEDY (J. Amer. Chem. Soc., 1929, 51, 1360—1366).—The critical temperatures of carbon dioxide as measured in capillary tubes of varying diameter down to 0.004 mm. is 30.96° , independent of the size of the tube.

S. K. TWEEDY.

Time variation of thermodynamic processes. N. VON RASCHEVSKY (Z. Physik, 1929, 54, 736—737).—Thermodynamics deals with a system the processes of which do not vary with time. The progress of entropy and free energy near this equilibrium state is followed formally, by two differential equations.

A. B. D. CASSIE.

Thermodynamics of solutions. V. FISHER (Z. Physik, 1929, 54, 715—723).—A general equation satisfied by usual thermodynamical parameters specifying a solution is deduced from equality of the thermodynamic potential for the pure solute and for the solute in solution. Appropriate simplifying assumptions give, (i) the law of partial pressure for a gaseous mixture, (ii) van't Hoff's laws and other equations for dilute liquid solutions. (ii) is applied to solutions of sucrose and calcium ferrocyanide in water.

A. B. D. CASSIE.

Semi-empirical vapour-pressure formula. V. KIREJEV (Z. Elektrochem., 1929, 35, 217—220).—The author has derived the formula $(a(1.10 - \tau)/\tau)d\tau = (1 - \tau/\pi)d\pi$, in which $a = L_b/RT_b(1.10 - \tau_b)$ (T = absolute temperature, T_c = critical temperature, T_b = b. p., P = pressure, P_c = critical pressure, L_b = latent heat of vaporisation at T_b , and $\tau = T/T_c$ and $\pi = P/P_c$) connecting vapour pressures, greater than about 0.3 atm., over a range of temperatures up to $\tau = 0.85$. A method of evaluating the integration constant of the expression in its integrated form, together with tables of appropriate data, are given. The expression is based on: (i) the Clausius-Clapeyron equation, (ii) a vapour-pressure formula obtained by Nernst ("Theoretische Chemie," 8—10 ed., p. 313), and (iii) an empirical formula which the author has found to connect the change in the heat of vaporisation with that of temperature.

H. T. S. BRITTON.

Shrinkage of glass threads during heating. I. SAWAI and Y. UEDA (*Z. anorg. Chem.*, 1929, **180**, 287—303; cf. A., 1928, 1085).—Using a soda-lime glass, measurements have been made of the changes in length on heating of glass threads of various diameters between 0.031 and 0.316 mm. As in the case of lead borate glasses, a contraction was found to occur at two temperatures. The first shrinkage disappears, however, by a preliminary heating at 500°. The temperature at which shrinkage commences is greatly dependent on the diameter of the thread, the load placed on it, and the rate of heating. From the shrinkage measurements the surface tension and viscosity of the glass thread can be calculated. The theoretical significance of the shrinkage temperature is discussed. O. J. WALKER.

Determination of internal friction of metals, especially mercury. F. SAUERWALD and W. RADECKER (*Z. Physik*, 1929, **54**, 844—847).—A number of experimental results are cited on the basis of which it is concluded that the values for the internal friction of mercury previously obtained must be correct within experimental error. A slip of any large dimensions cannot occur at the walls of the vessel. The value of the Hagenbach correction is discussed. A. J. MEE.

Gaseous effusion at high temperatures. F. R. BICHOWSKY and C. W. WILSON (*Physical Rev.*, 1929, [ii], **33**, 851—859).—A method of investigating the effusion of gases through a small orifice is described, and applied to helium for the range of temperature 1000—2100° Abs., and of pressure 0.2—0.8 mm. The kinetics of the problem is discussed. The effusion was found to follow Knudsen's formula. Correcting for viscosity and slip effects, the pressure varies with the absolute temperature when the rate of flow is constant. The apparatus thus serves as a gas thermometer. Experiments with hydrogen at high temperatures were inconclusive owing to the presence of atomic hydrogen. N. M. BLIGH.

Azeotropism in binary systems containing an acid. M. LECAT (*Ann. Soc. Sci. Bruxelles*, 1929, **49**, B, ii, 28—47).—Azeotropic data already published for binary systems containing one acid component are grouped systematically and reviewed. The general conclusion is that the azeotropic lowering, δ , for a given difference Δ between the b. p. of the components, diminishes rapidly with increasing mol. wt. of the acid, the degree of molecular association varying inversely with the mol. wt. For formic acid mixtures, the azeotropic lowering satisfies the equation $\delta = 20 - 0.589\Delta + 0.0045\Delta^2 - 0.0000024\Delta^3$; for acetic acid, the equation becomes $\delta = 10 - 0.61\Delta + 0.0134\Delta^2 - 0.00011\Delta^3$. For propionic, butyric, and isovaleric acids one equation is approximately valid, viz., $\delta = 7 - 0.562\Delta + 0.0185\Delta^2 + 0.000233\Delta^3$. The curves for benzoic and phenylacetic acids lie between those for acetic and propionic acid; δ_0 (i.e., for $\Delta = 0$) is about 8.7. H. F. GILLBE.

Binary azeotropes. XIII. M. LECAT (*Ann. Soc. Sci. Bruxelles*, 1929, **49**, B, ii, 17—27; cf. this vol., 255).—A further list is given of 167 positive azeotropes, 21 eutectics, and 2 negative azeotropes,

together with 10 euzetropes having approximately rectilinear isobars, 29 with isobars convex to the concentration axis, 8 with concave isobars, and 14 other azeotropes. H. F. GILLBE.

Alloys of gold and platinum. A. T. GRIGORIEV (*Z. anorg. Chem.*, 1929, **178**, 97—107).—See A. 1928, 955.

X-Ray study of the internal transformation of silver-zinc alloys. A. ROUX and J. COURNOT (*Compt. rend.*, 1929, **188**, 1399—1401).—The X-ray spectrum (A., 1928, 851) of an annealed silver-zinc alloy (30.23% Zn) is formed by juxtaposition of the spectra of the constituents, whilst that of the tempered alloy has characteristics only of the principal constituent. Deformation may be due to precipitation of the minor constituent. The authors' micrographic observations and general theory of tempering and recovery (*loc. cit.*) are confirmed. J. GRANT.

Critical solution temperature phenomena in the ternary system phenol-thymol-water. (Miss) K. W. WILCOX and C. R. BAILEY (*J. Physical Chem.*, 1929, **33**, 705—708).—The ternary system phenol-thymol-water has been investigated at 15°, 65°, 200°, and 250°, and the ternary diagram is reproduced. At 250°, the curve obtained is a critical saturation curve typical of the addition of a third substance soluble in one only of the partly miscible liquids; at 120°, the curve is of the type characteristic of the addition of a substance soluble to a considerable extent in both liquids. Thus, at high temperatures phenol reduces the solubility of thymol in water, and at low temperatures increases it. At the ordinary temperature, a mixture of equal weights of water and thymol can be rendered homogeneous by the addition of nearly twice the weight of phenol. L. S. THEOBALD.

Solubility of silicon in hydrofluoric acid. C. BEDEL (*Compt. rend.*, 1929, **188**, 1255—1257).—Solutions of silicon (89—96%) containing silica, traces of iron and aluminium, zinc, lead, silver, or magnesium in hydrofluoric acid of concentration corresponding with $\text{HF}, 2\text{H}_2\text{O}$ were concentrated by evaporation. The rate of dissolution rises to a maximum (1.25%/hr.) when the concentration of acid is 14% and then decreases to a minimum (0.3%/hr.) for 40% acid, after which it again increases. It is independent of the size of the particles and is far greater for silicon crystallised from silver than for that obtained by other methods. J. GRANT.

Conditions of solubility of silicon in hydrofluoric acid. C. BEDEL (*Compt. rend.*, 1929, **188**, 1294—1296; cf. preceding abstract).—The solubility of silicon in hydrofluoric acid is increased in the presence of oxidising agents (including air) and is influenced by the *E.M.F.* between the silicon and metallic impurities. In 30% acid silicon is electro-negative to platinum, silver, and copper, and electro-positive to lead, iron, zinc, magnesium, and aluminium. J. GRANT.

Life history of adsorbed atoms and ions. J. A. BECKER (*Amer. Electrochem. Soc.*, May, 1929. Advance copy. 21 pp.).—The condition of adsorbed atoms and ions is discussed in the light of recent

experimental work (cf. A., 1926, 988; 1928, 1303). From the way in which the electron work function of a surface is altered by adsorbed particles it is possible to calculate the ratio of adsorbed ions to adsorbed atoms. The fields due to adsorbed ions can exert appreciable forces on other adsorbed ions or atoms at distances of 10 or more atomic diameters, so that the possibility of evaporation of an adsorbed particle is greatly affected by the presence of neighbouring particles. Within a certain range of temperature the adsorbed particles migrate over the surface as a two-dimensional gas and may move over distances of several thousand atom diameters before evaporating.

H. J. T. ELLINGHAM.

Sorption of gases by minerals. I. Heulandite and chabazite. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1929, 4, 96—103).—Heulandite dehydrated at 350° absorbs ammonia fairly rapidly at 25°, the total amount taken up being approximately equivalent to the water lost on dehydration; ethylene and carbon dioxide are not appreciably absorbed. Dehydrated chabazite takes up carbon dioxide and ammonia very rapidly, and ethylene rather slowly. R. CUTHILL.

Adsorption [in gases]. II. W. KALBERER and C. SCHUSTER (Z. physikal. Chem., 1929, A, 141, 270—296; cf. this vol., 132).—The heats of adsorption of various gases (argon, carbon dioxide, nitrogen, ethylene) by silicic acid gels have been measured directly and compared with those deduced from the adsorption isotherms, from which information can also be obtained regarding the magnitude and properties of the adsorbing surface. In particular the steep rise of the first part of the carbon dioxide isotherm points to inhomogeneity of the surface, i.e., to "active centres," and evidence is adduced in favour of condensation in fine capillaries. A close connexion is shown to exist between the heat of adsorption and the volume of the adsorbed layer, expressed as the product of the area of the adsorbing surface and the mean amplitude of vibration of the adsorbed molecules at right angles to the surface; this volume (Adsorptions-raum) increases as the heat of adsorption decreases. The surface structure of silicic acid gel is in an extremely labile condition unless it has been strongly heated, and its area is approximately 10^6 cm.² per g. From an examination of the isotherms it is shown that the differential heat of adsorption should increase with fall of temperature, and this has been confirmed experimentally for carbon dioxide at high pressures, where the surface is not so labile. The heat of adsorption increases with increasing surface density of the adsorbed molecules, and is largely dependent on the previous history (heating, progressive extraction of gas, etc.) of the adsorbent, particularly at low pressures.

F. L. USHER.

Adsorption of water, ethyl alcohol, ethyl acetate, and acetic acid vapours by tungstic and zirconium oxides; bearing on heterogeneous catalysis. J. N. PEARCE and M. J. RICE (J. Physical Chem., 1929, 33, 692—704).—A continuation of previous work (A., 1925, ii, 381) in which thorium and alumina were the adsorbents. Comparison with the present results, obtained at 99.4°, shows that for unit volume of adsorbent the adsorption of water vapour

decreases in the order thorium, aluminium, tungsten, and zirconium oxides, which is also the order of the dehydrating power of these oxides towards alcohol. With ethyl acetate the order is reversed. It is inferred that in catalysed esterification the vapours of alcohol and acetic acid must be adsorbed simultaneously and that the catalytic effect increases as the adsorbing power for water vapour decreases.

L. S. THEOBALD.

Adsorption from aqueous solutions by silica. F. E. BARTELL and Y. FU (J. Physical Chem., 1929, 33, 676—687).—The adsorption of various organic and inorganic acids, bases, and salts from aqueous solution by pure dehydrated silica, prepared from silicon tetrachloride by the method of Ebler and Fellner (A., 1911, ii, 723), has been investigated. Inorganic bases are preferentially adsorbed in the order lithium > sodium > potassium > ammonium hydroxides, the order being the same as that of the hydration of ions and being due probably to the hydrophilic nature of silica. The commoner inorganic acids are not adsorbed, but organic acids are slightly adsorbed in amounts which decrease as a homologous series is ascended, e.g., formic > acetic > propionic > butyric acids. The greatest adsorption is obtained with salicylic and benzoic acids. The adsorption from aqueous salt solutions is hydrolytic, the base being adsorbed in all cases, and with the sodium salts of organic acids adsorption increases as an homologous series is ascended. An equilibrium exists between the base adsorbed and the acid in solution, the extent of the former being controlled by the hydrogen-ion concentration of the solution. This probably accounts for the greater adsorption of salts of organic acids than of inorganic salts. Data for the adsorption of benzoic acid by silica from solutions in carbon tetrachloride and benzene support the conclusion of Patrick and Jones (A., 1925, ii, 193) that greater adsorption corresponds with lower solubility of the solute adsorbed in the solvent. The degree of adsorption is also influenced by solid-liquid interfacial tension relationships, greater adsorption being obtained with the solvent which has the lower adhesion tension with the adsorbent (cf. A., 1923, ii, 464).

L. S. THEOBALD.

Adsorption of electrolytes by crystal faces. (Mlle.) L. DE BROUCKERE (Bull. Acad. roy. Belg., 1928, [v], 15, 170—184; cf. A., 1928, 831).—Experiments on the adsorption of chlorides by crystalline barium sulphate have been extended to cadmium, mercuric, lead, and lanthanum chlorides and previous results have been confirmed. The same results are obtained from whichever side the equilibrium is approached and whatever the analytical methods employed, and they are quite reproducible. Anions and cations are adsorbed in equivalent amounts. Comparison of the adsorption isotherms shows that the valency of the cation is unimportant, but that at saturation the isotherms are in the order of decreasing at. wt. of the cation. The isotherms agree with Freundlich's formula at low concentrations only. No analogy between the coagulation of colloidal solutions by electrolytes and the adsorption of electrolytes by crystal surfaces is apparent. Calculations of the

quantity of electrolyte adsorbed per unit surface at saturation support the idea of a film of unimolecular thickness on the crystal.

F. L. USHER.

Adsorption phenomena of silver iodide. II. A. OBRUTSCHEVA (Biochem. Z., 1929, 207, 25—27; cf. A., 1927, 617).—Further experiments show that the position of the point of maximum adsorption depends, not only on the nature of the adsorbent and of the adsorbed substance, but also on the concentration of the solution of the latter. The theoretical treatment previously given requires to be modified in view of the greater complexity now found to exist in the process.

W. MCCARTNEY.

Electric charge of [solid] silver iodide in saturated solutions of silver iodide. E. LANGE and P. W. CRANE (Z. physikal. Chem., 1929, A, 141, 225—248).—It is shown on thermodynamical grounds that a preferential adsorption of iodide ions is to be expected when solid silver iodide is in contact with its saturated aqueous solution. Measurements of the electrokinetic potential of silver iodide have been made with a differential endosmometer in which, by using a *P.D.* varying from 600 to 8000 volts, separate determinations could be completed in 30 sec. When the precipitate was formed from solutions containing excess of silver ions the potential was at first always more positive than when iodine ions were in excess, but after 80 washings the difference was reduced to 1 millivolt, whence it is inferred that no difference would be found in a perfectly washed precipitate. The electrokinetic potential of the substance in its saturated solution is -0.004 ± 0.001 volt at 20°. Figures are given showing the variation of this potential with concentration of silver ion. The isoelectric point lies at a concentration of about $4 \times 10^{-6} N$ -silver nitrate, above which the potential becomes positive. Similar measurements with silver bromide in its saturated solution gave a value of -0.0015 volt. The negative potential of the solid against its own solution is considered to be due to adsorption of the halogen ion, the stronger adsorption of iodine compared with bromine ions being ascribed to its greater deformability. Peculiarities in the behaviour of silver iodide, such as the unequal stabilising power of silver and iodine ions, and the ready formation of complex anions, receive a simple explanation in the displacement of the isoelectric point to the silver side of the equivalence point.

F. L. USHER.

Significance of the adsorption of ions by colloid particles in coagulation by electrolytes. H. FREUNDLICH, K. JOACHIMSOHN, and G. ETTISCH (Z. physikal. Chem., 1929, A, 141, 249—269).—The connexion between ionic adsorption and coagulation is shown to be less simple than was assumed in Freundlich's original theory. According to this the coagulation values for different ions correspond with their adsorption measured in equivalents, and the observed discrepancies cannot be ascribed to experimental errors. A new series of experiments with definitely hydrophobic sols (arsenious sulphide, gold) is described, in which the coagulation values for ions of different valency have been redetermined. The amounts of different cations adsorbed at this point

have been determined by sensitive potentiometric and colorimetric methods and found to be not only not equivalent, but even of different orders of magnitude. It is considered that the space distribution of ions round a colloidal particle is very specific and that the thickness of the double layer varies considerably; e.g., with colloidal gold the area occupied by electrolyte in the case of powerful ions with a small coagulation value is less than the total surface area of the gold and there is no ground for assuming a double layer thicker than unimolecular, whereas in the case of univalent ions the area is much greater and the adsorption layer consequently thicker. It is suggested that the lowering of the electrokinetic potential to a critical value need not be effected by adsorption of equivalent amounts of the oppositely charged ion, but may depend on the distribution of cations and anions on the surface of the particles. The amounts of hydrogen ion displaced when different cations are adsorbed have been measured and found to be of the same order of magnitude for all. It is confirmed that the coagulation value for univalent ions rises with dilution of the sol. The quantities of different cations adsorbed at the coagulation concentration by arsenious sulphide, in milli-equivalents per g., are: Na⁺ 5.80, H⁺ 4.28, Ba⁺⁺ 0.21, Zn⁺⁺ 1.50, Ni⁺⁺ 1.22, In⁺⁺⁺ 0.56, Fe⁺⁺⁺ 0.37, Th⁺⁺⁺⁺ 0.27, "neufuchsin" 0.08, methylene-blue 0.13.

F. L. USHER.

Capillarity. XI. Diffusion and concentration alterations in capillaries. K. SCHULTZE (Kolloid. Z., 1929, 48, 15—25).—The difficulties and sources of error in the measurement of the rise of salt solutions in capillaries of different dimensions are discussed.

E. S. HEDGES.

Drop-weight method for the measurement of surface tension. A. FERGUSON (J. Sci. Instr., 1929, 6, 163—167).—A discussion of the equation $mg = 2\pi r\gamma$ used by Quincke in the absolute determination of surface tension by the drop-weight method. Edwards' work (B., 1929, 400) is criticised.

C. W. GIBBY.

Measurement of the interfacial tension of oils. J. C. EDWARDS (J. Sci. Instr., 1929, 6, 167—168).—A reply to Ferguson (cf. preceding abstract).

C. W. GIBBY.

Change in the surface tension of some solutions of univalent chlorides with time. E. O. SEITZ (Ann. Physik, 1929, [v], 1, 1099—1108).—Kleimann's technique (A., 1926, 900) has been applied to potassium, lithium, and hydrogen chlorides. The alkali chlorides show with increasing concentration a linear increase in the static surface tension at constant temperature, whilst the acid exhibits a linear decrease in the surface tension α . In both cases the change of α with the temperature is -0.015 per degree. The effect of time is given by the relation $\delta\alpha = \Delta\alpha \cdot e^{-at}$, $\delta\alpha$ being the excess over the static value at any time, $\Delta\alpha$ that at $t=0$, and $1/a$ being the time occupied for $\delta\alpha$ to fall to the e^{th} part. Taking $1/a$ as τ , it is found that τ_0/τ (τ_0 being the value for pure water) shows a variation with concentration which is almost exactly in agreement with the variation of the Kohlrausch degree of dissociation Λ/Λ_∞ . This applies to the alkali salts at constant temperature, but not to hydrogen chloride in which τ and τ_0 are not very

different. As the temperature rises, the concentration being constant τ decreases linearly. The temperature coefficient of $-d\tau/\tau$ varies from 0.017 (hydrogen chloride) to 0.027 (lithium chloride).

R. A. MORTON.

Kinetic phenomena at metallic surfaces. G. VON HEVESY and M. BILTZ (*Z. physikal. Chem.*, 1929, **B**, 3, 271—281).—If a metal is dipped into a solution containing ions of the metal there is a transfer between the ions in the solution and the atoms of the metal. The transfer effect can be followed by a radioactive method. The kinetics of the change are investigated, the metals being both in the massive and the colloidal form. In the first instance the transfer between massive lead and lead ions was investigated, in one case active lead foil and inactive lead ions being used, and in the second inactive lead foil and active ions. The transfer is practically the same for both methods. The transfer between colloidal lead and lead ions was then determined. With lead sols there is no reversibility. In this case there is a considerable adsorption of lead ions on the colloidal particles. The velocity of transfer between adsorbed ions and ions in the solution is very small. The transfer between massive copper and silver ions is considered, together with the reverse case. The velocity of the change is greater and the effect of adsorption is less marked. A large proportion of the copper goes into solution as the univalent ion.

A. J. MEE.

Determination of the thickness of a film of oleic acid in the saturation state on water and of the saturation pressure of this film. F. EMIR (*Compt. rend.*, 1929, 188, 1284—1286).—The solubility of a film of oleic acid is greater on water than on 0.05*N*-hydrochloric acid and increases with the superficial density and with rise of temperature. The saturated film on water or acid has a thickness of 23 Å., a value in close agreement with that found by X-ray spectrography and which is independent of temperature (15—30°). The saturation pressure, which is 30.9 dynes/cm.² at 15° and increases with rise of temperature (cf. Marcelin, A., 1926, 120), seems to vary with the origin of the acid.

J. GRANT.

Molecular sieve membranes. L. MICHAELIS (5th Coll. Symp. Mon., 1928, 135—148).—A strong molecular sieve filter is obtained by allowing a solution of collodion to evaporate on a mercury surface. A method for determining the "fineness" of such a sieve is described, and relative values for various materials are recorded. The diameter of the pores is probably of the order of magnitude of single molecules. Relative velocities of diffusion through membranes separating water from 0.1*M*-solutions are: methyl alcohol 9.2, ethyl alcohol 3.0, propyl alcohol 1.0, carbamide 1.0, butyl alcohol 0.8, glycerol 0.22, chloral hydrate 0.11, monochlorohydrin 0.067, dextrose 0. NH_3 diffuses much more rapidly than NH_4 . The diffusion of electrolytes is extremely slow. With potassium chloride against sodium nitrate, diffusion of cations appears to proceed by "exchange," the anions diffusing but slightly, if at all. The valency of the anions has little influence.

CHEMICAL ABSTRACTS.

Osmosis of ternary liquids. General considerations. IX. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 254—263).—Theoretical. A continuation of the discussion (this vol., 392) of the influence of the composition of the liquids and the nature of the membrane on the direction of diffusion.

F. J. WILKINS.

Osmotic vapour-pressure. I. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 264—271).—Theoretical. A consideration of the relation between water vapour pressure and osmotic water vapour pressure and the influence of the latter on membrane diffusion.

F. J. WILKINS.

Effect of electrolytes on electro-endosmosis through wood membranes. A. J. STAMM (5th Coll. Symp. Mon., 1928, 361—368).—Dilute alkali solutions increase, and dilute acid solutions decrease, the rate of electro-endosmosis through wood membranes. Concentrated acids and bases permanently reduce the rate. Aqueous salt solutions show the normal effect of salts with anions and cations of different valency on negatively-charged membranes. Tervalent and quadrivalent cations cause a reversal of the direction of flow and of the sign of the contact potential. Multivalent anions increase the rate of flow and the negative contact potential.

CHEMICAL ABSTRACTS.

Preparation of collodion membranes. J. BÖSEKEN and O. MEYER (*Rec. trav. chim.*, 1929, **48**, 504—507).—Membranes which are capable of effecting the osmotic separation of dextrans from sugars may be prepared by precipitating copper ferrocyanide in a collodion membrane.

H. F. GILLBE.

Influence of solvent on rotatory dispersion. A. L. T. MOESVELD (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 344—355).—The rotatory dispersion of bornyl acetate in the liquid state, or when dissolved in various solvents, can be expressed by a one-term Drude equation. The values of the constant k of this equation have been determined for a set of six solvents and their binary combinations. The variations in its value are interpreted in terms of a deformation of solute molecules.

F. J. WILKINS.

Cryoscopic determinations of the molecular equilibria of resorcinol in aqueous solutions of sodium chloride. F. BOURION and C. TUTTLE (*Compt. rend.*, 1929, **188**, 1496—1498).—Solutions of resorcinol in 0.5*M*- or 1.225*M*-sodium chloride solutions show evidence of equilibria between simple and double or triple molecules for concentrations of resorcinol up to 0.625 and above 0.875, respectively. The cryoscopic constant, which is higher than for potassium chloride or aqueous solutions (this vol., 648), increases with the concentration of sodium chloride. Apparent contradictions to the author's thermodynamic treatment of such solutions (*loc. cit.*) are due to adsorption of water by the ions or molecules of the dissolved salt.

J. GRANT.

Change of volume on neutralisation. J. J. SASLAVSKY, E. G. STANDEL, and V. V. TOVAROV (*Z. anorg. Chem.*, 1929, **180**, 241—251).—The change of

volume on mixing solutions of acids and bases of various concentrations in different proportions has been measured for the following systems: potassium hydroxide-acetic acid, sodium hydroxide-acetic acid, -nitric acid, -sulphuric acid, ammonia-nitric acid. In most cases there is an increase in volume on neutralisation, the maximum change in volume corresponding with the neutral salt formation. With ammonia solutions there is a contraction in volume on neutralisation. Curves are given in which the percentage of alkali in the solution is plotted against the volume of the solution after mixing. In the case of the alkali-monobasic acid systems these curves show a sharp maximum at the point corresponding with complete neutralisation, and the two branches of the curve are symmetrical with respect to this point. The curvature of these two branches increases with the concentration of the solutions which are mixed. On mixing very concentrated solutions of alkali and acetic acid there is actually an initial contraction in volume. In the case of sulphuric acid the hydrogen sulphate stage of neutralisation is clearly shown on the curve.

O. J. WALKER.

Electrostriction by dissolved dipole molecules. G. JUNG (Z. physikal. Chem., 1929, B, 3, 204—208).—Mathematical. The electrostriction effect in solutions, due to dissolved particles which are electrically neutral dipoles is of the same order of magnitude as that due to ions.

O. J. WALKER.

Dispersoidal synthesis of gold by means of alkaline formaldehyde solutions. P. P. VON WEIMARN (Japan. J. Chem., 1929, 3, 165—215).—The paper summarises the results of many years' work on the production of gold sols, the experimental details of which have been published elsewhere. The influence of purity of the reagents in the preparation of red gold sols by reduction with formaldehyde is discussed: the only effect of increasing purity is to increase the concentration to which the red sols can be evaporated before they become blue. In several respects, the author's views are opposed to those of Zsigmondy. It is concluded that a large proportion of the work on dispersoidal gold synthesis should be repeated, not only quantitatively but qualitatively, that it is not possible to accept "coagulation values" obtained up to the present time, and that the identification of the synthesis of colloidal gold with spontaneous crystallisation is erroneous.

E. S. HEDGES.

Preparation of colloidal bismuth and arsenic soluble in water. A. F. GERASIMOV (J. Russ. Phys. Chem. Soc., 1929, 61, 269—274).—Colloidal bismuth and arsenic soluble in water were prepared from bismuth oxychloride and arsenic trichloride, respectively, by means of an acetic acid solution of "Paal's liquid" (A., 1902, i, 653, ii, 500). The colloids were purified by centrifuging, brought into solution by means of a 20% solution of sodium hydroxide, and evaporated to dryness on a water-bath. Both are powders, the bismuth colloid containing 17.9% of metal, the arsenic colloid 23—27% of metal. Both are negatively charged.

A. FREIMAN.

Tartaric acid method for synthesis of electro-negative sols. III. Adsorption of sodium

tartrate and succinate by aluminium hydroxide. A. DUMANSKI and A. JAKOVLEV (J. Russ. Phys. Chem. Soc., 1929, 61, 151—157, and Kolloid-Z., 1929, 48, 151—145).—See A., 1928, 1321.

Tartaric acid method for the synthesis of electronegative sols. V. Sulphide sols. A. DUMANSKI and A. BUNTIN (J. Russ. Phys. Chem. Soc., 1929, 61, 279—314).—Sols of lead, tin, ferric, and nickel sulphides have been prepared by the tartaric acid method, either from solutions of tartrates of the corresponding metals and hydrogen sulphide or from solutions of salts in tartaric acid and hydrogen sulphide. The conditions governing the formation of the sulphide sols, e.g., concentrations of starting materials etc., were also investigated. In the case of lead and tin sulphides the stability, density, relative viscosity, cataphoretic velocity, and behaviour towards alkalis, acids, and salts were also determined. It was found that there is no adsorption, peptisation, or chemical reaction between sodium tartrate and the sulphides.

A. FREIMAN.

Tartaric acid method of preparing negatively-charged sols. V. Physico-chemical properties of tartaric acid tungsten colloids. A. DUMANSKI and S. I. DIJATSKOVSKI (Kolloid-Z., 1929, 48, 49—57).—Measurements of the density, viscosity, angle of rotation, and conductivity of solutions prepared by mixing equivalent solutions of sodium tungstate and tartaric acid are recorded. An examination has been made of systems containing different ratios of tartaric acid to tungstate: colloidal solutions are readily obtained and some of the products have been analysed. The colloid solutions examined gelatinise and exhibit thixotropy. The gels also exhibit photochemical sensitivity. The complexes are hydrolysed by dilution.

E. S. HEDGES.

Desiccation of colloidal solutions of alumina and chromium oxide. P. BARY and J. V. RUBIO (Anal. Fis. Quím., 1929, 27, 273—284).—A more detailed account of work already published (this vol., 392).

Coalescence of an unfilterable precipitate of barium sulphate. H. M. TRIMBLE (Proc. Oklahoma Acad. Sci., Univ. Ok. Bull., 1928, [ii], No. 409, Studies Ser., No. 29, 197).—Large particles do not grow at the expense of smaller ones; aggregation of particles is followed by cementation.

CHEMICAL ABSTRACTS.

Changes in physico-chemical properties in the region between colloid and molecular disperse solutions. I. W. OSTWALD and A. QUAST (Kolloid-Z., 1929, 48, 83—95).—Measurements have been made of the diffusion coefficients of a number of dyes (night-blue, crystal-violet, new-fuchsin, brilliant-green, Congo-red, benzopurpurin, nerol, and sulphonecyanin) in mixtures of water and alcohol of varying composition, and from the results the relative sizes of particles of the dyes have been calculated by Einstein's equation. In all cases, the maximum degree of dispersion is obtained when mixtures of medium composition (40—60% of alcohol) are used as solvent. The radius of the particles may vary with the composition of the solvent mixture to the extent of 1:100.

E. S. HEDGES.

Influence of electrolytes on the viscosity of colloids. N. R. DHAR and S. GHOSH (*Kolloid-Z.*, 1929, 48, 43—49).—Measurements on more than 30 sols show that the viscosity of the sols is reduced by the addition of small quantities of electrolytes, and it is held that such a decrease in viscosity occurs whenever ions with the same charge as the sol are preferentially adsorbed. Conversely, viscosity rises with the purity of the sol and it is shown experimentally that sols of chromium hydroxide and of zirconium hydroxide are more viscous with increasing purity: the viscosity of a zirconium hydroxide sol was reduced to one half by addition of a 1% solution of zirconium oxychloride. The experiments support the authors' contention that the viscosity is the smaller the higher is the charge and that the uncharged material is more strongly hydrated than the charged sol. The conclusion is reached that the stability of a hydrophilic or hydrophobic sol is not connected with its degree of hydration. E. S. HEDGES.

Lyophilic colloids. II. Casein sol. H. R. KRUYT and H. LIER (*Koll.-Chem. Beih.*, 1929, 28, 407—450; cf. this vol., 136).—Measurements of the viscosity of solutions of purified casein in acids and in alkalis have been carried out and Poiseuille's law was found to be valid for all the solutions used. Measurements of relative viscosity were made with sols of casein of different concentration in presence of varying concentrations of bases, the hydrogen-ion concentrations of the sols being measured also. A viscosity maximum was observed at p_H 11.5, in agreement with the view that casein does not form a true solution, but contains polymolecular particles, of which only the surface molecules react. At a constant hydrogen-ion concentration, the increase in relative viscosity is parallel to the colloid concentration. In acid solution, sols of casein have a viscosity maximum at p_H 2.6. The acid sol is less stable than the basic sol. The addition of neutral electrolytes causes a decrease in viscosity, the valency of the cation being important in the alkaline sols and that of the anion being important in the acid sols. Observations on the flocculation of both the acid and basic sols show that these behave like typical suspension colloids. The alkaline sols are dehydrated in the usual way by alcohol and acetone, but the acid sols are not dehydrated under these conditions. The isoelectric point of casein lies between p_H 3.5 and 6.5. Only electrolytes of the type of sodium hydroxide and hydrochloric acid are able to peptise casein powder. E. S. HEDGES.

Osmometer for the measurement of the osmotic pressure of colloids. A. GRIGAUT and BOUTROUX (*J. Chim. phys.*, 1929, 26, 224—228).—An apparatus is described by which osmotic pressures of hydrosols may be measured accurately up to a pressure equal to 60 cm. of water. Two hemispherical cells are separated by a semi-permeable diaphragm, and from the glass walls of the cells two horizontal glass capillary tubes protrude perpendicularly to the diaphragm. A tap is inserted in one of these tubes. The hydrosol is placed in the cell which can be closed by the tap, whilst the cell on the opposite side of the diaphragm contains the ultra-filtrate of the sol.

Diffusion of the ultra-filtrate is allowed to occur through the diaphragm for some hours into the hydrosol while the tap in the capillary tube is kept closed; on opening the tap the diaphragm regains its initial condition and the water which has passed through it causes a displacement of the meniscus in the capillary tube. The pressure can be calculated from the increase in volume, or it may be measured directly on opening the tap by means of a pressure gauge connected to the end of the capillary tube.

H. T. S. BRITTON.

General colloid chemistry. XXIV. Colloid salt conductivity and colloid ion mobility. E. VALKÓ and N. WEINGARTEN (*Kolloid-Z.*, 1929, 48, 1—10).—The application of Hittorf's method of measuring ionic mobility to the study of colloid systems is discussed. Measurements have been made of the decrease in mobility of the colloid ions of an aluminium hydroxide sol when the chlorine ion is replaced by the sulphate ion, and a comparison with the decrease in conductivity is given. The colloid ions present in an aluminium hydroxide sol have a greater mobility when the sol is diluted. Reproducible sols, which can be characterised by electrochemical methods, have been prepared by incomplete precipitation of a solution of aluminium chloride by silver oxide. E. S. HEDGES.

Macroscopic method of determining the cataphoretic velocity of colloidal particles. A. E. ALEEV and A. F. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 275—277).—One of the conditions limiting the applicability of the macroscopic method (Gerasimov, A., 1927, 726) of determining the cataphoretic velocity of colloidal particles has been investigated. A. FREIMAN.

Kinetics of coagulation of colloids of the second order. K. JABŁCZYŃSKI and H. JASZCZOŁTOWNA (*Bull. Soc. chim.*, 1929, [iv], 45, 202—206).—See this vol., 506.

Influence of stirring on the rate of coagulation of colloids. K. JABŁCZYŃSKI and (MŁŁE.) G. SZAMES (*Bull. Soc. chim.*, 1929, [iv], 45, 206—210; cf. A., 1925, ii, 35).—The rate of coagulation of ferric oxide hydrosols by potassium chloride at the ordinary temperature has been followed spectrophotometrically at different rates of stirring. Both dialysed and undialysed sols were studied, and were aged for 6 months before use. Immediately after mixing with the electrolyte stirring increases the normal rate of coagulation, but afterwards diminishes it, the latter effect being more marked as the rate of stirring is increased. Diluting the sol tends to neutralise the effects of the stirring; whilst in the case of the undialysed sol, in which the ratio Fe:Cl was 1:0.22, the initial stage of acceleration was not observed, probably on account of its short duration. It is considered that this initial acceleration is due to the increased frequency of collisions between the primary particles, and the subsequent retardation to mechanical disruption of the larger aggregates produced during the first stage. The usual mathematical expression for the rate of coagulation cannot be applied when the liquid is stirred. F. L. USHER.

Mechanical coagulation of goethite sol. H. FREUNDLICH and S. LOEBMANN (Koll.-Chem. Beih., 1929, 28, 391—406).—The observation by Freundlich and Kroch (A., 1927, 18) that sols of goethite (prepared from iron carbonyl and hydrogen peroxide) are coagulated by mechanical agitation has been developed into a quantitative investigation, and the results have been compared with the similar mechanical coagulation of cupric oxide sols. With both sols the coagulation velocity is independent of the number of particles in the sol and of the volume of liquid stirred, whilst a quadratic relation exists between coagulation velocity and rate of stirring. Only a definite number of particles are coagulated by stirring a goethite sol, the rest remaining unaltered in the sol. A number of attempts at explanation of mechanical coagulation are shown to be improbable and the most likely explanation is that coagulation takes place at the surface of the solution, where a certain orderly arrangement of particles may exist: mechanical agitation effects a constant change of surface. The surface concerned need not be the sol-air interface, and experiments have shown that the effect is produced at any surface provided by a medium of low dielectric constant, whether it be a gas (e.g., air), a liquid (e.g., benzene), or a solid (e.g., powdered quartz). The effect of alcohols on the mechanical coagulation of goethite has also been examined. Propyl alcohol at low concentrations aids the coagulation, but has the reverse effect at higher concentrations: isoamyl alcohol favours coagulation at all concentrations, and methyl alcohol tends to prevent coagulation at all concentrations. The influence of electrolytes at small concentrations under the threshold value for coagulation is diminished and the amount of sol remaining uncoagulated is increased. Anions of high valency are particularly active in this respect.

E. S. HEDGES.

Flocculation of arsenious sulphide sols by thorium chloride. A. BOUTARIC and C. SEMELET (J. Chim. phys., 1929, 26, 195—204).—The following experiments are described: (1) Equal volumes of an arsenious sulphide sol were each mixed with water and solutions of thorium chloride of varying concentrations, such that the final volumes of the mixtures were the same and their thorium chloride contents equal. The mixtures which had been prepared from the more concentrated thorium chloride solutions flocculated in less time than did those in which more dilute solutions had been used. (2) Arsenious sulphide sols of the same concentration were mixed with equal volumes of thorium chloride solutions of varying concentration and the times taken by the mixtures to flocculate were observed. By plotting the logarithms of the concentrations of the thorium chloride solutions against the reciprocals of the times required, it was found possible to ascertain the concentration of thorium chloride below which coagulation could not be effected. (3) Equal volumes of thorium chloride solutions of the same concentration and of arsenious sulphide sols of varying concentrations were mixed and allowed to flocculate. The data show that the times required increases with the concentration of the colloid. (4) Sols having particles of different size

(an orange-coloured sol containing fine grains is obtained by passing a rapid flow of hydrogen sulphide through an arsenious acid solution, whereas a yellow, coarse-grained sol is produced with a slow supply) were investigated as in (2) and show that a smaller minimum concentration of thorium chloride is required for the flocculation of the coarse-grained sol as compared with the fine-grained sol. By employing the same concentration of thorium chloride less time was required to flocculate the former. (5) The time taken by a sol to flocculate under the influence of a given concentration of thorium chloride increases rapidly with rise of temperature. (6) Arsenious acid in the sulphide sol exerts a protecting influence against thorium chloride. (7) An excess of hydrogen sulphide in the sols reduces their stability towards thorium chloride. (8) Methyl alcohol, ethyl alcohol, and acetone each exercises a protective action on the sols against thorium chloride, whilst sucrose appears to be without effect.

H. T. S. BRITTON.

Effect of multivalent cations on some colloidal-chemical properties of kaolin. I. I. SHUKOV and M. N. SOKOLOVA (Kolloid-Z., 1929, 48, 71—78).—An investigation has been made of the relation between the stability of kaolin suspensions and electrolyte adsorption and capillary electric phenomena. Two kinds of kaolin (Gluchov and Gluchovetz) were employed and the electrolytes used were ferric chloride and thorium nitrate. In all cases the adsorption follows an anomalous course: the adsorption curve of thorium nitrate on Gluchov kaolin reaches a maximum and then continues as a straight line, but in the other cases the adsorption curve falls subsequently. These anomalies are believed to be due to the change in the degree of hydrolysis of the salt at different concentrations. The adsorption of both electrolytes is stronger by Gluchov than by Gluchovetz kaolin, in accordance with the higher negative charge and greater stability of the former. The sign of the charge is reversed with excess of the electrolytes, Gluchov kaolin requiring the higher concentration, and the concentration required is the same for both electrolytes when expressed in terms of normality. Gradual addition of ferric chloride to a Gluchovetz kaolin suspension causes a decrease in stability until the isoelectric point is reached, after which the reversed sol is stabilised. With Gluchov kaolin a second zone of decreasing stability is realised. Measurements of filtration velocity of suspensions of both kinds of kaolin show that the velocity is greater the smaller the stability.

E. S. HEDGES.

Peptisation of dyes by neutral salts. W. OSTWALD (Ber., 1929, 62, [B], 1194—1196).—The blue-black precipitate of the free dye acid of Congo-red is insoluble in water but dissolves to red solutions in about 0.5*N*-potassium chloride or magnesium chloride. The effect is even more marked when the blue sol is used which forms red or yellowish-red solutions with neutral chlorides, iodides, bromides, chlorates, nitrates, sulphates, etc. of uni- and multi-valent cations in concentration less than *N*. Ammonium chloride, nitrate, and sulphate do not exhibit this behaviour. In more concentrated salt solutions precipitation occurs.

H. WREN.

Relations between electrokinetic migration velocity, peptisation, and stability of coarsely disperse systems. A. VON BUZÁGH (Kolloid-Z., 1929, 48, 33—43).—Measurements of cataphoretic migration velocity have been carried out with suspensions of animal charcoal in picric acid solutions and with suspensions of kaolin and of bentonite in solutions of sodium hydroxide, using different concentrations of the electrolyte as peptiser and varying amounts of the solid phase. In each case, the migration velocity for a constant amount of solid phase rises at first with increasing concentration of the electrolyte, reaches a maximum, and then falls. A similar curve with a single maximum is obtained when a constant concentration of peptising agent is used and the migration velocity is plotted against the amount of solid phase. The similarity in the two curves is to be expected on the assumption that a definite electrical charge on the particles is necessary for peptisation and that this charge is related to a definite adsorbed amount of the peptising agent, for with small amounts of solid phase the relative amount of adsorbed electrolyte is too high, whilst with large amounts of solid phase there is insufficient electrolyte to stabilise the particles. The maximal value of migration velocity is practically the same, in agreement with the theory, whether obtained by varying the amount of the peptising agent or of the solid phase. A maximum is also observed in the curve connecting the degree of peptisation (*i.e.*, the ratio of peptised material to the total solid phase) with the amount of solid phase, the maximum corresponding with the maximum of electrical charge. In pure water, the migration velocity is independent of the amount of solid phase, and the degree of peptisation is constant for small amounts of solid phase, but later falls with increasing amounts of solid phase.

E. S. HEDGES.

Kinetic studies in the system colloidal ferric hydroxide-hydrochloric acid-water. E. HEYMANN (Kolloid-Z., 1929, 48, 25—33).—The ageing of solutions of ferric chloride has been followed by making conductivity determinations. The ageing is due to the slow condensation of the primary particles of hydrolysis product to form particles of ferric hydroxide of colloidal dimensions, and it was found that direct addition of ferric hydroxide to the system accelerates considerably the ageing process. Aluminium hydroxide does not exert this effect. The formation of the colloidal particles from the primary hydrolysis product is an autocatalytic process. The dissolution of the particles of ferric hydroxide by hydrochloric acid does not follow a unimolecular course and it is suggested that the reaction does not occur on the surface of the particles only. The ageing of solutions of sodium aluminate also is accelerated by the addition of aluminium hydroxide.

E. S. HEDGES.

Thixotropy of dispersions of small concentration. I. E. A. HAUSER (Kolloid-Z., 1929, 48, 51—62).—The influence of the dimensions of the containing vessel, the volume, and the concentration on thixotropy of natural bentonite suspensions is discussed. The destruction of the thixotropic properties of bentonite by dialysis and the possibility of

the thixotropy reappearing after addition of electrolytes are also discussed. An ultramicroscopic investigation of dialysed bentonite suspensions of low concentrations has shown that through the addition of increasing quantities of electrolytes, first the translation and then the rotation component of the Brownian movement is stopped. Further addition of electrolyte causes aggregation of the particles and finally flocculation.

E. S. HEDGES.

Syneresis. S. LIEPATOV (Kolloid-Z., 1929, 48, 62—63).—Polemical. Kuhn (this vol., 137) has misunderstood the author's results, some of the misunderstanding being due to misprints, which are now rectified.

E. S. HEDGES.

Syneresis. A. KUHN (Kolloid-Z., 1929, 48, 63).—A reply to Liepatov (preceding).

E. S. HEDGES.

Mol. wt. of cellulose. K. HESS (Rec. trav. chim., 1929, 48, 489—491).—The applicability of the mass action law to the cuprammonium-cellulose system expresses the kinetic individuality of the $C_6H_{10}O_5$ group, in contradiction to MacGillavry's assumption (this vol., 262).

H. F. GILLBE.

Mol. wt. of cellulose. D. MACGILLAVRY (Rec. trav. chim., 1929, 48, 492—493).—The optical behaviour of cellulose in cuprammonium solutions is explicable on the assumption of equivalent glucose residues, without having regard to the molecular size. Conversely, the latter cannot be determined from the optical behaviour.

H. F. GILLBE.

Orientation and pseudo-crystallisation phenomena resulting from the action of stretching in colloidal gels. J. J. TRILLAT (Compt. rend., 1929, 188, 1246—1248).—The X-ray examination of stretched films of cellulose, cellulose nitrate, and cellulose acetate affords evidence of molecular anisotropy as the stretching increases, the mean degree of molecular oscillation about the direction of stretch decreasing with increasing strain. Under high strains the diagrams are analogous to those of the corresponding crystalline substance, and it would seem that passage from the gel state occurs in stages, the final condition being that of pseudo-crystallisation in which the molecules occupy the same positions as in the crystal lattice but are not in perfect alignment. Modification of chemical properties may result as a consequence of change in orientation of active groups.

J. GRANT.

Magnetisation coefficient and structure of solutions of gelatin. M. FALLOT (Compt. rend., 1929, 188, 1493—1500).—The magnetisation coefficient of gelatin at 19° increases linearly with concentration (0—1.5%), but there is a sharp change in the direction of the line at the concentration (0.8%) corresponding with the maximum dielectric constant observed by Marinesco (this vol., 646). The magnetic and electric axes of the dipoles are probably perpendicular to one another.

J. GRANT.

Physico-chemical properties of pineapple-stem colloids. C. P. SIDERIS (Plant. Physiol., 1928, 3, 309—321).—Two proteins and a carbohydrate were identified in the expressed fluid, and their colloidal behaviour with solutions of sodium chloride and

hydroxide, respectively, was examined. It is suggested that the carbohydrate colloid has a hollow spherical structure, the shell being formed of aggregated micelles held together by electrostatic forces. Protein colloids may have similar structures, the carboxyl groups projecting inwards and the amino-groups outwards, or *vice versa*, according as the p_H of the solution is on the acid or alkaline side, respectively, of the isoelectric point.

CHEMICAL ABSTRACTS.

Qualitative reaction of protein. I. Reaction of acid in the acetic acid-sodium chloride test. S. OGATA (Hokkaido J. Med., 1928, 6, 26—36).—The amount of sodium chloride necessary to precipitate gelatin from aqueous solution decreases to a constant value, dependent on the gelatin concentration if below 3%, when acetic acid is added. In solutions more acid than p_H 9.6 the action of sodium chloride is not affected.

CHEMICAL ABSTRACTS.

Action of sodium chloride on collargol. G. S. VOZDVISCHENSKI and A. F. GERASIMOV (J. Russ. Phys. Chem. Soc., 1929, 61, 193—196).—Increase in the amount of albuminous matter present is found to decrease the protective action of sodium chloride on collargol, and this is more pronounced for non-dialysed collargol or non-dialysed solutions of albumin than for the dialysed substances. Dilution increases the effectiveness of sodium chloride and this action is also more pronounced in the case of non-dialysed samples. On dialysis an adsorptionally very sensitive portion of the albuminous matter passes out through the membrane.

A. FREIMAN.

Theory of vegetable tanning. IV. Separation into two liquid phases in systems hydrophylic colloid-water-polyphenol. H. G. B. DE JONG (Rec. trav. chim., 1929, 48, 494—503).—Dehydration of a gelatin sol at the isoelectric point by resorcinol occurs only between certain concentration limits of the latter. Over the same range, a fluid coagulum is produced, and if the mixture is kept for a time it separates into two layers, the one which is richer in gelatin containing the greater proportion of resorcinol. The separation process commences with a micro-separation of the resorcinol solution at the surface of the gelatin particles, followed by coalescence when conditions become favourable. A similar type of separation in gelatin sols has been observed with a number of phenols, with chebulic acid, digalloyl-glucose, and tannin, and also in agar and starch sols in presence of tannin.

H. F. GILLBE.

Layered sedimentation of suspensions of erythrocytes. V. DUCCESCHI (Kolloid-Z., 1929, 48, 78—79).—When the blood of various animals is added to the extent of 3—5% to a 1% solution of sodium chloride or Ringer's solution, the easily coagulable part settles in the course of 2—3 hrs. and the red corpuscles remain suspended for 24—48 hrs. During this time, the suspension of corpuscles frequently assumes a periodic structure, sedimentation taking place in layers. An explanation is not given.

E. S. HEDGES.

Chemistry of body processes. Nature of the action between gelatin and electrolytes. A. L.

FERGUSON (5th Coll. Symp. Mon., 1928, 159—178).—A discussion.

CHEMICAL ABSTRACTS.

Double refraction of stretched rubber. W. C. VAN GEEL and J. G. EYMERS (Z. physikal. Chem., 1929, B, 3, 240—246).—Two samples of rubber have been examined: (a) an unvulcanised plastic rubber and (b) an elastic rubber obtained by drying pure latex. In the case of the plastic rubber the double refraction is a linear function of the tension except with low tensions, where the rubber still has elastic properties. With elastic rubber much higher values of the tension are reached before the relationship becomes linear, and a formula is given which expresses the variation of double refraction with tension up to the limiting tension at which proportionality commences. At this limiting tension the extension of the rubber is 70%, which appears to be a characteristic magnitude for pure rubber.

O. J. WALKER.

Absolute zero of internal energy and entropy, and the corresponding inertness of matter. R. D. KLEEMAN (Science, 1928, 68, 235—236; cf. A., 1928, 1187).—The first and second differential coefficients with respect to temperature of the internal energy, pressure, and volume of a condensed substance at 0° Abs. either at constant volume or pressure or under its own vapour pressure are equal to zero. The inertness to changes in temperature possessed by matter at 0° Abs. indicates that at this temperature an atom differs considerably in its nature in virtue of a change in electronic configuration. A further proof that at 0° Abs. the internal heat of evaporation is zero is given.

L. S. THEOBALD.

Chemical combination as an electrostatic phenomenon. VI. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 224—228).—A mathematical discussion of recent attempts to deduce theoretically dissociation energies, heats of formation, and other intramolecular quantities.

S. I. LEVY.

Recent views on electrolytes. N. BJERRUM (Ber., 1929, 62, [B], 1091—1103).—A lecture.

H. WREN.

Equilibrium constant in double decompositions in aqueous solution. (MME.) LEMARCHAND and LEMARCHAND (Compt. rend., 1929, 188, 1289—1291).—The heat of reaction (10610 g.-cal.) for the double decomposition of barium chloride and sulphuric acid which is calculated from the equilibrium constants at 18° and 100° (this vol., 266) by means of the integrated van 't Hoff equation is in close agreement with thermochemical determinations (10100 g.-cal.).

J. GRANT.

Equilibrium, phosphoric acid-hydrogen fluoride-monofluophosphoric acid-water. W. LANGE (Ber., 1929, 62, [B], 1084—1088; cf. this vol., 662).—Weighed quantities of phosphoric acid and hydrogen fluoride are preserved at 20° in a platinum crucible with a tightly fitting lid. The mixture is poured into dilute potassium hydroxide solution at −10 in quantity sufficient for complete neutralisation and unchanged phosphoric acid is precipitated as silver phosphate. The incidence of the equilibrium $H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$ is established, but the dependence of the reaction on the concentration of

water can be explained only by the assumption that undissociated molecules, which are present in the concentrated acid but disappear on dilution with water, are involved.

H. WREN.

Polarity of halogens in solutions of pyridinium and allied dichloriodides. T. H. READE (J.C.S., 1929, 853—863).—Pyridinium, phenyltrimethylammonium, and allied dichloriodides dissolve in water to form solutions which are rich in hydrogen ions, chlorine ions, and hypiodous acid. Molecular chlorine and iodide ions are absent, but molecular iodine is present as a decomposition product of hypiodous acid. Unless treated with a reducing agent or some other special reagent, the solution does not immediately give a blue coloration with starch, but does so after some hours. A similar behaviour is observed with dichloriodides dissolved in solutions of sodium chloride or hydrochloric acid. The tendency of dichloriodides to ionise is retarded by the addition of a large excess of chlorine ions or hydrogen ions, the former having the greater effect. The rate of formation of hypiodous acid has been determined and is taken as a measure of the degree of dissociation of the dichloriodides. In 0.001*M*-solution, the dichloriodides behave like double salts which contain a highly reactive, positively-charged iodine atom, which forms hypiodous acid by combination with the hydroxyl ion of water. Hypiodous acid behaves similarly towards phenolic substances and aromatic amines.

E. S. HEDGES.

Dissociation constant of glutimic acid. V. ZAFOUK (Z. Zuckerind. Cechoslov., 1929, 53, 465—468).—From measurements of the electrical conductance of solutions of the sodium salt of glutimic acid at 25°, a mean value of 5.9×10^{-4} was found for the dissociation constant. The values calculated fell gradually from 5.93×10^{-4} in *M*/16 solution to 5.25×10^{-4} for *M*/1024 solution. From measurements of hydrogen-ion concentration in mixed solutions of glutimic acid and its sodium salt, values for the dissociation constant between 6.25×10^{-4} and 3.40×10^{-4} for *M*/75 and *M*/1000 solutions, respectively, were obtained.

F. G. TRYHORN.

Isomerism of the oximes. XXXIV. Dissociation constants of isomeric oximes and their influence on the production of the isomerides in alkaline solution. O. L. BRADY and N. M. CHOKSHI (J.C.S., 1929, 946—951).—Measurements of the dissociation constants of a number of oximes are given. Where there is little difference between the dissociation constants of two stereoisomeric oximes, both forms are produced on oximating the aldehyde or ketone in alkaline solution. The relation between the dissociation constants and the configuration of the isomerides is considered for the case of the ketoximes. If the analogy of the cinnamic acids be accepted, the results favour the old as against the new configurations of the ketoximes, but the analogy seems doubtful in view of the evidence in favour of the new configurations.

E. S. HEDGES.

Determination of the alkali-fixing capacity of the most important sugars. P. HIRSCH and R. SCHLAGS (Z. physikal. Chem., 1929, A, 141, 387—

412).—The acid properties of sugars are so feeble that the usual methods of determining dissociation constants are not trustworthy. The conductometric method of Hirsch (cf. A., 1926, 700) is applicable, using the formula $c = 100\Delta\kappa / (\Lambda_{\text{NaOH}} - \Lambda_{\text{NaX}})$, where *c* is the concentration of the alkali-sugar compound (NaX), $\Delta\kappa$ is the decrease in conductivity, and Λ the equivalent conductivity of the compound indicated. Sugar introduced into a solution of sodium hydroxide causes a decrease in conductivity due to the formation of a sodium-sugar salt. This decrease is accurately measurable and reproducible. Λ_{NaOH} was directly measured and it was assumed that sugar molecules have no influence on it. Λ_{NaX} must be obtained indirectly, since the salt is hydrolysed. To do this the conductivity of the solution of sugar and sugar salt with excess alkali was found directly, and the concentration of free alkali was determined potentiometrically on the basis of separate experiments conducted in the presence of different concentrations of various salts. The conductivity due to this free alkali could thus be calculated, and hence that of the sugar salt. Since the concentration of the latter is known from the difference in concentration of the free alkali at the beginning and end of the experiment, the equivalent conductivity could be calculated. By plotting the amount of alkali combined with 1 g.-mol. of sugar against the *p_H* of the liquid it was found that all the sugars investigated contain more than one acid group per molecule. The simplest assumption compatible with the experimental results is that the sugars are dibasic, and on this basis the dissociation constants of dextrose, laevulose, maltose, sucrose, and lactose have been calculated from Hirsch's formula. The experiments are not consistent with the enolisation theory of Michaelis as an explanation of the acid nature of sugars. By plotting the decrease in conductivity obtained on adding increasing amounts of sugar to a given concentration of alkali against concentration of sugar straight-line curves are obtained, from which the concentration of sugar solutions can be found quickly and accurately by determining the decrease in conductivity and reading off from the curves.

F. L. USHER.

Activity coefficients of certain acid-base indicators. J. SENDROY, jun., and A. B. HASTINGS (J. Biol. Chem., 1929, 82, 197—246).—Extensive series of comparative electrometric determinations of the hydrogen-ion activity and colorimetric determinations have been made with solutions of several indicators of the phenolsulphonaphthalein class in presence of neutral salts and of buffer mixtures. The indicators were found to behave like other weak acids in that the value of *pK'* is dependent on the total ionic strength of the solution, the quantitative connexion being expressed by the equation of Debye and Hückel. The relationship is influenced in a subsidiary degree by other factors such as the specific interionic effects of individual ions. The colorimetric determination of *p_{aH}* with the aid of bicolour standards is discussed in the light of these results.

C. R. HARRINGTON.

Effect of salts on weak electrolytes. III. Interaction of certain weak electrolytes. H. S.

SEIMS (J. Physical Chem., 1929, 33, 745—754; cf. A., 1928, 1093, 1326).—The inactivation of one weak electrolyte by another has been investigated by an examination of the effect of glycine on the dissociation index (pK_2) phosphoric acid. The presence of glycine lowers this value, the effect being decreased by the addition of magnesium or sodium chloride. With increasing amounts of glycine, this effect reaches a maximum and then decreases, indicating that neutral glycine inactivates the $\text{HPO}_4^{''}$ ion. The formula $k=c_g f/(1-f)$ can be applied, where c_g is the concentration of glycine and $1-f$ is the fraction of $\text{HPO}_4^{''}$ inactivated by glycine. Sodium monohydrogen phosphate, as is to be expected, increases the pK_2' of glycine, an effect which is also produced by the sulphate ion. At an ionic strength $\mu=0.2$, sodium oxalate, succinate, and citrate give curves parallel to that of the phosphate in their tendency to increase the pK_2' of glycine, but at $\mu=0.01$ these salts tend to decrease the dissociation index in the order oxalate > succinate > citrate > phosphate > sulphate. This order does not correspond with the size of the ions or with the distances between the charges. Analogous effects are obtained with succinimide when these salts are added. L. S. THEOBALD.

New kind of dehydration. D. BALAREV (Kolloid Z., 1929, 48, 63—70).—Previous work on the dehydration of gypsum is reviewed and shown to be contradictory. Some new experiments are described and these lead to the conclusion that the process of dehydration is a combination of two independent processes. The term "hemihydratic" is applied to this new form of dehydration. The apparently contradictory results of different investigators are explained on this view. E. S. HEDGES.

Equilibrium diagram of the cadmium-antimony system. T. MURAKAMI and T. SHINAGAWA (J. Study Met., 1928, 5, 283—296).—When the fused mass is rapidly cooled the β -phase, belonging to the metastable system, appears; on further cooling this is converted into the γ -phase of the stable system. When the cooling is slow, the γ -phase is formed directly. The β -phase is a solid solution containing the compound Cd_2Sb_2 and forms a eutectic (395° , 54% Sb) with cadmium. It is present in the range 40—45% Sb, and is converted into the γ -phase, a solid solution containing the compound CdSb (eutectics with cadmium and antimony) at 250° . The solid solubility limits of cadmium in antimony are 0.15% at the eutectic temperature and less than 0.1% at the ordinary temperature; the solubility of antimony in cadmium is less than 0.1% at either temperature.

CHEMICAL ABSTRACTS.

Action of gas on metals. II. The systems chromium-nitrogen and manganese-nitrogen. G. VALENSI (J. Chim. phys., 1929, 26, 202—218; cf. this vol., 664).—Measurements of the dissociation pressures under isobaric conditions, viz., under 760 mm., show that in the case of chromium the solid phase contains about 29% N between 500° and 870° ; 27% between 930° and 970° —this amount corresponds with CrN —and 12.6% between 1030° and 1200° . In the case of manganese the solid phase contains 15.4% N at 390° , and 6% at 1050° .

Chromium isotherms between 810° and 920° have ranges of constant pressures, which are probably the dissociation pressures of chromium nitride at the respective temperatures. No such constant pressure range occurs in the manganese isotherms. The dissociation pressure of chromium nitride can be calculated from the expression $\log p = 96.144 \log T + 88,444/T - 750.61$. H. T. S. BRITTON.

Ceramics of refractory substances. III. System $\text{ZrO}_2\text{--ThO}_2$. O. RUFF, F. EBERT, and H. WOITNEK (Z. anorg. Chem., 1929, 180, 252—256; cf. this vol., 650).—When zirconium and thorium dioxides are heated together in the solid state there is no change in the lattices of the two oxides up to 2400° , but at 2600° formation of mixed crystals begins. From cooled liquid mixtures of the two oxides two series of mixed crystals are obtained ($a=5.20$ and 5.51 \AA.). The m. p. of zirconium oxide is gradually increased by the addition of thorium oxide, and extrapolation gives a value of $3050^\circ \pm 25^\circ$ for the m. p. of the latter oxide. The presence of a lower oxide of thorium due to thermal decomposition or reduction could not be established. O. J. WALKER.

Binary system carbamide-ammonium nitrate. Molecular association in each component. W. J. HOWELLS (J.C.S., 1929, 910—915).—The equilibrium curve for the binary system ammonium nitrate-carbamide consists of two branches and exhibits a eutectic point at 44.7° and 47% of carbamide. The ammonium nitrate exhibits a transition point at 126° . Compound formation between these two substances does not occur at the temperatures involved. For dilute solutions, the molecular depression per 100 g. of carbamide is approximately 215. In molten carbamide, ammonium nitrate has an association factor approaching 2, and acetamide has an association factor approaching 3. For dilute solutions in molten ammonium nitrate, the molecular depression is about 221 per 100 g. In this solvent, water, carbamide, and lithium nitrate are all normal or nearly so, but sodium nitrate and acetamide are slightly associated. Potassium nitrate causes a sub-normal depression of the f. p., partly due to separation with the solvent in the form of mixed crystals. Calcium nitrate is slightly associated and ammonium chloride strongly associated in molten ammonium nitrate.

E. S. HEDGES.

Solubility in the gaseous phase, especially in the system $\text{NH}_3(\text{liq.})\text{--NH}_3(\text{gas})\text{--H}_2(\text{gas})\text{--N}_2(\text{gas})$. H. L. CUPPLES (J. Amer. Chem. Soc., 1929, 51, 1026—1033).—A "solubility effect" may be defined as a change in activity of one component caused by the presence of other components. No solubility effects are involved in the Poynting effect. Activity calculations for the system $\text{NH}_3(\text{liq.})\text{--NH}_3(\text{gas})\text{--H}_2(\text{g.})\text{--N}_2(\text{g.})$ at pressures up to 600 atm. and temperatures between -40° and 20° yield results for the percentage of ammonia formed from the free gases which agree substantially with the experimental results of Larson and Black (A., 1925, ii, 501, 852). There is no indication of a solubility effect of the gas phase for ammonia vapour. S. K. TWEEDY.

Thermal equilibrium between ethylene, iodine, and ethylene di-iodide. R. B. MOONEY and E. B.

LUDDAM (Proc. Roy. Soc. Edin., 1929, 49, 160—169).—The dissociation pressures corresponding with the co-existence of ethylene di-iodide and iodine as solid phase have been measured over the range 11—65°. The vapour pressures of ethylene di-iodide in the absence of dissociation have also been determined between 16° and 33° and the results indicate a molecular latent heat of vaporisation of 15,700 g.-cal. Using the data obtained, together with Baxter's values for the vapour pressure of iodine, the equilibrium constant K of the reaction $C_2H_4 + I_2 \rightleftharpoons C_2H_4I_2$ has been calculated for a series of temperatures. It is found that the relationship between $\log K$ and $1/T$ is not linear. The divergence from linearity is ascribed to the lowering of the vapour pressure of iodine by adsorbed ethylene and ethylene di-iodide.

F. J. WILKINS.

Thermal behaviour of phenols. II. The thermodynamics and the mechanism of the thermal decomposition of phenol and its homologues. A. HAGEMANN (Z. angew. Chem., 1929, 42, 503—508).—The behaviour of phenol and *m*-cresol during hydrogenation and in contact with hot catalysts (thermal decomposition) has been studied thermodynamically and the equilibria represented by equations. The results agree closely with those found experimentally.

A. R. POWELL.

Aqueous solutions of copper and ferrous sulphates. F. K. CAMERON and H. D. CROCKFORD (J. Physical Chem., 1929, 33, 709—716).—At 30°, the solubility of copper sulphate in water is depressed by sulphuric acid. Copper and ferrous sulphates mutually depress the solubility of each other in water, and the presence of sulphuric acid augments the depression. With regard to the two solid phases in contact with copper sulphate, ferrous sulphate, sulphuric acid, and water it is suggested that one consists of copper sulphate pentahydrate and the other of a solid solution of ferrous sulphate, sulphuric acid, and water. The brick-red salt $CuSO_4 \cdot FeSO_4 \cdot 2H_2O$ described by Etard (A., 1879, 104) could not be prepared.

L. S. THEOBALD.

System sodium iodate, sodium chloride, water. H. W. FOOTE and J. E. VANCE (Amer. J. Sci., 1929, [v], 17, 424—430).—Isotherms for this system have been determined at 35°, 25°, 15°, and 0°. The solid phases which occur are $NaCl$; $NaCl \cdot 2H_2O$; $NaIO_3 \cdot H_2O$; $NaIO_3 \cdot 5H_2O$; and a double salt $2NaIO_3 \cdot 3NaCl \cdot 10H_2O$. The solid phases at the characteristic temperatures are: $NaCl$; $NaIO_3 \cdot H_2O$, and double salt (24.6°); $NaIO_3 \cdot 5H_2O$; $NaIO_3 \cdot H_2O$, and double salt (6.8°); $NaCl \cdot 2H_2O$; $NaCl$, and double salt (0.04°). The ternary eutectic temperatures are: ice, double salt, $NaCl \cdot 2H_2O$ (−21.18°); ice, double salt, $NaIO_3 \cdot 5H_2O$ (−16.8° to −17°).

C. W. GIBBY.

Equilibria between water, the nitrates, and the sulphates of sodium and of potassium. E. CORNEC, H. KRONBACH, and A. SPACK (Compt. rend., 1929, 188, 1250—1253).—These equilibria have been studied between −2° and 90° and the results obtained represented schematically for ten temperature ranges. Darapskite ($Na_2SO_4 \cdot NaNO_3 \cdot H_2O$) is present between 10° and 74°, whilst glaserite appears at 90° but not at −2°, at which temperature a saturated solution of the four salts is obtained. Glauber's salt is present

below 32.4°. Hamid's conclusions (A., 1926, 245, 246) that a triple salt exists at 25° and that sodium nitrate and glaserite cannot coexist were not confirmed.

J. GRANT.

Systems $Al(NO_3)_3$ – $Fe(NO_3)_3$ – H_2O and KNO_3 – $Fe(NO_3)_3$ – H_2O at 0° and at 40°. G. MALQUORI (Atti R. Accad. Lincei, 1929, [vi], 9, 569—572).—In contact with solutions containing 37.81—12.33% of aluminium nitrate the stable solid phase at 0° is $Al(NO_3)_3 \cdot 9H_2O$. The phases $Al(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ are coexistent with a solution of composition 11.02% $Al(NO_3)_3$, 25.09% $Fe(NO_3)_3$, 63.89% H_2O . For solutions containing less than 11.02% of aluminium nitrate the stable phase is $Fe(NO_3)_3 \cdot 9H_2O$. At 40° the invariant system corresponds with 17.12% $Al(NO_3)_3$, 32.69% $Fe(NO_3)_3$, 50.19% H_2O , the stable phases being the same as at the lower temperature. In the second system at 0° an invariant point corresponds with 38.55% $Fe(NO_3)_3$, 3.92% KNO_3 , 57.53% H_2O , the stable phases being KNO_3 and $Fe(NO_3)_3 \cdot 9H_2O$. No invariant point occurs in this system at 40°.

F. G. TRYHORN.

Isotherms at 20° of the systems $La(NO_3)_3$ – $Mn(NO_3)_2$ – H_2O , $La(NO_3)_3$ – $Mg(NO_3)_2$ – H_2O , and $Mn(NO_3)_2$ – $Mg(NO_3)_2$ – H_2O . C. DI CAPUA (Gazzetta, 1929, 59, 164—169).—An examination of these isotherms for the presence of double salts yielded negative results. Saturated solutions at 20° of the nitrates of lanthanum, manganese, and magnesium contain respectively 60.13, 56.81, and 43.68% of the salts.

F. G. TRYHORN.

Individuality of heats of dilution of strong electrolytes. E. LANGE and J. MEIXNER (Naturwiss., 1929, 17, 273).—Preliminary. The integral heats of dilution V_c of uni-univalent strong electrolytes, even for concentrations below 0.01N, show definite differences, e.g., $LiF > KF$, $LiF > LiBr$, $KF > KCl > KNO_3$, $KCl > CsCl$, whilst the probable ionic diameters a show differences in the reverse order, $Li^+ < K^+ < Cs^+$; $F^- < Cl^- < Br^- < NO_3^-$. For lithium fluoride and calcium sulphate V_c is greater than would be expected from the limiting law in the Debye-Huckel theory ($a=0$). It is shown that it is unnecessary to assume negative a value for positive deviations.

R. A. MORTON.

Transference number of barium chloride as a function of the concentration. G. JONES and M. DOLE (J. Amer. Chem. Soc., 1929, 51, 1073—1091).—The Hittorf transport numbers, t , for barium chloride were determined over a hundred-fold concentration range in an improved apparatus of the Washburn type. The quantity $1/(1+t)$ is accurately a linear function of \sqrt{c} , the actual relationship being (i) $t+1 = A/(1+B\sqrt{c})$, where $A=1.4476$ and $B=0.07010$. Previous determinations of transport numbers over large concentration ranges have all been effected by means of the *E.M.F.* method and the results do not conform with (i). *E.M.F.* of cells of the type $Ag, AgCl/BaCl_2(0.05M)/BaCl_2(c)/AgCl, Ag$ were, therefore, determined at 25°, where c varies between 0.001 and 1.0M, but the potentials found agreed almost exactly with those of Lucasse (A., 1925, ii, 399). The erroneous transport numbers calculated by this author from his *E.M.F.* results are attributed therefore to

the complicated graphical procedure which he was compelled to use. An analytical method of computation is given. Lucasse's data for cells without liquid junctions yield the following equation for the mean activity coefficients of the ions of barium chloride at 25° (cf. Hückel, A., 1925, ii, 513): (ii) $\log f - 0.15266c = -1.734\sqrt{c}/(1 + 2.2318\sqrt{c})$. Combination of (ii) with (i) yields a relationship between α (activity) and c , which permits an integration of the fundamental thermodynamic equation (iii) $dE - (3RT/2F) d \ln \alpha$. When treated in this way Lucasse's data give $A = 1.4372$ and $B = 0.05409$ in (i). Combination of the authors' *E.M.F.* data with Lucasse's data gives $A = 1.4500$ and $B = 0.07135$ in (i). The analytical method, however, is regarded as the more trustworthy. S. K. TWEEDY.

Mobility of the hydrogen ion and the electrical conductivity of the halogen hydracids. (MILLER.) M. DE HLASKO (J. Chim. phys., 1929, 26, 125—148).—The electrical conductivities of aqueous solutions of hydrochloric, hydrobromic, hydriodic, bromic, and iodic acids have been measured at 25°. Values higher than those generally accepted have been obtained for the equivalent conductivities of hydrochloric, hydrobromic, and hydriodic acids at infinite dilution, being 431.5, 433.7, and 432.3, respectively. The mobility of the hydrogen ion is found to be 355.1. The densities and viscosities of the solutions used have been measured. The conductivities of aqueous solutions of bromic and iodic acids were calculated from the data for solutions of hydrobromic and hydriodic acids saturated respectively with bromine and iodine. Iodic acid is stronger than bromic acid. The constant for the hydrolysis of bromine in accordance with $2\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HBr}_3 + \text{HBrO}$, in solutions saturated with bromine, can be calculated with the aid of the law of mass action.

C. W. GIBBY.

Relation between electrical conductivity of solutions and their vapour pressure. T. DALHBLÖM (Teknisk Tidskr., 1928, 58, Kemi, 76—79; Chem. Zentr., 1928, ii, 2706—2707).—The expression $k \log p_0/p + rC = nF$, where C is the conductivity, p_0 and p are the vapour pressures of the solvent and salt solution of concentration n , respectively, and k , r , and F are constants, is derived. Hence $12.45\Delta t + rC = nF$, where Δt is the depression of the f. p. A theoretical explanation is offered.

A. A. ELDRIDGE.

Number of water and alcohol molecules associated with the silver ion. G. C. SCHMIDT and M. KELLER (Z. physikal. Chem., 1929, A, 141, 331—342).—The general question of the number of solvent molecules associated with ions is critically discussed. The presence of at least a few silver ions in alcoholic and aqueous solutions of silver nitrate is inferred from the fact that a current passes on the application of the smallest *E.M.F.* It has been shown by means of cryoscopic and conductivity experiments that both ammonia and pyridine when added to such solutions give rise to a complex ion AgX_2 , which is more soluble in alcohol than in water. Further addition does not result in the binding of more ammonia or pyridine. The transference numbers of these com-

plex silver ions have been determined and compared with those of the silver ion in both alcoholic and aqueous solutions of silver nitrate. The conclusion reached is that there are on the average two solvent molecules associated with the silver ion, assuming that the volumes occupied by the molecules of ammonia and water are in the ratio 94/85 as found by Grimm. Measurements of the conductivity when increasing amounts of ammonia and pyridine are added to dilute aqueous solutions of silver nitrate point to an equilibrium $\text{Ag}(\text{NH}_3)_2 \rightleftharpoons \text{Ag}(\text{H}_2\text{O})_2$. In aqueous solutions there appears to be an equilibrium between the ions $\text{Ag}(\text{H}_2\text{O})_2$, $\text{Ag}(\text{H}_2\text{O})$, and Ag , and similarly for the alcoholic solution. F. L. USHER.

Electrochemistry of the system AlBr_3 -KBr in benzene. V. A. PLOTNIKOV and S. I. JAKUBSON (J. Russ. Phys. Chem. Soc., 1928, 60, 1585—1592).—See this vol., 144.

Electrochemistry of solutions of phosphorus pentachloride in bromine. V. A. PLOTNIKOV and S. I. JAKUBSON (J. Russ. Phys. Chem. Soc., 1928, 60, 1505—1512).—See this vol., 144.

Single potential of the copper electrode. E. NEWBERRY (J. Amer. Chem. Soc., 1929, 51, 1315—1322).—The varying values which have been recorded for the potential of the copper electrode are attributed to the rapid formation of a thin film of basic salts, and a method is described whereby the potential may be ascertained before this film has had time to form. The single potentials of pure copper and of two-phase copper amalgam are found experimentally to be identical, whence, from the work of Nielsen and Brown (A., 1927, 1144), the standard potential of copper referred to the normal hydrogen electrode is 0.3502 volt.

S. K. TWEEDY.

Single potential of the nickel electrode. E. NEWBERRY (J. Amer. Chem. Soc., 1929, 51, 1429—1436).—The potential of nickel in a solution of its ions is uninfluenced by the purity of the nickel salt and by metallic impurities or gaseous oxygen in the electrode, but it is very much affected by the physical state of the electrode surface and by the presence of gaseous hydrogen. The electrode appears to react somewhat with the electrolyte. The potential was investigated by observations on a cell of the type $\text{Ni}|\text{NiSO}_4 \cdot 0.5M|\text{Hg}_2\text{SO}_4|\text{Hg}$, special precautions and technique being adopted. For each abrading material used to polish the electrode there is a definite limiting potential. Constant and reproducible values are obtained only when the nickel is treated anodically with a small current density insufficient to produce passivity. It is suggested that two allotropes of nickel exist, one, preponderating in amorphous nickel, having a potential of 0.45 volt or more (referred to *N*-hydrogen electrode) and the other a potential of 0.05 volt or less; the equilibrium of these allotropes in ordinary nickel accounts for the third observed potential, 0.17 volt. This hypothesis also affords an explanation of the retardation phenomena observed during the electrolytic deposition of nickel and of the electrodeposition of polished nickel. It is probable that the true reversible potential of a metal giving rise to hydrated ions cannot be directly determined.

S. K. TWEEDY.

Electrolytic potentials of some metals. L. BOUCHET (Compt. rend., 1929, 188, 1237—1239).—The electrolytic potentials of magnesium, zinc, hydrogen, copper, and silver are -1.766 , -1.052 , -0.281 , 0.041 , and 0.502 , respectively, compared with the *N*-calomel electrode at $18-24^{\circ}$. Slight variations with the salt used were obtained in the case of zinc.

J. GRANT.

Calcium amalgam electrode in dilute aqueous solutions. R. J. FOSBINDER (J. Amer. Chem. Soc., 1929, 51, 1345—1356).—The activity coefficients of calcium chloride up to $3.3M$ were determined from *E.M.F.* measurements on cells of the type: $Ag|AgCl|CaCl_2(c)|Ca \text{ amalgam}|CaCl_2(0.0099M)|AgCl|Ag$, the results, up to $1M$, being in agreement with those of Lucasse (A., 1925, ii, 399). An apparatus suitable for determining the activity coefficients of calcium ions, including a dropping calcium amalgam electrode, is described, and used for determining the said coefficients from 0.01 to $0.001M$ in calcium sulphate, lactate, hydroxide, chloride, and acetate solutions at about 25° . The results are in approximate agreement with the requirements of the Debye-Hückel theory. Addition of electrolyte or protein lowers the potential of the calcium amalgam electrode. Experiments on dog's blood show that the electrode is useless for determining calcium-ion activity in any solution containing cations other than calcium. Proteins probably form a skin over the electrode, thus hindering the establishment of true electrochemical equilibrium.

S. K. TWEEDY.

Potential of inert electrodes in solutions of sulphurous acid and its behaviour as an oxidising and reducing agent. A. A. NOYES and H. H. STEINOUR (J. Amer. Chem. Soc., 1929, 51, 1409—1428).—Experiments relating to the potential *E* of a platinised platinum electrode in solutions containing sulphite and hydrogen ions (cf. Carter and James, A., 1925, ii, 134) are described. Under quiet conditions *E* is fairly constant, but on prolonged agitation of the solution it becomes more negative and then gradually increases to the quiet-state value. A combination of catalytic and adsorption effects at the electrode is the possible explanation. The potential is not accidental; at 25° it is given empirically by $-0.37 - 0.0296 \log [H]^{4/3}$. It is due to sulphurous acid and some decomposition product of this acid. It is independent of the initial condition of the electrode and is scarcely affected by the presence of sulphuric, hydrochloric, and dithionic acids. The aforesaid decomposition product is probably hyposulphurous acid ($H_2S_2O_4$, which the authors, in accordance with a systematic nomenclature which they propose for certain sulphur acids, rename "dithionous acid"), and the nearly constant value of *E* is said to be due to the rate of production of this acid from sulphurous acid, being equal to the rate at which it spontaneously decomposes. Addition of sulphur has no influence on *E* at low temperatures, but at higher temperatures it may affect the potential because of the accelerated rate of decomposition of the hyposulphurous acid. The potential is complicated by the presence of oxygen, since this latter assists the decomposition of the hyposulphurous acid. A quantitative interpretation of the chemical

behaviour of sulphurous acid is given, and the free energy changes of several ionic reactions involving sulphur acids are calculated.

S. K. TWEEDY.

Electromotive behaviour of aluminium and its amalgams. R. MÜLLER (Z. Elektrochem., 1929, 35, 240—249).—The potentials set up between aluminium and aluminium amalgams, respectively, and non-aqueous solutions containing aluminium bromide have been investigated by comparing them with the potentials of certain silver comparison electrodes. In one case, the liquid phase consisted of fused aluminium bromide and potassium bromide, whilst in another, aluminium bromide was dissolved in pyridine. The data show that the potential of aluminium and its amalgams with regard to a particular solution is the same and is independent of the composition of the amalgam.

Several experiments were made to ascertain the decomposition potentials of aluminium and bromine from non-aqueous solutions, using either platinum or mercury as cathode.

H. T. S. BRITTON.

Behaviour of the antimony electrode in buffered and unbuffered solutions. V. G. LAVA and E. D. HEMEDDES (Philippine Agric., 1928, 17, 337—349).—Antimony electrodes, which are recommended for sugar solutions but not for soils, were tested in buffer solutions of potassium dihydrogen phosphate and sodium hydroxide and in mixtures of $0.01N$ -sodium hydroxide and $0.01N$ -hydrochloric acid at $26-29^{\circ}$; the p_H is given by $E = 0.052 + 0.057 p_H$.

CHEMICAL ABSTRACTS.

Influence of the solvent on the *E.M.F.* of silver halide cells. I. Water-ethyl alcohol mixtures. A. S. AFANASIEV (Z. Elektrochem., 1929, 35, 220—222, and J. Russ. Phys.-Chem. Soc., 1929, 61, 613—618).—Measurements were made of the *E.M.F.* of cells of the type $Ag|AgCl, KCl|KBr, AgBr|Ag$ in the half-elements of which various solvent media, consisting of mixtures of water and ethyl alcohol in differing proportions, were used. The *E.M.F.* found were in good agreement with those obtained by calculation, using Brodsky's formula (A., 1926, 688) which he developed for the *E.M.F.* of similar mercurous halide concentration cells containing various non-aqueous solvents.

H. T. S. BRITTON.

Oxidation-reduction. XIV. Equilibrium potentials of sodium 2:6-dibromobenzeneindophenol-2'- and -3'-sulphonates, 2:6:2'-trichlorobenzeneindophenol, and 2:6-dimethylbenzeneindophenol. W. L. HALL, P. W. PREISLER, and B. COHEN (U.S. Public Health Rep., Suppl. 71, 1928, 26 pp.).—The equilibrium potentials and dissociation constants of the four compounds mentioned in the title have been determined at 30° by methods previously described (cf. A., 1923, ii, 726; 1924, ii, 597). Deflexions in the $E'_0 - p_H$ curves (where E'_0 is the potential corresponding with an equimolecular mixture of oxidant and reductant) denote detectable dissociation, and when the change in slope ($-dE/dp_H$) is negative, the dissociation causing the change is assigned to the reductant: when the change is positive, dissociation is attributed to the oxidant. The first three of the above compounds occupy positions on the extreme electropositive side (i.e., most easily reducible) of the indophenol series. The effect of

substituting sulfo-, chloro-, and methyl groups is discussed, and a list of 13 useful oxidation-reduction indicators is given together with values of E'_0 at p_H 5.0—9.0 and 30°.

H. BURTON.

Polarographic studies with the dropping mercury cathode. I. Amphoterity of ferrous hydroxide. B. SCHRAGER (Coll. Czech. Chem. Comm., 1929, 1, 275—281).—Measurements with the polarograph show that ferrous hydroxide dissolves slightly in aqueous solutions of sodium hydroxide, owing to the reaction $\text{Fe}(\text{OH})_2 + \text{OH}' \rightarrow \text{Fe}(\text{OH})'_3$, the ratio $[\text{Fe}(\text{OH})'_3]/[\text{OH}']$ having the value 5×10^{-5} . From the value for the deposition potential of ferrous iron in the solution, the value of the product $[\text{Fe}''][\text{OH}]^2$ is calculated to be 7×10^{-13} . Cobaltous and manganous hydroxides also show acidic properties.

R. CUTHILL.

Tervalent chromium. (MME.) N. DEMASSIEUX and J. HEYROVSKY (J. Chim. phys., 1929, 26, 219—223).—Polarisation curves obtained with the "polarograph" during the electrolysis of tervalent chromium salt solutions of different concentrations, in which the dropping mercury electrode is used, are described, and the inflexions are attributed to either $\text{Cr}''' \rightarrow \text{Cr}'' + F$ or $\text{Cr}''' \rightarrow \text{Cr} + 3F$. The curves are stated to show that the less hydrated chromium ions in the green salts (according to Werner's theory) are reduced and discharged at potentials which are more positive than those at which the more hydrated chromium ions in the violet salts become reduced. This is true of the chloride and sulphate solutions, although with the latter the abnormally great displacements of the potentials at which reduction occurs indicate that the complexity of the ions varies with dilution in passing from the green to the violet form. The potentials at which reduction occurs in potassium and rubidium chrome alum solutions are coincident, and indicate, it is believed, the progressive dissociation of the anion complexes. The constitution of chrome alums is compared with that of simple salts. No reduction occurs in alkaline chromium hydroxide solutions, which is regarded as proof of the colloidal nature of the hydroxide, in contrast with solutions of zincates and plumbites in which reduction has been observed.

H. T. S. BRITTON.

Influence of glycine on the electrical conductivity of salt solutions. T. MURAYASU (Hokkaido J. Med., 1928, 6, 328—336).—The reduction of the conductivities of 0.0*M*-solutions on the addition of glycine diminishes in the order: hydrogen chloride, sodium chloride, cobalt nitrate, sodium carbonate, calcium chloride, potassium dichromate, barium chloride, aluminium chloride, ammonium chloride; with ferric chloride, chromic chloride, zinc sulphate, copper sulphate, magnesium sulphate, potassium ferrocyanide there is an increase in conductivity which diminishes in the order given.

CHEMICAL ABSTRACTS.

Anodic behaviour of aluminium. W. J. MÜLLER and K. KONOPICKY (Z. physikal. Chem., 1929, 141, 343—377; cf. A., 1928, 247).—The theories hitherto advanced to explain the anodic passivity and valve action of aluminium electrodes are critically examined. Measurements have been made of the

rate of decrease of the current under a constant *P.D.* and Meserve's observation, that after the lapse of a certain time this is inversely proportional to the square of the current strength, has been confirmed. It is therefore improbable that the action is due to the formation of a protective film of oxygen, which according to the authors' results can occur only if the aluminium is made chemically passive. The gas evolved at an aluminium anode has been examined and shown to contain a varying quantity of hydrogen, a result in agreement with the theory that the anodic passivity is due to a layer of hydroxide, since aluminium even when highly anodically polarised is still chemically active and capable of liberating hydrogen from the electrolyte. The oxygen produced is not formed at the surface of the metal but on the skin of hydroxide covering it. It has further been shown that the hydroxide layer is the seat of both resistance and capacity, and it cannot therefore be assumed that the latter is due to a film of oxygen. The dissipation of the charge in a formed anode follows the normal course of the discharge of a condenser through a resistance as long as the electrolyte is approximately neutral. The conclusion reached is that, as an anode, aluminium becomes covered with a gelatinous layer of hydroxide which must be negatively charged and consequently pressed against the metal, whilst the electrolyte is expressed from the pores of this gel by cataphoresis. The reverse process occurs when the aluminium becomes the cathode. An expression based on this view has been deduced giving a relation between current strength and time which is in complete agreement with the experimental results.

F. L. USHER.

Application of reduced equations to chemical reactions. W. SWIENTOSLAWSKI and J. G. ZAWIDZKI (Rocz. Chem., 1929, 9, 246—265).—Curves expressing the velocity of chemical reactions are plotted using the reduced co-ordinates x' and τ , where τ is the time necessary for the reaction of a definite fraction ($x' = 1/n = 1/4, 1/2$, or $3/4$) of the substrate. Using these co-ordinates, the initial concentration of substrates and the velocity coefficient are eliminated from the velocity equation, so that one single curve is obtained for all equations of the same order for a given value of n . The value of this simplification for the investigation of the problems of kinetics is discussed.

R. TRUSZKOWSKI.

Ignition of combustible gas with three-part spark. T. TERADA, K. YUMOTO, and R. YAMAMOTO (Proc. Imp. Acad. Tokyo, 1929, 5, 125—126).—The three-part spark is a special type of long spark produced when a spark gap is charged up gradually by a static machine, when the ratio of the gap to the diameter of the spherical electrodes is greater than 2, and the potential of the positive electrode is lowered by earthing, or by a needle-point leakage. The spark is tripartite, the positive and negative parts being smooth and continuous, whilst the centre is split and of greater luminosity. Ignition of coal gas occurs easily in the positive or negative portions of the spark, but the character of the spark is altered during the process. Minimum frequency of ignition was found at the junctions of the positive and negative

portions with the middle of the spark. A maximum occurs at a point slightly to the negative side of the centre of the spark. Frequency of ignition approaches 100% at the surface of the negative electrode, and falls nearly to zero at the positive surface.

F. G. TRYHORN.

Explosive gas mixtures. P. H. PRAUSNITZ.—See B., 1929, 421.

Ignition temperatures of mixtures of carbon monoxide and air. M. PRETTE and P. LAFFITTE (Compt. rend., 1929, 188, 1403—1405).—The authors' method (this vol., 271) shows that the ignition temperature of air containing 10—40% of carbon monoxide is approximately 655°, but that it rises rapidly for higher concentrations. The higher is the temperature of the mixture the greater are its limits of inflammability. Traces of residual burnt gases do not affect the results as in the case of hydrogen (*loc. cit.*), but water vapour and traces of hydrogen lower the ignition temperature, the latter to an extent increasing with its concentration (*e.g.*, 80° for 0.005 part).

J. GRANT.

Photographic investigation of flame movements in carbon monoxide-oxygen explosions. W. A. BONE and R. P. FRASER (Phil. Trans., 1929, A, 228, 197—234).—A camera for photographing explosion waves is described. The film is fixed to the periphery of a wheel 6" in diameter, which can be driven by a friction drive at any speed between 30 and 12,000 r.p.m. The flame velocity in mixtures of carbon monoxide and oxygen is diminished by intensive drying, but the mixture could still be ignited after 240 days' drying. The effects of intensive drying can be overcome by applying an electric field throughout the duration of the explosion. There is always an induction period when feeble sources of ignition are used. With condenser discharges the general flame speed is not greatly accelerated by considerable increases in spark intensity, but combustion was retarded when violent flame oscillations were set up by very heavy sparks. The flame oscillations are held to be due either to repeated reflexions of the two opposite compression waves from the ends of the explosion tube or else to compression of unburnt gas in front of the flame and/or contraction of the burnt gas behind it. Flame speeds may be raised by "shock waves" from one uniform rate to another by abrupt steps.

C. W. GIBBY.

Role of electrical carriers in the explosion of combustible gases mixed with air. F. HABER (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 11, 162—170).—The deformation of the explosion zone and the effect on the velocity of transmission of ignition produced by the passage of explosive mixtures with air through the continuous field of a wedge-shaped condenser have been studied. The deformation is not a general property of flame and occurs only in gas mixtures which are good conductors. It diminishes when the continuous field is replaced by an alternating field of high frequency. From the results obtained with mixtures of various gases with air it is concluded that uncharged radicals and not electrical particles are responsible for the process of combustion and especially for the velocity

of propagation of ignition. The uncharged radicals are produced with less expenditure of energy than the charged, and only in the case of the groupings C-C and possibly CH, which possess low excitation potentials, is the ionisation potential low enough to bring about in an air flame an appreciable fission into ions and electrons. The essential source of ionisation is the chemical energy of the elementary processes of combustion.

L. S. THEOBALD.

Unimolecular reactions. D. G. BOURGIN (Proc. Nat. Acad. Sci., 1929, 15, 357—362).—The new quantum mechanics is applied to the study of unimolecular reactions, with special reference to the N_2O_5 molecule, and the problem is shown to be closely allied to that of thermionic emission and radioactive disintegration. A particular mode of decomposition described by the severing of a certain linking is considered and an intermediate region in which the energy exceeds the dissociation energy is assumed. The molecular motion is described by a Schrodinger wave equation and an expression for the reaction velocity is finally obtained in which the parameters may be determined from band spectra data as well as from reaction rate experiments. A means is provided for estimating the equilibrium point of the unimolecular decomposition.

N. M. BLIGH.

Oxidation of iodide ion by persulphate ion. I. Effect of tri-iodide ion formation on the reaction velocity. E. JETTE and C. V. KING (J. Amer. Chem. Soc., 1929, 51, 1034—1047).—The kinetics of the reaction $2KI + K_2S_2O_8 = 2K_2SO_4 + I_2$ have been studied. The results indicate that the tri-iodide ion reacts with the persulphate ion, and at a rate which is approximately one half of that of the iodide ion (*cf.* Kiss and Zombory, A., 1927, 632, etc. which work is criticised), so that the observed velocity is the sum of the velocities of two reactions. The tri-iodide ion probably does not act as a catalyst for the main reaction.

S. K. TWEEDY.

Oxidation of iodide ion by persulphate ion. II. Effect of removing the products of the reaction on the reaction velocity. C. V. KING and E. JETTE (J. Amer. Chem. Soc., 1929, 51, 1048—1057).—The results previously obtained (preceding abstract) were confirmed and found to hold for higher concentrations also. The confirmation was effected by conducting experiments in which the iodine was removed either by means of organic solvents or by reaction with sodium hydroxide. The reaction was also studied in presence of neutral salts (nitrates of magnesium, calcium, sodium, and barium; sulphates of calcium and potassium). Removal of the sulphate ion (as barium or calcium sulphate) probably does not increase the velocity of the main reaction. The equilibrium constant of the reaction $I_2 + I' \rightleftharpoons I_3'$ in 0.1M-potassium nitrate solution was also determined.

S. K. TWEEDY.

Kinetics of oxidation of organic compounds by bromine. II. Action of bromine on formic acid. E. JOSEFOWICZ (Rocz. Chem., 1929, 9, 309—325).—The velocity of reaction between dilute aqueous solutions of bromine and formic acid is expressed approximately by the equation $dx/dt = k(a-x)^2/2x$, where a is the initial concentration of formic acid

and x that of hydrogen bromide at time t . The value of k diminishes progressively. The velocity equation in the presence of excess of hydrogen bromide is $dx/dt = k(a-x)^2/(c+2x)$, c being the initial concentration of hydrogen bromide. In the presence of excess of hydrogen chloride or nitric acid, $dx/dt = k(a-x)^2/(0.75c+2x)$. The addition of bromides, chlorides, or nitrates has little influence on the reaction velocity, which is, however, considerably accelerated by the addition of sodium sulphate, which increases the p_H of the solution. The velocity of this reaction is unaffected by light. Its temperature coefficient for the interval 20–30° is 2.26. The reaction takes place between bromide and formate ions. The retardation of reaction by hydrogen bromide is due partly to diminution of dissociation of formic acid owing to hydrogen ions and partly to combination of bromide ions with molecules to yield inactive tribromide ions. R. TRUSZKOWSKI.

Concentration of sugar and rate of hydrolysis in an acid medium. H. COLIN and A. CHAUDUN (Compt. rend., 1929, 188, 1291–1292; cf. A., 1925, i, 233).—The ratio k_{40}/k_5 for the hydrolysis of sucrose (*loc. cit.*) which decreases with the concentration of acid (for hydrochloric, sulphuric, oxalic, or acetic acid) may be less than unity at high dilutions and bears no simple quantitative relation to the p_H value. The arbitrary nature of Moran and Lewis' correction for the volume of water liberated on hydrolysis (*loc. cit.*) is indicated. J. GRANT.

Decomposition of sodium sulphate. (MLLE.) G. MARCHAL (Bull. Soc. chim., 1929, [iv], 45, 225–228).—The rate of decomposition of sodium sulphate has been studied by heating the anhydrous substance in a resistance furnace in a stream of dry nitrogen, the amount of change being ascertained from the loss of weight. By heating alone at 1300° the loss of weight was 4.23% in 4 hrs. Admixture of silica or of alumina greatly increased the initial rate of decomposition, the loss of weight after the first hour being 14.14% for silica and 22.03% for alumina, using equimolecular proportions in each case. The reaction can be utilised for the preparation of alumina in a pure state from minerals containing it.

F. L. USHER.

Reactions [and corrosion phenomena] at high pressures. E. BERL.—See B., 1929, 419.

Oxidation of iron and steel at high temperatures. L. B. PFEIL.—See B., 1929, 437.

Effect of cold-working on corrosion of iron and steel. H. ENDÔ.—See B., 1929, 437.

Corrosion of steel by acid solutions. H. ENDÔ.—See B., 1929, 437.

Corrosion of aluminium. J. CALVET.—See B., 1929, 438.

Corrosion of aluminium alloys. QUILLARD and BASCOU.—See B., 1929, 477.

Application of the logistic function to experimental data. L. J. REED and J. BERKSON (J. Physical Chem., 1929, 33, 760–779).—Mathematical. In view of the erroneous conceptions which exist concerning this function, the basic properties of the

equation are reviewed. Applications to autocatalytic reactions, bimolecular reactions, and to oxidation and reduction potentials are discussed.

L. S. THEOBALD.

Catalysis of the reaction between persulphate and iodine ions. II. Velocity of ionic reactions. A. VON KISS (Rec. trav. chim., 1929, 48, 508–516).—The results originally obtained (A., 1927, 632) have been confirmed, and an error in Saal's calculation (A., 1928, 484) is demonstrated. Measurements have been made of the velocity of the reaction between the ferric and iodide ions in dilute solution.

H. F. GILLBE.

Autocatalytic decomposition of thiosulphuric acid. II. K. JABŁCZYŃSKI and S. FRENKENBERG (Bull. Soc. chim., 1929, [iv], 45, 210–217; cf. A., 1926, 913).—The influence of sulphur nuclei, of "sulfidale" (a medicinal preparation of finely divided sulphur), and of mastic on the rate of decomposition of thiosulphuric acid solutions has been studied by measuring the opacity of acidified solutions of sodium thiosulphate, gum arabic being present in all cases. The addition of sulphur nuclei, obtained by dialysing a reaction mixture left over from a previous experiment, caused the time of half change (t) to decrease. The difference between the values of t without and with sulphur nuclei is nearly proportional to the quantity of nuclei added. When this quantity is very large the reaction ceases to be autocatalytic and becomes unimolecular, the sulphur as it is produced being deposited on the nuclei already present, and no fresh nuclei being formed. "Sulfidale," in which the sulphur particles have an average diameter of 1.54 μ , and a colloidal suspension of mastic also exert an accelerating influence on the reaction, and to about an equal extent, but the period of induction is longer than when colloidal sulphur is added. It is considered that the colloidal sulphur liberated during the reaction acts by destroying the condition of supersaturation, whereas "sulfidale" and mastic behave at first like indifferent solids, becoming catalytically active only after they have adsorbed a sufficient quantity of colloidal sulphur.

F. L. USHER.

Reaction kinetics of heterogeneous catalysis. W. FRANKENBURGER (Z. Elektrochem., 1929, 35, 278–283).—A theoretical discussion of the mechanism of the various stages, their temperature coefficients and reaction orders, of decompositions occurring at the surfaces of catalysts. H. T. S. BRITTON.

Decomposition reactions during catalytic hydrogenation in presence of nickel. Role of the catalyst in heterogeneous catalysis. A. A. BALANDIN (Z. physikal. Chem., 1929, B, 3, 167–194).—From an examination of a large amount of experimental data on the catalytic hydrogenation of organic compounds in presence of nickel (cf. Senderens) it is shown that there is a definite order in which the various atomic groups are eliminated from the original molecule (compounds involving only the six elements hydrogen, carbon, nitrogen, oxygen, chlorine, and bromine are considered). The linkings which are most easily broken are not those which are most unstable in the free molecule. The ease with which

a particular atom or group of atoms is eliminated from the molecule depends on its affinity towards the catalyst, which acts by weakening the linking between that atomic group and the rest of the molecule. The nature of the catalyst is therefore an important factor. This view is illustrated also by means of a number of other reactions which are catalysed by nickel, *e.g.*, dehydrogenation of hydrocarbons, amines, and alcohols, hydrogenation of double linkings, dehydration of alcohols, and many condensation reactions.

O. J. WALKER.

Promoter action of copper and copper oxide on the reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$. I. Oxidation velocity of copper. II. Reduction of cupric oxide. III. Autocatalysis in the heterogeneous system. Y. OKAYAMA (J. Soc. Chem. Ind. Japan, 1928, 31, 300—306, 399—406, 407—410.)—I. The velocity of oxidation of copper in the atmosphere of oxygen at 0.12 mm. was investigated. The surface of the bulb of a mercury thermometer was covered with the thin layer of copper. Through the bulb a thin glass capillary spiral tube was passed, and sealed at its ends to the wall of the bulb. This capillary tube carried in it an electrically heated spiral of platinum wire (10 cm. \times 0.1 mm.). Thus the mercury in the bulb, together with the thin layer of copper on it, could be heated to any desired temperature. The reaction velocity was determined by the change of pressure, which was measured by means of the McLeod manometer. The velocity of oxidation increased with time, according to the equation $-dp/dt = kpt$, where p and t are the pressure and time, respectively. This increase was thought to be caused by the catalytic action of copper oxide, which was formed by the reaction, the action taking place at the copper-copper oxide interface. After some time, the velocity of oxidation decreased, owing to the decrease in the surface of copper and in the pressure of oxygen. The relation between the velocity of oxidation and temperature was given by the equation $\log k = -3823/T + 5.5$, where k and T are the velocity coefficient and absolute temperature, respectively.

II. The reduction of cupric oxide by hydrogen is autocatalytic even above 200° . The reaction is retarded by the presence of water vapour. When hydrogen is passed over cupric oxide the weight of the latter increases at first and then decreases. This initial increase in weight is due to surface adsorption of water vapour. By measuring the decrease in pressure and condensing the water vapour formed by liquid air, the velocity of reduction was found to be given by the equation $-dp/dt = kpt/(p_0 - p)$, where p_0 and p were the initial pressure of hydrogen and the pressure at the time t , respectively. The velocity coefficient k at T° Abs. is given by: $\log k = -5257/T + 7.38$.

III. The autocatalysis in the heterogeneous reaction can be easily explained by Volmer's nucleus theory, but it still remains doubtful whether all autocatalytic actions in a heterogeneous system are due to the removal of the difficulty of the formation of nuclei. There are two possibilities, namely, (1) facilitation of the rate of the molecular change, and (2) the removal of the difficulty of nucleus formation. Y. NAGAI.

Catalytic action of some compounds containing iron. H. VON EULER, H. NILSSON, and D. RUNEHELM (Svensk Kem. Tidskr., 1929, 41, 85—92).—The catalase activity of hæmin and of certain allied compounds on solutions of hydrogen peroxide (0.008—0.009*M*) has been determined and the constant $K = k/[\text{millimol. Fe}]$ calculated, where k is the velocity coefficient of the reaction and (millimol.Fe) the concentration in millimols. per litre of the iron-containing compound under examination. The values found are for hæmin $K = 0.06$, for pyratin, $\text{C}_{30}\text{H}_{28}\text{O}_4\text{N}_4\text{FeCl}$ (prepared by heating hæmin with resorcinol at 180 — 190°) $K = 0.8$, mesohæmin $K = 1.1$ — 1.7 , and deuterohæmin $K = 1.0$. The buffers used appear to influence the values of the constants. All these substances bring about the oxidation of reduced phenolphthalein by hydrogen peroxide, their activities being approximately proportional to 100, 1000, 125, and 200, respectively.

W. O. KERMACK.

Catalytic reduction of carbon monoxide under normal pressure. I. Investigation of catalytic activity of metals by means of heating curves. II. Investigation of effect of foreign substances on catalytic activity of cobalt by means of heating curves. S. KODAMA (Bull. Inst. Phys. Chem. Res., Japan, 1929, 8, 277—283, 284—287).—I. The catalytic effect on the reduction of carbon monoxide with hydrogen of metals obtained by reduction of their oxides has been examined at temperatures up to 450° by means of heating curves. Copper reduced at 180° has no action. Nickel brings about the formation of hydrocarbons, whilst cobalt causes separation of carbon in addition. With cobalt, but not with nickel, the catalytic activity depends on the temperature at which the metallic oxide was reduced. Iron is oxidised with separation of carbon, and no hydrocarbons are formed. Cobalt, nickel, and the oxidised iron decompose pure carbon monoxide.

II. If the cobalt is charged with thoria, no carbon separates, but hydrocarbons are still formed. Charging with copper has a similar effect, but the activity of this catalyst is rather less. Aluminium oxide and manganous oxide have a deleterious influence on the activity, and potassium carbonate favours the separation of carbon.

R. CUTHILL.

Nature of carbon produced by catalytic decomposition of carbon monoxide with iron. T. WATANABE (Bull. Inst. Phys. Chem. Res., Japan, 1929, 8, 288—292).—The carbon produced by the catalytic decomposition of carbon monoxide proves, from X-ray examination, to be of a graphitic nature. The higher is the temperature of its formation, the more does it approximate to the normal structure of graphite, the smaller is its adsorptive power, and the higher its density.

R. CUTHILL.

Thermal decomposition of methane. I. Decomposition in silica bulbs. G. C. HOLLIDAY and H. C. EXELL (J.C.S., 1929, 1066—1074).—The decomposition of methane on silica at temperatures between 800° and 1200° has been studied. Extremely slow decomposition follows a very rapid initial one, and a practically stable mixture is obtained containing more methane than is present at true equilibrium.

The lower is the initial pressure the greater is the final amount of decomposition. Hydrogen added initially behaves in the same way as that produced in the reaction. It is considered that the retardation is due to preferential adsorption of hydrogen, protecting the surface. Similar results were obtained with porcelain; no retardation was observed with a nickel catalyst. The effect of temperature on the false equilibrium is analogous to that on a true equilibrium. Ethane gave the same false equilibrium mixture as methane. C. W. GIBBY.

Kinetics of the catalytic dehydrogenation of decahydronaphthalene. N. D. ZELINSKI and A. A. BALANDIN (Bull. Acad. Sci. U.S.S.R., 1929, No. 1, 29—52).—The degree of dehydrogenation of decahydronaphthalene was determined by measuring the volume at *N.T.P.* of hydrogen evolved on passing a known volatilised quantity of decahydronaphthalene over a layer of a suitable catalyst heated in an electric furnace. The catalysts used were platinised charcoal (30% Pt), platinum-black (30%) on asbestos, and nickelised asbestos (72% Ni). In the case of platinised charcoal it was found that dehydrogenation is almost complete (99%) at 333° and that it is much more effective than platinum-black on asbestos. The same method was used for investigating the dehydrogenation of *cyclohexane* using platinised charcoal, palladised asbestos, and nickelised asbestos as catalysts and the dehydrogenation of piperidine using platinised asbestos and palladised asbestos as catalyst. By using Arrhenius' relation $k = k_0 e^{-Q/RT}$, values of k_0 and Q for dehydrogenation of decahydronaphthalene are obtained as follows: using platinised charcoal $k_0 = 7.128 \times 10^{10}$, $Q = 18890$ g.-cals., using platinum-black on asbestos $k_0 = 2.202 \times 10^{10}$, $Q = 18990$ g.-cals., and using nickelised asbestos $k_0 = 3.63 \times 10^4$, $Q = 9990$ g.-cals. For the dehydrogenation of *cyclohexane* using platinised charcoal $k_0 = 1.12 \times 10^9$, $Q = 18040$ g.-cals., using palladised asbestos $k_0 = 5.754 \times 10^7$, $Q = 15300$ g.-cals., and using nickelised asbestos $k_0 = 1.143 \times 10^2$, $Q = 9710$ g.-cals. From the data of Zelinski and Pavlov (A., 1923, i, 767) for the use of platinised asbestos, $k_0 = 1.122 \times 10^9$, $Q = 18040$ g.-cals. Dehydrogenation of piperidine using platinised asbestos gives $k_0 = 5.00 \times 10^8$, $Q = 19930$ g.-cals., and by using palladised asbestos $k_0 = 6.026 \times 10^8$, $Q = 16250$ g.-cals. From these results the authors conclude that the energy of activation (Q) as well as the temperature coefficient of the reaction velocity (k_0) are independent of the nature of the catalysed substance and depend only on the catalyst used. By plotting the reciprocal of the temperature against the logarithm of the percentage of hydrogen evolved they obtain, instead of straight lines, lines bent upwards at a temperature of about 270° and explain this as being due to a much larger decomposition of the hydrocarbon with a consequent formation of a thin, invisible layer of carbon on the catalyst, the catalytic activity of which is therefore lowered. Different experiments at temperatures below 270° give in all cases the same volumes of hydrogen, whilst by heating at temperatures above 270° and subsequently determining the volume of hydrogen evolved on dehydrogenation at temperatures below 270° the volume of hydrogen evolved is less.

The authors also investigated the effect of addition of pure naphthalene on the dehydrogenation of decahydronaphthalene and of the addition of benzene on the dehydrogenation of *cyclohexane*. The effect was measured by determining the volume at *N.T.P.* of hydrogen evolved and also by the increase in density and of the refractive index of the different mixtures. They conclude that the effects of addition of one of the products of the reaction are rather complicated and that the effects of adsorption are of the greatest importance. A. FREIMAN.

Topochemical reactions. V. KOHLSCHUTTER (Helv. Chim. Acta, 1929, 12, 512—529).—A lecture, giving a general account of topochemical reactions, i.e., reactions which are localised at a particular point in a reacting system, as distinct from reactions which take place throughout a homogeneous gaseous or liquid phase. The process of crystallisation is dealt with in particular. O. J. WALKER.

Electrolysis of [solutions of electrolytes in] water with alternating current. A. CANAUD (Compt. rend., 1929, 188, 1397—1398).—The volumes of hydrogen evolved during the electrolysis of 0.001*M.* aqueous solutions of electrolytes with electrolytic iron electrodes, by an alternating current of 50 cycles at 110 volts, have been redetermined under more refined conditions (cf. A., 1928, 489). The volume decreases slightly with increase in mobility of the cations for the non-hydrolysable sulphates, and is high and low in the presence of hydrogen and hydroxyl ions, respectively. The electrodes are attacked in the former case, but not in the latter. J. GRANT.

Alkaline electrolytic iron. S. J. LLOYD—See B., 1929, 438.

Electrochemical corrosion of painted or lacquered steel. A. R. EVANS—See B., 1929, 437.

Electrolytic formation of sodium arsenate. O. ESSIN (Z. Elektrochem., 1929, 35, 234—240).—On electrolysis of an alkaline solution of arsenious oxide, containing 80.5 g. of oxide and 100.6 g. of sodium hydroxide per litre, between iron electrodes in a cell without a diaphragm, with a *C.D.* of both anode and cathode equal to 0.03 amp./cm.², about 50% of the oxide underwent oxidation at the anode, whilst about 12% became reduced at the cathode. This was prevented by interposing a diaphragm between the electrodes and using sodium hydroxide solution as catholyte. A solid crust of sodium arsenate appeared around the anode through the anolyte becoming supersaturated when certain concentrations of electrolyte were employed. A series of experiments was performed in a diaphragm cell with an electrolyte containing about 70 g. of arsenious oxide and 87.5 g. of sodium hydroxide per litre, with anode *C.D.* ranging from 0.003 to 0.03 amp./cm.² and with equal current concentrations. The yields of arsenate varied from 0 to 100%, the maximum corresponding with each *C.D.* being indicated by the liberation of oxygen at the anode. H. T. S. BRITTON.

Electrodeposition of chromium from aqueous solutions of chromic acid. J. ROUDNICK (Z. Elektrochem., 1929, 35, 249—254).—Experiments were carried out to ascertain the conditions under

which a constant ratio of trivalent chromium to hexavalent chromium could be obtained during the electrodeposition of chromium from a 20% solution of chromic acid in which an amount of sodium sulphate equal to 0.2% of that of the chromic anhydride was dissolved. Copper was used as cathode, and as anode either lead or platinum was employed. The electrode reactions were investigated partly by analysing the gases evolved. Anodic oxidation of the trivalent chromium produced at the cathode was greater at a lead anode than at a platinum anode. The platinum anode became coated with a greenish-yellow diaphragm, composed of both trivalent and hexavalent chromium oxides, which was not attacked by dilute hydrochloric acid or sodium hydroxide solution. An increase in the deposit of chromium by increasing the trivalent chromium content of the electrolyte could not be obtained.

H. T. S. BRITTON.

Theory of the electrodeposition of chromium from aqueous chromic acid solutions. III. E. MÜLLER and J. STSCHERBAKOV (*Z. Elektrochem.*, 1929, 35, 222—234).—Solutions of pure chromic acid alone and also together with various proportions of sulphate ion, introduced in the form of sodium sulphate, were electrolysed, using either a bright platinum wire as cathode or a copper plate on which electrolytic chromium had been deposited. The equilibrium potential of the cathode was measured before electrolysis, whilst during the passage of the current the potentials assumed with varying currents were found, and they were determined again one minute after the current had been switched off. Despite the strong oxidising action of chromic acid, it appears that when it is absolutely pure it cannot be reduced electrolytically, but may be reduced in the presence of sulphate ions. The results obtained are considered to point to the formation of an invisible, non-conducting film over the cathode. The layer is formed by the reduction of the chromic acid, has fine pores, and contains sulphate-ions. The difference in the behaviour of bright platinum and chromium cathodes is discussed on the basis of the theory.

H. T. S. BRITTON.

Electrolytic copper obtained from electrolytes containing gelatin. Determination of water-content. Hygroscopic and catalytic properties. C. MARIE and P. JACQUET (*J. Chim. phys.*, 1929, 26, 189—194).—Marie and Buffat (*A.*, 1927, 840) found that the deposits formed on the cathode in the electrolysis of copper sulphate solutions containing gelatin were contaminated with gelatin and copper sulphate. The present experiments deal principally with the water contents of rapidly dried deposits; these are proportional to the excess in the weights of the cathodic deposits over those calculated for pure copper from the voltameter readings. They were equal to the sum of the normal water contents of the constituents, gelatin and hydrated copper sulphate comprising the extra amounts. Difficulty was experienced in obtaining concordant results of the water contents by drying the deposits in a current of hydrogen owing to the catalytic action, which was promoted by the exceedingly fine and porous

copper deposits, between the hydrogen and the small amount of oxygen which it contained as impurity.

H. T. S. BRITTON.

Cause of periodic phenomena in electrolysis. E. S. HEDGES (*J.C.S.*, 1929, 1028—1038).—The anodic dissolution of copper in hydrochloric acid has been studied, using a rotating anode. The frequency of the periods is independent of current density over a certain range, and above that falls almost linearly with increasing current density. The frequency is independent of the rate of dissolution of the metal, and directly proportional to the speed of rotation. Evidence has been obtained showing that a critical concentration of chloride ions is necessary before the anode film can be dissolved. The author's theory of anodic polarisation is amplified.

C. W. GIBBY.

Electrosynthesis of hydrocarbons. L. BERMEJO and L. BLAS (*Anal. Fis. Quim.*, 1929, 27, 228—235).—Peroxides are formed at the anode during the electrolysis of sodium benzoate, but no diphenyl is formed. On the other hand, no peroxides can be recognised at the anode during the electrolysis of acetates, and the formation of hydrocarbons does not appear to be a result of anodic oxidation (cf. Fairweather and Walker, *A.*, 1927, 119). A quantitative yield of ethane is obtained by the electrolysis of saturated zinc acetate solution with platinum electrodes at 15° with a current density of 1 amp. per cm.² In the electrolysis of lead acetates it is found that the tetra-acetate is formed only in anhydrous acetic acid solution. Aqueous acid or neutral solutions yield at the anode lead peroxide, formed by decomposition of the tetra-acetate. Alkaline solutions of basic lead acetate yield at the anode lead sesquioxide, formed by oxidation of the basic acetate. No ethane is formed in these cases.

R. K. CALLOW.

Electrolysis of ammonium acetate and ammonium hexoate. F. FICHTER and W. LINDENMAIER (*Helv. Chim. Acta*, 1929, 12, 559—572).—The electrolysis of ammonium acetate in an aqueous solution containing free acetic acid with a platinum anode gives an approximately 90% yield of ethane and a small amount of acetamide, the yield of which can be increased by cooling the anode. It is suggested that the acetamide is formed by the action of free ammonia, resulting from hydrolysis of ammonium carbonate or acetate, on the primarily formed acetyl peroxide: $(\text{CH}_3\cdot\text{CO}_2)_2 + \text{NH}_3 = \text{CH}_3\cdot\text{CO}_2\text{OH} + \text{CH}_3\cdot\text{CO}\cdot\text{NH}_2$. Similarly, hexoamide is obtained by the electrolysis of ammonium hexoate. When an ammoniacal solution of ammonium acetate is electrolysed with a platinum-iridium anode a dark brown resinous condensation product is formed, which is soluble in water and insoluble in alcohol. In addition, methyl alcohol and formaldehyde are found in the solution. With a graphite anode very small amounts of methylamine are formed, probably by the action of free ammonia on the peracetic acid: $\text{CH}_3\cdot\text{CO}_2\text{OH} + \text{NH}_3 = \text{MeNH}_2 + \text{CO}_2 + \text{H}_2\text{O}$. In support of this view it was found that the explosion of acetyl peracid in an atmosphere of ammonia also produces small quantities of methylamine. Carbamide is always formed during the electrolysis of ammonium acetate solutions. This is due to a secondary reaction, the

ammonium carbonate which is first formed being converted into carbamide at the anode.

O. J. WALKER.

Electrolytic reduction of benzoic acid. F. SOMLÓ (Z. Elektrochem., 1929, 35, 264—265).—The supposition of Baur and Müller (A., 1928, 490) that the oil having the empirical formula C_6H_8O was cyclohexenone obtained by the cathodic reduction of benzoic acid is adversely criticised, on the grounds that no such product was prepared by Mettler (A., 1906, i, 851) in the electrolytic reduction of phthalic acid under similar conditions. H. T. S. BRITTON.

Electrolysis in gels. I. P. HAPPEL, R. E. LIESEGANG, and O. MASTBAUM (Kolloid-Z., 1929, 48, 80—82).—When a layer of gelatin containing sodium chloride and litmus is electrolysed between two platinum wires, the region round the cathode becomes coloured blue, whilst the anodic region develops a red colour. While the current is flowing these regions are not circular, diffusion of the hydrogen and hydroxyl ions taking place most readily along the axis joining the two poles. The coloured regions become circular when the current is interrupted.

E. S. HEDGES.

Test of the radiation hypothesis of chemical reaction. W. URE and R. C. TOLMAN (J. Amer. Chem. Soc., 1929, 51, 974—983).—The rate of racemisation of *d*-pinene in the liquid state at temperatures (near the b. p.) at which the thermal reaction is just appreciable is uninfluenced by infra-red radiation up to 3μ , the density of which has been largely increased over that prevailing in a hohlraum at the reacting temperature of the pinene. Mayer's experiments (A., 1928, 140) do not prove the ineffectiveness of radiation up to 13μ .

S. K. TWEEDY.

Light- and dark-reactions involving reversible and consecutive reactions. R. WEGSCHEIDER (Monatsh., 1929, 51, 285—324; cf. A., 1923, ii, 49).—The theory of photochemical processes of the type $M \rightleftharpoons M'$, $M' \rightarrow X$, where M' is an activated intermediate product formed under the influence of light in accordance with the law of photochemical equivalence, and M is the only molecular species which absorbs light, has been investigated mathematically by the methods of the classical kinetic theory. The intensity of the light proves to enter into the equation for the rate of formation of X not as the first power but as a power which gradually diminishes to zero as the intensity increases. It appears probable, however, that the total absorption from the start of the reaction until M is exhausted is independent of the intensity. The number of quanta absorbed per mol. of X formed will vary considerably during the course of the reaction, so that the figures determined over a selected interval are more or less fortuitous. Only if the second reaction is unimolecular and the first reaction irreversible will the quantum number approximate to unity. The concentration of M' does not remain constant during the reaction, as some have assumed in order to account for photochemical reactions the velocity of which is proportional to the square root of the intensity of the light, e.g., the formation of hydrogen bromide from its elements (cf. Skrabal, A., 1927, 188). Nevertheless, the square

root law may be explained if the activation reaction is unimolecular and the reverse reaction bimolecular, provided that the ratio of the square of the concentration of M' to the concentration of M remains sensibly constant during the reaction, although not necessarily equal to the equilibrium constant. With favourable values of the velocity coefficients, this condition is, indeed, fulfilled during a large portion of the reaction period.

R. CUTHILL.

Role of the walls of the vessel in the photochemical reaction $H_2 + Cl_2$. A. TRIFONOV (Z. physikal. Chem., 1929, B, 3, 195—203).—Velocity measurements have been made of the photochemical formation of hydrochloric acid in cylindrical vessels of different dimensions. At low pressures (about 10 mm.) the quantum yield is proportional to the square of the diameter of the vessel. This is ascribed to the cessation of the chain reactions $H_2 + Cl = HCl + H$, $H + Cl_2 = HCl + Cl$ at the walls of the vessel due to adsorption of hydrogen and chlorine atoms. With increase of pressure the formation of hydrochloric acid becomes independent of the dimensions of the vessel.

O. J. WALKER.

Budde effect in bromine and chlorine. G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1929, 51, 1395—1399).—The Budde effect for bromine and chlorine undergoes no change when these halogens are purified and dried (cf. Brown and Chapman, A., 1928, 469). Hydrogen readily reduces pyrex glass at the temperature of the softening point of the latter.

S. K. TWEEDY.

Effect of pressure on the photochemical formation of hydrogen bromide. I. W. JOST and G. JUNG (Z. physikal. Chem., 1929, B, 3, 83—94).—According to a formula worked out on the assumption of triple collisions, the reaction velocity of the photochemical formation of hydrogen bromide should depend on the total pressure. Experiments of Bodenstein and Lütkemeyer (A., 1925, ii, 218), do not indicate this. Experiments and apparatus to test the validity of the equation are described, and it is found that the reaction velocity is inversely proportional to the square root of the total pressure.

A. J. MEE.

Effect of pressure on the photochemical formation of hydrogen bromide. II. W. JOST (Z. physikal. Chem., 1929, B, 3, 95—127).—The photochemical formation of hydrogen bromide is studied especially from the points of view of dependence on pressure, the walls of the vessel, and the wave-length of light used. An apparatus which can be used for this and similar purposes is described. The velocity of formation was measured over a large pressure range and with light of the continuous spectrum and of the wave-length of absorption of bromine. The velocity of formation in the continuous and band spectra is almost the same. The accurate kinetics of the reaction are derived mathematically, equations found in the previous paper (cf. preceding abstract) being developed and extended. The activated bromine atoms formed primarily in the light affect the reaction like inactive atoms and become deactivated before entering into the reaction. The walls exert a characteristic effect on the reaction velocity com-

parable with that observed by Bodenstein, Lehner, and Wagner for carbonyl chloride. The velocity coefficients for the part reactions are calculated.

A. J. MEE.

Radio-chemical synthesis of ammonia. E. PONSAERTS (Bull. Soc. Chim. Belg., 1929, 38, 110—120).—The value of the ratio of the number of molecules of ammonia formed to the number of ion pairs produced when mixtures of nitrogen and hydrogen are exposed to radon rises rapidly as the partial pressure of nitrogen is increased, to a maximum value of 0.32 at 25%. It remains steady until the nitrogen partial pressure reaches 75%, after which it decreases rapidly again. Doubling the total gas pressure or raising the temperature by 20° has no marked influence on the maximum value of the ratio.

Nitrogen under the influence of radon reacts with mercury to form a brown solid which is possibly a mercury nitride.

F. J. WILKINS.

Influence of the variation of intensity [of light] on the velocity of the decomposition of ferric thiocyanate and the bleaching of neocyanine and some other photochemical reactions. A. K. BHATTACHARYA and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 197—205).—From experiments with a 1000-watt gas-filled tungsten lamp it is shown that the velocities of the decomposition of ferric thiocyanate, of the bleaching of neocyanine, and of the reactions between chromic acid and citric and tartaric acids are proportional to the square root of the intensity of the incident radiation, whereas the velocities of the reactions between lactic and chromic acids and between iodine and sodium lactate and tartrate are directly proportional to the intensity of the radiation.

A. R. POWELL.

Reaction of excited mercury with oxygen. Addendum. A. J. LEIPUNSKI and A. W. SAGULIN (Z. physikal. Chem., 1929, B, 3, 215—216).—Tables of time and pressure values omitted from the original paper (this vol., 155) are given.

O. J. WALKER.

Photochemical reaction between dextrose and hydrogen peroxide in acid medium with tungstic acid sol as photocatalyst. I. J. C. GHOSH and J. MUKHERJEE (J. Indian Chem. Soc., 1929, 6, 231—238).—The rate of oxidation of dextrose by hydrogen peroxide in presence of tungstic acid sol (prepared from sodium tungstate and an excess of hydrochloric acid) is almost negligible in the dark, but exposure to radiations in the immediate ultra-violet (330—400 μ) causes a rapid increase. Oxidation of 1 mol. of dextrose corresponds with the decomposition of 1 mol. of hydrogen peroxide. A study of the change shows that the reaction velocity is unimolecular with respect to the peroxide, and the velocity coefficient varies inversely as the square root of the concentration of free hydrochloric acid for the same concentration of tungstic acid, increases slightly with increased dextrose concentration, and with increased sodium tungstate concentration first increases, passes through a maximum, and then diminishes rapidly. The results are discussed assuming that adsorption of hydrogen-ions and peroxide molecules on the tungstic acid sol occurs, with subsequent activation of the peroxide.

H. BURTON.

Effect of short-wave radiation on proteins. M. SPIEGEL-ADOLF (Klin. Woch., 1928, 7, 1592—1596; Chem. Zentr., 1928, ii, 2483).—Seralbumin, serum, other blood proteins, and egg-albumin, when exposed to ultra-violet light, undergo an increase of absorption in a certain wave-length range in the ultra-violet. Addition of alkali or acid increases the effect, but addition of acid to non-irradiated protein produces a shift of the absorption towards the shorter wave-lengths. Preparations irradiated by radium show increased absorption towards the shorter wave-lengths.

A. A. ELDRIDGE.

High-pressure syntheses of carbonates and silicates. W. EITEL and W. SKALIKS (Naturwiss., 1929, 17, 316—319).—A progress report on technique and results in the attempts to prepare naturally occurring minerals of the dolomite type and complex silicate-carbonates. The following double compounds have been prepared: $\text{Na}_2\text{CO}_3, \text{CaCO}_3$, $\text{K}_2\text{CO}_3, \text{CaCO}_3$, $\text{Na}_2\text{CO}_3, \text{MgCO}_3$, $\text{K}_2\text{CO}_3, \text{MgCO}_3$, etc. The last compound can be obtained in a vitreous state. Subsequent heating of the glass to 200—400° causes the appearance of crystals of the trigonal or hexagonal form common to the other double carbonates. Attempts to make dolomite were unsuccessful, magnesium carbonate acting on the sodium calcium carbonate so as to form the sodium magnesium double compound with calcium carbonate set free.

R. A. MORTON.

Oxidation of alkali sulphites to dithionates. R. HAC (Coll. Czech. Chem. Comm., 1929, 1, 259—262).—The normal sulphites of sodium and potassium in aqueous solution are oxidised to dithionates when warmed with lead dioxide, which is reduced to red lead; manganese dioxide does not react.

R. CUTHILL.

Preparation of potassium nitrate. A. L. MEHRING, W. H. ROSS, and A. R. MERZ.—See B., 1929, 430.

Copper oxide in the borax bead. W. D. BANCROFT and R. L. NUGENT (J. Physical Chem., 1929, 33, 729—744).—When copper oxide is used to colour a boric acid glass, some reduction to cuprous oxide occurs. The percentage of cupric oxide in the mass increases with increasing alkalinity and decreases with a rise in temperature. Cupric oxide colours a glass blue, whilst the green colour is due to cuprous oxide. The cuprous copper in borax glasses can be determined by treatment with ferric sulphate solution and by titrating the ferrous iron produced. The coloration of glazes, glass, and certain minerals is discussed.

L. S. THEOBALD.

Berthollet's explosive silver and the formation of silver mirrors. F. BAUM (Chem.-Ztg., 1929, 53, 354—374).—A discussion of the various theories which have been advanced to explain the formation of an explosive compound of silver by the interaction of silver oxide and ammonia and of silver nitrate and ammonia in the presence of an alkali hydroxide.

A. R. POWELL.

Basic phosphate of calcium and of strontium and the adsorption of calcium hydroxide by basic calcium phosphate and by tricalcium phosphate. J. R. LORAH, H. V. TARTAR, and

(Miss) L. WOOD (J. Amer. Chem. Soc., 1929, 51, 1097—1106).—The final product of the hydrolysis of calcium phosphate is $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$. Strontium phosphate hydrolyses similarly. Hydrolysis proceeds more rapidly in alkaline solution. Basic barium phosphate appears not to exist. Isotherms (25°) are given for the adsorption of calcium hydroxide by basic calcium phosphate and by tricalcium phosphate. The curves are of the type given by Freundlich's adsorption isotherm equation. In the case of the basic phosphate either the calcium hydroxide penetrates the phosphate very slowly or else solid solutions are formed. S. K. TWEEDY.

Co-ordination number 5 in hydrates. F. SIERRA (Anal. Fis. Quím., 1929, 27, 220—227).—Zinc sulphate hexahydrate is obtained by evaporating a saturated solution of the heptahydrate at $45\text{--}50^\circ$. In a current of dry air at 50° it yields the monohydrate, from which no further water is lost below 150° . The hexahydrate has d_4^{25} 2.0537, molecular volume 131.1. Hence, the molecular volume of the water is 15 for the first five molecules, and 9.7 for the last. This is in agreement with the constitution $\text{Zn}(\text{H}_2\text{O})_5(\text{SO}_4 \cdot \text{H}_2\text{O})$ for the hexahydrate (Moles, A., 1926, 336). The hexahydrate cannot be prepared by desiccating the heptahydrate at $40\text{--}50^\circ$, since the former already loses water at that temperature. R. K. CALLOW.

Strontium thiosulphate. R. PORTILLO (Anal. Fis. Quím., 1929, 27, 243—250).—Strontium thiosulphate is prepared by mixing cold concentrated solutions of strontium chloride and sodium thiosulphate. It separates from aqueous solution when alcohol is added as the pentahydrate, d_4^{25} 2.202; molecular heat of solution in 800 mols. of water -7.34 g.-cals. at 17° . Water is lost slowly on keeping, and rapidly at 50° , to yield the monohydrate, d_4^{25} 2.916, molecular heat of solution in 800 mols. of water $+2.38$ g.-cals. at 17° . This can be dehydrated only at 180° with decomposition. R. K. CALLOW.

Tetrathionates. I. Barium tetrathionate. R. PORTILLO (Anal. Fis. Quím., 1929, 27, 236—242).—Barium tetrathionate is prepared by triturating a paste of barium thiosulphate and water with iodine and extracting the iodide with alcohol, and is purified by separation from the aqueous solution by addition of alcohol. It forms needles ($+\text{H}_2\text{O}$), d_4^{25} 2.777, molecular heat of solution in 800 mols. of water -7.0 g.-cals. at 17° . The water of crystallisation is removed only at 60° with decomposition. The aqueous solution decomposes when kept or warmed. The aqueous-alcoholic solution is stable. R. K. CALLOW.

[Preparation of] pure carbon monoxide. J. G. THOMPSON.—See B., 1929, 431.

The "Ditte reaction." L. RODRIGUEZ PIRE (Anal. Fis. Quím., 1929, 27, 192—219).—A quantitative study, using pure materials, has been made of the oxidation of carbon monoxide by iodine pentoxide (Ditte, Ann. Chim. Phys., 1870, 13, 318). Carbon monoxide, prepared from pure formic acid and sulphuric acid, is absorbed practically completely by ammoniacal cuprous chloride provided that proper precautions are taken in the preparation of the reagent

and in the manipulation. Iodic acid prepared from sulphuric acid and barium iodate cannot be obtained free from traces of sulphate (cf. Guichard, A., 1909, ii, 477). Pure iodic acid is best prepared by the action of purified fuming nitric acid on purified iodine. It separates in different crystalline forms from concentrated and from dilute nitric acid. Dehydration takes place in two stages: first, rapidly, at 110° , and then slowly to completion at 200° (cf. Baxter and Tilley, A., 1909, ii, 225). The loss of weight of the product in a stream of pure, dry air at $25\text{--}60^\circ$ is of the order of 0.00005% per hr. The completeness of the oxidation of carbon monoxide by iodine pentoxide depends primarily on the rate at which the gas is passed. The amount unchanged was 0.000007% at 100° , 0.000087% at 25° , and 3% at 0° . The reaction being exothermic, the incompleteness of the reaction at 0° is attributed to the formation of a layer of iodine on the pentoxide. The decomposition of pure iodine pentoxide does not take place below 270° . In presence of a little sulphuric acid, unstable, complex products are formed. Preliminary determinations of the at. wt. of iodine from the ratio $\text{I}_2:\text{O}_5$ from the Ditte reaction gave figures of the same order as the accepted value. R. K. CALLOW.

Reactions of the halogens with carbon sulphidoselenide. H. V. A. BRISCOE, J. B. PEEL, and P. L. ROBINSON (J.C.S., 1929, 1048—1050).—Carbon sulphidoselenide reacts with chlorine and bromine at ordinary temperatures, giving respectively thiocarbonyl tetrachloride and selenium tetrachloride, and thiocarbonyl tetrabromide and selenium tetrabromide, or, under certain conditions, the compound $\text{C}_2\text{S}_2\text{SeBr}_6$. C. W. GIBBY.

Rapid concentration of germanium and gallium contained in zinc oxide carrying them. C. JAMES and H. C. FOGG (J. Amer. Chem. Soc., 1929, 51, 1459—1460).—A solution of the zinc oxide in hydrochloric acid is filtered and the hot filtrate rendered basic by the slow addition of some of the original zinc oxide. The mixture is filtered and the residue dissolved in acid, the solution being distilled and treated in the usual manner to obtain the two elements. S. K. TWEEDY.

Zirconium. IV. Precipitation of zirconium by phosphates. R. D. REED and J. R. WITHROW (J. Amer. Chem. Soc., 1929, 51, 1311—1315; cf. A., 1928, 858).—A five-fold excess of ammonium phosphate, phosphoric acid, or microcosmic salt in presence of 0.344*M*-sulphuric acid efficiently removes zirconium from solution as phosphate, but sodium phosphate is inefficient except when used in forty-fold excess. Acid must be present; sulphuric acid is preferable to hydrochloric or nitric acid. Zirconium sulphate yields a precipitate with sodium cobaltinitrite. S. K. TWEEDY.

Preparation and properties of the ammonium phosphates. W. H. ROSS, A. R. MERZ, and K. D. JACOB.—See B., 1929, 431.

Synthesis of arsenic phosphates. S. M. HORSCH and G. BETSIS (Prakt. Acad. Athenes, 1928, 3, 216—219; Chem. Zentr., 1928, ii, 2632).—Arsenic orthophosphate, AsPO_4 , is obtained by the interaction

of arsenious oxide and pyrophosphoric acid at 230—245° and then at 280°; the compound $4\text{AsPO}_4 \cdot 3\text{H}_4\text{P}_2\text{O}_7$ is similarly obtained. A. A. ELDRIDGE.

Antimony phosphate. S. M. HORSCH (Prakt. Acad. Athenes, 1927, 2, 517; Chem. Zentr., 1928, ii, 2632—2633).—When orthophosphoric acid is heated at 330° with powdered antimony, vigorous reaction with liberation of antimony hydride takes place. After heating at 370° and extraction with water, crystals of *antimony phosphate*, $5\text{SbPO}_4 \cdot 2\text{H}_2\text{O}$, are obtained. The compound may also be produced by interaction of antimony chloride with pyrophosphoric acid or ammonium hydrogen phosphate (affording $\text{SbPO}_4 \cdot 2\text{H}_2\text{O}$). A. A. ELDRIDGE.

Salts of bismuth and sodium phosphate. O. CALCAGNO (An. Of. Quim. Prov. Buenos Aires, 1928, 2, 1—22).—The mechanism of the formation of normal bismuth phosphate when a solution of di- or tri-sodium phosphate is added to a bismuth nitrate solution containing up to three molecules of free nitric acid is discussed. The action of sodium acetate in bringing about the precipitation of bismuth "subnitrate" from a nitric acid solution of bismuth nitrate is described: a considerable excess of concentrated sodium acetate solution causes the precipitate to redissolve owing to the formation of the compound $(\text{AcO})_2(\text{BiOH})$, which, however, breaks up immediately into acetic acid and basic bismuth acetate. The reactions between solutions of di- and tri-sodium phosphates and bismuth nitrate in presence of nitric and acetic acids and sodium acetate, and the conditions governing the precipitation of normal and basic bismuth phosphates from glycerol solutions of sodium bismuthite are described. H. F. GILLBE.

Reaction between sulphur dioxide and nitrogen peroxide. W. MANCHOT and H. SCHMID (Ber., 1929, 62, [B], 1261—1263; cf. A., 1927, 32).—Re-examination of the interaction between sulphur dioxide and nitrogen dioxide or trioxide at a high temperature or between sulphur trioxide and nitric oxide confirms the conclusion of Briner (this vol., 40) that the compound $\text{S}_2\text{N}_2\text{O}_5$ is formed; the constitution $2\text{SO}_3 \cdot \text{NO}$ ascribed previously to it is incorrect. A compound with nitrogen content exceeding the ratio S : N = 1 : 1 does not appear to be formed by the action of liquid sulphur dioxide on an excess of liquid nitrogen peroxide. The action of nitrosyl chloride on silver sulphate gives products with the ratio S : N = 1 : 1.94, 1.24, 1.22, and 1.73, but it is difficult to ascertain whether the excess of nitrogen is due to unremoved nitrosyl chloride. H. WREN.

Preparation of selenic acid and its salts. E. R. HUFF and C. R. McCROSKY (J. Amer. Chem. Soc., 1929, 51, 1457—1458).—Selenious acid, or a salt, is reduced with 30% hydrogen peroxide for about 3 hrs. (cf. Meyer and Heider, A., 1915, ii, 630). About 90% oxidation is obtained. S. K. TWEEDY.

Molybdates. V. G. ARANDA (Anal. Fis. Quím., 1929, 27, 165—168).—Preparation of normal barium, strontium, and lead molybdates by fusion of the chloride of the metal with normal sodium molybdate yields on prolonged heating or on employment of a

sufficiently high temperature crystalline molybdates, d 4.9747, 4.6624, and 6.9208, respectively.

H. F. GILLBE.

Molybdates. V. G. ARANDA (Anal. Fis. Quím., 1929, 27, 251; see preceding abstract).—Grey lead molybdate has d_{25}° 6.6933. R. K. CALLOW.

Silicododecatungstic acid. I. Preparation of silicotungstic acid. A. G. SCROGGIE (J. Amer. Chem. Soc., 1929, 51, 1057—1062).—In the isolation of silicotungstic acid (Drechsel, A., 1887, 703) the ether may be replaced by many esters, ketones, and aldehydes. This fact supports Rosenheim's suggestion that the acid is of the oxonium salt type (A., 1918, ii, 77). Further, the hydrochloric acid may be replaced by nitric acid, 20% sodium chloride, and solutions of some lithium salts. The silicotungstic acid is efficiently isolated by means of common salt and ethyl acetate alone. In the analysis of the acid, the sample is preferably ignited at 400—500°, and titrations are best carried out with very dilute alkali solutions, using chlorophenol-red as indicator. The acid prepared by North's directions is impure (J. Amer. Pharm. Assoc., 1924, 13, 1001). Dehydration of the acid is best effected by dehydrating agents under reduced pressure; 4 mols. of water are held tenaciously. The acid reacts with alkali as follows: $4\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 4\text{H}_2\text{O} + 24\text{NaOH} = \text{H}_2\text{SiO}_3 + 12\text{Na}_2\text{WO}_4 + 19\text{H}_2\text{O}$. An improved method of preparing the acid is given. S. K. TWEEDY.

Preparation of oxygen fluoride. P. LEBEAU and A. DAMIENS (Compt. rend., 1929, 188, 1253—1255).—A gas containing 70% of the compound F_2O (A., 1927, 1044) is obtained by the passage of fluorine in fine bubbles at the rate of 1 litre/hr. through a 2% solution of sodium hydroxide 1 cm. deep by means of a platinum tube 2 mm. in diameter. The gas (b. p. -167°) formed according to the equation $2\text{F}_2 + 2\text{NaOH} = 2\text{NaF} + \text{F}_2\text{O} + \text{H}_2\text{O}$ is collected over water, liquefied in liquid air, and fractionated. There is evidence of the formation of an unstable intermediate compound with marked oxidising properties.

J. GRANT.

Oxidations with fluorine. XIII. Action of fluorine on alkaline acetate solutions. F. FICHTER and E. BRUNNER (Helv. Chim. Acta, 1929, 12, 573—576; cf. A., 1926, 925).—When fluorine is passed into a solution of potassium acetate made alkaline with excess of potassium carbonate small quantities of methyl alcohol and traces of formaldehyde are formed. The gaseous products contain ethylene and ethane. With an alkaline solution of potassium propionate ethyl alcohol is obtained. The formation of alcohols from alkaline solutions of fatty acid salts, which is known to take place electrolytically, also occurs by the action of fluorine. O. J. WALKER.

Fluorides of manganese and of cadmium. P. NUKA (Z. anorg. Chem., 1929, 180, 235—240).—Contrary to the statements found in the literature, manganous fluoride is not insoluble in water. This salt can be prepared as a white powder by heating in a stream of carbon dioxide at 290—300° the double fluoride of manganese and ammonium, NH_4MnF_3 , which can be obtained by precipitating a solution of manganous chloride with a large excess of ammonium

fluoride. The solubilities of manganous fluoride at 40, 60, and 100° are 0.66, 0.44, and 0.48 g. per 100 g. of solution. By allowing a solution of manganous fluoride to crystallise at the ordinary temperature a hydrate, $\text{MnF}_2 \cdot 4\text{H}_2\text{O}$, was obtained. The solubility of this substance at 20° is 1.05 g. of the anhydrous salt in 100 g. of solution. A hydrate of the double fluoride of manganese and ammonium could not be obtained. The corresponding double fluorides of potassium and sodium are obtained as white precipitates by adding excess of a saturated solution of the alkali fluoride to a solution of manganous chloride. The solubility of ammonium manganofluoride at 20° is 1.2 g. per 100 g. of solution; the solubilities of the alkali double fluorides are somewhat smaller.

By adding ammonium fluoride to a very concentrated solution of cadmium nitrate at the ordinary temperature a white, glistening precipitate of the hydrate $\text{CdF}_2 \cdot 2\text{H}_2\text{O}$ was obtained. This substance loses water on long keeping, or on heating at 50°. The solubility of the dihydrate could not be determined, and it appears probable that it can exist in several modifications. As in the case of manganous fluoride, solutions of cadmium fluoride become turbid on heating due to precipitation of the anhydrous salt.

O. J. WALKER.

Oxidation of halogen acids by sulphuric acid. K. PROSKOURIAKOFF (J. Physical Chem., 1929, 33, 717—719).—The temperatures and acid concentrations at which iodine or bromine is liberated from potassium iodide or bromide, respectively, and sulphuric acid have been determined. At 100°, 60°, 50°, 45°, and 36° iodine can be detected with concentrations of sulphuric acid which are 25%, 30%, 35%, 40%, and 50%, respectively. With potassium (?) bromide the temperatures are 169°, 100°, 46°, and 36° for the detection of bromine with 60%, 70%, 80%, and 90% sulphuric acid, respectively. At 100°, 70% sulphuric acid is necessary to oxidise hydrobromic acid. Mercuric sulphate does not catalyse the liberation of iodine by sulphuric acid between 36° and 100°.

L. S. THEOBALD.

Polyhalides. I. Chloroiodic acid, $\text{HICl}_4 \cdot 4\text{H}_2\text{O}$. V. CAGLIOTI (Atti R. Accad. Lincei, 1929, [vi], 9, 563—568).—The analogy between iodine and the noble metals is extended by the preparation of a chloroiodic acid, $\text{HICl}_4 \cdot 4\text{H}_2\text{O}$, by passing chlorine through a suspension of iodine in concentrated hydrochloric acid. The reddish-orange solution so obtained crystallises almost completely at 0° into tabular orange-yellow crystals of the free acid, which has a high vapour pressure and an irritating odour. The derivation of such salts as KCl_2I_2 , RbCl_2I_2 , CsCl_2I_2 , and $\text{MgCl}_2 \cdot 2\text{ICl}_3 \cdot 8\text{H}_2\text{O}$ from this acid is confirmed by the possession by such compounds of a common absorption band.

F. G. TRYHORN.

Mechanism of oxidative processes. XVI. Rusting of iron. H. WIELAND and W. FRANKE.—See B., 1929, 476.

Reactions between ferrous compounds and nitric oxide. I. L. CAMBI and A. CLERICI (Atti R. Accad. Lincei, 1929, [vi], 9, 519—523).—Addition of an alkali hydroxide solution to a solution of nitric

oxide in aqueous ferrous sulphate ($\text{NO} : \text{FeSO}_4 = 0.8 : 1$) precipitates a black compound which rapidly becomes red, and causes foaming through evolution of nitrogen and nitrous oxide. Even at 0° the precipitate decomposes with the evolution of nitrous oxide, and after 48 hrs. is completely converted into ferric hydroxide, although kept in an atmosphere of nitric oxide. It is suggested that compounds of ferrous salts with nitric oxide may decompose according to the equations $2[>\text{Fe}-\text{NO}] \rightarrow 2\text{Fe}^{\text{III}} + \text{N}_2\text{O}$, $2[>\text{Fe}-\text{NO}] \rightarrow 2\text{Fe}^{\text{III}} + \frac{1}{2}\text{N}_2 + \text{NO}$, and $2[>\text{Fe}-\text{NO}] \rightarrow \text{Fe}^{\text{II}} + 2\text{NO}$. Decomposition occurs by the first process in alkaline solution and by the second alone in acid media. The third process also occurs to some extent in acid solution.

F. G. TRYHORN.

Action of oxalic acid and malonic acid on tetramminocobaltic complexes and analogous compounds. W. SOHRAMM (Z. anorg. Chem., 1929, 180, 161—183; cf. A., 1927, 33, 542).—A comparison is made of the action of oxalic and malonic acids on cobaltic compounds having a complex cation which contains the group CoA_4 , where A represents an equivalent of ammonia, ethylenediamine, or phenylenediamine. Oxalic acid displaces the groups H_2O , OH , Cl , Br , NO_3 , CO_3 , and $\text{C}_3\text{H}_2\text{O}_4$ more or less readily from the complex forming the corresponding oxalato-compounds, $[\text{CoA}_4\text{C}_2\text{O}_4]\text{X}$, which are stable towards the free mineral acid formed at the same time. The malonato-group in the compound $[\text{Co}(\text{NH}_3)_4\text{C}_3\text{H}_2\text{O}_4]\text{Br}$ is not attacked by oxalic acid, whilst the nitrito-groups in the substance $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$ are displaced only with difficulty. The primary action of malonic acid on the complex salts is in general to displace mineral acid from the anion of the complex salt. This acid is then taken up by the complex cation. With dinitro-tetramminocobaltic nitrate and with oxalato-complex compounds of the type $[\text{CoA}_4\text{C}_2\text{O}_4]\text{X}$ malonic acid does not react as a rule. Malonato-complex compounds, $[\text{CoA}_4\text{C}_3\text{H}_2\text{O}_4]\text{X}$, are obtained only when the displaced mineral acid is removed from the solution hydrolytically, as in the case of the carbonic acid in the carbonato-complex salts, $[\text{CoA}_4\text{CO}_3]\text{X}$. The iodide $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{I}$, however, is exceptional and does not react with malonic acid. The malonate, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]_2\text{C}_3\text{H}_2\text{O}_4$, forms with malonic acid the diaquo-salt, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{C}_3\text{H}_2\text{O}_4)_3$. The corresponding oxalate shows a similar change with oxalic acid. Although the sulphito-group of the compounds of the type $[\text{CoA}_4\text{SO}_3]\text{X}$ can be removed from the solution by hydrolysis, such compounds do not form malonato- and oxalato-complex salts by the action of malonic and oxalic acids, respectively, because the free sulphurous acid reduces the tervalent cobalt. The preparation of the following compounds is also described: malonatotetramminocobaltic chloride and nitrate and the compounds $[\text{Co en}_2\text{C}_2\text{O}_4]\text{Cl} \cdot \text{H}_2\text{O}$, $[\text{Co pn}_2\text{C}_2\text{O}_4]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$, and $[\text{Co pn}_2\text{C}_2\text{O}_4]\text{Cl} \cdot 3\text{H}_2\text{O}$ (en=ethylenediamine, pn=propylenediamine).

O. J. WALKER.

Spinels of the type $\text{M}_2^{\text{II}}\text{M}^{\text{IV}}\text{O}_4$. G. NATTA and L. PASSERINI (Atti R. Accad. Lincei, 1929, [vi], 9, 557—563).—Cobaltous orthostannate, d 6.108, greenish-blue, has been prepared by calcining at 900° the

precipitate produced by the addition of sodium hydroxide solution to a solution of stannic chloride and cobalt chloride. Magnesium orthostannate, white, d 4.378, was prepared analogously. X-Ray examination of these products shows that cobaltous orthostannate crystallises in the cubic system and possesses a unit cell containing 8 mols., of edge $8.605 \pm 0.005 \text{ \AA}$, and of volume $637.16 \times 10^{-24} \text{ c.c.}$, 6.307 . Magnesium orthostannate is isomorphous with the cobalt salt and has a unit cell with edge $8.580 \pm 0.007 \text{ \AA}$, and with volume $631.63 \times 10^{-24} \text{ c.c.}$, $d_{\text{calc.}} 4.864$. Calculation of the structure factor shows that these compounds belong to the type of the spinels, viz., 8f, 16c, 32b (space-group O_i-7). The preparation of these compounds confirms the generalisation that the ionic diameters of the anions and cations determine the possibility of the formation of compounds of the spinel type. F. G. TRYHORN.

Nitrites. I. Nitrites of nickel and cobalt; "pyridinates." L. LE BOUCHER (Anal. Fis. Quím., 1929, 27, 145—156).—Compounds of heavy metal nitrites with pyridine have been prepared by addition of a concentrated solution of sodium nitrite to an aqueous solution of a salt of the metal in presence of pyridine; the precipitate which is formed contains, after washing with a mixture of water and pyridine, variable proportions of the two solvents. In a dry atmosphere containing pyridine vapour anhydrous compounds are produced. The following compounds are described: $\text{Ni}(\text{NO}_2)_2 \cdot 6\text{C}_5\text{H}_5\text{N}$, deep blue, m. p. 57° ; $\text{Ni}(\text{NO}_2)_2 \cdot 4\text{C}_5\text{H}_5\text{N}$, light blue, m. p. 74° ; $\text{Co}(\text{NO}_2)_2 \cdot 6\text{C}_5\text{H}_5\text{N}$, red, m. p. 57° ; $\text{Co}(\text{NO}_2)_2 \cdot 3\text{C}_5\text{H}_5\text{N}$, violet-red, m. p. about 90° ; $\text{Co}(\text{NO}_2)_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, deep red, m. p. about 100° with partial decomposition. The densities are 1.325, 1.400, 1.256, 1.446, and 1.594, respectively. H. F. GILLBE.

Dissociation of hydrated nitrates. J. G. VIANA and E. MOLES (Anal. Fis. Quím., 1929, 27, 157—164).—Systematic dehydration of the hexahydrates of cobalt and nickel indicates that loss of nitric acid sets in only after 4 mols. of water have been lost, i.e., when the composition of the salt corresponds with that of a salt of orthonitric acid. H. F. GILLBE.

Chloropyridino-derivatives of rhodium. Rhodium tripyridinotrichlorides and dipyridinotetrachlorides etc. M. DELEPINE (Bull. Soc. chim., 1929, [iv], 45, 235—249).—Rhodium gives two series of dipyridinotetrachlorides which are similar in properties to the corresponding *cis*- and *trans*-iridium compounds (A., 1923, i, 89, 135, 243, 480, 944; 1927, 433), differing mainly in stability and in reaction velocities. The *cis*-rhodium salts are orange and the *trans*-derivatives red, the *trans*-pyridine salt being sparingly and the *cis*-salt moderately soluble. The silver salts are insoluble, the alkali salts soluble. Sodium rhodium hexachloride when warmed with pyridine is converted into *tripyridinorhodium trichloride*, $(+2\text{CHCl}_3)$, soluble in chloroform; a second isomeride was not obtained. When heated with pyridine at 130° for 8 hrs. the trichloride is converted into *tetrapyridinorhodium dichloride* $(+6\text{H}_2\text{O})$ (cf. Jorgensen, A., 1883, 1058). Cold pyridine in presence of pyridine hydrochloride converts sodium rhodium hexachloride into a mixture of *cis*- and *trans*-*dipyridinorhodium*

tetrachlorides, in which the *cis*-salt preponderates. The isomerides are separated by washing and decantation with cold water, the mother-liquors being concentrated at 40° , and treated with pyridine hydrochloride, or by dissolution in ammonia. The following *cis*-dipyridino-derivatives, $\text{Rh}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4 \cdot \text{M}$, are described: *potassium* $(+\text{H}_2\text{O})$, *pyridinium*, *ammonium*, and *silver*. The pyridine salt on crystallisation from water affords *cis-dipyridinoaquorhodium trichloride* $(+\text{H}_2\text{O}$, lost at $120-125^\circ$), which with silver nitrate gives *silver dipyridinonitratorhodium trichloride*, $[\text{Rh}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_3 \cdot \text{NO}_3] \cdot \text{Ag} \cdot 2\text{H}_2\text{O}$; the corresponding potassium salt undergoes immediate decomposition into dipyridinoaquorhodium trichloride. The following *trans*-dipyridino-derivatives are described: *pyridinium*, *potassium* $(+\text{H}_2\text{O})$, *ammonium* $(+\text{H}_2\text{O})$, and *silver*. Boiling water converts the dipyridine salt into *trans-dipyridinoaquorhodium trichloride* $(+\text{H}_2\text{O}$ lost at 110° ; at 130° $1.5\text{H}_2\text{O}$ is lost, giving the insoluble complex $\text{Rh}_2(\text{H}_2\text{O})(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_6$], yielding *silver trans-dipyridinonitratorhodium trichloride*, with silver nitrate, converted by hydrochloric acid or chlorides into the dipyridinoaquotrichloride. The *trans*-derivative is less stable than the *cis*-isomerides. Cold pyridine (6 mols.) alone converts sodium rhodium hexachloride into a mixture of *cis*- and *trans*-dipyridino-derivatives and a complex rose compound, probably the *trans*-dipyridino-tetrachloride of a tripyridinoaquorhodium trichloride, $[\text{Rh}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4][\text{Rh}(\text{C}_5\text{H}_5\text{N})_3(\text{H}_2\text{O})\text{Cl}_2]$. Ammonia converts the *cis*- or *trans*-dipyridinotetrachlorides or the dipyridinoaquotrichlorides into pentammoniochlororhodium dichloride, pyridine similarly affording the tetrapyridinorhodium dichlorides, the *trans*-isomeride yielding the insoluble intermediate complex compound, $[\text{Rh}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4][\text{Rh}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2]$. Attempts to obtain the quadrivalent rhodium complex, $\text{Rh}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4$, by syn-crystallisation of *cis*-ammonium dipyridinorhodium tetrachloride and *cis*-dipyridinoplatinous dichloride failed. R. BRIGHTMAN.

Some complex ammonio-pyridines of iridium. M. DELEPINE and J. PINEAU (Bull. Soc. chim., 1929, [iv], 45, 228—235).—Potassium pyridinoiridium pentachloride with ammonia (d 0.923) in 15 hrs. at 100° gives traces of the chloropentammine, $[\text{IrCl}(\text{NH}_3)_5]\text{Cl}_2$, and a non-crystalline product, converted through the *mercurichloride*, $\text{Cl}_2[\text{IrCl}(\text{NH}_3)_4\text{C}_5\text{H}_5\text{N}] \cdot 2\text{HgCl}_2$, into *chlorotetramminopyridinoiridium chloride*, $\text{Cl}_2[\text{IrCl}(\text{NH}_3)_4\text{C}_5\text{H}_5\text{N}] \cdot 2\text{H}_2\text{O}$ (*picrate*, *dichromate*, and *sulphate*). Potassium mercuri-iodide also affords a precipitate. *trans*-Dipyridinoiridium tetrachloride similarly affords the double salt, $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4]_2[\text{IrCl}(\text{NH}_3)_4\text{C}_5\text{H}_5\text{N}]$, and pyridinoiridium pentachloride the double salt, $[\text{Ir}(\text{C}_5\text{H}_5\text{N})\text{Cl}_5][\text{IrCl}(\text{NH}_3)_4\text{C}_5\text{H}_5\text{N}]$. *trans*-Sodium dipyridinoiridium tetrachloride and ammonia in 30 hrs. afford the complex double salt (A), $[\text{Ir}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4]_3[\text{Ir}(\text{NH}_3)_3\text{H}_2\text{O}(\text{C}_5\text{H}_5\text{N})_2] \cdot 6\text{H}_2\text{O}$, decomposed by pyridine hydrochloride in boiling solution into pyridine dipyridinoiridium tetrachloride and *dipyridinoaquotriamminoiridium trichloride* $(+3\text{H}_2\text{O})$, which gives precipitates with potassium ferriocyanide, sodium pyrophosphate, mercuric salts, picric acid, tannin, potassium bromide and iodide, and is con-

verted at 115° in 3 hrs. into dipyridinotriamminochloroiridium dichloride. When heated with 12 times its weight of ammonia (d 0.92) at 100° for 36 hrs. the complex double salt (A) affords 80% of chlorodipyridinotriamminoiridium dichloride ($-2\text{H}_2\text{O}$), which with sodium bromide and iodide affords the corresponding *halides*, $\text{X}_2[\text{IrCl}(\text{NH}_3)_3(\text{C}_5\text{H}_5\text{N})_2]\cdot\text{H}_2\text{O}$. The *sulphate*, $\text{SO}_4[\text{IrCl}(\text{NH}_3)_3(\text{C}_5\text{H}_5\text{N})_2]\cdot 3\text{H}_2\text{O}$, is obtained by double decomposition. R. BRIGHTMAN.

Dissolution of metals and alloys. M. CENTNERSZWER (Z. physikal. Chem., 1929, A, 141, 297—320).—A summary of the general results of work carried out in the author's laboratory during the past 10 years. F. L. USHER.

Quantitative emission spectrum analysis. W. GERLACH and E. SCHWEITZER (Z. anal. Chem., 1929, 77, 213—217).—Polemical against Thurnwald (this vol., 530). The presence of potassium, nickel, or iron in the solution interferes with the accurate comparison of the zinc and silver lines, and absorption of the solution in carbon electrodes leads to variations in the concentration of the dissolved salts.

A. R. POWELL.

Use of 0.1*N*-hydrochloric acid for standardising electrometric p_{H} measurements. N. F. MACLAGAN (Biochem. J., 1929, 23, 309—318).—The advantages of using hydrochloric acid are pointed out. Some of the factors influencing the *P.D.* at the liquid junction 0.1*N*-HCl|sat. KCl have been investigated and a simple method of forming the junction is described which is reproducible to ± 0.05 millivolts or ± 0.001 p_{H} . A new type of flowing junction for these solutions is also described. The degree of reproducibility of junctions formed with agar bridges and with ground glass surfaces is considered. Observations on the time change at the junction 0.1*N*-HCl|sat. KCl, x *N*-HCl are presented. Impurities of a certain sample of potassium hydrogen phthalate which could not be removed by recrystallisation affected the p_{H} of the 0.05*N*-solution.

S. S. ZILVA.

Use of cresol-red in acid solutions. F. R. McCURMB and W. R. KENNY (J. Amer. Chem. Soc., 1929, 51, 1458—1459).—Attention is directed to the use of cresol-red as an indicator in acid solutions. Some applications and advantages are given.

S. K. TWEEDY.

Accuracy of titrations, critical concentration of the burette liquid, and sensitivity of indicators. H. RUOSS (Z. anal. Chem., 1929, 77, 175—185).—Mathematical expressions are deduced to show the magnitude of the errors involved in acidimetric titrations by varying the concentration of the acid and to express the sensitivity of various indicators under different conditions. A. R. POWELL.

Change in colour of indicators at boundary surfaces. A. THIEL (Z. Elektrochem., 1929, 35, 266—267).—The variations in the colour of indicators at phase boundaries, observed by Deutsch (A., 1928, 1183), such that lower p_{H} values are indicated, are discussed particularly in regard to those indicators that owe their colour-changes to basic functions, *e.g.*, tropæolin-OO, thymol-blue. H. T. S. BRITTON.

Determination and control of acidity in the crystallisation of ammonium sulphate. J. A. CRANSTON and (Miss) J. STOCKDALE.—See B., 1929, 430.

Determination of chloride in bromides. R. K. MCALPINE (J. Amer. Chem. Soc., 1929, 51, 1065—1073).—A method previously described (Berg. A., 1926, 1017) is modified so that potassium permanganate may be used in place of bromate. The bromide is converted into bromoacetone and the chloride is then determined gravimetrically as silver chloride.

S. K. TWEEDY.

Iodo-oxidimetric determinations. A. SCHWICKER (Z. anal. Chem., 1929, 77, 161—169).—Acid iodate solutions may be titrated directly with potassium hydrogen sulphite solutions stabilised with 5—10% of alcohol. This reaction may be utilised for several indirect titrations, *e.g.*, the determination of hydrazine, ferrocyanide, thiocyanate, arsenic trioxide, and antimony trioxide. In every case an excess of iodate solution is added to the acidified solution, containing tartaric acid in the case of antimony, and, after 5—10 min., the liberated iodine and excess of iodate are titrated with hydrogen sulphite.

A. R. POWELL.

Determination of small amounts of dissolved oxygen [in water]. F. R. McCURMB and W. R. KENNY.—See B., 1929, 456.

Determination of small quantities of hydrogen sulphide in gases. H. BACH.—See B., 1929, 422.

Volumetric determination of sulphate ion. D. KOSZEGI (Z. anal. Chem., 1929, 77, 203—209).—The sulphate solution is treated at 80—100° with 0.1*N*-barium chloride solution in slight excess. 5 c.c. of sodium acetate are added followed by sufficient standard potassium dichromate to precipitate excess of barium used, and finally the excess dichromate is determined iodometrically in filtered solution. If iron or alumina is present solution is made ammoniacal before addition of barium chloride.

A. R. POWELL.

Electrolytic analysis of nitrates. M. A. RABINOVITSCH and A. S. FOKIN (J. Russ. Phys. Chem. Soc., 1929, 61, 315—318).—Nitrates are reduced in an alkaline solution by hydrogen to ammonia. The hydrogen is prepared by the decomposition of sodium amalgam by an alkali solution in the presence of tungsten, vanadium sulphate, or chloroplatinic acid as catalysts. The amalgam is prepared continuously in the course of the analysis.

A. FREIMAN.

Colorimetric determination of phosphoric acid. C. BORDEIANU (Ann. sci. Univ. Jassy, 1929, 15, 372—379).—The method previously described (B., 1927, 422) can be applied to urine, glycerophosphates, and glucose syrup, and to hypophosphites after oxidation with nitric acid. Free phosphoric acid in the presence of glycerophosphates can be determined, since the observation of Bally and Gaume that nitric acid does not decompose glycerophosphates is confirmed. The total phosphate in glycerophosphates is determined after warming for 1 hr. with a mixture of nitric and sulphuric acids. Glucose syrup is purified and decolorised by filtration

through charcoal which may, if very active, lower the phosphate content somewhat. The errors introduced when the difference in concentration between the standard and the solution to be analysed is appreciable may be marked but do not reach the values found by Defay with cystine (A., 1926, 1115). Results obtained by the new method are compared with those obtained by established methods.

L. S. THEOBALD.

Quantitative analysis of phosphoric acid. IV. Gravimetric and volumetric determination as ammonium phosphomolybdate. M. ISHIBASHI (Mem. Coll. Sci. Kyoto, 1929, 12, 135—153).—To determine the conditions under which phosphoric acid can be accurately determined gravimetrically as ammonium phosphomolybdate the influence of temperature, concentration of nitric acid, amount of ammonium nitrate and molybdate, and quantity of phosphate taken was examined. Results accurate to $\pm 0.05\%$ are obtained by precipitating ammonium phosphomolybdate from dilute nitric acid solution, containing a concentration of ammonium nitrate between 0.6 and 2.5*N*, at 40—65°. The precipitate is washed with 2% nitric acid, heated gently for 10 min., then at 250—300° for 0.5 hr., and cooled over freshly-fused calcium chloride. The P_2O_5 is determined from the weight of phosphomolybdate by using the theoretical factor 0.0378. The molar ratio of ammonium molybdate to ammonium phosphate should be between 1.5 and 3.0, and 0.01—0.13 g. of ammonium phosphate should be taken for analysis. The influence of a number of substances on the precipitation was studied. Hydrochloric, sulphuric, tartaric, oxalic, and citric acids should be excluded. Pemberton's method for the volumetric determination of phosphoric acid precipitated as ammonium phosphomolybdate was found to give accurate results when the factor 0.0003030 was substituted for the theoretical value 0.0003089.

C. J. SMITHELLS.

Analytical application of complex-chemical and induced reactions. F. FEIGL and P. KRUMHOLZ (Ber., 1929, 62, [B], 1138—1142; cf. A., 1928, 1107).—Silicic acid is detected by mixing 1 c.c. of the solution in dilute nitric or hydrochloric acid (the acidity must not exceed 0.2—0.5*N*) heating to incipient ebullition with 2 drops of a solution of ammonium molybdate in nitric acid, cooling, treating with 1—2 drops of a 0.25% solution of benzidine or benzidine hydrochloride in 10% acetic acid, and then with an equal volume of saturated sodium acetate. A blue precipitate or coloration is produced which, with very minute amounts, is best observed after extraction with amyl alcohol. The extreme sensitiveness of the reaction (1 in 8×10^6) requires the use of Jena glass vessels and blank tests. In the presence of phosphoric the preliminary removal of the insoluble phosphomolybdate is necessary. The reaction is adapted for the detection of fluorine by warming the substance under investigation with quartz sand and concentrated sulphuric acid in a porcelain crucible covered with a watch glass on which hangs a drop of water; the is tested for silica as described above. The smallest amount of fluorine so detected is 0.005 mg.

The reduction of lead salts to metallic lead by alkali

stannite solution is enormously accelerated by the presence of traces of bismuth, the precipitated bismuth obviously acting as nucleus for the lead, otherwise slowly separated. A method which permits the detection of 0.02 μ g. of bismuth is given. Reduction of antimony salts to metallic antimony is also accelerated by the presence of bismuth, as, to a smaller extent, is that of copper hydroxide. Detection of bismuth in the presence of copper is effected by treating the acid solution with 25% sodium hydroxide until copper hydroxide is precipitated, dissolution of the precipitate with 5% potassium cyanide, and addition of 1 drop of 3% lead acetate and 3 c.c. of stannite solution; 2 parts of bismuth in the presence of 50,000 parts of copper are detected in 3 min.

H. WREN.

Uranyl zinc acetate as reagent for the detection and determination of sodium. I. M. KOLTHOFF (Chem. Weekblad, 1929, 26, 294—298; cf. Barber and Kolthoff, A., 1928, 859).—The reagent is specific, and very delicate; 0.03 mg. of sodium in 1 c.c. of solution gives a perceptible precipitate. Potassium salts do not interfere unless present in great excess, but lithium must first be removed as the fluoride by addition of ammoniacal ammonium fluoride solution and alcohol. The use of the reagent for the detection and determination of traces of sodium is briefly reviewed.

S. I. LEVY.

Analysis of fluorspar. G. E. F. LUNDELL and J. T. HOFFMAN.—See B., 1929, 471.

Sensitive test for magnesium. W. L. RUIGH (J. Amer. Chem. Soc., 1929, 51, 1456—1457).—One drop of a 0.5% solution of *op*-dihydroxyazo-*p*-nitrobenzene in 1% sodium hydroxide solution is added to the magnesium solution rendered slightly acid with hydrochloric acid and excess of dilute sodium hydroxide is then added. A sky-blue magnesium lake is formed. Nickel and cobalt behave similarly; excess of ammonium salts must be absent (cf. Suitsu and Okuma, J. Soc. Chem. Ind. Japan, 1926, 29, 132).

S. K. TWEEDY.

Ceric sulphate in volumetric analysis. VI. Oxidation of hydrogen peroxide by ceric sulphate. Indirect determination of lead. N. H. FURMAN and J. H. WALLACE, jun. (J. Amer. Chem. Soc., 1929, 51, 1449—1453; cf. this vol., 669).—The titration of ceric sulphate with hydrogen peroxide, and *vice versa*, is accurate in solutions containing moderate amounts (e.g., 2—5*N*) of sulphuric or nitric acid. The forward reaction is also accurate in solutions containing hydrochloric acid up to 5*N*. Lead dioxide may thus be indirectly determined by utilising the fact that hydrogen peroxide reacts with the dioxide in presence of nitric acid (Schlossberg, A., 1903, ii, 184).

S. K. TWEEDY.

Determination of thallous salts using potassium permanganate in a hydrochloric acid medium. A. JILEK and J. LUKAS (Chem. Listy, 1929, 23, 155—162).—Titration at 75° following the above procedure does not give accurate results unless 2 g. of potassium chloride are added per 150 c.c. of reaction mixture containing 0.2 g. of thallium; the acidity of such mixtures may be doubled without affecting the result. The function of potassium

chloride is to maintain sparingly soluble thallium chloride in solution; the chlorides of lithium, rubidium, and caesium, but not of sodium and ammonium, act equally well in this respect.

R. TRUSZKOWSKI.

Iodometry. III. Copper as a standard in iodometry. S. POPOV, (Miss) M. JONES, C. TUCKER, and W. W. BECKER (*J. Amer. Chem. Soc.*, 1929, 51, 1299—1306; cf. A., 1925, ii, 1093).—The reaction between copper sulphate and potassium iodide solutions was investigated. In neutral solutions, variation of the iodide concentration between 4 and 12% has no appreciable influence on the amount of copper sulphate decomposed, although cuprous iodide may absorb iodine to a slight extent (Bray and MacKay, A., 1910, ii, 996). When 4% potassium iodide solution is used, the order of mixing the reactants, keeping for 10 min., and the presence of cuprous iodide are without influence. The amount of iodine liberated is always raised with increased hydrogen-ion concentration; the effect is possibly due to atmospheric oxidation of the cuprous ions. An improved electrolytic method of determining copper is described; solvent action on the platinum anode may be avoided by having 0.3 c.c. of sulphuric acid or 0.15 c.c. of this acid and 0.15 c.c. of nitric acid in 200 c.c. of electrolyte (0.1*N*-copper sulphate). Specific directions are given for carrying out the hæmoxylol test for copper (cf. Mendel and Bradley, A., 1905, ii, 737). The results indicate that, provided the salt and acid concentrations are kept very small, pure copper or copper sulphate solution may be used as a standard in iodometry. S. K. TWEEDY.

Iodometry. IV. Potassium permanganate as a standard in iodometry. S. POPOV and A. H. KUNZ (*J. Amer. Chem. Soc.*, 1929, 51, 1307—1311; cf. preceding abstract).—In the thiosulphate-iodine titration there is no appreciable oxidation of the iodide ion by air in a solution containing 6% of potassium iodide and 0.1*M*-sulphuric acid, even after 10 min., providing the titrations are performed in the dark; the presence of manganous and potassium sulphates, and the rate and mode of addition of the permanganate also are without influence. The potassium iodide used must be free from alkali. The slight difference in the permanganate-thiosulphate ratio produced by using potassium iodide at different concentrations (2% and 6%) is attributable to "loss of oxygen" by the permanganate during the reduction process. For standardisation purposes, 6% potassium iodide must be used; the acid concentration may be 0.1*M*-sulphuric acid.

S. K. TWEEDY.

Quantitative spectral analysis of solutions. F. GROMANN (*Z. anorg. Chem.*, 1929, 180, 257—274).—The amount of mercury present in small quantities of mercuric sulphide is determined by dissolving the sulphide in aqua regia, placing the solution in the lower of two electrodes across which a spark is formed, and examining the intensity of photographic blackening by certain persistent lines of the mercury spectrum. The following general precautions must be observed in quantitative spectral analysis: The electrodes must not get worn; the upper electrode

must be kept dry; spirting of the solution in the lower electrode must be avoided and only a small portion of it allowed to evaporate; the surface of the solution must be kept at the same level in comparative measurements. For the lower electrode containing the aqua regia solution an alloy of 60% Pb and 40% Cd was used, the upper electrode being made of nickel. A special form of spark gap and exciter is described. The sensitivity of the method is increased by the addition of cupric sulphide to the mercuric sulphide. By comparison of the intensity of blackening by the mercury resonance line 2536.52 and the copper line 2618.4 it is possible to estimate approximately the concentration of a solution containing mercury without using comparison solutions. The smallest concentration that can be determined is 0.0004% mercury. The concentrations of the solutions examined were 0.01, 0.02, 0.04, 0.1, 0.2, 0.4% mercury and under the best conditions the accuracy is within $\pm 10\%$. O. J. WALKER.

Determination of very small quantities of mercury. A. STOCK and W. ZIMMERMAN (*Z. angew. Chem.*, 1929, 42, 429—430; cf. A., 1928, 726; Thilenius and Winzer, this vol., 531).—The effect of carbamide in the colorimetric determination by means of diphenylcarbazone is apparent if the acidity of the test solution is kept low. S. I. LEVY.

Mercury poisoning and its chemical detection. FRIEDERICH and BUHR (*Süddeut. Apoth.-Ztg.*, 1928, 68, 702—703; *Chem. Zentr.*, 1928, ii, 2739).—Chlorine is passed through urine (1000 c.c.) which is simultaneously evaporated (to 150 c.c.). The excess of chlorine is removed with carbon dioxide, the cold liquid is filtered, treated with a few drops of copper sulphate solution, slightly acidified with hydrochloric acid, and treated with hydrogen sulphide. The centrifuged precipitate, suspended in water, is redissolved with the aid of chlorine, carbon dioxide is passed, and the sulphide is reprecipitated. After redissolution and removal of chlorine, ammonium oxalate is added until the copper oxalate redissolves, the mercury is deposited on a copper wire, and identified as iodide. It is determined electrolytically in a solution containing ammonium oxalate and oxalic acid. A. A. ELDRIDGE.

Molybdomanganimetry of iron salts. Its mechanism and limitations. P. FLEURY and J. MARQUE (*J. Pharm. Chim.*, 1929, [viii], 9, 479—488; cf. Fontes and Thivolle, A., 1926, 1282; 1923, ii, 583).—The reaction of ferrous salts with the phosphomolybdate reagent is reversible, the blue colour being reduced by ferric salts. The equilibrium is only slowly established, and for the determination of small amounts of ferrous salts in presence of ferric salts the method is unsatisfactory. In the determination of ferrous salts large errors are produced by the presence of hydrochloric acids, but these can be corrected by the previous addition of manganese sulphate. The presence of either sulphuric acid or sodium sulphate considerably weakens the intensity of the blue colour. The reduction of ferric salts by copper in presence of either small quantities of hydrochloric acid or organic material containing phosphorus such as blood-serum or glycerophosphates, gives rise to large errors in the

titration. Addition of manganese sulphate does not correct the errors if the hydrochloric acid is present before the reduction. These difficulties are not apparent if zinc be substituted for copper.

E. H. SHARPLES.

Titration of potassium ferrocyanide, using diphenylamine as internal indicator. I. M. KOLTHOFF (Chem. Weekblad, 1929, 26, 298—301; cf. Moll, this vol., 165; Cone and Cady, A., 1927, 1046).—Potassium ferrocyanide may be very accurately titrated by means of zinc sulphate solution, which has been standardised against a known ferrocyanide solution. It is added to the ferrocyanide solution to be titrated, in presence of sulphuric acid, potassium ferricyanide, and the indicator. Sulphides, thiosulphates, and thiocyanates present in the ferrocyanide interfere, and are first oxidised by addition of sodium hydroxide and hypobromite; excess of the latter is reduced by addition of arsenious acid.

S. I. LEVY.

Qualitative analysis of a mixture of ferrocyanide, ferricyanide, and thiocyanate. P. C. BANERJEE (J. Indian Chem. Soc., 1929, 6, 259—262).—The cold neutral solution of the three acids is treated with a solution of cerous nitrate which precipitates ferrocyanide, the filtrate is treated with nickel nitrate to remove ferricyanide, and finally thiocyanate is detected by addition of ferric chloride. The cerous nitrate precipitate is treated with sodium hydroxide and ferrocyanide confirmed by adding ferric chloride. Ferricyanide is confirmed by treating the nickel precipitate similarly and adding ferrous chloride.

A. R. POWELL.

Rapid method of detecting elements of groups II—IV by means of organic reagents. P. AGOSTINI (Annali Chim. Appl., 1929, 19, 164—173).—The method described serves for the detection of all metals giving chlorides soluble in hydrochloric acid with the exception of the alkali and alkaline-earth metals and magnesium.

T. H. POPE.

Analysis of chrome ores. T. R. CUNNINGHAM and T. R. MCNEILL.—See B., 1929, 478.

Rapid method for dissolving high-chromium steels for determination of sulphur. B. S. EVANS.—See B., 1929, 476.

Gravimetric determination of tungsten in presence of vanadium. A. JÍLEK and J. LUKAS (Coll. Czech. Chem. Comm., 1929, 1, 263—274).—To determine tungstate in presence of vanadate, 1 c.c. of concentrated hydrochloric acid is added to 100 c.c. of the neutral solution, and the vanadium reduced to the quadrivalent state with hydroxylamine hydrochloride at the b. p., and then after addition of a 2% solution of arsenic acid the tungsten is precipitated at the b. p. as quinine arsenotungstate by means of a 2% solution of quinine hydrochloride. The precipitate is then ignited to give tungsten trioxide, and weighed. The organic matter in the filtrate is destroyed by treatment with sulphuric acid and cupric oxide, and after reduction of the arsenic acid with sulphur dioxide copper and arsenic are separated as sulphides. By treatment of the alkaline solution with hydrogen peroxide, the vanadium is re-oxidised

to vanadate, then precipitated with mercurous nitrate and weighed as vanadic oxide after ignition.

R. CUTHILL.

Colorimetric micro-determination of uranium salts. M. TISSIER and H. BENARD (Compt. rend. Soc. Biol., 1928, 99, 1144—1146; Chem. Zentr., 1928, ii, 2582).—The reaction with potassium ferrocyanide is employed.

A. A. ELDRIDGE.

Volumetric determination of vanadium by means of potassium iodate. E. H. SWIFT and R. W. HOEPFEL (J. Amer. Chem. Soc., 1929, 51, 1366—1371).—To 25 c.c. of vanadate solution in an atmosphere of carbon dioxide hydrochloric acid is added so that, after the subsequent addition of a slight excess of standard potassium iodide solution, the mixture contains 6 to 8M-hydrochloric acid: $2\text{H}_3\text{VO}_4 + 2\text{HI} + 4\text{HCl} = 2\text{VOCl}_2 + \text{I}_2 + 6\text{H}_2\text{O}$. Five c.c. of carbon tetrachloride are then added and the whole is titrated with standard potassium iodate solution: $2\text{I}_2 + \text{HIO}_3 + 5\text{HCl} = 5\text{ICl} + 3\text{H}_2\text{O}$; $2\text{HI} + \text{HIO}_3 + 3\text{HCl} = 3\text{ICl} + 3\text{H}_2\text{O}$. Hydrochloric acid must be added during the titration so that the solution is always 6M in acid, for at this concentration quadrivalent vanadium is not oxidised by the iodine monochloride formed in the titration. Phosphate, arsenate, or ferric iron may be present. Tungstic acid may also be present if it is kept in solution by phosphoric acid.

S. K. TWEEDY.

Simple viscosimeter. R. A. VAN LINGE (Chem. Weekblad, 1929, 26, 301).—A pipette having a capillary tube in place of the lower limb is provided at the upper end with a three-way tap, which permits of easy filling to a constant level; a half turn allows the measured quantity to flow through the capillary.

S. I. LEVY.

Preparation of a stabilised electrode and its use in the determination of halogens. N. JOASSART and E. LECLERC (Bull. Soc. chim. Belg., 1929, 38, 121—131).—A method for the determination of halogens in acid solution using an electrode in a medium containing gelatin is described.

F. J. WILKINS.

Apparatus for extraction with filtration. A. KULMAN (Oil Fat Ind. Russia, 1928, No. 8, 7—11; Chem. Zentr., 1929, i, 110).—An apparatus for the determination of loss of weight on extraction is described.

A. A. ELDRIDGE.

Bending glass tubing. R. N. ALLEN (Phillipine J. Sci., 1929, 38, 299).—Asbestos fibre is tamped tightly into the bore of the tube where the desired bend is to be made; the glass may be then heated and bent without any collapse occurring. The fibre may be removed when cool with a piece of wire, as it does not fuse into the glass.

B. W. ANDERSON.

Modern chemical balances. L. RAMBERG (Svensk Kem. Tidskr., 1929, 41, 106—119).—A discussion of the relative advantages and disadvantages of the various types of balances employed in chemical work. With regard to the usual form of micro-balance, it is pointed out that a serious error, which may amount to 0.005 or even 0.01 mgm., may easily arise through the practical impossibility of ensuring that the rider always takes up exactly the same

position in any notch on the graduated rider arm (cf. A., 1925, ii, 319). H. F. HARWOOD.

Gas analysis [apparatus]. J. T. DONNELLY, C. H. FOOT, and J. REILLY.—See B., 1929, 421.

Modified Hempel gas burette. G. H. W. LUCAS.—See B., 1929, 457.

Crucible tongs for analytical work. L. RAMBERG (Svensk Kem. Tidskr., 1929, 41, 78—79).—An improved form of crucible tongs is described. The lower ends are formed from nickel wire, 2 mm. thick, shaped so as to permit of crucibles of different sizes being encircled and lifted. Owing to the special construction of the nickel ends, even the thinnest and smallest platinum crucibles can be handled without risk of deformation, whilst the tongs can also be employed for lifting dishes up to 6 cm. diameter.

H. F. HARWOOD.

Ebullioscopic and tonometric determinations. W. SWIENTOSLAWSKI (Rocz. Chem., 1929, 9, 266—308).—A description of various ebullioscopic apparatus designed by the author, and of the technique of their application to a number of problems.

R. TRUSZKOWSKI.

Barium sulphate as an indicator of the degree of hydration of sulphuric acid in drying apparatus. G. BOEHM (Chem.-Ztg., 1929, 53, 323).—Sulphuric acid containing 1% of barium sulphate is clear until diluted to about 93% concentration; between 93% and 84%, needle crystals of the compound $\text{BaSO}_4 \cdot 2\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ separate freely; on further dilution, the needle crystals change to the fine crystals of barium sulphate. This change is easily detected, and may be used as an indication that the acid is too dilute for further effective drying. S. I. LEVY.

Two laboratory rotating furnaces. F. HEINRICH (Chem. Fabr., 1929, 173—174).—The simpler model is intended for rotation in a gas-fired muffle furnace, the larger for direct heating by gas.

S. I. LEVY.

Micro-determination of vapour density. J. B. NIEDERL (Z. anal. Chem., 1929, 77, 169—174).—An apparatus for the determination of the vapour density of liquids of low b. p. comprises a cylindrical container (50 c.c.) filled with mercury and provided with a capillary tube reaching to the bottom inside and bent outside in the form of an inverted U leading into a collecting cylinder in which the displaced mercury is collected. After heating the apparatus to 10° above the b. p. of the liquid the vapour density of which is required, the weight of mercury displaced by expansion and collected in the cylinder is determined. The apparatus is cooled and again filled with mercury, about 5 mg. of liquid are introduced in a fine capillary tube into the middle of the mercury in the container, and the heating is repeated. The additional weight of mercury collected is a measure of the volume of the vapour of the liquid tested.

A. R. POWELL.

Electrically heated thermostat. P. VAN CAMPEN (Z. Elektrochem., 1929, 35, 265—266).—Difficulty often arises in the ordinary electrical controlling device of the heating of a thermostat through the formation of sparks between the mercury surface and the platinum wire in the regulator. A method is

described in which very small currents, 10^{-4} to 10^{-5} amps., are allowed to pass through the regulator and then on to the grid of an amplifying thermionic valve. The amplified current activates an electrical relay. The temperature can be regulated to $\pm 0.002^\circ$.

H. T. S. BRITTON.

Pulfrich step-photometer as a turbidity measurer. S. GARTNER (Kolloid-Z., 1929, 48, 10—15).—A modification of the Pulfrich step-photometer, which enables the instrument to be used as a nephelometer, is described. Some experimental results, obtained with the modified instrument, are given.

E. S. HEDGES.

Apparatus for continuous automatic measurement of the alveolar carbon dioxide. REGELBERGER (Z. ges. exp. Med., 1928, 61, 747—756; Chem. Zentr., 1928, ii, 2671).

Determination of available oxygen by the Bunsen method. T. W. PARKER and P. L. ROBINSON (J.C.S., 1929, 1106—1108).—The tendency of potassium iodide solution to be sucked back, in the usual procedure of Bunsen's method, and the necessity of transferring the solution to another vessel for titration, can be obviated. A detachable absorption flask contains a wide tube, ground in and filled with glass beads, serving as a reservoir for potassium iodide solution if the pressure rises, and as an inlet for air if it falls.

C. W. GIBBY.

Improved calcium chloride tube. D. V. N. HARDY (J.C.S., 1929, 1108).—A U-tube is fitted with two stopcocks, by rotating which access of air can be prevented. The interior of one of them is shaped so as to act as a water trap.

C. W. GIBBY.

Solid and liquid states of helium. W. H. KEESOM (Natuurwetensch. Tijds., 1929, 11, 65—79).—An account is given of the work of Kamerlingh Onnes on the liquefaction of helium, and of the apparatus employed to attain the lowest recorded temperature of 0.8 — 0.9° Abs. By increasing the pressure over liquid helium at very low temperatures, solid helium has been obtained, and the pressure-temperature curve for solid helium mapped, from 4.2° Abs. at 126 atm. to 1.2° Abs. at 25 atm. The curve bends sharply at the lower end, becoming nearly parallel with the T -axis, so that it does not cut the vapour-pressure curve for liquid helium; it is therefore impossible to solidify helium by cooling alone, and solid helium below the critical temperature must always melt before vaporising. The experiments were carried out first in metal containers, later in glass vessels, but although the presence of solid helium was conclusively proved by the arrest of a magnetically controlled stirrer, no difference in appearance or refractive index and no line of demarcation between solid and liquid could be observed. The existence of two liquid modifications of helium, with a transition point at 2.3° Abs. and 38 mm., has been proved from the dielectric constant, specific gravity, and surface-tension curves, all of which show change of direction at 2.3° Abs., and by recording the rate of change of vapour pressure with rising and falling temperature. The modification stable at the lower temperatures has the lower density and surface

tension, and the higher latent heat of vaporisation; the heat of transformation is calculated as 0.13 g.-cal. per g. The transition temperature is that at which the triple point was to have been expected for solid-liquid-gas phases; the existence of the second liquid modification with this transition temperature indicates

a triple point of a character hitherto unknown for elementary substances, and the possibility that the new liquid modification may be crystalline. It is probable also that there is a second triple point corresponding with the co-existence of the solid and both liquid modifications.

S. I. LEVY.

Geochemistry.

Helium in New Zealand. C. C. FARR and M. N. ROGERS (New Zealand J. Sci. Tech., 1929, 10, 300—308).—Analyses are given of natural gas from a large number of sources in New Zealand. Helium is an almost universal constituent. C. W. GIBBY.

Larnite (calcium orthosilicate, a new mineral) and associated minerals from a limestone contact-zone in Co. Antrim. C. E. TILLEY (Min. Mag., 1929, 22, 77—86).—At the contact of dolerite with chalk on Scawt Hill, near Larne, the finely granular rock shows an unusual assemblage of minerals, including spurrite ($2\text{Ca}_2\text{SiO}_4 \cdot \text{CaCO}_3$), larnite (Ca_2SiO_4), merwinite ($3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), gehlenite, spinel, and calcite. Optical data are given for each of these. The larnite is readily decomposed with gelatinisation by weak acids, and it is slowly attacked by water with the production of calcium hydroxide. It is monoclinic with optical characters agreeing with the artificial $\alpha\text{-Ca}_2\text{SiO}_4$. When the larnite-rock is heated to dull redness and allowed to cool it falls to powder, due to the inversion to $\gamma\text{-Ca}_2\text{SiO}_4$. These contact-metamorphic minerals were probably formed at a high temperature, followed by rapid cooling.

L. J. SPENCER.

Renardite. A. SCHOEF (Bull. Soc. Franç. Min., 1928, 51, 247—252; Chem. Zentr., 1929, i, 374).—Renardite, a new uranium mineral from Chinkolobwe, has d greater than 4, n_a 1.715, n_b 1.736, n_c 1.739 (± 0.003), and contains: insol. (quartz) 2.11, PbO 12.26, P_2O_5 8.15, $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{CoO}$ 3.68, MoO₃ 0.74, UO_3 64.82, H_2O 8.74%, corresponding with the formula $\text{PbO} \cdot 4\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$. A. A. ELDRIDGE.

Friedelite, schallerite, and related minerals. L. H. BAUER and H. BERMAN (Amer. Min., 1928, 13, 341—348).—Chemical analyses and physical properties are recorded.

CHEMICAL ABSTRACTS.

Dipyrite and associated contact minerals from the Franklin mountains of Texas. J. T. LONSDALE (Amer. Min., 1929, 14, 26—32).

Larsenite, calcium-larsenite, and associated minerals at Franklin, N.J. C. PALACHE, L. H. BAUER, and H. BERMAN (Amer. Min., 1928, 13, 334—340).—Larsenite, H_3 , has $a:b:c = 0.4339:1:0.5234$. Chemical analyses are recorded.

CHEMICAL ABSTRACTS.

Zircon from North Burgess, Ont. C. PALACHE and H. V. ELLSWORTH (Amer. Min., 1928, 13, 384—391).—Zircon has $a:c = 1:0.6429$. Heating increases the density and reduces the refractive index. A chemical analysis is recorded.

CHEMICAL ABSTRACTS.

Nature and origin of the amphibole asbestos of S. Africa. M. A. PEACOCK (Amer. Min., 1928, 13,

241—286).—Analyses of blue crocidolite correspond with the formula $3\text{H}_2\text{O} \cdot 2\text{Na}_2\text{O} \cdot 6(\text{Fe}, \text{Mg})\text{O} \cdot 2\text{Fe}_2\text{O}_3 \cdot 17\text{SiO}_2$; amosite, grey, is an orthorhombic amphibole with ferrous oxide as the dominant base. Optical data and chemical analyses are recorded.

CHEMICAL ABSTRACTS.

Uranium/thorium ratio in Monazites. S. IMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 229—236).—The fact that the thorium/uranium ratio in some uranium-rich minerals increases with the geological age of the specimen has led to the conclusion that the parent of the thorium disintegration series is an isotope of uranium (thorium-uranium, at. no. 92). An attempt has been made to find whether an analogous relation exists in monazite pebbles, crystals, and sands from known localities, i.e., in uranium-poor minerals. Although the results do not conflict with the theory of Riss (Sitzungsber. Akad. Wiss. Wien, 1924, 133, 91), they are not considered sufficient to support it in view of experimental difficulties and the lack of data. No noteworthy connexion has been found between the uranium/thorium ratio and the amounts of thorium and uranium present. This ratio, although of the same order of magnitude for all the specimens analysed, was not constant. Determinations of uranium gravimetrically and by the radium emanation method have given results which agree within the limits of experimental error, showing that in the samples used no detectable amount of any uranium isotope outside the uranium-radium series was present.

F. L. USHER.

Dyscrasite and the silver-antimony constitution diagram. G. M. SCHWARTZ (Amer. Min., 1928, 13, 495—503).—Dyscrasite is considered to have the formula Ag_3Sb , a known compound in the system silver-antimony. The origin of an intergrowth, as found in ores at Cobalt, Ont., is discussed.

CHEMICAL ABSTRACTS.

X-Ray study of lateritic rocks and of sporogelite. W. F. DE JONG (Z. Krist., 1928, 66, 303—308; Chem. Zentr., 1928, ii, 2545).—A scheme for the weathering of magmatic rocks is based on X-ray studies of bauxite, kaolinite, diaspore, feldspar, and hydrargillite, and of desiccated aluminium hydroxide.

A. A. ELDRIDGE.

Heating curves of manganite. N. KURNAKOV and V. ČERNÝCH (Zentr. Min. Geol., 1928, A, 359—361; Chem. Zentr., 1929, ii, 2342).—Loss of water, without loss of oxygen, occurs when manganite, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$, is heated at 365—400°.

A. A. ELDRIDGE.

Hydrotalcite and pyroaurite. N. KURNAKOV and V. ČERNÝCH (Zentr. Min. Geol., 1928, A, 353—

359; Chem. Zentr., 1928, ii, 2341—2342).—Hydro-talcite, $9\text{Mg}(\text{OH})_2 \cdot 4\text{Al}(\text{OH})_3 \cdot 8\text{H}_2\text{O}$, has d 2.027—2.210, H 2; in pyroaurite, d 2.049—2.083, the alumina is replaced by iron. Water is eliminated from limonite at 180° , hydrargillite at 240° , brucite at 410° , diaspore (hydro-talcites) at 540° ; magnesium carbonate is decomposed at 700° . A. A. ELDRIDGE.

Formation of cupriferous "black earths," Niari, French Congo. R. BURKHARDT (Arch. Sci. phys. nat., 1929, [v], 11, 59—82).—Analyses are given of sandstones, limestones, "black earths," and "red earths" occurring in the French Congo. The two latter contain small quantities of copper.

C. W. GIBBY.

Constitution of the augite of Monti Rossi (Etna). G. G. CRISTALDI and G. COLUMBA (Annali Chim. Appl., 1929, 19, 173—182).—Crystals of this augite contain (1) nitrides and yield, on the average, 0.1493% of ammonia on hydrolysis, and (2) a magnetic ilmenite, d 4.32, with the ratio $\text{FeTiO}_3 : \text{Fe}_2\text{O}_3$ nearly 1. The residual portion of the augitic mass has a composition differing appreciably from those published and may be regarded as containing diopside-hedenbergite 89.93, spinels 5.42, and pseudo-giadeite 4.65%. T. H. POPE.

[Gudmudite, plumbferite, hæmatophanite, and jacobsite.] K. JOHANSSON (Z. Krist., 1928, 68, 87—118; Chem. Zentr., 1928, ii, 2449).—Gudmudite, FeSbS , from Gudmunstorp, near Sala, silver-white to steel-grey, H 6, contained Fe 26.83, Sb 57.76, S 15.41%; $a : b : c = 0.6729 : 1 : 1.1868$, rhombic. Plumbferite, d 6.07, from Jakobsberg contained PbO 33.03, FeO 0.71, MnO 1.41, CaO 0.40, MgO 0.34, K_2O 0.13, Na_2O 0.17, Fe_2O_3 63.01, Sb_2O_3 0.25, FeTiO_3 0.15, insol. 0.15%, corresponding with the formula $(\text{Pb}, \text{etc.})\text{O}_2\text{Fe}_2\text{O}_3$; hexagonal, $a : c = 1 : 3.9719$. The unit cell, $a = 11.82$, $c = 47.14$ Å., contains 42 mols. Hæmatophanite, d 7.70, occurring with plumbferite, contained PbO 73.26, FeO 0.22, MnO 0.29, CaO 0.26, MgO 0.06, K_2O 0.17, Na_2O 0.38, Fe_2O_3 22.01, FeTiO_3 0.20, Cl 2.17, H_2O 0.73, insol. 0.42%, corresponding with the formula $\text{Pb}(\text{Cl}, \text{OH})_2 \cdot 4\text{PbO} \cdot 2\text{Fe}_2\text{O}_3$; tetragonal-holohedral, $c : a = 1.95 : 1$; the unit cell, $a = 7.801$, $c = 15.23$ Å., contains 3 mols. Jacobite, H 6, d 4.76, from Jakobsberg, Wermland, contained MgO 9.26, MnO 13.94, FeO 2.49, 2.57, FeTiO_3 0.17, Fe_2O_3 73.96%, corresponding with the formula $\text{MgFe}_2\text{O}_4 \cdot (\text{Mn}, \text{Fe})\text{Fe}_2\text{O}_4$; cubic, $a = 8.42$ Å., the unit cell containing 4 mols.;

space-group O_4 . Analyses of a disintegration product of jacobite, and of a yellowish-green garnet are given. A. A. ELDRIDGE.

Occurrence of germanium in topaz. J. PAPISH (Science, 1928, 68, 350—351).—Germanium was detected in all the specimens of cassiterite and topaz examined. CHEMICAL ABSTRACTS.

Norbergite from Franklin, N.J. E. S. LARSEN, L. H. BAUER, and H. BERMAN (Amer. Min., 1928, 13, 349—353).—Norbergite is orthorhombic; optical properties, and an analysis of a specimen, d 3.20, H 5.5, are recorded. CHEMICAL ABSTRACTS.

Humite group. E. S. LARSEN (Amer. Min., 1928, 13, 354—359).—Chemical and optical data are recorded. CHEMICAL ABSTRACTS.

Formula of glauconite. A. F. HALLIMOND (Amer. Min., 1928, 13, 589—590).—A discussion. CHEMICAL ABSTRACTS.

Chemistry, optics, and genesis of the hastingsite group of amphiboles. M. BILLINGS (Amer. Min., 1928, 13, 287—296).

"Bauxite" from Kashmir. T. V. M. RAO (Min. Mag., 1929, 22, 87—91).—Six analyses of material from the "bauxite" deposits of Jammu in Kashmir show the extreme values: Al_2O_3 61.70—80.74, H_2O 12.15—14.99, SiO_2 0.84—14.07, TiO_2 2.48—4.36, Fe_2O_3 0.75—3.56, with small amounts of alkalis, lime, magnesia, and carbon. The material is hard enough to scratch glass and has an average density of 3.2. Under the microscope it is very dense and opaque, and although some diaspore was detected optically, the bulk of the material is thought to be the monohydrate ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) called bœhmite (A., 1927, 748). L. J. SPENCER.

Petrology of the Whin sill. S. I. TOMKELEV (Min. Mag., 1929, 22, 100—120).—The Whin sill of the north of England (A., 1928, 1211), although very uniform in texture and in chemical and mineralogical composition over a wide area, shows at times some variations. Descriptions with analyses are given of a coarse gabbroid type occurring as bands and streaks in the normal dolerite, of a coarse rock with red granophyric spots, of red felsitic veins, and of spheroidal aplitic inclusions. The coarsely crystallised varieties evidently contained more volatile constituents, and it is suggested that they represent a "wet" differentiation portion of the magma before injection took place in the sill. L. J. SPENCER.

Organic Chemistry.

Asymmetric synthesis. R. BOUSSET (Compt. rend., 1929, 188, 1407—1410).—A theoretical discussion of the conditions under which asymmetric synthesis may be effected. J. W. BAKER.

Electrosynthesis of hydrocarbons. L. BERMEJO and L. BLAS.—See this vol., 775.

Preparation of free methyl. F. PANETH and W. HOREDITZ (Ber., 1929, 62, [B], 1335—1347).—When a rapid stream of hydrogen or nitrogen charged

with lead tetramethyl is passed at a very low pressure through a heated quartz tube a mirror of lead is obtained. When the gaseous products of the decomposition of lead tetramethyl are passed over such a lead mirror at a suitable distance from the point of decomposition, the mirror disappears, but another mirror is produced if the tube is heated at a further point. The product formed by the action of the vapours on the lead mirror can be condensed in a tube cooled in liquid air and, after volatilisation, can be

decomposed by heat. The ability of the vapours to combine with lead vanishes very rapidly, but it is possible by suitably heating a tube containing a lead mirror to cause the appearance and disappearance of the mirrors to occur at a distance of 30 cm. Attempts to condense the vapour by liquid air are accompanied by complete loss of activity. The "solvent" action of the vapours on their own lead mirror is apparent, since the edge of the latter on the side opposite to the flame is sharply defined. It appears therefore that the thermal decomposition of lead tetramethyl results in the very transitory production of a gaseous material capable of converting lead into a substance closely similar to, if not identical with, lead tetramethyl. Insight into the nature of the agent is derived from the observation that it transforms an antimony mirror into two substances, m. p. below -20° and $+13.5^{\circ}$, respectively, and a zinc mirror into zinc dimethyl. Since the possible decomposition products of lead tetramethyl, methane, ethane, ethylene, and acetylene are inactive towards metallic mirrors, whether cold or heated, the phenomena can be accounted for only by regarding the aggressive agent as the free methyl radical which has a short, but measurable, life period. Attempts to measure the latter constant are based on the passage of lead tetramethyl vapour under constant conditions through a tube heated at one point and observation of the relationship between the distance between standard antimony mirrors and this point and the time required for the complete disappearance of the antimony mirrors. In a hydrogen atmosphere at 2 mm. pressure, the concentration of free methyl sinks to its half value in approximately 0.006 sec. and free methyl consequently disappears practically completely in 0.1 sec.

The formation of metallic hydrides by the action of the silent discharge in mixtures of hydrogen and methane is probably accompanied to a greater or less extent by that of metallic methyls, and the latter substances are probably necessary intermediates in the production of the hydrides in those cases in which the action is not observed without the presence of methane.

H. WREN.

Action of sulphur on *n*-heptane and *n*-butane. R. B. BAKER and E. E. REID (J. Amer. Chem. Soc., 1929, 51, 1566—1567).—*n*-Heptane and sulphur at 150 – 250° or at 300 – 350° give a very small yield of a thiophen, (?) $C_7H_{10}S$, b. p. 160 – 161° , d_4^{25} 0.9221, but no mercaptans or sulphides. *n*-Butane and sulphur at 335° give a trace of thiophen (cf. Friedmann, A., 1916, i, 735).

H. E. F. NOTTON.

Isomeric heptanes. I. Preparation [with R. E. MARKER]. **II. Properties.** G. EDGAR and G. VANIGAERT (J. Amer. Chem. Soc., 1929, 51, 1483—1540—1550).—The preparation for the first time of considerable quantities of the pure isomeric heptanes is described. *n*-Heptane (1), b. p. 98.4° (all b. p./760 mm.), m. p. -90.5° , is obtained from Jeffery pine oil (Kremers, A., 1921, i, 705). β -Methylhexane (2), b. p. 90.0° , m. p. -119.1° ; α - γ -methylhexane (3), b. p. 91.8° ; γ -ethylpentane (4), b. p. 93.3° ; $\beta\delta$ -dimethylpentane (7), b. p. 80.8° , m. p. -123.4° ; *dl*- $\beta\gamma$ -dimethylpentane (6), b. p. 80.9° , m. p. -123.4° ; and $\beta\beta\gamma$ -trimethylbutane (9), b. p. 80.9° , m. p.

-25.0° , are prepared by the method of Chavanne (A., 1919, i, 380; 1922, i, 417; 1924, i, 1025). The unsaturated hydrocarbons obtained by dehydrating $\beta\delta$ -dimethylpentan- γ -ol and $\gamma\gamma$ -dimethylpentan- β -ol both yield mixtures of heptanes when hydrogenated. $\beta\beta$ -Dimethylpentane (5), b. p. 78.9° , m. p. -125.6° , is obtained conveniently, but in small yield, from magnesium *n*-propyl bromide and *tert*-butyl chloride in presence of mercuric chloride, and $\gamma\gamma$ -dimethylpentane (8), b. p. 86.0° , m. p. -135.0° , from magnesium ethyl bromide, *tert*-amyl chloride, and mercuric chloride. The properties of the products are compared with published data.

The values of 27 fundamental and derived constants (some taken from previous papers; cf. Smyth and Stoops, A., 1928, 935; Stewart, A., 1928, 1079; Freyer and others, this vol., 637), all determined on the same material, are given for each of the above isomerides. The density, refractive index, dielectric constant, coefficient of expansion, and dispersion and derived constants are affected by changes in constitution in the following way. The values for isomerides containing β -methyl groups are smaller, and for those containing γ - or $\beta\gamma$ -substituents greater, than those for *n*-heptane. With two or more substituents the effect is additive. The order of increasing magnitude of these constants is, therefore: 5, 7, 2, 1, 3, 9, 8, 6, 4. On the other hand, constants related to the internal pressure, e.g., surface tension, b. p., a (van der Waals), and critical solution temperature in aniline, also, less regularly, critical temperature, velocity of sound, adiabatic and isothermal compressibilities, give the order: 5, 7, 9, 2, 8, 3, 6, 1, 4. The two orders differ only in the positions of *n*-heptane and $\beta\beta\gamma$ -trimethylbutane. The critical pressures and viscosities show no relation to other properties. The X-ray diffraction results are discussed. Available data for the hexanes, octanes, nonanes, and decanes are tabulated. In general, these show the same relationships between structure and physical properties as do the heptanes. The results should be of value in the identification of new paraffin hydrocarbons.

H. E. F. NOTTON.

Determination of unsaturation with potassium bromide-bromate mixture. F. CORTESE (Rec. trav. chim., 1929, 48, 564—567).—Francis' method (B., 1926, 811) for the determination of unsaturation by titration with a potassium bromide-bromate mixture is found to be trustworthy for aliphatic olefines and diolefines whether these contain conjugated linkings or not, but is not trustworthy for certain ring structures and for substances of unknown constitution. Thus the values so obtained for furan and a phenylbutadiene polymeride were only half the true values.

J. W. BAKER.

Unsaponifiable matter from oils of elasmobranch fish. V. Constitution of squalene as deduced from its degradation products. I. M. HEILBRON, W. M. OWENS, and I. A. SIMPSON (J.C.S., 1929, 873—883).—The conclusions of André and Canal (B., 1927, 416) that squalene is not a single substance or a dihydrotriterpene are contested. Under all methods of attack squalene gives decomposition products typical of those expected from a

triterpene hydrocarbon. No definite evidence of the existence of any single monoterpene in the fraction obtained by distillation of squalene at 300–350 mm. in a current of nitrogen can be obtained, only constant-boiling mixtures of mono- and di-hydromonoterpenes being produced. Repetition of the hot-wire decomposition (Chapman, J.C.S., 1923, 123, 769) has failed to confirm the existence of heptarene, $C_{10}H_{18}$, although a squalene fraction, b. p. 60–100/20 mm., when heated with 99% formic acid, gives a liquid, b. p. 125–130°/3 mm., d^{20}_D 0.9098, n^{20}_D 1.4998, probably a diterpene (dimyrcene?).

Majima and Kubota's ozonolysis experiments (A., 1923, i, 1, 174) are mainly confirmed; their two unidentified substances, m. p. 195° and 136°, are laevulaldehyde peroxide and methylheptenone peroxide, respectively.

Oxidation of squalene in acetone solution at the ordinary temperature by solid potassium permanganate has led to the isolation of succinic acid, methylheptenone, and dihydro- ψ -ionone; this proves the presence in squalene of the carbon skeleton:

$C-C(C):C-C-C-C(C):C-C-C-C(C):$. Treatment of squalene with chromyl chloride leads chiefly to the production of resins, but some formaldehyde, acetaldehyde, and succinic acid can be isolated.

Squalenes obtained from *Centrophorus granulosus* or from *Scymnorhinus lichia* in ethereal solution, by bromination at –25°, give a crude squalene dodecaboromide resolvable into two dodecaboromides, m. p. 198° and 178°, insoluble and soluble, respectively, in ethyl acetate; the first and more stable dodecaboromide definitely has the formula $C_{30}H_{50}Br_{12}$. It is concluded that squalene exists as an isomeric mixture of dihydrotriterpenes to which the formulae

$CMe_2 \cdot CH \cdot CH_2 \cdot [CH_2 \cdot CMe \cdot CH \cdot CH_2]_4 \cdot CH_2 \cdot CMe \cdot CHMe$

and

$CMe_2 \cdot CH \cdot CH_2 \cdot [CH_2 \cdot C(CH_3) \cdot CH_2 \cdot CH_2]_4 \cdot CH_3 \cdot CMe$

CHMe are given.

R. J. W. LE FEVRE.

Unsaponifiable matter from oils of elasmo-branch fish. VI. Constitution of squalene as deduced from a study of the decahydrosqualenes. I. M. HEILBRON and A. THOMPSON (J.C.S., 1929, 883–892).—Squalene is treated with hydrogen in the presence of nickel catalyst until 5 mols. are absorbed. The hydrogenation is selective, isomeric decahydrosqualenes being formed accompanied by about 25% of dodecahydrosqualene (squalane): evidently products hydrogenated to a lower degree than decahydrosqualene are also formed. The mixed hydrosqualenes, b. p. 227–230°/3 mm., were ozonised in chloroform solution; the ozonide had $d < 1$. Decomposition of the ozonide by boiling water in an atmosphere of nitrogen leads to the following products: (1) neutral, methyl isohexyl ketone (semicarbazone, m. p. 149–150°), hexahydro- ψ -ionone, a ketone, $C_{19}H_{38}O$, probably $\gamma\eta\lambda$ -trimethylhexadecan- α -one, b. p. 136–139°/1.5 mm., n^{20}_D 1.4461 (semicarbazone, m. p. 71.5–73.5°), and a ketone, $C_{24}H_{48}O$, probably $\gamma\eta\lambda\alpha$ -tetramethyleicosan- τ -one, b. p. 195–205°/3 mm., mixed with squalene; (2) acid, γ -methyl- n -valeric acid, 80-dimethylnonoic acid, b. p. 105–108°/3 mm. (amide, m. p. 80–81°) (also obtained from synthetic hexahydro- ψ -ionone by the action of chromic acid in acetic acid

solution) and an $C_{17}H_{34}O$, probably $\gamma\eta\lambda$ -trimethyltetradecic acid, b. p. 182–192°/5 mm. In some experiments 80-dimethylnonaldehyde (?) (semicarbazone, m. p. 115–116°) can be isolated.

In connexion with the identity of the ketone $C_{19}H_{38}O$ (above) farnesol was hydrogenated at 100° by hydrogen in the presence of nickel on charcoal: the hexahydrofarnesol, b. p. 125–128°/3 mm., d^{20}_D 0.8361, n^{20}_D 1.4469, obtained is converted successively into hexahydrofarnesyl bromide, b. p. 122°/4 mm., d^{20}_D 1.001, n^{20}_D 1.4605, ethyl hexahydrofarnesylacetacetate, b. p. 175–178°/3 mm., d^{20}_D 0.9014, n^{20}_D 1.4484, and 5 α -trimethyl-5-pentadecanone, b. p. 142–143°/3 mm., 0.8403, n^{20}_D 1.4435 (semicarbazone, m. p. 70–70.5°).

It is concluded that in addition to the structures I and II given (preceding abstract), squalene exists in a third isomeric form,

$CMe_2 \cdot CH \cdot CH_2 \cdot CH = CMe \cdot [CH_2]_2 \cdot CH \cdot CMe \cdot [CH_2]_3 \cdot CH \cdot CMe \cdot [CH_2]_2 \cdot CH \cdot CMe \cdot [CH_2]_3 \cdot CMe \cdot CHMe$. The addition of hydrogen to the squalene molecule probably proceeds from the terminal grouping $CMe \cdot CHMe$ common to the three forms. R. J. W. LE FEVRE.

Hepta- α -di-inene and nona- α -di-inene. LESPICHAU and JOURNAUD (Compt. rend., 1929, 188, 1410–1411).—The action of the magnesium compound of $\beta\delta$ -dibromo- Δ^{α} -butene on epidibromohydrin yields β -dibromo- Δ^{α} -heptadi-inene mixed with its higher homologue. Separation is difficult, so that on conversion into the diacetylene a mixture of C_7 and C_9 hydrocarbons is obtained. Heptadi-inene, $CH_2[CH_2]_n \cdot C \equiv CH$ ($n=3$), b. p. 111.5–112.5°, d^{20}_D 0.8164, n^{20}_D 1.451, and nonadi-inene ($n=5$), b. p. 55–55.5°/13 mm., m. p. –21°, d^{20}_D 0.8159, n^{20}_D 1.452, are readily obtained by the action of monosodioacetylene on, respectively, tri- and penta-methylene bromide, the reaction proceeding smoothly under ordinary pressure (cf. Lebeau and Picon, A., 1913, i, 438). With alcoholic silver nitrate these diacetylenes yield disilver derivatives (each combined with $AgNO_3$) which react with iodine to yield the hexaiodides $(Cl_2 \cdot Cl)_2(CH_2)_n$, m. p. 75.5–76.5° and 107–108°, respectively. J. W. BAKER.

Characteristic reaction of primary *aci*-nitro-compounds. H. WIELAND and Z. KITASATO (Ber., 1929, 62, [B], 1250–1253).—Methazonic acid in anhydrous pyridine is converted by benzoyl chloride at –15° to –5° into dibenzoylchloroglyoxime, $OBz \cdot N \cdot CH \cdot COCl \cdot N \cdot OBz$, m. p. 165°, the constitution of which is established by its formation from anti-chloroglyoxime, whereas *amphi*-chloroglyoxime affords a chlorinated dibenzoyl derivative, m. p. 165°, which depresses the m. p. of the compound from methazonic acid. Under similar conditions, *ac*-phenylnitromethane gives the chloride of benzoylbenzhydroxamic acid, m. p. 109°, prepared also from benzhydroxamyl chloride. Secondary *aci*-nitro-derivatives do not appear to undergo this change but to be normally benzoylated. H. WREN.

Methyl alcohol from hydrogen and carbon monoxide. II. Dimethyl ether. R. L. BROWN and A. E. GALLOWAY.—See B., 1929, 426.

Rapid dehydration of alcohol using barium oxide and metallic calcium. G. F. SMITH.—See B., 1929, 449.

Configuration of pentaerythritol. III. J. BORSEKEN and B. B. C. FÉLIX (Ber., 1929, 62, [B], 1310—1316; cf. A., 1928, 616, 1213).—In reply to Kenner (this vol., 171) and Semenzov (*ibid.*, 538), who have pointed out that a pyramidal arrangement of the groups in pentaerythritol is not incompatible with an asymmetric configuration, it is maintained that such molecules would only with difficulty retain their unsymmetrical nature in solution and would pass by oscillation through symmetrical phases which would render impossible fission into optical antipodes. Until evidence of *cis-trans*-isomerism of the acetals is forthcoming the optical resolution is regarded as establishing the tetrahedral configuration.

Aminoacetaldehyde diethylacetal is condensed with pentaerythritol by hydrogen chloride in absolute alcohol to the compounds $[\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{O}_2\text{C}_2\text{H}_5)_2]_2\text{C}$, m. p. 62—64°, and $(\text{OH}\cdot\text{CH}_2)_2\text{C}\cdot\text{C}_2\text{H}_4\text{O}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$, m. p. 124°. The former compound is resolved by malic acid into the *l*-base, m. p. 60—70°, $[\alpha]_D^{20} -0.43^\circ$ in water, and m. p. 72—74°, $[\alpha]_D^{20} +0.95^\circ$ in water.

Camphor does not react in the usual manner with pentaerythritol, whereas its diethylacetal gives the *d*-camphoracetal, m. p. 156°, $[\alpha]_D^{20} -29.3^\circ$ in chloroform, and *monocamphoracetal*, m. p. 135°, $[\alpha]_D^{20} -18.6^\circ$ in chloroform. Indications of the existence of isomerides are not obtained.

p-Cresol is hydrogenated under pressure in presence of nickel to 4-methylcyclohexanol, which is transformed by phosphorus tribromide into the corresponding bromide, b. p. 55°/15 mm. Successive treatment with magnesium and ethyl orthoformate transforms the bromide into *hexahydro-p-tolualdehyde-diethylacetal*, b. p. 110°/15 mm., $d_4^{20} 0.8801$, $n_D^{20} 1.4572$, which is hydrolysed, converted into the *aldehyde sodium hydrogen sulphite* compound, and condensed with formaldehyde in the presence of potassium hydroxide to 4:4-dihydroxymethyl-1-methylcyclohexane, b. p. 105°/0 mm.; m. p. 45°. The last-mentioned compound condenses with pyruvic acid to the *spiran*, $\text{C}_8\text{H}_{16}\text{Me}_2\text{C}_3\text{H}_4\text{O}_2\cdot\text{CMe}\cdot\text{CO}_2\text{Et}$, b. p. 82—89°/0 mm., $d_4^{20} 1.044$ (1.049), $n_D^{20} 1.4635$ (1.4638); the corresponding acid, m. p. 111°, is partly resolved into its optical antipodes by means of quinine. H. WREN.

Trifluoro-alcohols. II. Trifluoroisopropyl alcohol. F. SWARTS (Bull. Soc. chim. Belg., 1929, 38, 99—109; cf. A., 1927, 1055).—Trifluoroisopropyl alcohol, b. p. 77.7° (corr.)/754 mm., m. p. -52°, $d_4^{20} 1.2799$, $n_D^{20} 1.3172$, is prepared by an improved method of catalytic hydrogenation of trifluoroacetone under pressure. The alcohol has acidic properties. Its dissociation constant in water is 2×10^{-7} at 25°. It reacts with potassium carbonate to yield the *potassium* derivative. No ethylenic compound can be obtained from the alcohol by treatment with zinc chloride, oxalic acid, or concentrated sulphuric acid. The last reagent yields *trifluoroisopropylsulphuric acid*, isolated as the *barium* salt (+2H₂O), which decomposes when kept or heated to give the alcohol, barium sulphate, and sulphuric acid. Hydrogen bromide not attack the alcohol. The action of phosphorus tribromide yields *trifluoroisopropylphosphorous bromide*, $\text{C}_3\text{H}_5\text{F}_3\text{OPBr}_2$, m. p. 48°, b. p. 156—157°, $d_4^{20} 1.988$. When this compound is treated with

bromine (1 mol.) and the product distilled, decomposition takes place partly with the formation of *trifluoroisopropyl bromide*, b. p. 49°, $d_4^{20} 1.633$. The distillation residue, containing the phosphorous bromide compound, yields when treated with water *trifluoroisopropylphosphorous acid*, isolated as the *barium* salt. *Trifluoroisopropyl acetate* has b. p. 85.6°/75 mm., $d_4^{20} 1.1823$, $n_D^{20} 1.3314$. The *allophanate* has m. p. 159.7° (decomp.). The physical properties of trifluoro-alcohols are compared and discussed.

R. K. CALLOW.

Acetylene oxides and α -lactones. W. MADE-LUNG and M. E. OBERWEGNER (Naturwiss., 1929, 17, 430).—The isolation of phenylacetylene oxides, and hydroxy- and alkyloxy-derivatives of these, which in the enol form have α -lactone structures, is mentioned.

S. I. LEVY.

$\alpha\alpha'\beta\beta'$ -Tetrabromoethyl ether and so-called "tetrabromobutaldehyde." H. HIBBERT, S. Z. PERRY, and K. A. TAYLOR (J. Amer. Chem. Soc., 1929, 51, 1551—1555).—Vinyl ether, conveniently prepared by the continued action of $\beta\beta'$ -dichloroethyl ether on strongly heated powdered potassium hydroxide, gives with bromine in chloroform $\alpha\alpha'$ -tetrabromoethyl ether, m. p. 63—65°. This is, as suggested by Stepanov (A., 1927, 42; cf. A., 1923, i, 439), identical with the compound described by Freundler (A., 1907, i, 285) as tetrabromobutaldehyde. With ethylene glycol at 100° it gives β -bromoethylidene ethylene ether (57% of the theoretical). H. E. F. NOTTON.

Mechanism of organic reactions. I. Wandering of acyl groups in glyceryl esters. H. HIBBERT and N. M. CARTER (J. Amer. Chem. Soc., 1929, 51, 1601—1613).—Reactions of glyceryl esters which are accompanied by acyl wandering are reviewed (cf. Fairbourn and Cowdrey, this vol., 292). Hydrolysis of $\alpha\gamma$ -benzylideneglyceryl benzoate (A., 1928, 1213) with aqueous alcohol containing a little hydrochloric acid and *p*-nitrobenzoylation of the oily product yields a mixture of glyceryl α -benzoate β -*p*-nitrobenzoate and glyceryl α -benzoate $\beta\gamma$ -di-*p*-nitrobenzoate (Bergmann, A., 1921, i, 444). Similarly, $\alpha\gamma$ -benzylideneglyceryl *p*-nitrobenzoate, m. p. 156°, $\alpha\beta$ -benzylideneglyceryl *p*-nitrobenzoate, m. p. 90—91°, and $\alpha\beta$ -isopropylideneglyceryl *p*-nitrobenzoate are all hydrolysed by dilute hydrochloric acid to glyceryl α -*p*-nitrobenzoate; whilst $\alpha\gamma$ -benzylideneglyceryl *p*-bromobenzoate, m. p. 146°, $\alpha\beta$ -benzylideneglyceryl *p*-bromobenzoate, m. p. 72°, and $\alpha\beta$ -isopropylideneglyceryl *p*-bromobenzoate, m. p. 39—40°, are all hydrolysed to glyceryl α -*p*-bromobenzoate, m. p. 70°. These results illustrate the tendency of β -acyl groups to migrate to the α -position in reactions involving the use of acids. The mechanism of the change is discussed. Conclusions as to the constitution of polyhydroxy-derivatives, based on the progressive hydrolysis of their acyl derivatives must, accordingly, be regarded as 'untrustworthy'. The structure of glyceryl $\alpha\gamma$ -ditrityl ether (cf. Helferich, A., 1928, 44) has been confirmed by the hydrolysis of its *methyl ether*, m. p. 158.5°, by hydrogen bromide in glacial acetic acid at 0° to β -methyl glyceryl ether.

H. E. F. NOTTON.

Reactions in liquid hydrogen sulphide. VI. Reactions with organic compounds. R. W.

BORGESON and J. A. WILKINSON (J. Amer. Chem. Soc., 1929, 51, 1453—1456; cf. A., 1928, 961).—Saturated aromatic hydrocarbons and vaseline, ethyl ether, phenols, saturated monobasic acids, alkyl and aryl halides, amides (picramide reacts slowly) and alkylamines are all soluble and non-reactive. Amylene and trimethylethylene are miscible with and non-reactive towards liquid hydrogen sulphide unless the temperature is raised to about 18°, when an unstable white solid separates on re-cooling to -77°. The odour of a mercaptan is produced on dissolution of unsaturated compounds. Aldehydes react as follows: $R \cdot CHO + H_2S \rightarrow R \cdot CH(OH) \cdot SH \rightarrow R \cdot CHS + H_2O$, the water forming white crystals of $H_2S \cdot xH_2O$. Sugars are insoluble. Grignard reagents react vigorously, liberating the corresponding hydrocarbon. Alkylamines react to form unstable viscid liquids or crystalline solids. Phenylhydrazine yields yellow crystals of $NHPh \cdot NH_2 \cdot H_2S$. Acyl halides react as follows: (i) $R \cdot COCl + H_2S \rightarrow R \cdot CO \cdot SH + HCl$; (ii) $R \cdot CO \cdot SH + H_2S \rightarrow R \cdot CS \cdot SH + H_2O$. *Dithioacetic acid thioanhydride*, $(CSMe)_2S$, m. p. 225°, is obtained by dissolving acetyl chloride or bromide in liquid hydrogen sulphide. S. K. TWEEDY.

Formylmethanedisulphonic and bromoformylmethanedisulphonic acids. H. J. BACKER (Rec. trav. chim., 1929, 48, 571—576).—Formylmethanedisulphonic acid (I) [*silver* + H_2O (cf. Schroeter, A., 1898, i, 614) and *thallous* + H_2O , salts] is best prepared by Rathke's method (A., 1872, 388), when it is obtained as its *potassium hydrogen sulphite* derivative (solubility, in absence of air at 25°, 2.12 g./100 g. of water). The solubilities of the potassium + H_2O , and barium + $4H_2O$ (lit. + $2H_2O$) and anhydrous, salts at 25° are respectively 1.02, 0.3935, and 0.3245 g./100 g. of water. Bromoformylmethanedisulphonic acid [potassium + H_2O (solubility, 8.92 g./100 g. of water at 25°) and barium + $2H_2O$ salts] is obtained by bromination of I, its potassium hydrogen sulphite derivative, or its barium salt at 100°, but interaction of potassium bromoformylmethanedisulphonate and potassium hydrogen sulphite yields only the hydrogen sulphite derivative of I in accordance with the equation $C(CH_3O)Br(SO_3K) + 2KHSO_3 + H_2O = KHSO_4 + OHC \cdot CH(SO_3K)_2 + KHSO_4 + HBr$. J. W. BAKER.

Electrolysis of ammonium acetate and ammonium hexoate. F. FICHTER and W. LINDENMAIER.—See this vol., 775.

Thiocyanogen value of fats. H. P. KAUFMANN [with A. BROCKE].—See B., 1929, 441.

Preparation of unsaturated acids and esters. E. PHILIPPI (Monatsh., 1929, 51, 277—279).—Elaidic acid and its ethyl ester are best obtained (45% yield) by von Farnsteiner's method (A., 1899, ii, 705). Ethyl $\beta\beta$ -dimethylacrylate, b. p. 61.5°/30 mm., is obtained in 75% yield by Weinig's method (A., 1895, i, 17) from ethyl α -bromoisovalerate, b. p. 106—108°/30 mm. (Schleicher, A., 1892, 427). Ethyl Δ^7 -pentenolate is obtained from allyl alcohol (Coffey and Ward, J.C.S., 1921, 119, 1303) through allyl bromide, and ethyl allylacetoacetate, b. p. 118—121°/26—33 mm. (Brühl, A., 1894, ii, 433), hydrolysis of the latter being best accomplished by the (slightly modified) method of

Zeidler (A., 1877, iii, 437). Vinylacetic acid is obtained in slightly less than the stated yield by Bruylant's method (A., 1924, i, 1053) using allyl chloride in place of the bromide or iodide. Sorbic acid is obtained in 63% yield by Doebner's method (A., 1900, i, 536) if the starting material is carefully purified, and Δ^8 -hexenoic acid is best obtained by Fittig's method (A., 1872, 486). J. W. BAKER.

Action of ammonia and amines on the esters of unsaturated acids. E. PHILIPPI and E. GALTER [and, in part, M. ZORZI and E. BERTEL] (Monatsh., 1929, 51, 253—266; cf. Philippi and Spenner, A., 1915, i, 222).—Interaction of unsaturated esters with ammonia, methylamine, and piperidine at a lower temperature favours amide formation, whilst addition occurs mainly with the use of a solvent (alcohol or water) at a higher temperature. With $\alpha\beta$ -unsaturated acids addition is the main reaction, with $\beta\gamma$ -acids amide formation preponderates, whilst $\gamma\delta$ -acids in general show very little tendency to react. Examples of the following types of possible action are given: (1) simple addition, (2) amide formation, (3) (1) and (2) combined, (4) abnormal reactions such as ring formation or rearrangement of the position of the double linking, (5) no action. Thus ethyl crotonate and anhydrous ammonia at the ordinary temperature give a 55% yield of ethyl β -amino-butyrate, whilst with piperidine a 60% yield of ethyl β -piperidinobutyrate, b. p. 125°/15 mm. (decomp. into its components by distillation under atmospheric pressure), is obtained. Ethyl acrylate and piperidine give ethyl β -piperidinopropionate, b. p. 104—106°/12—13 mm. (yield 87%). Amide formation alone occurs with methyl Δ^8 -hexenoate and ammonia, yielding Δ^8 -hexenoamide, m. p. 75°, and with ethyl phenylisocrotonate, whilst methyl sorbate yields only 10% of the amide together with unidentified products. With anhydrous methylamine ethyl crotonate yields ethyl β -methylaminobutyrate together with β -methylaminobutyrmethylamide, b. p. 146°/56 mm., whilst ethyl Δ^7 -pentenolate (allylacetate) yields only a trace of the acid amide, most of the ester being recovered unchanged. Rearrangement occurs when ethyl $\beta\beta$ -dimethylacrylate reacts with ammonia or methylamine, the products being, respectively, ethyl β -amino- and β -methylamino-isovalerate, b. p. 71.5—72°/11 mm., accompanied in the latter case by β -methylamino-isovalermethylamide, b. p. 138—140°/15 mm. No action occurs between ammonia (or methylamine) and ethyl oleate, elaidate, and α -ethylacrylate, or between piperidine and ethyl $\beta\beta$ -dimethylacrylate. J. W. BAKER.

Esters of butenoic acids. P. BRUYLANTS (Bull. Soc. chim. Belg., 1929, 38, 133—143; cf. A., 1928, 401, and Auwers, A., 1923, i, 746).—Ethyl vinylacetate, b. p. 124.0—124.2°/755 mm., d_4^{20} 0.91224, n_D^{20} 1.41054, is best prepared by esterification of the acid, using sulphuric acid. Esterification of the nitrile by alcohol and sulphuric acid yields a product containing ethyl crotonate and unchanged nitrile. The product obtained from $\beta\gamma$ -dibromobutyronitrile by esterification and treatment with zinc contains unchanged nitrile. Ethyl vinylacetate is isomerised completely to ethyl crotonate by boiling with sodium phenoxide.

Ethyl crotonate, b. p. 136.6—136.8°/749 mm., d_4^{20} 0.91752, n_D^{20} 1.42524, is best obtained by esterification of the acid. Dehydration of ethyl β -hydroxybutyrate in chloroform solution by phosphoric oxide yields ethyl crotonate accompanied by ethyl vinylacetate. Ethyl isocrotonate, b. p. 125.5—126°/749 mm., d_4^{20} 0.91820, n_D^{20} 1.42423, is prepared by treatment of pure sodium isocrotonate in alcohol with ethyl iodide. Ethyl methacrylate, b. p. 118.4—118.6°/753 mm., d_4^{20} 0.91063, n_D^{20} 1.41472, may be obtained either from ethyl β -chloroisobutyrate by interaction with pyridine in presence of a little sodium iodide, followed by dry distillation, or from ethyl α -bromoisobutyrate by interaction with diethylaniline. *cyclo*Propanecarboxylic acid has d_4^{20} 1.0885, n_D^{20} 1.43901. The nitrile has d_4^{20} 0.8946, n_D^{20} 1.42293. The ethyl ester has b. p. 132.4—132.6°/750 mm., d_4^{20} 0.96078, n_D^{20} 1.41902.

R. K. CALLOW.

Highly unsaturated acids of sardine oil. I. New acid, $C_{18}H_{26}O_2$, and the highly unsaturated C_{18} -acids. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1929, 4, 83—91).—The highly unsaturated acids from Japanese sardine oil were separated by the method already described (A., 1925, i, 1129; B., 1927, 83) and converted into the methyl esters; by distillation of the product in a vacuum, a lower fraction, b. p. 215°/15 mm., was obtained together with a higher fraction [saponification value, 198.8; iodine value (Rosenmund and Kuhnemann) 179.6°, n_D^{20} 1.4628] containing considerable quantities of admixed esters of a low degree of unsaturation. Bromination of the lower-boiling ester fraction affords an ether-insoluble bromide, m. p. 220° (decomp.), separated by benzene into a soluble fraction (A) [Br=66.52%, sinters 165°, m. p. 198°] and an insoluble fraction (B) [Br=69.25%, darkens above 200°, m. p. 240° (decomp.)].

By treatment with zinc and glacial acetic acid for 5 hrs. at 100° in an atmosphere of carbon dioxide, A gives a 74% yield of esters, from which two fractions (E and F) are obtained by distillation; E consists essentially of *methyl hiragonate*, $C_{17}H_{28}O_2$, b. p. 180—190°/15 mm., d_4^{15} 0.9160, n_D^{15} 1.4792, giving an ether-insoluble *bromide*, $C_{17}H_{28}O_2Br_2$, m. p. 180° (yield 57%), and affording by hydrolysis *hiragonic acid*, $C_{16}H_{26}O_2$, 0.9324, n_D^{15} 1.4876, which by bromination gives a 57% yield of a *bromide*, $C_{16}H_{26}O_2Br_2$, m. p. 190°. By hydrogenation *hiragonic acid* yields palmitic acid accompanied by small quantities of acids with more than 16 C-atoms. Fraction F contains a *methyl ester*, $C_{19}H_{32}O_2$, b. p. 205—215°/15 mm., d_4^{15} 0.9168, n_D^{15} 1.4856, giving a 49% yield of a *bromide*, $C_{19}H_{32}O_2Br_2$, m. p. 215° (decomp.), and affording by hydrolysis a product consisting mainly of an *acid*, d_4^{15} 0.9329, n_D^{15} 1.4935, giving a 49% yield of a $C_{18}H_{30}O_2Br_2$ or $C_{18}H_{30}O_2Br_2$, m. p. 215° (decomp.). Hydrogenation affords mainly stearic acid, accompanied by small quantities of C_{16} - and C_{20} -acids.

By debromination with zinc and glacial acetic acid, F gives a 76% yield of a product from which, after removal of unsaponifiable matter, distillation furnishes two fractions (G), b. p. 205—215°/15 mm., and (H), b. p. 215—230°/15 mm.; G appears to consist of a mixture of methyl esters, $C_{19}H_{30}O_2$ and $C_{19}H_{32}O_2$, in which the

former predominates, d_4^{15} 0.9172, n_D^{15} 1.4862, giving a *bromide*, $C_{19}H_{30}O_2Br_2$, m. p. 215° (decomp.), and affording by hydrolysis a mixture of acids, $C_{18}H_{28}O_2$ and $C_{18}H_{30}O_2$, d_4^{15} 0.9332, n_D^{15} 1.4942. The acid $C_{18}H_{28}O_2$ predominates, and bromination affords a *bromide*, $C_{18}H_{28}O_2Br_2$, m. p. 220° (decomp.); hydrogenation yields stearic acid with small quantities of C_{16} -acids. Fraction H was not examined further.

C. W. SHOPPEE.

Iwashi (sardine) acid. M. TSUJIMOTO (Bull. Inst. Tokyo Ind. Res. Lab., 1928, 23, No. 3, 1—23).—For the acid, $C_{22}H_{34}O_2$, d_4^{15} 0.9410, n_D^{15} 1.5057, iodine value (bromopyridine method) 388.8, the following alternative formulæ are deduced from ozonisation experiments

(i) $CH_3Et[CH \cdot [CH_2]_2 \cdot CH]_3 \cdot CH \cdot CH_2 \cdot CH \cdot CH \cdot [CH_2]_6 \cdot CO_2H$, (ii) $CH_3Et[CH \cdot [CH_2]_2 \cdot CH]_5 \cdot CH \cdot CH_2 \cdot CH \cdot CH \cdot CH \cdot [CH_2]_2 \cdot CH \cdot CH \cdot [CH_2]_2 \cdot CO_2H$.

CHEMICAL ABSTRACTS.

Lactic acid tests. H. V. ARNY and M. C. DIMLER (J. Amer. Pharm. Assoc., 1929, 18, 459—462).—From an examination of published tests for the determination of lactic acid in presence of other organic acids the most satisfactory was found to be a combination of extraction with ethyl acetate (Ohlsson, A., 1916, ii, 542) and the resorcinol test of Brauer (A., 1920, ii, 517).

E. H. SHARPLES.

Active molecule of oxalic acid. F. OBERHAUSER and J. SCHORMULLER (Annalen, 1929, 470, 111—128; cf. Oberhauser and Hensinger, A., 1928, 505; Tschitschibabin, this vol., 48).—A qualitative test for manganese, sensitive for 0.1 mg. of manganese per litre consists of treating a manganese salt with hydrogen peroxide, mercuric chloride, and oxalic acid, when precipitation of mercurous chloride occurs. Activation of oxalic acid may be carried out by treating the anhydrous acid with potassium permanganate in acetone, showing that the nature of the solvent is of little importance. Prolonged exposure of a mixture of a ferrous salt, oxalic acid, and mercuric chloride to air causes a separation of mercurous chloride. Oxygen facilitates the change, whilst an inert gas prohibits it. A convenient method for the preparation of activated oxalic acid consists in treating the acid with hydrogen peroxide in presence of a small amount of a ferrous salt (ferric salts have no effect). The reduction of mercuric chloride by such a mixture has been studied in detail, and it is found that 1 g.-atom of ferrous iron causes precipitation of 100—500 mols. of mercurous chloride. No stoichiometrical relationship exists between the ferrous iron and (or) hydrogen peroxide, and the activated oxalic acid. The order of addition of the reagents is important: no precipitation of mercurous chloride occurs when the ferrous salt is added to the mixture. No formic acid is formed during the activation (cf. Krauss and Bruchhaus, this vol., 541), and the activated oxalic acid is the stronger reducing agent. The active acid is also produced during the anodic oxidation of oxalic acid, by the action of nitrites, and by ammonium or potassium persulphates. In this last case activation is presumably due to Caro's acid, since hydrogen peroxide and sulphates have no action. When a mixture of oxalic acid and ammonium oxalate is heated no activation occurs, but exposure of

such a solution to a mercury-quartz arc lamp gives an active product. The activated acid loses its activity when heated for a short time, and addition of mercuric chloride to an activated solution shows that the activity is less than that of a solution previously treated with the chloride. Attempts to isolate the active acid were negative, and the absorption spectra of ordinary and active oxalic acids are identical. The reduction of mercuric chloride is considered to be a chain reaction. The constitution of the active acid is discussed briefly.

H. BURTON.

Mechanism of the cleavage of ethyl $\alpha\delta$ -dibromoadipate by secondary amines. New synthesis of cyclobutane derivatives. R. C. FUSON and T. Y. KAO (J. Amer. Chem. Soc., 1929, 51, 1536—1539).—Evidence in favour of the mechanism proposed for this reaction (A., 1928, 738; this vol., 425) is afforded by the formation of ethyl 1-cyanocyclobutane-1:2-dicarboxylate, b. p. 152—154°/9 mm., n_D^{20} 1.1103, n_D^{25} 1.4519, from ethyl *ms*- $\alpha\delta$ -dibromoadipate and sodium cyanide in boiling absolute alcohol. This yields, after hydrolysis, decarboxylation, and treatment with hydrochloric acid at 190°, *trans*-cyclobutane-1:2-dicarboxylic acid (Perkin, J.C.S., 1894, 65, 580).

H. E. F. NOTTON.

Stereochemistry of the glutamic acids. I. R. MALACHOWSKI (Ber., 1929, 62, [B], 1323—1326).—*trans*-Glutamic acid is converted by boiling acetic anhydride into the hydroxyanhydride, which is gradually added to water at 10—12°; as soon as the solution ceases to give a green colour with ferric chloride, it is evaporated as rapidly as possible under greatly diminished pressure at the ordinary temperature, thus yielding *cis*-glutamic acid, m. p. 136—136.5° (corr.) [when mixed with the ordinary glutamic acid, m. p. 111—114°]. When solid or dissolved in ether the new acid can be preserved for weeks, whereas in aqueous solution or when melted it passes into the ordinary acid. The two acids are closely similar in m. p. and solubility, but differ completely from one another in crystalline form. The dissociation constant of the *cis*-acid is $k^0 = 1.43 \times 10^{-4}$, of the *trans*-acid $k^0 = 1.74 \times 10^{-4}$. At 15—20° about 40% of the *cis*-acid is transformed into the *trans*-acid in aqueous solution within 16 hrs. Acetic anhydride at 40° effects almost quantitative conversion of the *cis*-acid into the anhydride, whereas the *trans*-acid is only slightly anhydridised under these conditions.

H. WREN.

$\gamma\gamma$ -Dimethylpimelic acid. G. KOMPFA (Ber., 1929, 62, [B], 1371—1372).—4:4-Dimethylpiperidine hydrochloride is converted by benzoyl chloride and excess of alkali into 1-benzoyl-4:4-dimethylpiperidine, b. p. 174—177°/10 mm., $d_4^{16.5}$ 1.0511, $n_D^{16.5}$ 1.54534, converted by phosphorus pentachloride into benzonitrile and $\alpha\alpha$ -dichloro- $\gamma\gamma$ -dimethylpentane, b. p. 58—59°/8 mm., d_4^{15} 1.0917, n_D^{15} 1.48990. $\gamma\gamma$ -Dimethylpimelonitrile, m. p. 123°, from the dichloride and potassium cyanide, is hydrolysed by concentrated hydrochloric acid at 120° to $\gamma\gamma$ -dimethylpimelic acid, m. p. 83° (*dianilide*, m. p. 165°; *diamide*, m. p. 176°).

H. WREN.

Composition of sodium bismuth tartrate. J. H. YOE and J. H. MOTE (J. Amer. Pharm. Assoc.,

1929, 18, 450—459).—Sodium bismuth tartrate prepared by the action of bismuth hydroxide on tartaric acid in presence of excess of cold alkali is a sodium tetrabismuth tartrate.

E. H. SHARPLES.

Action of cyanogen chloride, bromide, and iodide on ethyl sodiomalonate. Synthesis of ethane- and ethylene-tetracarboxylic esters. G. MIGNONAC and O. W. RAMBECK (Compt. rend., 1929, 188, 1298—1301).—The action of a very slow current of cyanogen chloride on an alcoholic solution of ethyl sodiomalonate gives, instead of ethyl cyanomalonate (cf. Haller, A., 1882, 1189), ethyl ethylmalonate, presumably owing to alcoholysis of the sodium derivative. In an ethereal suspension, pure ethyl cyanomalonate, b. p. 138—140°/14 mm., d_4^{25} 1.1128, n_D^{25} 1.4295 (cf. Haller, *loc. cit.*), is obtained. Little of the substance is formed if cyanogen bromide is used in alcohol or ether; hydrogen cyanide is lost, giving ethyl ethylenetetracarboxylate, with some ethyl ethane-tetracarboxylate. With cyanogen iodide, hydrogen cyanide is not evolved, and ethyl ethanetetracarboxylate is almost exclusively formed. E. W. WIGNALL.

Constitution of gum arabic. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1929, 51, 1519—1525).—The λ -arabinosic acid (O'Sullivan, J.C.S., 1884, 45, 41) obtained by hydrolysing arabic acid with 2% sulphuric acid shows all the reactions of an aldobionic acid. It yields on hydrolysis galactose, and on oxidation (Heidelberger and Goebel, A., 1927, 1114) saccharic acid, and is, therefore, a *d*-galactosido-*d*-glycuronic acid, $[\alpha]^{25} + 2.5^\circ$, changing to $+1.71^\circ$ with lactonisation (calcium salt). It is oxidised by barium hypoiodite to a *glycuronogalactonic acid* (calcium salt). A preliminary examination of arabic acid indicates that it contains *d*-galactose (2 mols.), aldobionic acid (1 mol.), *l*-arabinose (3 mols.), and rhamnose (1 mol.) residues, approximately in the proportions stated.

H. E. F. NOTTON.

Claisen ester condensation with ethyl thioacetate. R. B. BAKER and E. E. REID (J. Amer. Chem. Soc., 1929, 51, 1567—1570).—Ethyl thioacetate, Ac·SEt (Michler, A., 1875, 761), b. p. 116—117°, d_4^{25} 0.9755, n_D^{25} 1.4503, and sodium at 50° give ethyl acetothioacetate (15% of the theoretical yield), CH₃Ac·CO·SEt, b. p. 60°/2 mm., d_4^{25} 1.0684, n_D^{25} 1.4885, which contains 31% of the enolic modification (bromine titration). Its copper salt is stable, but those of other metals decompose, giving metallic sulphides. It undergoes acid and ketonic hydrolysis in the same way as ethyl acetoacetate and readily decomposes when heated into dehydracetic acid. A mixture of ethyl acetate and ethyl thioacetate (equal mols.) gives with sodium a product containing 98% of ethyl acetothioacetate and 2% of ethyl acetoacetate. Ethyl thioacetate does not condense with acetone in presence of sodium, but with acetonitrile it gives cyanoacetone (7% of the theoretical yield).

H. E. F. NOTTON.

Constitution of substances of high mol. wt. R. O. HERZOG (Naturwiss., 1929, 17, 271).—The small elementary cell recorded in X-ray studies of substances of high mol. wt. is equally consistent with long chains or small molecules. Constitutional formulæ may

exceed and extend outside the elementary cell and the classical conception of a molecule is of little service in the study of substances of high mol. wt. Staudinger (*ibid.*, 141) misunderstands the position.

R. A. MORTON.

Tests for acetone and acetaldehyde. H. LEFFMANN (*Amer. J. Pharm.*, 1929, 101, 337—340).—The newer reagents suggested in recent literature have been examined, and found to have no great advantages.

S. I. LEVY.

Hydrogenation of acetaldehydeacetals. M. CABANAC (*Compt. rend.*, 1929, 188, 1257—1259).—When the vapour of acetaldehydediethylacetal, mixed with hydrogen, is passed over finely-divided nickel, reaction begins at about 200°. At 210° ethyl alcohol and ether are formed. Acetaldehydedipropylacetal yields similarly ethyl propyl ether and propyl alcohol, and the dibutylacetal yields ethyl butyl ether and butyl alcohol.

R. K. CALLOW.

Action of potassium cyanide on chloroaldehydes. F. D. CHATTAWAY and H. IRVING (*J.C.S.* 1929, 1038—1048).—The following compounds were prepared in the yields stated by the rapid interaction of a solution of anhydrous chloral in the requisite alcohol on a suspension of potassium cyanide in the same alcohol: methyl dichloroacetate (84%), ethyl dichloroacetate (88%), *n*-propyl dichloroacetate, b. p. 176° (70%), and *allyl* dichloroacetate, b. p. 175.5° (64%). The yields of dichloroacetates are greatly reduced when the reaction conditions are modified to favour the formation of chloral cyanohydrin (e.g., slow addition of the cyanide to chloral alcoholate in alcoholic solution) or when potassium cyanide acts on an alcoholic solution of chloralcyanohydrin itself.

Addition of dichloroacetaldehyde ethyl alcoholate to potassium cyanide-ethyl alcohol suspension led to a 38% yield of ethyl chloroacetate. Similar treatment of monochloroacetaldehyde with either aqueous or alcoholic potassium cyanide gave not more than 10% yields of ethyl acetate.

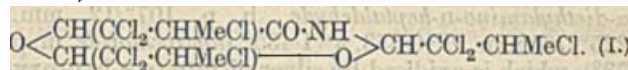
By the action of potassium cyanide on a solution of *butyl* chloral hydrate in ethyl alcohol ethyl α -chlorocrotonate, ethyl $\alpha\beta$ -dichlorobutyrate (which rapidly lost hydrogen chloride at the ordinary temperature, generating the previous ester), and *butyl* chloralcyanohydrin, m. p. 101—102°, were obtained. By using exactly 1 mol. of potassium cyanide the following α -chlorocrotonates were prepared in the yields indicated: ethyl (90%), methyl (85%), *n*-propyl (67%), *n*-butyl (70%). *Butyl* chloralcyanohydrin itself reacted with potassium cyanide in alcoholic solution, giving ethyl α -chlorocrotonate.

Potassium cyanide and *butyl* chloral hydrate, in aqueous solution, gave *butyl* chloralcyanohydrin accompanied by α -chlorocrotonic acid; potassium cyanide and chloral-ammonia suspended in aqueous ammonia reacted with formation of dichloroacet-

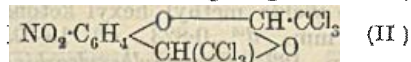
Similar treatment of *butyl* chloral hydrate led to α -chlorocrotonamide. Chloral diacetate and potassium cyanide reacted violently, in presence of alcohol, affording ethyl acetate and dichloro-

Addition of potassium cyanide to a solution of *butyl* chloral hydrate in benzene gave, after 10 days, *cyclo-2:4:7-tri-($\alpha\beta$ -trichloropropyl)cyclo-2:4:6:7-*

tetramethylene-1:3:5-dioxamine, I, (?) m. p. 99.5—100.5°.



Previous mechanisms for these reactions are destructively criticised and the theory is advanced that the potassium cyanide first causes the elimination of hydrogen chloride from the aldehyde-hydrate, -alcoholate, or -ammonia, probably by the intermediate replacement of a chlorine atom by a cyanogen group [e.g., removal of 1 mol. of hydrogen chloride by potassium cyanide from 6-nitro-2:4-bis(trichloromethyl)-1:3-benzdioxin, giving 6-nitro-2(or 4)-di-



chloromethylene-4(or 2)-trichloromethyl-1:3-benzdioxin, II, m. p. 136.5°], followed by elimination of the very slightly ionisable hydrogen cyanide, leaving an unsaturated compound which by intramolecular rearrangement gives an acid, an ester, or an acid amide: $\text{CCl}\cdot\text{CH}(\text{OH})\cdot\text{OH}(\text{OR})(\text{NH}_2) \xrightarrow{\text{KCN}} \text{C}\cdot\text{C}(\text{OH})\cdot\text{OH}(\text{OR})(\text{NH}_2) \rightarrow \text{CH}\cdot\text{CO}\cdot\text{OH}(\text{OR})(\text{NH}_2)$.

R. J. W. LE FÈVRE.

α -Bromoaldehydes and their derivatives. A. KIRRMANN (*Ann. Chim.*, 1929, [x], 9, 223—286).—A detailed account of work some of which has been published previously (A., 1927, 340, 442). The following data seem to be new or revised. The *dimethylacetals* of propaldehyde, b. p. 89°, d^{20}_4 0.849, n^{20}_D 1.3799 (Newbury and Barnum, A., 1891, 284); butaldehyde, b. p. 114°, d^{20}_4 0.847, n^{20}_D 1.3900; *n*-hexaldehyde, b. p. 52—53°/12 mm., 158°/760 mm., d^{20}_4 0.846, n^{20}_D 1.406, are obtained from the aldehyde in the usual manner, whilst the *diethylacetal* of *n*-valeraldehyde, b. p. 59°/12 mm., d^{20}_4 0.829, n^{20}_D 1.4029, is obtained directly by the action of triethoxymethane on magnesium butyl bromide. From these are obtained α -bromopropaldehyde, d^{20}_4 1.595, n^{20}_D 1.4804 (yield very small), together with its *dimethylacetal*, b. p. 49—50°/12 mm., 151° (corr.)/760 mm., d^{20}_4 1.360, n^{20}_D 1.4482, and some dibrominated products; α -bromo-*n*-butaldehyde, d^{20}_4 1.469, n^{20}_D 1.4683, together with its *dimethylacetal*, b. p. 64°/12 mm., d^{20}_4 1.303, n^{20}_D 1.4509, *para*- α -bromo-*n*-butaldehyde, m. p. 98°, and $\alpha\alpha'$ -*di*-bromo-*n*-butaldehyde, b. p. 53°/17 mm., d^{20}_4 1.862, n^{20}_D 1.5098; α -bromo-*n*-hexaldehyde, b. p. 63—64°/12 mm., d^{20}_4 1.292, n^{20}_D 1.463; α -bromo-*n*-heptaldehyde, d^{20}_4 1.239, n^{20}_D 1.4623 (65—75% yield) (*diurethane*, m. p. 112°), together with $\alpha\alpha'$ -*di*-bromo-*n*-heptaldehyde, b. p. 96°/11 mm., d^{20}_4 1.565, n^{20}_D 1.496 (not pure); and α -bromo-*n*-valeraldehyde, d^{20}_4 1.368, n^{20}_D 1.4640 (which polymerises to the corresponding *aldol*, b. p. 195°/5 mm., d^{20}_4 1.479, n^{20}_D 1.497, depolymerisation occurring during distillation under ordinary pressure), together with the unstable $\alpha\alpha'$ -*di*-bromo-*n*-valeraldehyde, b. p. 65°/11 mm., d^{20}_4 1.735, n^{20}_D 1.5035. They exhibit the usual aldehydic properties, but, contrary to Franke (A., 1900, i, 427), are stable to boiling water and are only partly attacked by sodium methoxide in boiling methyl alcohol or toluene, or by sodium acetate and acetic acid. They react normally with amines in ethereal solution. Thus α -bromo-*n*-heptaldehyde and trimethylamine yield the quaternary ammonium salt,

m. p. 126°, decomp. 150°, with elimination of trimethylamine hydrobromide; diethylamine yields α -diethylamino-*n*-heptaldehyde, b. p. 107°/12 mm., 225°/760 mm., d^{20}_4 0.853, n^{20}_D 1.4352 (hydrochloride, m. p. 73°), which is oxidised by silver nitrate to α -hydroxy-*n*-heptic acid (barium salt + 0.5H₂O) and heptic acid; whilst ethylamine and ammonia react similarly, although in these cases it is not possible to isolate the α -aminoaldehyde. In the following reactions the α -bromoaldehydes behave abnormally. Magnesium alkyl bromides react to yield ketones of the type CH₂R·CO·R', which further react to yield the tertiary alcohols, CH₂R·CR'(OH), the latter being partly dehydrated to the olefines, CHR:CR'. Thus α -bromo-*n*-heptaldehyde yields methyl hexyl ketone (20%), b. p. 64°/12 mm., d^{16}_4 0.823, n^{16}_D 1.4195 (semicarbazone, m. p. 123°), dimethylhexylcarbinol, b. p. 81°/13 mm., d^{19}_4 0.823, n^{19}_D 1.4299, β -methyl- Δ^2 -octene (5%), b. p. 42°/14 mm., 146° (corr.)/760 mm., d^{16}_4 0.738, n^{16}_D 1.4243, and the bromohydrin, b. p. 106—107°/12 mm., d^{16}_4 1.207, n^{16}_D 1.4751, the last being obtained by a normal reaction. Similar results are obtained with zinc methyl. From α -bromo-*n*-valeraldehyde is obtained (?) γ -ethyl- Δ^2 -*n*-heptene, b. p. 144° (corr.), d^{16}_4 0.742, n^{16}_D 1.4259. By the action of lead or silver hydroxides α -bromo-*n*-heptaldehyde is converted into *n*-heptic acid, thus reacting as if it possessed the structure of α -heptoyl bromide, b. p. 80°/12 mm., d^{18}_4 1.211, n^{18}_D 1.4605, with which, however, it is not identical. An electronic explanation of these reactions is discussed and it is assumed that in the abnormal reactions ketens intervene as unisolated intermediates. By the action of sodium on the vinyl bromides CHR:CHBr and CRBr:CH₂ (*loc. cit.*) are obtained mixtures of the ethylene CHR:CH₂ and the acetylene CR·CH, whilst magnesium yields the ethylene and a magnesium vinyl bromide, the presence of the latter being shown by its action with water and iodine.

J. W. BAKER.

Action of metallic sodium on brominated cyclic acetals. H. S. HILL and G. J. C. POTTER (J. Amer. Chem. Soc., 1929, 51, 1509—1514).—Acetaldehyde and ethylene glycol in presence of excess of dry hydrogen bromide give ethylene γ -bromopropylidene ether (65% of the theoretical yield), b. p. 72—73°/10 mm. (slight decomp.). This is converted by sodium in boiling ether into (a) β -hydroxyethyl Δ^2 -*n*-propenyl ether, b. p. 60—61°/16 mm.; (b) adipylidene diethylene ether, crystals, b. p. 139—140°/10 mm., identified as described by Read and Hibbert (A., 1924, i, 709), and (c) ethylene propylidene ether, probably formed as a secondary product from (a). Ethylene γ -bromobutylidene ether (56% yield), b. p. 76—78°/10 mm., prepared from crotonaldehyde, yields with sodium (a) β -hydroxyethyl Δ^2 -*n*-butenyl ether, b. p. 60—65°/10 mm., (b) β -dimethyladipylidene diethylene ether (?), b. p. 150—170°/15 mm., and (c) ethylene butylidene ether. Thus, unlike the β -brominated cyclic acetals (A., 1928, 1213), the γ -bromo-derivatives undergo in part a Wurtz condensation in presence of sodium. The new unsaturated ethers (a) are readily, but not explosively, isomerised by 50% sulphuric acid to ethylene propylidene and butylidene ethers.

H. E. F. NOTTON.

Chlorides of α -ethylenic alcohols. C. COURTOT and J. PIERRON (Compt. rend., 1929, 188, 1501—1504; cf. this vol., 802).—Oxidation of ethyl- and propyl-vinylcarbinols with a mixture of chromic and sulphuric acids at 34—35° gives, respectively, 40 and 45% yields of ethyl vinyl ketone, b. p. 68—70°/200 mm., 0.8524, 1.4233 (picrate of diethylamine additive compound, m. p. 78°), and propyl vinyl ketone, b. p. 88—90°/150 mm., d^{14}_4 0.8518, n^{14}_D 1.4275 (picrate of diethylamine additive compound, m. p. 81°). α -Chloro- α -phenylpropane is similarly oxidised at 68° directly to phenyl ethyl ketone (yield 77%), at which temperature the chloro-compound suffers 97% hydrolysis in 75 min., whilst only 24.5% hydrolysis occurs in 48 hrs. at the ordinary temperature.

J. W. BAKER.

Action of organomagnesium compounds on ethyl ethylcyanoacetate. A. MAVRODIN (Compt. rend., 1929, 188, 1504—1506).—Ethyl ethylcyanoacetate reacts in its enolic form with the Grignard reagent in boiling ether, the hydrocarbon being eliminated and the unchanged cyano ester being recovered after hydrolysis. In boiling toluene, however, the cyano-group also reacts, the ultimate product being a β -diketone formed thus:

$$\begin{aligned} \text{CHEt}(\text{CN})\cdot\text{CO}\cdot\text{Et} &\xrightarrow{\text{MgR}^X} \text{C}(\text{CN})\cdot\text{C}(\text{OMgX})\cdot\text{OEt} + \text{RH} \\ &\xrightarrow{2\text{RMg}^X} \text{CR}(\text{NMGX})\cdot\text{C}(\text{MgX})\cdot\text{CR}(\text{OEt})(\text{OH}) \longrightarrow \\ &\text{R}\cdot\text{CO}\cdot\text{CHET}\cdot\text{CO}\cdot\text{R} \end{aligned}$$

Thus with magnesium ethyl iodide is obtained γ -diketo- δ -ethyl-*n*-heptane, b. p. 91—92°/10 mm. (25—30% yield), converted by semicarbazide acetate into 3:4:5-triethylpyrazole-1-carboxamide, m. p. 98°; and with magnesium phenyl bromide a 60% yield of $\alpha\gamma$ -diketo- $\alpha\gamma$ - δ - β -ethylpropane (Behal and Auger, A., 1890, i, 388) is obtained. This is converted by semicarbazide acetate into 3:5-diphenyl-4-ethylpyrazole, m. p. 167° (picrate, m. p. 161°), and by hydroxylamine into 2:4-diphenyl-3-ethylisooxazole, m. p. 93—94°.

J. W. BAKER.

Complex compounds of diacetyldioxime. J. V. DUBSKY and F. BRYCHTA (Pub. Fac. Sci. Univ. Masaryk, 1928, No. 103, 28 pp.).—See this vol., 543.

Sulphite-cellulose process. I. Action of hydrogen sulphite solutions on sugars. T. MARUSAWA, D. NAITO, and J. UCHIDA (Mem. Ryojo Coll. Eng., 1929, 1, 351—393; cf. Marusawa, B., 1917, 868; 1918, 52; Hagglund, this vol., 297, 428).—An investigation has been made of the products formed in solutions containing about 0.08 mol. per litre of dextrose, mannose, xylose, or levulose and 0.3 mol. per litre of sodium hydrogen sulphite, with varying additions of sodium sulphite or sulphurous acid. At the ordinary temperature dextrose, mannose, and xylose form loose compounds, largely dissociated, with sodium hydrogen sulphite, and the sulphur dioxide they contain may be directly determined after treatment with acid or alkali. The dissociation constants of the hydrogen sulphite compounds under the specified conditions are, respectively, 0.38, 0.12, and 0.15. Levulose forms no compound under these conditions. When the solutions are heated at 130°, the amounts of sugar and hydrogen sulphite rapidly diminish, and thiosulphate is formed. If the hydrogen-ion concentration is lowered by the

addition of sodium sulphite, very little thiosulphate is formed, and the rate of decomposition of the hydrogen sulphite ions is diminished. Addition of sulphurous acid causes an increase in the rate of decomposition of the hydrogen sulphite ions with formation of thiosulphate, accompanied by sulphate and polythionates, and there is less loss of sugar. The formation of thiosulphate is greatest with dextrose and least with lavulose. It is suggested that on heating the hydrogen sulphite combines with the sugar in equimolecular proportions to form stable compounds, different from those formed at low temperatures. These compounds are of two types, one of which (*A*) is decomposed by heating with dilute hydrochloric acid, with the formation of thiosulphate, whilst the other (*B*) is stable to hydrochloric acid and is only slowly decomposed by heating with alkaline hypobromite solution. The acidic *A*-compound is formed first, and decomposes to a greater or smaller extent, according to the conditions, as shown in the equation $2R \cdot C(OH) \cdot SO' = 2R \cdot CO_2H + S_2O_3'' + H_2O$, hydrogen ions favouring this decomposition. In presence of sodium sulphite the neutral *B*-compound, which is probably cyclic, is formed, probably from the *A*-compound by intramolecular change. The *B*-compound may be decomposed by sodium hydroxide and sodium peroxide and its sulphur content then determined. The decomposition of hydrogen sulphite ions is catalysed by the thiosulphate formed by decomposition of the *A*-compound, and the former decomposition is decreased by addition of sodium sulphite, in the first place, because of the decreased formation of thiosulphate from the *A*-compound, and, secondly, because of the decreased activity of the thiosulphate in absence of hydrogen ions. The reaction between sugars and hydrogen sulphites is, therefore, best studied at low hydrogen-ion concentrations. The "loosely combined" sulphur dioxide, determined, in solutions which have been heated, by titration with iodine, includes thiosulphate and polythionates. At the point at which free sulphur begins to separate, the "loosely combined" sulphur dioxide, then principally thiosulphate and polythionates, reaches a maximum.

R. K. CALLOW.

Compounds of alkaline-earth hydroxides with sugars. J. E. MACKENZIE and J. P. QUIN (J.C.S., 1929, 951—964).—Notwithstanding the discordant literature of the subject the following definite compounds can be prepared: monolime-monosucrose (penta- or hexa-hydrate, dihydrate, and anhydrous), dilime-monosucrose (hexahydrate and anhydrous), trilime-monosucrose (hexahydrate and anhydrous), monostrontia-monosucrose (hexahydrate), distrontia-monosucrose (anhydrous), monobaryta-monosucrose (anhydrous), monolime-monoglucose (monohydrate), monolime-monofructose (hexahydrate, dihydrate), monolime-monomaltose (monohydrate), monolime-monolactose (anhydrous). For these are given: analytical data, solubilities, rotations, and results of diffusion experiments. Attempts to obtain compounds containing larger proportions of the earths than those mentioned were unsuccessful. The methylglucosides, -fructosides, -maltosides, and -lactosides

were unaffected by calcium hydroxide. The constitution attributed to lime-glucose is

$OH \cdot CH_2 \cdot (CH \cdot OH)_4 \cdot CH \cdot \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} Ca$ and that to the corresponding compounds of other reducing sugars either $R \cdot CH \cdot \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} Ca$ or $R \cdot C \left(\begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} Ca \right) \cdot CH_2OH$ (R =residue of sugar molecule). The alkaline earth-sucrose compounds are probably of similar nature to those formed by combination of sucrose with sodium or potassium chlorides.

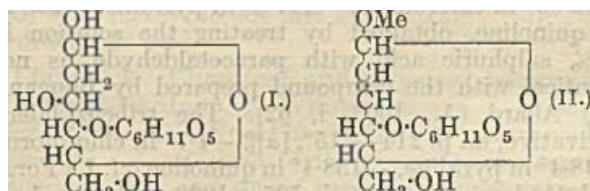
R. J. W. LE FÈVRE.

Determination of reducing sugars in presence of hydrocyanic acid. H. HÉRISSEY and A. CHALMETA (Ann. Falsif., 1929, 28, 214—223).—See A., 1928, 1358.

Determination of reducing sugars by the ferricyanide method. A. IONESCU-MATIU (Ann. Sci. Univ., Jassy, 1929, 15, 363—371).—See A., 1928, 398.

Unsaturated reduction products of sugars.

XI. 2-Deoxycellobiose (cellodesose) and derivatives of 2:3-bisdeoxycellobiose. XII. Reduction products of sugars. M. BERGMANN and W. BREUERS (Annalen, 1929, 470, 38—51, 51—61).—XI. When cellobial (A., 1921, i, 648; 1924, i, 265) is shaken with 2*N*-sulphuric acid at 0° and then freed from acid by barium hydroxide and carbonate, there is obtained 2-deoxycellobiose [cellodesose (cf. A., 1922, i, 227)] (I), decomp. 200° (corr.) after sintering at 184°, $[\alpha]_D^{25} + 23.2^\circ$ in water, $[\alpha]_D^{25} + 9.82^\circ$ in pyridine after 5 min. $\rightarrow +37.8^\circ$ after 24 hrs. The reducing power (Fehling's solution) of this sugar is only one third of that of cellobiose. When I is treated with methyl alcohol containing 1% of hydrogen chloride two 2-deoxymethylcellobioses [methylcellodesosides], *A*, m. p. 169—171° (corr.), $[\alpha]_D^{25} + 40^\circ$ in water, and *B*, m. p. about 220° (decomp.), $[\alpha]_D^{25} - 19.9^\circ$ in water, are produced. Fission of an equimolecular mixture of *A* and *B* with 0.01*N*-hydrochloric acid at 100° is almost complete after 30 min. Treatment of pentaacetyl- ψ -cellobial (A., 1921, i, 648) with methyl alcohol containing 0.25% of hydrogen chloride and subsequent acetylation of the residue with acetic anhydride and pyridine give penta-acetyl- ψ -cellobial- α -methyl-lactolide, m. p. 131.5—132.5° (corr.), $[\alpha]_D^{25} + 65.4^\circ$ in *s*-tetrachloroethane: in the absence of acetylation a tetra-acetate, m. p. 203—205° (corr.), results. Hydrolysis of the penta-acetate with barium hydroxide and aqueous-acetone yields ψ -cellobial- α -methyl-lactolide (II), m. p. 112—113° (corr.), $[\alpha]_D^{25} + 97.3^\circ$ in water. This is very sensitive towards acids and the dry substance readily absorbs water. Reduction of II with hydrogen and a palladium catalyst in presence of methyl alcohol affords 2:3-bis-



deoxy- α -methylcellobiose, m. p. 147—148° (corr.), $[\alpha]_D^{25} + 90.4^\circ$. Hydrolysis of this with 0.001*N*-hydro-

chloric acid proceeds rather more readily than a mixture of the deoxymethylcellobioses under the same conditions.

XII. Reduction of triacetyl- ψ -glucal (A., 1924, i, 266) with hydrogen in presence of acetic acid and palladium-black (cf. Wieland, A., 1912, i, 247; Tausz and Putnoky, A., 1920, ii, 61) affords $\alpha\epsilon$ -anhydro-n-hexane- $\alpha\delta\epsilon\zeta$ -tetrol diacetate (III), b. p. 102—103°/0.7 mm., n_D^{20} 1.4511, together with dihydro- ψ -glucal triacetate, b. p. 150—157°/1.2—1.5 mm., n_D^{20} 1.4545. Diacetyl- ψ -glucal is reduced in presence of platinum-black (Willstätter, A., 1921, ii, 185) to III and dihydro- ψ -glucal diacetate. Hydrolysis of III with barium hydroxide in aqueous acetone gives $\alpha\epsilon$ -anhydro-n-hexane- $\alpha\delta\epsilon\zeta$ -tetrol (IV), b. p. 122°/1.5 mm., n_D^{20} 1.4832, which when treated with thionyl chloride and pyridine yields an ester, $C_6H_{10}O_4S$, m. p. 99°, $[\alpha]_D^{25} +8.62^\circ$ in *s*-tetrachloroethane. With benzaldehyde and zinc chloride at 100°, IV yields a benzylidene derivative, $C_{13}H_{16}O_3$, m. p. 137—137.5° (corr.). $\alpha\epsilon$ -Anhydro- $\delta\zeta$ -dichlorohexane- $\alpha\epsilon$ -diol has b. p. 55°/0.8 mm. Reduction of hexa-acetyl- ψ -cellobial (A., 1921, i, 648) in presence of acetic acid and palladium-black (Tausz-Putnoky) gives $\alpha\epsilon$ -anhydro- δ -glucosidyl-n-hexane- $\alpha\delta\epsilon\zeta$ -tetrol penta-acetate (V), m. p. 133—134° (corr.), $[\alpha]_D^{25} +18.1^\circ$ in *s*-tetrachloroethane, also formed together with bisdeoxycellobiose penta-acetate, m. p. 153—155° (corr.), $[\alpha]_D^{25} +32.1^\circ$ in *s*-tetrachloroethane, by similar reduction of penta-acetyl- ψ -cellobial. If this last substance is reduced by Willstätter and Waldschmidt-Leitz's method (A., 1921, ii, 185), $\alpha\epsilon$ -anhydro- δ -glucosidyl- Δ^8 -hexene- $\alpha\delta\epsilon\zeta$ -tetrol penta-acetate, m. p. 109—110° (corr.), $[\alpha]_D^{25} +20^\circ$ in *s*-tetrachloroethane, results; with an active catalyst, however, V is produced. When diacetyl-arabinal (Gehrke and Aichner, A., 1927, 544) is boiled with water and the dry residue is acetylated with acetic anhydride and pyridine in the cold, diacetyl- ψ -arabinal, b. p. 120—124°/0.6 mm., n_D^{20} 1.4625, is obtained.

H. BURTON.

Microcolorimetric determination of lactose. F. GONZALEZ and A. GIMENO (Anal. Fis. Quím., 1929, 27, 39—47).—The micro-method of Folin and Wu for the determination of dextrose may be satisfactorily employed for lactose. H. F. GILLBE.

Derivatives of volemitol. V. ETTTEL (Coll. Czechoslov. Chem. Comm., 1929, 1, 288—293).—Volemitol, m. p. 153—154°, extracted from *Lactarius volemus* by an improved method, is best purified by crystallisation from a mixture of pyridine and alcohol. The trimethylene derivative, m. p. 212—213°, $[\alpha]_D^{25} -13.84^\circ$ in chloroform, is obtained by heating with formaldehyde and hydrochloric acid. The triethylidene derivative, m. p. 161—162°, $[\alpha]_D^{25} -72.35^\circ$ in chloroform, -117.6° in pyridine, -225.2° in quinoline, obtained by treating the solution in 50% sulphuric acid with paracetaldehyde, is not identical with the compound prepared by Bougault and Allard (A., 1903, i, 62). The tribenzylidene derivative, m. p. 214—215°, $[\alpha]_D^{25} -1.7^\circ$ in chloroform, -48.4° in pyridine, -138.4° in quinoline (cf. La Forge and Hudson, A., 1920, i, 595; 1928, 1213), is best obtained by the action of benzaldehyde in alcoholic hydrochloric acid. The hepta-acetate has m. p.

120—121°, $[\alpha]_D^{25} +20.7^\circ$ in chloroform, pyridine, or acetic acid (cf. Bourquelot, A., 1896, i, 273; Bougault and Allard, *loc. cit.*). The heptaphenylurethane, m. p. 266° (decomp.), is obtained by the action of phenyl-carbimide in pyridine. The action of acetone or chloral yields no crystalline products.

R. K. CALLOW.

Digitalis glucosides. III. Gitoxigenin and isogitoxigenin. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1929, 82, 403—409).—An improved yield of isogitoxigenin is obtained by treatment of gitoxigenin with stronger alkali than that previously employed (A., 1928, 1376); the "isogitoxigenonic acid methyl ester" formerly obtained (*loc. cit.*), by oxidation of isogitoxigeninic acid methyl ester with chromic acid, has now been found to contain a relatively resistant lactone group, and is re-named methyl isogitoxigonate. When oxidised with hypobromite, isogitoxigeninic acid yields a lactone acid, isogitoxigenic acid, $C_{23}H_{34}O_6$ (not $C_{21}H_{30}O_6$ as previously stated), m. p. 260°, $[\alpha]_D^{25} -50^\circ$ in 95% alcohol, which, with concentrated hydrochloric acid, gives anhydroisogitoxigenic acid, $C_{23}H_{32}O_5$, m. p. 215°. Methyl isogitoxigeninate gives, with hydroxylamine, an oxime, m. p. 287°; isogitoxigenin, when oxidised with chromic acid, yields isogitoxigenone, m. p. 278—279°. The apparent structural dissimilarities between gitoxigenin and the other cardiac aglucones, suggested by the previous work (*loc. cit.*), therefore disappear.

C. R. HARRINGTON.

Starch. XXII. Amylose and amylopectin. H. PRINGSHEIM and A. STEINGROEVER (Ber., 1929, 62, [B], 1352—1359).—If amylose acetate is heated with naphthalene at 260—270°, an acetate with the initial specific rotation remains. Hydrolysis of this product with alcoholic potassium hydroxide followed by very cautious desiccation of the resulting material with alcohol and ether affords an amylosan with the unchanged specific rotation of amylose which has no reducing action, is hydrolysed by amylase, and yields a blue colour with iodine. The preparation dissolves easily at the atmospheric temperature in water to a clear solution which appears stable. Cryoscopic determinations indicate an increase in mol. wt. with each measurement of the f. p., so that the minimum value, about 600, must be regarded only as an upper limit of the actual mol. wt. Freezing favours aggregation until the substance ultimately separates in an insoluble form. The same product is prepared by boiling a solution of amylose acetate in chloroform with benzenesulphonic acid, followed by precipitation with alcohol and hydrolysis. The ash content of the preparations is invariably less than 0.5% and cannot therefore account for the depression of f. p.; they cannot be regarded as causative of disaggregation, since this effect is not produced by sodium thio-cyanate in *M*/1000 solution. The b. p. of water is not raised by either preparation, but depressed by several hundredths of a degree. Determinations of mol. wt. by the Barger-Rast method indicate the formula $(C_6H_{10}O_5)_2$, whereas the cryoscopic method indicates $(C_6H_{10}O_5)_4$.

Amylopectin is converted by acetic anhydride and pyridine into a product which, after successive treatment with ice and dehydration with alcohol, yields

to boiling ethyl acetate a material identical in solubility with amylose triacetate. The portion insoluble in ethyl acetate, after purification by means of chloroform, gives *amylopectin triacetate*, which slowly yields homogeneous solutions in cold chloroform or glacial acetic acid; these are too viscous and cloudy to allow polarimetric measurement. Degradation of amylopectin triacetate with benzenesulphonic acid in chloroform could not be effected satisfactorily; the acetate which slowly separates from the solution is hydrolysed to a non-reducing product, $[\alpha]_D +165^\circ$, which gives a red colour with iodine and has a mol. wt. corresponding with $(C_6H_{10}O_5)_2$ to $(C_6H_{10}O_5)_3$ in freezing water. When large amounts of acetic anhydride are added to the chloroform and benzenesulphonic acid the solution remains homogeneous. Addition of alcohol to the solution precipitates a product, $[\alpha]_D +172.5^\circ$ in chloroform, with all the properties of amylose triacetate. This is hydrolysed to a material only partly soluble in water and giving a blue colour with iodine.

H. WREN.

Constitution of starch. K. H. MEYER, H. HOPFF, and H. MARK (Ber., 1929, 62, [B], 1103—1112).—The formation of maltose derivatives from starch by enzymatic degradation and also by the action of acetyl bromide leads to the conclusion that maltose is present in some form as a component of starch. α -Linkings must therefore be present in starch, possibly alternating with β -linkings. Application of Hudson's rules to β -maltose and β -glucose establishes that all the increments of β -glucose are present in β -maltose and the latter substance contains a dextrose residue corresponding exactly with a residue present in a chain with α -1:4-linking. Examination of various carefully dried starches in formamide shows that pure wheat starch has $[\alpha]_D +220^\circ$, whilst other varieties have somewhat lower values which approximate to those of wheat starch as their purity increases. For exclusive α -1:4-glucosyl residues the value $[\alpha]_D +226^\circ$ is calculated, so that it appears that in starch the dextrose residues are united to one another solely by α -bridges; this is true also for glycogen. Extension of the comparison to aqueous solution necessitates the use of the highest observed values for $[\alpha]_D$, since the activity first increases and then falls on boiling the solution, as a consequence of slow dispersion and incipient hydrolysis. The maximal value is $[\alpha]_D +212^\circ$, which is probably below the theoretical, whereas the calculated datum is about $+230^\circ$.

The assumption of the presence in starch of a small, uniform unit which builds the different varieties of starch by differing types of association is regarded as improbable. The great variability of starches and non-homogeneity of starch preparations indicates

in general that much greater variations occur in the length of the main valency chains than in those of cellulose. Examination of the kinetics of the hydrolysis of starch by acids shows that the action has the same order of magnitude in the initial stages and subsequently and proceeds at about the same rate as a glucosidic hydrolysis. The temperature coefficient of the change indicates that it is a normal chemical reaction and not a diffusion phenomenon,

as might be expected from the complicated structure of the amylose used. The occurrence of maltose as the final product of the degradation of starch by enzymes and acetyl bromide appears incompatible with the presence exclusively of dextrose residues, but the enzymatic action is certainly very complex and does not permit conclusions with regard to the constitution of starch, whilst the change with acetyl bromide is effected with undissolved starch, so that steric influences may play a part. The structure of starch is therefore considered to resemble in principle that of cellulose in an arrangement of dextrose residues as a diagonal screw. The cellobiose chain thus appears stretched, whereas the maltose chain has a zig-zag formation. The remarkable difference in behaviour of cellulose and starch towards water is thus explained. The observation that starch micelles can be oriented only with difficulty if at all suggests that the main valency chains are shorter than in cellulose and not arranged in longitudinal bundles, but according to some unrecognised principle of structure.

H. WREN.

"Salt hydrolysis" of starch. N. IVANOVSKY (Zhur. exp. Biol. Med., 1928, 10, 292—294).—"Salt hydrolysis" of starch to erythrodextrin was not observed. Starch is not affected by hæmin, hæmoglobin, or hæmolysed red blood cells.

CHEMICAL ABSTRACTS.

Allylcelluloses. I. SAKURADA (Z. angew. Chem., 1929, 42, 549—550).—See this vol., 430.

Celluloseglycollic acid. I. SAKURADA (Z. angew. Chem., 1929, 42, 640—643).—See this vol., 430.

Cellulosexanthoacetic acid. T. NAKASHIMA (Z. angew. Chem., 1929, 42, 546—549).—See this vol., 430.

Cellulosexanthamides. T. NAKASHIMA (Z. angew. Chem., 1929, 42, 643—645).—See this vol., 430.

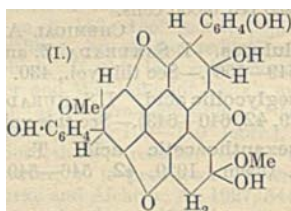
Constitution of cellulose xanthate. II. T. LIESER (Annalen, 1929, 470, 104—110).—Treatment of cellulose xanthate (B., 1928, 742) with nitrosomethylurethane in methyl alcohol affords a *monomethylcellulose*, $(C_6H_{10}O_5)(C_6H_9O_4OMe)$, insoluble in organic solvents, which swells in sodium hydroxide solution. Similar treatment of cellulose gives products containing 0.75 and 0.87% OMe. Hydrolysis of the methylated cellulose first with 75% sulphuric acid at the ordinary temperature and then with hot 8% sulphuric acid (by dilution) gives dextrose and 2-methylglucose [*phenylhydrazone*, m. p. 176° (uncorr.)]. This last compound is also obtained by hydrolysis of 3:4:6-triacetyl-2-methylmethylglucoside, m. p. 121° (uncorr.) [obtained by methylation of 1-chloro-3:4:6-triacetylglucose (Brigl, A., 1922, i, 225) with methyl iodide and silver oxide], with 10% hydrochloric acid.

H. BURTON.

Lignin. I. Chemical and physical behaviour of phenol-lignins. E. WEDERKIND and J. R. KATZ (Ber., 1929, 62, [B], 1172—1177; cf. Hillmer, B., 1926, 46).—Acetylation of the simple phenol-lignins leads smoothly and under varied experimental conditions to compounds of constant analytical composition, and the simple acetylphenol-lignin, like acetyl-

resorcinol-lignin and methylphenol-lignin, has relatively great solubility in a variety of organic media. Determinations of mol. wt. in glacial acetic acid give values of 250—270 for less than 0.5% solutions which increase rapidly with increasing concentrations. In phenol and naphthalene the minimal mol. wt. 1800 is observed. In bromoform and chloroform, the compound gives colloidal solutions. Unexpectedly this is found to be the case also in glacial acetic acid, acetone, and alcohol, so that osmotic measurements are here valueless. Analytical results indicate $C_{19}H_{20}O_6$ as the simplest possible formula for acetylphenol-lignin, whence $C_9H_{10}O_3$ for lignin. Since, however, this expression is not compatible with any constitution assigned to lignin and it has not previously been assumed that less than two methoxyl groups are present in the simplest lignin, the formula for acetylphenol-lignin is doubled ($C_{38}H_{40}O_{12}$), and thus after subtraction of two methoxyls, four acetyls, and two phenols, the expression $C_{16}H_{16}O_6$ is derived for the simplest lignin skeleton. For acetylresorcinol-lignin the constitution

$C_{16}H_{11}O_4Ac_2(OMe)_2[C_6H_3(OAc)_2]_2$ is similarly obtained. The addition of phenol to lignin is considered to occur at the double linking, thus leading to the constitution I for phenol-lignin, based on the lignin formula of Jonas.



Judged by its Röntgen spectrum, phenol-lignin appears amorphous. Acetylphenol- and acetylresorcinol-lignin have rings of which the identity periods are approximately 4 Å., thus indicating a naphthalene or conjugated benzene system. Willstätter lignin exhibits two rings, the inner, smaller, one being indistinct and not present in the phenol-lignin. Willstätter lignin derived from radial and tangential sections of wood shows no marked effect of direction, but a slight asymmetry. Röntgenographic examination of various species of wood gives essentially only the diagram of cellulose. The solubility of derivatives of phenol- and resorcinol-lignin in chloroform, benzene, etc. permits their examination in unimolecular films on water. The molecules appear to be large discs either lying flat on the water surface or overlapping like tiles. It is very probable that macro-molecules in Staudinger's sense exist and have a disc form, thus being differentiated sharply from the linear form of the cellulose molecule.

H. WREN.

Preparation of salts of methylguanidine stable in air. W. TRAUBE and K. GORNIK (Z. angew. Chem., 1929, 42, 379—381).—Molecular proportions of dicyanodiamide and methylamine hydrochloride are fused together, the cooled mass is dissolved in absolute alcohol and treated with sodium ethoxide, the solution separated from sodium chloride, and

neutralised with sulphuric acid. The crude sulphate is separated from hygroscopic impurities by dissolving in a little water and reprecipitating with alcohol, and finally crystallised from water; the pure salt, m. p. 238°, is no longer hygroscopic, and easily yields the stable picrate, m. p. 198—199°, and nitrate, m. p. 148—149°. By employing formic in place of sulphuric acid, the somewhat hygroscopic formate, m. p. 122°, is obtained. The *nitrite* forms stable prisms, m. p. 150°. *Acetylmethylguanidine*, m. p. 171—172°, is obtained in needles and elongated plates by warming the free base in alcoholic solution with ethyl acetate; its hydrochloride has m. p. 172. *Benzoylmethylguanidine*, obtained in the same way from ethyl benzoate, crystallises from hot water in hexagonal prisms, m. p. 156°; the hydrochloride forms needles, m. p. 220—221°. *Oxalymethylguanidine*, m. p. 205—209° (decomp.), and *iminomalonylmethylguanidine*, obtained from the free base by the action of ethyl oxalate and ethyl cyanoacetate, respectively, are both soluble in water; the latter separates with 1 mol. water of crystallisation, m. p. 162° (decomp.), and forms a red *isonitroso*-compound. S. I. LEVY.

β-Chloro-substituted organic compounds of arsenic. V. V. NEKRASSOV and A. S. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1929, 61, 71—78).—See A., 1928, 1230.

Hydrogenation and decomposition of organic compounds of silicon at high temperatures and pressures. V. IPATIEV and B. DOGLOV (Ber., 1929, 62, [B], 1220—1226).—Tetraethylsilane suffers 50% decomposition after 3 days at 350° according to the scheme $2SiEt_4 = C_2H_6 + Et_3Si \cdot SiEt_3$. The gaseous products contain also methane and silicon tetrahydride, whilst the formation of a difficultly volatile, viscous oil indicates more profound condensation. Triethylsilane appears to be formed. Phenyltriethylsilane suffers only 15% decomposition after 24 hrs. at 450°, 60% after 3 days at 350°. The product contains benzene, unchanged phenyltriethylsilane, triethylsilicic acid (due to presence of atmospheric oxygen in the bomb), tetraethylsilane, and diphenyldiethylsilane. A dimeride of phenyltriethylsilane is also formed. Tetraphenylsilane is extremely stable over the range 300—450°, being unaffected except for the production of 2—3% of oil after 8 days at 450°. At 490°, the molecule becomes completely degraded, probably suffering profound condensation. The crystalline substance so obtained cannot be melted, sublimed, distilled, or dissolved in any medium.

H. WREN.

Yields of Grignard reagents. I. **Alternating properties of *n*-alkyl bromides.** II. **Effect of rapid addition of halide on yield.** H. GILMAN, E. A. ZOELLNER, and J. B. DICKEY (J. Amer. Chem. Soc., 1929, 51, 1576—1583, 1583—1587).—The yields of Grignard reagents obtained from 14 alkyl bromides and from nine other halides by an improved optimum procedure have been accurately determined by an acid titration method (cf. Gilman and others, A., 1923, ii., 272; 1928, 1212; this vol., 546). The *n*-alkyl halides containing an even number of carbon atoms appear to give higher yields than the preceding homologues. A slight decrease in yield is noted with

increasing mol. wt. For a given alkyl group the order of decreasing yield is *n*-, *sec*-, *tert*-alkyl, and bromides give higher yields than the corresponding iodides. The method gives good yields of magnesium α - and β -naphthyl bromides.

The decrease in the yield of Grignard reagent caused by adding all the alkyl halide to the magnesium at once, instead of in the course of 30–35 min., has been determined for the above 23 halides. With alkyl halides the decrease is about 10–18% of the theoretical yield, with the aryl halides 3–7%, and with benzyl chloride only 0.3%. The alkyl iodides show a greater decrease than the bromides, and the branched alkyl a greater than the *n*-alkyl halides.

H. E. F. NOTTON.

Active magnesium-copper alloys for the preparation of Grignard reagents. H. GILMAN and L. L. HECK (Bull. Soc. chim., 1929, [iv], 45, 250–254).—Further comparative experiments on the use of active magnesium-copper alloys for the preparation of Grignard reagents from β -bromostyrene, *n*-butyl chloride, and pinene hydrochloride show that alloys containing 13.3, 14.5, and 19.6% of copper are more efficient than activated magnesium, the alloy containing 14.5% of copper being superior to that containing 12.75% of copper (A., 1928, 253). The results indicate maximum efficiency for an alloy containing 15% of copper. The colour reaction previously described (A., 1928, 160) was used in determining the rate of formation of the Grignard compound. Treatment of activated magnesium or magnesium-copper alloys with dry hydrogen at 360° (cf. Ray and Dutt, A., 1928, 630) reduced their catalytic activity.

R. BRIGHTMAN.

Formation of di-*p*-tolyl in preparation of magnesium benzyl chloride. Preliminary formation of free radicals in preparation of Grignard reagents. H. GILMAN and J. E. KIRBY (J. Amer. Chem. Soc., 1929, 51, 1571–1576).—The hydrocarbon, m. p. 119–120°, obtained in small yield in many reactions involving the use of magnesium benzyl chloride (cf. A., 1925, i, 802) is now shown to be di-*p*-tolyl. It is also obtained when this reagent reacts with cupric chloride, azobenzene, or formaldehyde, and must, therefore, be present in the reagent itself. It is probably formed from the free benzyl radicals, which are the initial products of the reaction (cf. this vol., 179). This is confirmed by the presence of di-*p*-tolyl (0.2% yield; also traces of *o*-tolyl derivatives, oxidised to phthalic acid) in the product from magnesium benzyl chloride and hydrochloric acid at

The possibility that the di-*p*-tolyl might have arisen from traces of *p*-chlorotoluene in the benzyl chloride was excluded by a special test. Difficulty was experienced in obtaining a negative Beilstein test for chlorine on samples of benzoic acid.

H. E. F. NOTTON.

Forced reaction between some hydrocarbons and organomagnesium halides. H. GILMAN and J. A. LEERMAKERS (Rec. trav. chim., 1929, 48, 577–579).—No action can be detected between magnesium benzyl chloride or magnesium ethyl bromide and *o*-, *m*- or tri-phenylmethane when they are refluxed in benzene, toluene, or xylene under varying conditions,

almost the whole of the hydrocarbon being recovered in the pure state.

J. W. BAKER.

Thermal decomposition of organo-magnesium alkoxides. D. IVANOV (Compt. rend., 1929, 188, 1259–1260).—A study of the thermal decomposition of magnesium ethoxy-, *n*- and *iso*-propoxy-, *iso*- and *tert*-butoxy-, cyclohexyloxy-, and phenoxy-bromides, and of the *n*-amyloxy- and benzyloxy-chlorides shows that the decomposition temperature is 330–350° for derivatives of primary alcohols, 190–220° for those of secondary, 140–160° for those of tertiary alcohols, 380–400° for the benzyloxy-, and 500° for the phenoxy-derivative. It is suggested that the initial reaction is a double decomposition between two molecules of the alkoxide with the formation of magnesium oxide and halide, the corresponding ethylenic hydrocarbon, and the alcohol. These are actually the principal products, accompanied by polymerisation products of the hydrocarbon and traces of other compounds. The magnesium halide catalyses the dehydration of the alcohol.

R. K. CALLOW.

Reactions of organic mercury compounds with organic halides. II. F. C. WHITMORE and E. N. THURMAN (J. Amer. Chem. Soc., 1929, 51, 1491–1503).—Organic halides have been refluxed with mercury diphenyl, or di-*p*-tolyl in toluene, carbon tetrachloride, or chloroform for 300 hrs., or until reaction has taken place. The following do not react: ethylidene, benzylidene, and benzoyl chlorides, dodecyl, ethylene and cyclohexyl bromides, tetrachloro- and hexachloro-ethane, *sec*-, butyl, allyl, benzyl, and 2:4:6-trinitrophenyl iodides, benzotrichloride, phenyl β -bromoethyl ether, phenyl γ -bromopropyl ether, ethyl dichloroacetate, methyl α -bromo-*isobutyrate* and α -bromocamphor. The following give with mercury diaryls arylmercuric halides (I) and tarry products: bromonitromethane, acetyl iodide, dibenzoylmethyl bromide, ω -bromoacetophenone, phenylacetylenyl iodide, and iodoacetoneitrile. Ethyl bromomalonate reacts partly, giving I, ethyl malonate, *p*-bromotoluene, and (?) ethyl ethylene-tetracarboxylate. On the other hand five halides undergo definite reactions of four types. (a) Diphenylmethyl bromide gives with mercury di-*p*-tolyl, diphenyl, and di-*n*-butyl, respectively, diphenyl-*p*-tolylmethane (80%), triphenylmethane (90%), and $\alpha\alpha$ -diphenylpentane (35% of theory). (b) *tert*-Butyl bromide gives almost quantitatively *isobutylene*, I, and toluene. *tert*-Amyl iodide and ethyl α -bromo-ethane- $\alpha\beta$ -tricarboxylate yield similarly trimethyl-ethylene and ethyl ethylenetricarboxylate, respectively. (c) 9-Bromofluorene with mercury diaryls gives 9:9'-difluorenylidene and I. (d) Stilbene dibromide gives stilbene, I, and *p*-tolyl bromide. Thus, in general, mercury diaryls react with organic halides similarly to, but much less readily than other types of bases. Contrary to the statement of Kharasch (A., 1922, i, 189), 2:4:6-trinitrophenylmercuric chloride and mercury bis-2:4:6-trinitrophenyl react normally with iodine, giving iodo-2:4:6-trinitrobenzene, but no hexanitrodiphenyl.

H. E. F. NOTTON.

1:2-Dimethylcyclopropanes. J. BAUDRENGHEIN (Bull. Acad. Roy. Belg., 1929, 15, 53–80).—

1 : 2-Dimethylcyclopropanes have been prepared from $\beta\delta$ -dibromopentane, obtained by either of the following processes : (1) Condensation of magnesium methyl bromide and crotonaldehyde and decomposition of the product with water gives a 75% yield of Δ^r -pentene- β -ol, (I), b. p. 122—122.1°/760 mm., d^{20} 0.8962, n_D^{20} 1.4163, but if sulphuric acid is used in the decomposition of the product a relatively large proportion of the ether $(CHMe:CH:CHMe)_2O$, b. p. 158—158.5°, d^{20} 0.8047, n_D^{20} 1.4306 (also prepared by the action of 10% sulphuric acid on the alcohol), is obtained. Anhydrous hydrogen chloride converts I into β -chloro- Δ^r -pentene, b. p. 100.5°/771.6 mm., d^{20} 0.9004, n_D^{20} 1.4322, which, since it is readily hydrolysed, is best obtained by direct distillation of the alcoholic solution without washing. Hydrogen bromide slowly converts this into the bromopentene (also obtained by direct action of hydrogen bromide on I), which is very readily hydrolysed and is converted by further treatment with hydrogen bromide (after distillation to remove an antecatalyst) into a mixture of $\beta\gamma$ - and $\beta\delta$ -dibromopentanes. A similar mixture is obtained by the action of hydrogen bromide on the acetate of I obtained by the action of potassium acetate on the bromopentene, but with the acetate, b. p. 138.5—139°/753 mm., d^{20} 0.8962, n_D^{20} 1.4163, prepared by the action of acetic anhydride on I, the main product is the bromopentene, further absorption of hydrogen bromide being extremely slow. By the action of phosphorus tribromide on I only 69% of monobrominated products are obtained, isomerisation occurring, since conversion into the acetates yields a mixture which was not further investigated. By the action of zinc and boiling 80% alcohol on the mixed dibromopentanes a mixture of Δ^s -pentene (44% from the dibromopentanes obtained from the chloropentene, 16% from the mixture obtained from the acetate) and stereoisomeric 1 : 2-dimethylcyclopropanes, which is separated by conversion of the former into $\beta\gamma$ -dibromopentane by the action of bromine in potassium bromide solution, and distillation of the cyclic hydrocarbons, b. p. 30—36°. (2) By the action of hydrogen chloride on aldol only resins are obtained, and only a 50% yield of β -chloro-*n*-butaldehyde results with crotonaldehyde. (3) Pentane- $\beta\delta$ -diol is obtained by reduction of methyl β -hydroxypropyl ketone (Claisen, A., 1899, i, 667) with platinum-black and hydrogen, and hence is converted into $\beta\delta$ -dibromopentane and the dimethylcyclopropanes. (4) Pentane- $\beta\delta$ -diol, obtained by the action of magnesium methyl bromide on aldol (Franke and others, A., 1907, i, 171), is difficult to separate from magnesium salts by extraction with ether, but the product is readily converted directly by the action of 48% hydrobromic acid into a mixture of the bromohydrin and dibromopentane, which yields a mixture of dibromopentanes by the action of hydrogen bromide at 100°, since by the action of zinc it yields a mixture of the ethylenic and cyclic hydrocarbons. (5) Catalytic reduction of acetylacetone with platinum-black yields a mixture of pentan- β -ol and pentane- $\beta\delta$ -diol (30%), and with active platinum containing a trace of iron a mixture of the diol and methyl β -hydroxypropyl ketone is obtained. Reduction with sodium and alcohol, however, gives a 70% yield of the diol. The dibromopentanes ob-

tained from this, on treatment with zinc, yield only 1% of the ethylenic derivative, the main product being 1 : 2-dimethylcyclopropane. By repeated fractional distillation of the 1 : 2-dimethylcyclopropanes, b. p. 30—36°, the two stereoisomeric forms, b. p. 28.8—29°, d^{20} 0.6769, 1.37129, and b. p. 37.2—37.4°, d^{20} 0.6928, n_D^{20} 1.38223, respectively, are obtained. The latter form is more resistant to the action of bromine. Exaltation of the molecular refractivities for various wave-lengths are tabulated and discussed.

J. W. BAKER.

Oxidation of organic halogen compounds. C. COURTOT and J. PIÉRON (Bull. Soc. chim., 1929, [iv], 45, 286—293).—The oxidation of α -olefinic secondary chlorides to ketones is related to the mobility of the halogen in presence of water. Thus, 1-chloro- Δ^2 -cyclohexene, b. p. 65—66°/40 mm., obtained in 93% yield by the action of dry hydrogen chloride on $\Delta^{1:3}$ -dihydrobenzene at -5° to -8° , is hydrolysed by water at 15° in 48 hrs. and at 60—65° in 75 min. Oxidation with sulphuric acid and sodium dichromate at 60—65° gives 60% of Δ^1 -cyclohexen-1-one, b. p. 63°/14 mm. Chlorocyclohexane is only partly (8.7%) hydrolysed at 90—95°, and on oxidation at 40—45° affords adipic acid. Chlorocyclopentane is neither hydrolysed nor oxidised at 50—55°; at 90—95° 71% is hydrolysed and oxidation gives glutaric acid. Similarly 9-chlorofluorenone is neither oxidised nor hydrolysed at 15°, but at 95—97° is rapidly hydrolysed, and oxidation affords fluorenone. δ -Chloro- Δ^s -hexene, b. p. 65—67°/110 mm., obtained in 81% yield by saturating Δ^s -hexen- δ -ol with hydrogen chloride at 0°, does not combine with halogen hydride. Hydrolysis is complete in 90 min. at 40° and 81% is hydrolysed in 48 hrs. at 15°. Oxidation at 60—65° gives 55% of Δ^s -hexen- δ -one, b. p. 137—140° (2 : 4-dinitrophenylhydrazones, m. p. 100—101°), converted by hydrogenation in presence of platinum-black into ethyl propyl ketone, b. p. 121—124° (semicarbazone, m. p. 112°). γ -Chloro- δ -methyl- Δ^s -heptene, b. p. 75—78°/53 mm., obtained by the action of hydrogen chloride on δ -methyl- Δ^s -hepten- γ -ol at 0°, is readily hydrolysed, 93% at 15° in 48 hrs., 90% at 45—50° in 75 min., and at 45—50° is oxidised to δ -methyl- Δ^s -hepten- γ -one, b. p. 96—98°/70 mm., 170—172°/735 mm. (semicarbazone, m. p. 167°, 2 : 4'-dinitrophenylhydrazones, m. p. 147°). some δ -methyl- Δ^r -heptadiene being also formed. Δ^s -Hexen- δ -one and δ -methyl- Δ^s -hepten- γ -one do not react with magnesium methyl iodide at the ordinary temperature, and accordingly do not exist in the enolic form. Oxidation of the Δ^s -sec.-chloride accordingly offers an alternative route for preparing the Δ^s -ketone.

R. BRIGHTMAN.

***p*-Bromoethylenic derivatives of benzene and their magnesium organo-compounds.** II. R. QUELET (Bull. Soc. chim., 1929, [iv], 45, 255—274).—*p*-Bromostyrene does not react with magnesium activated by bromine in ether. With *p*-bromopropenylbenzene reaction is incomplete, about 10% of the bromide being recovered unchanged, and the normal magnesium derivative undergoes partial condensation. *p*-Bromo- Δ^a -butenylbenzene, *p*-bromoallylbenzene, and *p*-bromo- Δ^r -butenylbenzene behave similarly and the yield of magnesium derivative at the

ordinary temperature as determined by Gilman's method (A., 1923, ii, 272) is considerably higher than that found by Job and Reich's method. The formation of the complex magnesium derivative is accelerated by heat. On decomposition with water, magnesium *p*-propenylbenzene bromide affords 43% of propenylbenzene, b. p. 68°/12 mm., d_4^{20} 0.918, n_D^{20} 1.558 (dibromo-derivative, m. p. 66.5°), and some *pp'*-dipropenylbenzene, m. p. 186°, together with a non-crystalline semi-fluid substance, probably the decomposition product of the complex magnesium derivative. Δ^a -Butenylbenzene, b. p. 80°/12 mm., d_4^{20} 0.907, n_D^{20} 1.550, allylbenzene, b. p. 154°/730 mm., and Δ^a -butenylbenzene, b. p. 65°/12 mm., are similarly obtained accompanied by similar uncrystallisable non-volatile products. About 20% of the *p*-bromoallylbenzene is recovered unchanged.

The following have been prepared from the above magnesium derivatives by the usual methods: *p*-allylphenol, b. p. 120°/12 mm., 235°/732 mm., *p*-allylbenzoic acid (yield 25%), m. p. 104—105° (silver salt, dibromo-derivative, m. p. 154°), *p*-diallylbenzene, b. p. 94°/12 mm., d_4^{20} 0.915, n_D^{20} 1.526 (tetrabromo-derivative, m. p. 109°), *p*-allylbenzaldehyde (with ethyl orthoformate, yield 12%), b. p. 113°/12 mm., n_D^{20} 1.555 (semicarbazone, m. p. 197°, bromo-derivative, b. p. 193—195°/15 mm. (decomp.)), *p*-propenylphenol, m. p. 93°, b. p. 136—137°/12 mm., *p*-propenylbenzoic acid (yield 30%), m. p. 215°, sublimes above 190° (silver salt), *p*-propenylallylbenzene (from magnesium *p*-propenylbenzene bromide and allyl bromide), b. p. 107—108°/11 mm., d_4^{20} 0.918, n_D^{20} 1.559 (tetrabromo-derivative, m. p. 73°), *p*-propenylbenzaldehyde (yield 10%), b. p. 132°/17 mm., d_4^{20} 1.044, 1.607 (semicarbazone, m. p. 230°), and *p*-propenylphenylethylcarbinol, m. p. 57°, b. p. 143—145°/11 mm. (phenylurethane, m. p. 235—236°), which on dehydration with phosphoric anhydride in benzene affords *p*-dipropenylbenzene, m. p. 63—64°, b. p. 123—125°/12 mm. (tetrabromo-derivative, m. p. 168—169°). Comparison of the *p*-diallyl-, *p*-dipropenyl-, and *p*-allylpropenylbenzene shows that under 12 mm. migration of the double linking from the β - to the α -position raises the b. p. by 15°. The low m. p. of the tetrabromo-derivative of *p*-allylpropenylbenzene is attributed to dissymmetry of the molecule and is not really an exception to the rule that the bromides of Δ^a -derivatives have higher m. p. than the bromides of the Δ^b -derivatives.

R. BRIGHTMAN.

2-Methylnaphthalenes. III. K. DZIEWOŃSKI and A. WULFSOHN (Bull. Acad. Polonaise, 1929, A, 143—148).—Sulphonation of 2-methylnaphthalene with an equimolecular quantity of chlorosulphonic acid in nitrobenzene at 30—40° gave 2-methylnaphthalene-8-sulphonic acid (sodium salt; chloride, m. p. 96°; amide, m. p. 172—174°; anilide, m. p. 162—164°). Its constitution was established by conversion into 7-methyl- α -naphthol, m. p. 109—111° [acetate, m. p. 39—41°; azo-derivative with *p*-nitroaniline, m. p. 250° (decomp.)], by fusion of the sodium salt with potassium hydroxide. A. I. VOGEL.

2:3- and 1:4-Dinitronaphthalene. L. K. CHUDOZHLOV (Coll. Czech. Chem. Comm., 1929, 1, 302—305).—See A., 1927, 49.

Pyrogenic decomposition of the perhydrides of fluorene and acenaphthene under pressure of hydrogen. M. A. ORLOV and M. A. BELOPOLSKY (Ber., 1929, 62, [B], 1226—1234).—Hydrogenation of fluorene at 210—230° with initial pressure 60—70 atm., twice in presence of nickel oxide, and then in that of a mixture of nickel oxide and hopcalite (mixture of oxides of silver, manganese, copper, and cobalt), affords a complex mixture of products. Treatment of the mixture at 380°/70—75 atm. initial pressure leads to the gasification of about 32% of it and the production of monocyclic and, probably, dicyclic naphthenes. The presence of perhydroindenes in the fractions of higher b. p. is established by their conversion when passed through a tube heated at 750° into indene, cyclopentadiene, naphthalene, and chrysene; under similar conditions, these products are obtained also from perhydroindene. When distilled with aluminium chloride, fluorene affords coke and diphenyl.

Perhydroacenaphthene is remarkably stable towards heat, but, at about 450° yields gases and petroleum hydrocarbons containing benzenoid compounds. When passed through a tinned iron tube at 650° it gives ethylene and propylene, cyclopentadiene, toluene, indene, and methyldiene. The presence of indenenes in coke-oven tar and primary tar is probably due to the decomposition of fluorene hydrides, the presence of which has been established in coal.

H. WREN.

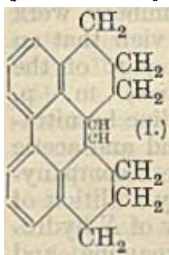
meso-Derivatives of anthracene and dianthryl.

V. I. MINAEV and B. P. FEDOROV (J. Russ. Phys. Chem. Soc., 1929, 61, 143—150).—Sodium sulphite and 9-nitroanthracene react to form sodium anthracene-9-sulphonate, which on treatment with alkali hydroxide yields anthranol, and 9-anthramine on heating with ammonia in a sealed tube. Sodium dianthryl 9-sulphate is also obtained as a by-product, which can be easily reduced to the parent hydrocarbon, dianthryl, hydrolysed to give 9-hydroxydianthryl, and, on heating with ammonia in a sealed tube, made to yield 9-dianthrylamine, m. p. 305° (decomp.).

M. ZVEGINTZOV.

[Pyrogenic decomposition of chrysene under pressure of hydrogen.] N. ORLOV and N. LICHTACHEV (Ber., 1929, 62, [B], 1378; cf. this vol., 549).—A correction. H. WREN.

Perylene and its derivatives. XXII. A. ZINKE and N. SCHNIDERSCHITSCH (Monatsh., 1929, 51, 280—284).—Catalytic reduction of perylene with hydrogen and palladised charcoal in acetic acid at 990—1000 mm. yields octahydroperylene (I), m. p. 159—161°, whilst



by extraction of the residual catalyst with acetic acid hexahydroperylene (Zinke and Unterkreuter, A., 1920, i, 541) is obtained. Similar reduction of perylene-3:10-quinone yields the corresponding hexahydroperylene-3:10-diol, m. p. 298—300° (diacetate, m. p. 342—343°), whilst from the 1:12-quinone is obtained hexahydroperylene-1:12-diol, m. p. 260° (decomp.) (diacetate, m. p. 192—194°), together with a small quantity of a substance, m. p. 146—150° (possibly the octa-

hydrodiol). Similar reduction of perylene-3 : 9-quinone yields an unidentified substance, m. p. 251—253°.

J. W. BAKER.

Nitration of bromoanilines in sulphuric acid. R. LUKEŠ and J. FRAGNER (Coll. Czech. Chem. Comm., 1929, 1, 294—301).—Nitration of *o*-bromoaniline in concentrated sulphuric acid yields 6-bromo-*m*-nitroaniline. *m*-Bromoaniline, under the same conditions, yields 3-bromo-*p*-nitroaniline, m. p. 175—176°, accompanied by 5-bromo-*o*-nitroaniline, m. p. 151—152°, in small quantity. The constitution of 3-bromo-*p*-nitroaniline is confirmed by bromination to 2 : 3 : 6-tribromo-*p*-nitroaniline, m. p. 159°, by conversion into 2 : 4-dibromonitrobenzene, m. p. 61°, and by conversion into *o*-bromonitrobenzene, m. p. 44—45° (lit. 41°), by the action of nitrous fumes. 3-Bromo-*p*-nitroaniline has also been prepared by the nitration of *m*-bromoacetanilide and converted into 2 : 3 : 6-tribromo-*p*-nitroaniline as described by Claus and Wallbaum (A., 1898, i, 18), who give m. p. 172° and 131°, respectively.

R. K. CALLOW.

Transformation of phenylnitroamines into nitroanilines. I. A. E. BRADFIELD and K. J. P. ORTON (J.C.S., 1929, 915—921).—The isomeric change of aromatic nitroamines into nitroanilines under the influence of mineral acids in aqueous or aqueous acetic acid media (cf. Orton and Pearson, J.C.S., 1908, 93, 725; Orton, Reed, and Thomas, Brit. Assoc. Repts., 1912, 117; Chem. News, 1912, 106, 236) has been re-examined. Quantitative measurements (using a colorimetric method) of the velocity of transformation of the nitroamines derived from 2 : 4-dichloro- and 2 : 4-dibromo-aniline, and 3-bromo-*p*-toluidine, in 50% and 98% acetic acid media, show that although the appropriate nitroaniline is the main product, by-products arise, one of which is a substance capable of diazo-coupling with a phenol. The formation of the nitroaniline and by-products proceeds as a reaction of the first order and no stoichiometrical relation exists between the proportions of the products; the ratio varies with the experimental conditions, but in general has the same value for equivalent concentrations of different catalysing acids. By contrast with the chloroamine transformation (A., 1928, 628), the anion of the acid catalyst is not fundamentally concerned in the reaction, and the chlorination of an anilide by the chloroamine of another finds no complete and simple parallel, although it is sometimes possible for the nitro-group to migrate from a nitroamine to a carbon atom of another aniline or anilide. The catalytic behaviour of nitric acid for the transformation is anomalous, but this is not due to nitration effects. The results confirm the preliminary work (*loc. cit.*), and are in harmony with the view that an intramolecular process is the essential part of the transformation. 3-Bromo-*p*-tolylnitroamine, m. p. 65°, was prepared from 3-bromo-*p*-toluidine by nitration with nitric acid (*d* 1.50) in acetic acid and acetic anhydride at 0°, and separated from the accompanying 3-bromo-5-nitro-*p*-tolylnitroamine by addition of three-quarters of the calculated quantity of *N*-hydrochloric acid; 2 : 4-dichlorophenylnitroamine and 2 : 4-dibromophenylnitroamine, m. p. 77°, were obtained by the method of Orton (J.C.S., 1902, 81, 806;

A., 1907, i, 205). These nitroamines are highly sensitive to light.

C. W. SHOPPEE.

Pyridine as catalyst in production of dimethyl- α -naphthylamine. F. G. GERMUTH (J. Amer. Chem. Soc., 1929, 51, 1555—1557).—Addition of 4 c.c. of pyridine to each g.-mol. of α -naphthylamine increases the yield of dimethyl- α -naphthylamine obtainable by treatment with methyl sulphate (2 mols.) and 40% sodium hydroxide from 51.3% to 65.8%. Larger amounts produce no further increase.

H. E. F. NOTTON.

Constitution of Bandrowski's base. J. J. RITTER and G. H. SCHMITZ (J. Amer. Chem. Soc., 1929, 51, 1587—1589).—The constitution assigned by Bandrowski (A., 1889, 973; cf. Erdmann, A., 1904, i, 778, 935) to the base, m. p. 238°, obtained by oxidising *p*-phenylenediamine with potassium ferricyanide is confirmed by the observation that 1 mol. of the base, when oxidised with lead peroxide and 25% sulphuric acid, yields 1 mol. of *p*-benzoquinone. A compound analogous to that formed from *p*-toluidine (Green, J.C.S., 1893, 63, 1395) should give 2 mols. of quinone.

H. E. F. NOTTON.

Reduction of esters of benzeneazohydroxybenzoic acids. E. PUXEDDU (Gazzetta, 1929, 59, 212—218).—Reduction of an alkyl benzeneazophenolcarboxylate involves, in addition to the loss of the benzeneazo-group, the removal of the alkyl group. Thus methyl 5-benzeneazosalicylate (Limpricht, A., 1891, 1036) (methyl ether, m. p. 66°) is reduced by phenylhydrazine or by tin and hydrochloric acid to 5-aminosalicylic acid, which is also obtained from ethyl 5-benzeneazosalicylate, m. p. 100° (methyl ether, m. p. 64°), or from the phenyl ester, m. p. 149°.

E. W. WIGNALL.

Stereochemistry of aromatic compounds.
VIII. Optically active heterocyclic compounds and azo-dyes of the dinaphthyl series. R. KUHN and P. GOLDFINGER (Annalen, 1929, 470, 183—200; cf. Mascarelli, this vol., 181).—Azo-2 : 2'-naphthalene is reduced by stannous chloride and alcoholic hydrogen chloride (cf. Jacobsen, A., 1922, i, 589) to 2 : 2'-diamino-1 : 1'-dinaphthyl (I), m. p. 193° (corr.). When I is treated with *d*-camphorsulphonic acid in alcoholic chlorobenzene, *d*-2 : 2'-diamino-1 : 1'-dinaphthyl *d*-camphorsulphonate, m. p. 243° (corr.), $[\alpha]_D^{25} + 491.8^\circ$ in pyridine, separates. *d*-2 : 2'-Diamino-1 : 1'-dinaphthyl (II), m. p. 242.5—243° (corr.), $[\alpha]_D^{25} + 149.5^\circ$ in pyridine, exhibits *laevo*-rotation ($[\alpha]_D^{25} - 30^\circ$) in *N*-hydrochloric acid. The *l*-isomeride (III) has m. p. 243°, $[\alpha]_D^{25} + 46.8^\circ$ in 2*N*-hydrochloric acid. Resolution of I is not readily effected with α -bromo- γ -camphorsulphonic acid. Condensation of 6 : 6'-diaminoditolyl (Meisenheimer and Horing, A., 1927, 766) with benzil at 180—200° affords a condensation product, m. p. 213° (corr.): the corresponding substances from I, II, and III have m. p. 277.5° (corr.), yielding a turbid liquid which becomes clear at 291.5°, m. p. 295°, $[\alpha]_D^{25} - 1910^\circ$ in pyridine, and m. p. 281°, $[\alpha]_D^{25} + 823.4^\circ$ in pyridine, respectively. The *dibenzylidene* derivative of II has m. p. 146° (corr.), $[\alpha]_D^{25} + 129^\circ$ in pyridine, -130° in sulphuric acid, whilst the condensation product with dinitrobenzil has m. p. 335, $[\alpha]_D^{25} - 1611^\circ$ in pyridine. Acetylation of an optically

impure specimen of III with acetic anhydride and pyridine gives a *diacetyl* derivative, m. p. 237°, $[\alpha]_D^{25} +151.6^\circ$ in acetic acid, which when reduced with hydrogen in presence of platinum oxide and acetic acid, yields an inactive product. Similar results are obtained with the *diacetyl* derivative, $[\alpha]_D^{25} -92^\circ$ in acetic acid, and the benzil condensation product, of II. Racemisation of II is not effected by heating with *N*-hydrochloric acid at 100°, but at 135° some optically inactive naphthocarbazole, m. p. 157° (Meisenheimer and Witte, A., 1904, i, 193) (picrate, m. p. 221°), is formed. When II is diazotised and coupled with resorcinol, a deep-red *azo-dye*, $C_{22}H_{22}O_4N_4$, darkens and decomp. about 300°, $[\alpha]_{D589}^{20} -1730^\circ$ in pyridine, is obtained. The rotation-dispersions of most of the above optically active compounds, for different wave-lengths, are given.

H. BURTON.

Volatility and structures of azides and aliphatic diazo-compounds. N. V. SIDGWICK (J.C.S., 1929, 1108—1110).—Comparison of the b. p. of azides and aliphatic diazo-compounds with the corresponding halides and nitro-compounds, shows that the b. p. of the former lie near those of the bromides, or between these and the iodides (cf. Forster and Newman, *ibid.*, 1910, 97, 2572), whilst the b. p. of the latter lie very near those of the chlorides. The open-chain formulæ $R \cdot N \cdot N \cdot N$, $R_2C \cdot N \cdot N$, contain semi-polar double linkings, the presence of which always causes a rise in the b. p.; the b. p. would therefore be expected to lie near those of the nitro-compounds rather than the chlorides or bromides. The results appear to indicate that the ring formulæ should be retained for both azides and diazo-compounds. C. W. SHOPPEE.

Constitution of normal diazotates and diazo-hydrates. A. HANTZSCH (Ber., 1929, 62, [B], 1235—1241).—The observation of Cambi and Szegő (A., 1928, 1369) that the absorption curves of normal and *iso*-diazotates are differentiated by the presence or absence of a characteristic band has been anticipated by Hantzsch and Lifschitz (A., 1912, ii, 1116), who have been led to the conclusion that the light absorption of the *azo*-group in *azo*-compounds $R \cdot N \cdot N \cdot R$ and particularly in the isomeric diazo-compounds, $Ar \cdot N_2 \cdot SO_3H$, $Ar \cdot N_2 \cdot CN$, and $Ar \cdot N_2 \cdot OMe$, is so unusually variable that no certain interpretation with regard to constitution can be based on the absorption curves. Cambi and Szegő's assertion that "normal and *iso*-diazotates cannot possibly be stereoisomerides" is without foundation and their method of determining constitution by optical means leads to untenable conclusions when applied to other *azo*-compounds such as tolueneazodimethylamine and potassium hyponitrite. Reply is made to Angeli (A., 1928, 1129).

H. WREN.

Introduction of the triphenylmethyl group into phenols. II. D. V. N. HARDY (J.C.S., 1929, 1000—1011).—Phenols and phenolic ethers fall into three groups according to their behaviour towards an acetic-sulphuric acid solution of triphenylmethylcarbinol (the Baeyer-Villiger reaction). Those which condense (Group I) include phenol, anisole, phenetole, *o*-cresol, *o*-tolyl methyl ether, *o*-tolyl ethyl ether, *m*-cresol, pyrocatechol, guaiacol, veratrole, resorcinol

and its dimethyl ether, quinol, pyrogallol and its trimethyl ether, thymol, α - and β -naphthol; those which reduce the carbinol to triphenylmethane (group II) include *p*-cresol, *p*-tolyl methyl and ethyl ethers, *m*- and *p*-chlorophenol, quinol dimethyl ether. To group III, those which do not react, belong *o*- and *p*-nitrophenol, picric acid, *o*- and *p*-nitroanisole, salicylic acid, methyl salicylate, trichlorophenol, trichloroanisole, tribromophenol. *o*-Chloro- and *o*-bromo-phenol exhibit anomalous behaviour, condensing and yielding triphenylmethane simultaneously. Mechanisms for the Baeyer-Villiger reaction suggested by the author (with Boyd, A., 1928, 516) and by van Alphen (*ibid.*, 57) are discussed. It is considered that the primary reaction is between the triphenylmethyl cation and the undissociated phenol, since phenolic ethers react similarly to phenols. It is suggested that the formation of triphenylmethane by members of group II is preceded by elimination of triphenylmethyl as the anion from an intermediate complex, and the nature of the subsequent oxidation products, in particular those derived from *p*-cresol, is discussed. A number of reactions which appear to involve the triphenylmethyl anion are instanced. In general, the triphenylmethyl group enters the nucleus para to hydroxyl or methoxyl, but occasionally *o*-substitution occurs. Contrary to the statement of Schorigin (A., 1928, 59), di-triphenylmethylation has been observed for α -naphthol and 1:3-dimethoxybenzene. The preparation of the following tetraphenylmethanes is described: 4-ethoxy-, m. p. 191°, converted by boiling acetic-hydriodic acid into 4-hydroxy-, 3:4-dihydroxy-, m. p. 262° (cf. *lit.*); 3:4-dimethoxy-, m. p. 170° (*lit.*), converted by acetic-hydriodic acid into the foregoing hydroxy-compound; 2:4-dihydroxy-, m. p. 268° (decomp.) (*lit.*); 1:3-dimethoxy-, m. p. 180° (*lit.*), together with 1:3-dimethoxy-4:6-bistriphenylmethylbenzene, m. p. 271°; 3:4:5-trihydroxy-, m. p. 255° (decomp.) after darkening at 230° (compound + 2COMe₂); 3:4:5-trimethoxy-, m. p. 178°; 4-hydroxy-2-methyl-5-isopropyl-, which is dimorphous, α -form, m. p. 106—107°, β -form, m. p. 157°; 3-chloro-4-hydroxy-, m. p. 193.5°, together with triphenylmethane (I), m. p. 93°; 3-bromo-4-hydroxy-, m. p. 186—187°, together with I. Guaiacol yields a mixture of 4-hydroxy-3-methoxy- and 3-hydroxy-4-methoxy-tetraphenylmethanes hydrolysed by acetic and hydriodic acids to 3:4-dihydroxytetraphenylmethane, m. p. 262°. α -Naphthol affords 4-triphenylmethyl- α -naphthol, m. p. 204—204.5° (compound + 1EtOH), together with 2:4-bistriphenylmethyl-1-naphthol, m. p. 235—236°; β -naphthol gives 1-triphenylmethyl- β -naphthol, m. p. 228°. *m*-Chloro- and *p*-chloro-phenol, quinol dimethyl ether, *p*-tolyl ethyl ether, and *p*-tolyl methyl ether all give I as the sole identifiable product: the yield is 98.4% in the last case. *p*-Cresol yields I together with an acidic substance, isolated as a brown, amorphous powder, shrinking about 85°, and melting at 100—110° (decomp.). *o*-Tolyl ethyl ether affords 4-ethoxy-3-methyltetraphenylmethane, m. p. 144° (cf. van Alphen, A., 1927, 867), also obtained synthetically as follows: triphenylcarbinol and *o*-toluidine were condensed with acetic and hydrochloric acids, and the product was hydrolysed to 4-amino-3-methyltetra-

phenylmethane; the diazonium sulphate of the latter, when treated with boiling ethyl alcohol, gave the above ethoxy-compound, m. p. 143°. By the Sandmeyer reaction, the foregoing diazonium sulphate affords 4-chloro-3-methyltetraphenylmethane, m. p. 160°. *o*-Diphenylenephenylcarbinol condenses with phenol to yield *o*-diphenylene-4-hydroxydiphenylmethane (lit.), converted by acetic-hydriodic acid into *o*-diphenylenephenylmethane, m. p. 145°. Diphenyldiphenylcarbinol similarly affords *diphenyl-4-hydroxytriphenylmethane*, m. p. 183°, also prepared from diphenyldiphenylmethyl chloride and phenol; it is stable toward acetic and hydriodic acids.

The stability of tetraphenylmethane derivatives (cf. Boyd and Hardy, *loc. cit.*) has been further investigated, and a tabular summary is given. The decompositions mentioned are analogous to those of 2-hydroxytriphenylmethane (Schmidt, Diss., Heidelberg, 1898) and of the hexamethyl ether of phloroglucinolphthalein (A., 1928, 884), and afford additional evidence of the reversibility of the Baeyer-Villiger reaction. C. W. SHOPPEE.

Germicidal action of hydroxydiaryl sulphides. G. E. HILBERT and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 1526—1536).—*p*-Methoxydiphenyl sulphide, b. p. 194—195°/13 mm., prepared by modifications of (a) Hinsberg's (A., 1903, i, 251; 1908, i, 875; 1909, i, 6) and (b) Ziegler's (A., 1890, 1292) methods, is converted by a mixture of 48% hydrobromic acid and acetic anhydride at 80—90° into *p*-hydroxydiphenyl sulphide (115), m. p. 50—51°, b. p. 164—165°/3 mm. (*p*-nitrobenzoate, m. p. 74—75°), and by 21% hydrobromic acid in glacial acetic acid at 60°, or by boiling 48% aqueous hydrobromic acid into diphenyl disulphide and *p*-bromophenol. The new phenol may also be obtained directly from benzenesulphinic acid and phenol [cf. (a)], or from magnesium *p*-anisyl bromide and chlorothiolbenzene, but not from *p*-hydroxybenzenediazonium chloride and sodium phenyl sulphide. *o*-Methoxy-, b. p. 150—152°/3 mm.; *m*-methoxy-, b. p. 156°/4 mm., *diphenyl sulphides*, and *p*-methoxyphenyl *p*-tolyl sulphide, m. p. 45—46°, b. p. 181—182°/4 mm., prepared by method (b), are demethylated to *o*-hydroxydiphenyl sulphide (33), b. p. 140°/3 mm. (*p*-nitrobenzoate, m. p. 72—73°); *m*-hydroxydiphenyl sulphide (68), b. p. 159—161°/3 mm. (*p*-nitrobenzoate, m. p. 103°), and *p*-hydroxyphenyl *p*-tolyl sulphide (50), m. p. 67—68°, b. p. 178—180°/3 mm. A new method, probably of general application, for preparing diphenyl sulphide is by decomposing the yellow intermediate product from benzenediazonium chloride and sodium phenyl sulphide at 5° with copper powder. *p*-Methoxydiphenylsulphone is demethylated to *p*-hydroxydiphenylsulphone (<10), m. p. 136—137°. The high phenol coefficients (given in parentheses) and low toxicities of the hydroxydiphenyl sulphides are noteworthy. H. E. F. NOTTON.

Esters of hydrogenated aromatic alcohols [cyclohexyl stearate]. R. H. VAN SCHAACK, jun.—See B., 1929, 427.

Manufacture of condensation product from *m*-cresol and acetone [2:2'-dihydroxy-4:4'-dimethyl-ββ-diphenylpropane]. SCHERING-KAHLBAUM A.-G. and H. JORDAN.—See B., 1929, 467.

Reactivity of the nitro-group in 4:5-dinitroveratrole towards sodium methoxide at 35° and 45°. A. H. PARIJS (Rec. trav. chim., 1929, 48, 560—563).—The velocity of the bimolecular reaction between 4:5-dinitroveratrole and sodium methoxide has been determined at 35° and 45° by titrating the unchanged sodium methoxide with acetic acid. The bimolecular velocity coefficients at 35° and 45° are, respectively, 0.0029 and 0.0088 min.⁻¹. The corresponding values for *o*-dinitrobenzene (cf. Steger, A., 1899, i, 745, whose values need to be halved) are 0.0242 and 0.0695, respectively, hence the introduction of two methoxy-groups into *o*-dinitrobenzene retards the reaction with sodium methoxide to a greater extent than does the introduction of a single methoxy- or ethoxy-group in the 5-position in 1-chloro-2:4-dinitrobenzene. The solubility of 4:5-dinitroveratrole in absolute methyl alcohol at 15°, 25°, 35°, and 45° is, respectively, 7.66, 10.54, 18.21, and 24.95 g. per litre. J. W. BAKER.

Hydroxy-β-orscinol [2:3:5-trihydroxy-*p*-xylenes]. Y. ASAHINA and E. ISHIBASHI (Ber., 1929, 62, [B], 1207—1208; cf. this vol., 818).—*p*-Xyloquinone is converted by acetic anhydride and concentrated sulphuric acid into *hydroxy-β-orscinol triacetate*, m. p. 108°, from which *hydroxy-β-orscinol*, m. p. 158°, is derived; the corresponding *tribenzoate* has m. p. 156°. H. WREN.

Hoesch synthesis of phenolic ketones. II. Condensation of arylglyoxylonitriles with phloroglucinol. W. BORSCHKE, C. WALTER, and J. NIEMANN (Ber., 1929, 62, [B], 1360—1366).—Contrary to the observations of Marsh and Stephen (A., 1925, i, 1158), the condensation of arylglyoxylonitriles with phloroglucinol leads to the formation of imino lactones,
$$\begin{array}{c} (\text{OH})_3\text{C}_6\text{H}_2 \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C}(\text{NH})\text{O} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_2(\text{OH})_3 \end{array} \quad (\text{I}).$$

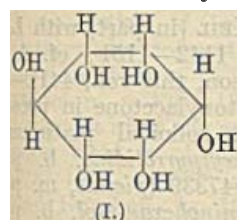
Treatment of a solution of benzoyl cyanide (1 mol.) and phloroglucinol (2 mols.) in ether with hydrogen chloride affords 2:4:6:2':4':6'-hexahydroxytriphenylacetiminolactone (I; Ar=Ph), m. p. 286—287° [monohydrate; hydrochloride, m. p. 215—220° (decomp.); penta-acetate (also dihydrate), m. p. 181°]. Similarly, 4-methoxybenzoyl cyanide yields 2:4:6:2':4':6'-hexahydroxy-4''-methoxytriphenylacetiminolactone (I; Ar=OMe-C₆H₄), m. p. 259—260° after blackening (also monohydrate). 4-Chlorophenylacetone nitrile and *p*-nitrosodimethylaniline in boiling methyl alcohol in presence of sodium hydroxide afford the 4-dimethylaminoanil of 4-chlorobenzoyl cyanide, m. p. 146—174°, converted by *o*N-hydrochloric acid into 4-chlorobenzoyl cyanide, b. p. 117—118°/16 mm., m. p. 40—41°, which with phloroglucinol yields 4''-chloro-2:4:6:2':4':6'-hexahydroxytriphenylacetiminolactone (I, Ar=Cl-C₆H₄), decomp. 270—280° after blackening (hydrochloride, decomp. 235—240° when rapidly heated; penta-acetate, m. p. 265—267° after softening at 255° and then darkening). Resorcinol and 4-chlorobenzoyl cyanide afford 4''-chloro-2:4:2':4'-tetrahydroxytriphenylacetolactone, decomp. 276° after becoming red.

4-Chloro-oximinoacetophenone, m. p. 158—160°, from 4-chloroacetophenone and isoamyl nitrite, is converted by acetic anhydride into 4-chlorobenzoic acid.

Similarly, 4-bromo-oximinoacetophenone, m. p. 161°, yields 4-bromobenzoic acid. H. WREN.

Configuration of inactive inositol. S. POSTERNAK and T. POSTERNAK (Compt. rend., 1929, 188, 1296—1298).—The synthesis of *i*-inositol by Wieland and Wishart (A., 1914, i, 953) did not decide its stereochemical structure; the preparation of a levorotatory tetraphosphoric acid of the substance (A., 1928, 271) showed, however, that it could not have the structure — and the optical inactivity of the monophosphoric acid (Anderson, A., 1914, i, 1191) excluded the structure

The action of fuming nitric acid on a mixture of inositol-mono- and -di-phosphoric acids gives a product of the composition of a tartaric acid phosphate, which is hydrolysed to *r*-tartaric and mesotartaric acids; since the structure $\frac{1,3,5}{2,4,6}$ contains only *trans*-hydroxyl groups, it is now excluded. Further, the oxidation of inositol by alkaline potassium permanganate at 0° gives, in addition to trihydroxyglutaric and tetrahydroxyadipic acids, *allomucic* acid [new m. p. 176° (decomp.), identical with a specimen prepared from mucic acid and freed from the latter by treatment of the aqueous solution of the ammonium salt with alcohol]; the only remaining structure for inositol



consistent with this is —, i.e. (I). Anderson's monophosphoric acid is accordingly $\frac{3}{2}$ -inositol-3(or 6)-phosphoric acid, and the *l*-diphosphoric acid contains its second phosphoric acid group on a 1, 2, 4, or 5 carbon atom. To form *allo*-

mucic acid, the ring opens at the 5,6 or 6,1 linking; other products are probably formed by ring-fission elsewhere. It is suggested that natural inositol should be considered as a reserve carbohydrate which by its special configuration can break down to various substances, according to the point of ring-fission as determined by the positions at which phosphoric acid is attacked.

E. W. WIGNALL.

Synthesis of isomeric ephedrine and their homologues. W. N. NAGAI and S. KANAO (Annalen, 1929, 470, 157—182).—Benzaldehyde condenses with nitroethane in presence of 25% aqueous potassium hydrogen carbonate, yielding β -nitro- α -phenylpropyl alcohol, b. p. 123—124°/4 mm., reduced by zinc dust and 25% acetic acid to β -hydroxylamino- α -phenylpropyl alcohol, m. p. 78—79°. Treatment of this with aqueous formaldehyde affords the methyl-enitrone, $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{N}\langle\text{CH}_2\text{O}\rangle$, m. p. 100°,

reduced by zinc dust and acetic acid to a mixture of *dl*-ephedrine (I), m. p. 75° [hydrochloride, m. p. 187—188°; chloroplatinate, m. p. 199°; chloroaurate, m. p. 112—113°; N-*p*-nitrobenzoyl derivative, m. p. 162°; quaternary ammonium iodide, $\text{C}_{12}\text{H}_{20}\text{ONI}$, m. p. 228—229°, from I (1 mol.) and methyl iodide (4.5 mols.)], and *dl*-isoephedrine (II), m. p. 118° [hydrochloride, m. p. 164°; oxalate, m. p. 218° (decomp.); chloroaurates, m. p. 117° and 194°; copper oxide compound, $2\text{C}_{10}\text{H}_{15}\text{ON}\cdot\text{CuO}\cdot 2\text{H}_2\text{O}$, m. p. 129° (decomp.), N-*p*-nitrobenzoyl derivative, m. p. 165—

166°; quaternary ammonium iodide, $\text{C}_{12}\text{H}_{20}\text{ONI}$, m. p. 183°, by the action of methyl iodide]. When I is treated with *d*-tartaric acid in warm methyl alcohol, *l*-ephedrine *d*-hydrogen tartrate (+MeOH), m. p. 69°, separates on cooling: evaporation of the residue and further cooling affords *d*-ephedrine *d*-hydrogen tartrate, m. p. 145—146°. *l*-Ephedrine, m. p. 40—40.5°, $[\alpha]_D^{20} -34.69^\circ$ in water (hydrochloride, m. p. 216—217°; N-*p*-nitrobenzoyl derivative, m. p. 187—188°, $[\alpha]_D^{20} -51.77^\circ$ in chloroform, which on heating with concentrated hydrochloric acid gives *d*-isoephedrine *O*-*p*-nitrobenzoate), is identical with the natural product from Ma Huang. *d*-Ephedrine (hydrochloride, m. p. 216—217°; N-*p*-nitrobenzoyl derivative, m. p. 187—188°, $[\alpha]_D^{20} +51.12^\circ$ in chloroform) has m. p. 40—40.5°, $[\alpha]_D^{20} +34.42^\circ$ in water. Treatment of II with aqueous tartaric acid yields *l*-isoephedrine *d*-hydrogen tartrate, m. p. 178° (decomp.), furnishing *l*-isoephedrine, m. p. 118—118.5°, $[\alpha]_D^{20} -51.93^\circ$ in alcohol (hydrochloride, m. p. 182—182.5°, $[\alpha]_D^{20} -61.88^\circ$ in water; N-*p*-nitrobenzoyl derivative, m. p. 177°, $[\alpha]_D^{20} -140.47^\circ$ in chloroform), and purification of the residual base with *l*-tartaric acid gives *d*-isoephedrine, m. p. 117—118°, $[\alpha]_D^{20} +51.87^\circ$ in alcohol [hydrochloride, m. p. 182—182.5°, $[\alpha]_D^{20} +61.61^\circ$ in water; oxalate, m. p. 219° (decomp.); N-*p*-nitrobenzoyl derivative, m. p. 177°, $[\alpha]_D^{20} +140.85^\circ$ in chloroform], identical with the natural product.

Reduction of β -nitro- α -phenylpropyl alcohol with iron and aqueous-alcoholic sulphuric acid below 45°, or with tin and hydrochloric acid yields a mixture of *dl*-norephedrine [β -amino- α -phenylpropyl alcohol], m. p. 104—105° [hydrochloride, m. p. 194°; sulphate, m. p. 285—286°; oxalate, m. p. 245° (decomp.); dioxalate, m. p. 182—183° (decomp.); chloroplatinate, m. p. 221.5°; chloroaurate; copper oxide compound, m. p. 169° after darkening at 120°; N-acetyl derivative, m. p. 135°, converted by heating with concentrated hydrochloric acid into *dl*-norisoephedrine; N-*p*-nitrobenzoyl derivative, m. p. 189°], and *dl*-norisoephedrine, m. p. 71° [hydrochloride, m. p. 169°; sulphate, m. p. 290—291° (decomp.); oxalate, m. p. 235°; dioxalate, m. p. 171° (decomp.); chloroplatinate, m. p. 199.5° (decomp.); chloroaurate, m. p. 132—133°; copper oxide compound, m. p. 154° (decomp.); acetyl derivative, m. p. 85—86°; N-*p*-nitrobenzoyl derivative, m. p. 170°]. Resolution of these amines is accomplished by *d*- and *l*-tartaric acids. *d*-Norephedrine, m. p. 52°, $[\alpha]_D^{20} +14.76^\circ$ in alcohol [*d*-hydrogen tartrate (+EtOH), m. p. about 160°, $[\alpha]_D^{20}$ (alcohol free) +34.69°; hydrochloride, m. p. 171—172°, $[\alpha]_D^{20} +33.4^\circ$ in alcohol; sulphate (+2H₂O), m. p. (anhydrous) 285—286° (decomp.), $[\alpha]_D^{20} +31.51^\circ$; oxalate, m. p. 245°; chloroplatinate, m. p. 221.5° (decomp.); chloroaurate, m. p. 188°; N-*p*-nitrobenzoyl derivative, m. p. 175—176°, $[\alpha]_D^{20} +49.95^\circ$ in chloroform, when heated with concentrated hydrochloric acid gives *l*-norisoephedrine *p*-nitrobenzoate], *l*-norephedrine, m. p. about 50°, $[\alpha]_D^{20} -14.56^\circ$ in alcohol [*l*-hydrogen tartrate (+EtOH), m. p. 160° after sintering at about 130°, $[\alpha]_D^{20}$ (alcohol free) -34.46°; hydrochloride, m. p. 171—172°, $[\alpha]_D^{20} -33.27^\circ$; sulphate (+2H₂O), m. p. (anhydrous) 285—286° (decomp.), $[\alpha]_D^{20} -31.99^\circ$; oxalate, m. p.

245° (decomp.); *chloroplatinate*, m. p. 221° (decomp.); *chloroaurate*, m. p. 188°; N-p-nitrobenzoyl derivative, m. p. 175—176°, $[\alpha]_D^{25}$ —49.58° in chloroform, converted by treatment with concentrated hydrochloric acid into *d*-norisoephedrine *p*-nitrobenzoate; *trimethylammonium iodide*, m. p. 211—212°, $[\alpha]_D^{20}$ —22.23°, obtained also from *l*-ephedrine and methyl iodide], *l*-norisoephedrine, m. p. 77.5—78°, $[\alpha]_D^{20}$ —32.64° in alcohol [d-hydrogen tartrate, m. p. 202° (decomp.); $[\alpha]_D^{20}$ —13.39°; *hydrochloride*, m. p. 180—181°, $[\alpha]_D^{20}$ —42.68°; *sulphate*, m. p. 290—291° (decomp.), $[\alpha]_D^{20}$ —39.99°; *oxalate*, m. p. 235°; *chloroplatinate*, m. p. 199°; *chloroaurate*, m. p. 137—138°; N-p-nitrobenzoyl derivative, m. p. 199°, $[\alpha]_D^{20}$ —105.13° in chloroform], and *d*-norisoephedrine, m. p. 77.5—78°, $[\alpha]_D^{20}$ +33.14° in alcohol [l-hydrogen tartrate, m. p. 202°, $[\alpha]_D^{20}$ +13.36°; *hydrochloride*, m. p. 180—181°, $[\alpha]_D^{20}$ +42.53°; *sulphate*, m. p. 290—291° (decomp.), $[\alpha]_D^{20}$ +40.12°; *oxalate*, m. p. 235° (decomp.); *chloroplatinate*, m. p. 198; *chloroaurate*, m. p. 137—138°; N-p-nitrobenzoyl derivative, m. p. 199.5°, $[\alpha]_D^{20}$ +104.96° in chloroform; *trimethylammonium iodide*, m. p. 216—216.5°, $[\alpha]_D^{20}$ +36.65°, are described. When dl-N-benzoylnorephedrine, m. p. 143°, is treated with concentrated sulphuric acid, 2:5-diphenyl-4-methylloxazoline (III) [*picrate* (IV), m. p. 140—141°], results. This is converted by boiling with dilute hydrochloric or sulphuric acid into dl-norisoephedrine O-benzoate [*hydrochloride* (V), m. p. 220°; *sulphate*, m. p. 182° (decomp.); *picrate*, m. p. 186° (decomp.)], also obtained by crystallising IV from hot alcohol]. Treatment of V with concentrated sulphuric acid gives III; with ammonia, dl-N-benzonorephedrine, m. p. 128°, is obtained.

Reduction of β -nitro- α -phenylpropyl alcohol with zinc dust and 50% acetic acid in presence of 2 mols. of formaldehyde affords a mixture of dl-methyl-ephedrine [β -dimethylamino- α -phenylpropyl alcohol], m. p. 63.5—64.5° (*hydrochloride*, m. p. 207—208°; *oxalate*, m. p. 170—171°; *picrate*, m. p. 124—125°; *chloroaurate*, m. p. 137°), and dl-methylisoephedrine, b. p. 135.5° (corr.)/16 mm., d_4^{20} 1.5143 (*picrate*, m. p. 148—148.5°; *oxalate*), separated by means of the difference in solubility of the hydrochlorides in acetone. *l*-Methylephedrine, m. p. 87—87.5°, $[\alpha]_D^{20}$ —29.2° in methyl alcohol [d-hydrogen tartrate, m. p. 87—88°, $[\alpha]_D^{20}$ —6.77°; *hydrochloride*, m. p. 192° after sintering at 189°, $[\sigma]_D^{20}$ —29.95°; *oxalate*, m. p. 187° (decomp.); *picrate*, m. p. 142°; *chloroaurate*, m. p. 128—129°; *copper oxide* compound, m. p. 86—87°], *d*-methylephedrine, m. p. 87—87.5°, $[\alpha]_D^{20}$ +29.17° in methyl alcohol [l-hydrogen tartrate, m. p. 87—88°, $[\alpha]_D^{20}$ +6.6°; *hydrochloride*, m. p. 192°, $[\alpha]_D^{20}$ +30.07°; *oxalate*, m. p. 187°; *chloroaurate*, m. p. 127—128°; *methiodide*, m. p. 211°, $[\alpha]_D^{20}$ +22.1°], *d*-methylisoephedrine, b. p. 145—145.5° (corr.)/24 mm., m. p. 28—28.5°, d_4^{20} 0.98566, n_D^{20} 1.5109, $[\alpha]_D^{20}$ +48° in methyl alcohol [d-hydrogen tartrate, m. p. (+2H₂O) 83.5—84°, (anhydrous) about 150°; *chloroaurate*, m. p. 127°], and *l*-methylisoephedrine, b. p. 145° (corr.)/24 mm., m. p. 28—28.5°, d_4^{20} 0.9854, n_D^{20} 1.5108, $[\alpha]_D^{20}$ —48.34° in methyl alcohol [l-hydrogen tartrate, m. p. (+2H₂O) 83.5—84°, (anhydrous) about 150°; *chloroaurate*, m. p. 128°; *hydrochloride*; *oxalate*; *methiodide*, m. p. 216—216.5°,

$[\alpha]_D^{20}$ —36.1°], are described. *d*- and *l*-Methylephedrine are also obtained from *d*- and *l*-ephedrine and methyl iodide.

H. BURTON.

A homologue of ephedrine. J. SAEM and B. SANCHEZ (Bull. Soc. chim., 1929, [iv], 45, 284—286).—*p*-Tolyl ethyl ketone, b. p. 234—235° (yield 60% from propionyl chloride and toluene in presence of aluminium chloride and carbon disulphide; cf. Klages, A., 1902, i, 611), is converted by bromination in benzene in a current of carbon dioxide into α -bromoethyl *p*-tolyl ketone, m. p. 80° (yield 75%), which with an 8% solution of methylamine in benzene affords (yield 45%) *p*-tolyl α -methylaminoethyl ketone *hydrochloride*, m. p. 232° (*methiodide*, m. p. 199—200°; *picrate*, m. p. 170°). By hydrogenation in presence of platinum-black the latter is converted into *p*-tolyl- α -methylaminoethylcarbinol, b. p. 114° (*hydrochloride*, m. p. 222°; *methiodide*, m. p. 175°; *picrate*, 179°), which is rather more toxic for rabbits than natural ephedrine, but exerts a smaller hypertension (cf. Hyde, Browning, and Adams, A., 1928, 1143).

R. BRIGHTMAN.

Formation of bases from carbonyl compounds. III. **Synthesis of *dl*-ephedrine and other aminoalcohols.** A. SKITA and F. KEIL [in part, with L. BOENTE] (Ber., 1929, 62, [B], 1142—1151; cf. A., 1928, 1228; Manske and Johnson, this vol., 441).—Catalytic hydrogenation of acetonylacetone in presence of cyclohexylamine and colloidal platinum affords 2:5-dimethyl-N-cyclohexylpyrrolidine, b. p. 100°/16 mm., d_4^{20} 0.8927, n_D^{20} 1.47339 (*picrate*, m. p. 111—114°), and ϵ -cyclohexylaminoheptan- β -ol, b. p. 153°/21 mm., m. p. 76—77° (*picrate*, m. p. 76—77°). γ -Methylacetylacetone and cyclohexylamine similarly afford δ -cyclohexylamino- γ -methylpentan- β -ol, b. p. 104—106°/1 mm. (*picrate*, m. p. 157—159°). Benzoylacetone and methylamine analogously yield the diastereoisomeric γ -methylamino- α -phenylbutan- α -ols (I), b. p. 155—156°/16 mm., d_4^{20} 1.0107, 1.52032 (pale yellow *picrate*, m. p. 193—194°), and (II) b. p. 155—156°/16 mm., d_4^{20} 1.0079, n_D^{20} 1.52298 (dark yellow *picrate*, m. p. 118—119°). Benzil and methylamine give β -methylamino- $\alpha\beta$ -diphenylpentan- α -ol, b. p. 195—200°/20 mm., m. p. 134° (*hydrochloride*, m. p. 250°; *acetate*, m. p. 144—145°, whilst β -cyclohexylamino- $\alpha\beta$ -diphenylethan- α -ol, m. p. 162—163° (*hydrochloride*, m. p. 264—265°), is derived from benzil and cyclohexylamine. Methyl propyl diketone and methylamine afford β -methylaminohexan- γ -ol, b. p. 81°/18 mm., m. p. 78° (*hydrochloride*, m. p. 146—147°), and 4-hydroxy-1:4-dimethyl-5-propyl-2- α -hydroxybutylpyrrolidine, b. p. 154—156°/15 mm. (*diacetyl* derivative, m. p. 165—168°/16 mm.). Phenyl methyl diketone and methylamine give β -methylamino- α -phenylpropan- α -ol (*dl*-ephedrine), m. p. 75°, in 50% yield. Hydrogenation of *dl*-ephedrine in presence of formaldehyde and colloidal platinum gives almost quantitatively β -dimethylamino- α -phenylpropan- α -ol (N-methylephedrine), m. p. 63—64.5° (*hydrochloride*, m. p. 205°). Acetylacetone and dimethylamine in presence of ammonium chloride and colloidal platinum are hydrogenated to δ -dimethylaminopentan- β -ol, b. p. 61—62°/11 mm.

H. WREN.

Action of chlorine compounds on cholesterol.
VII. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 302—304).—Iodine trichloride and cholesterol in ether yield an amorphous substance, m. p. 72—73°, containing no hydroxyl group, apparently a mixture of an iodo- and a chloro-compound. By the action of sulphur monochloride at 100°, followed by treatment with water, a reddish-brown product, m. p. 72—85°, containing 26.37% S, 3.61% Cl, is obtained. The sulphur is probably present as $\cdot\text{CH}\cdot\text{SH}\cdot$, being eliminated by aqueous potassium hydroxide or concentrated nitric acid. In chloroform solution, antimony trichloride after 2 hrs. gives a violet coloration (cf. Steidle and Kahlenberg, A., 1926, 633). Calcium chloride gives an additive compound. Stannic chloride in excess in benzene at the ordinary temperature affords a brown product, m. p. 65—70°, containing chlorine, which gives Liebermann's reaction, yields a non-crystalline bromide, and contains no hydroxyl group. Stannic chloride alone gives the same product.
 R. BRIGHTMAN.

Sterol group. III. Acetylation and catalytic hydrogenation of ergosterol. I. M. HEILBRON and W. A. SEXTON. **IV. Existence of isomeric ergosterols.** I. M. HEILBRON, W. A. SEXTON, and F. S. SPRING (J.C.S., 1929, 921—926, 926—931).—Catalytic hydrogenation of ergosterol using palladium-black in ether at 15° or in alcohol at 70° yields α -ergosterol, m. p. 130—131°; the process is selective and by arrest after the addition of 2 atoms of hydrogen a good yield is obtained of dihydroergosterol, m. p. 173°, $[\alpha]_{\text{D}}^{20} -21.7^\circ$ (acetate, m. p. 180°) (cf. Windaus and Brünken, A., 1928, 424). Use of glacial acetic acid as solvent at 70° affords allo- α -ergostanyl acetate, m. p. 144—145° (cf. Reindel and Walter, A., 1928, 295), hydrolysed by 10% alcoholic potassium hydroxide to allo- α -ergostanol monohydrate, m. p. 144—145° (cf. Reindel and Walter, *loc. cit.*).

When a solution of ergosterol in glacial acetic acid is treated with anhydrous potassium acetate at 100° for 5—6 hrs. in an atmosphere of carbon dioxide ergosteryl α -acetate, m. p. 132—133°, is obtained; it regenerates ergosterol by hydrolysis with 5% alcoholic potassium hydroxide. The α -acetate passes into ergosterol β -acetate by treatment with boiling acetic anhydride, or when heated above its m. p., and by catalytic hydrogenation with palladium-black in ether furnishes α -ergostenyl acetate, m. p. 109—110°. The authors suggest that the third double linking, which is hydrogenated only in hot glacial acetic acid, joins two quaternary carbon atoms, since this behaviour is reminiscent of that of abietic acid (cf. A., 1922, i, 547; 1925, i, 1419.)

IV. Homogeneous samples of ergosterol obtained from two different sources, although possessing identical m. p. and closely similar optical properties, behave differently towards catalytic hydrogenation. Thus with palladium-black in ether at 15°, Bohringer's product (I), m. p. 161—162°, $[\alpha]_{\text{D}}^{25} -159.3^\circ$, absorbs 4 atoms of hydrogen to yield α -ergosterol, m. p. 130—131°, $[\alpha]_{\text{D}}^{25} +18.0^\circ$, whilst Boot's product (II), m. p. 161—162°, $[\alpha]_{\text{D}}^{25} -171.0^\circ$, slowly absorbs slightly less than 2 atoms of hydrogen. Hydrogenation of II is completed by addition of fresh catalyst,

yielding a tetrahydro-derivative, separable into β -ergosterol, m. p. 114—116° (acetate, m. p. 94—96°), and α -ergosterol, m. p. 130—131°. Failure to obtain complete hydrogenation with the first portion of the catalyst is not due to poisoning, since the same specimen of catalyst rapidly converted I into α -ergosterol. Acetylation of either I or II with acetic anhydride affords products possessing identical m. p. and specific rotations, provided that the duration of treatment is the same: with increasing time the m. p. falls and the specific rotation rises. The difficulty of hydrogenating I persists after acetylation, but both I and II furnish α -ergostenyl acetate, m. p. 109—110°, $[\alpha]_{\text{D}}^{25} +6.3^\circ$ by treatment with palladium-black. Hydrolysis of the ergosteryl β -acetate from II, m. p. 172—174°, with 5% alcoholic potassium hydroxide affords an ergosterol, m. p. 161—162°, $[\alpha]_{\text{D}}^{25} -160.0^\circ$, hydrogenated rapidly and completely in the presence of palladium-black to α -ergosterol, m. p. 130—131°, $[\alpha]_{\text{D}}^{25} +19^\circ$; the form of the hydrogen-absorption-time curve is precisely similar to that given by I. Another specimen of ergosterol, $[\alpha]_{\text{D}}^{25} -161.2^\circ$, obtained from Boot's when treated with twice the amount of catalyst used to hydrogenate I, absorbed 4 atoms of hydrogen without any marked break at the dihydro-stage, to yield α -ergosterol, m. p. 129—131°.

C. W. SHOPPEE.

Zymosterol, a dextrorotatory sterol of yeast. H. PENAU and G. TANRET (Compt. rend., 1929, 188, 1317—1319; cf. following abstract).—Zymosterol has the formula $\text{C}_{27}\text{H}_{42}\text{O}_2\cdot\text{H}_2\text{O}$, i.e., that of a hydroxy-ergosterol (cf. Maclean, A., 1928, 329); after losing water above 80°, it has m. p. 100—101°, rising after several resolidifications to 106—108°. In alcoholic chloroform at 16° the values $[\alpha]_{\text{D}}^{20} +60.5^\circ$, $[\alpha]_{\text{D}}^{25} +39.9^\circ$, $[\alpha]_{\text{D}}^{5780} +34.8^\circ$ are found (cf. Maclean); the dispersion ratio $[\alpha]_{\text{D}}^{4360} : [\alpha]_{\text{D}}^{5780}$ is thus 1.73 (cf. the value 2.85 for ergosterol). The iodine value (190—201) confirms the presence of three ethylenic double linkings; the acetyl derivative, $\text{C}_{27}\text{H}_{40}(\text{OAc})_2$, has m. p. 115°, $[\alpha]_{\text{D}}^{25} +20^\circ$; the digitonin complex contains 28.6% of zymosterol. Zymosterol in acetic anhydride and sulphuric acid gives the green Liebermann reaction, with a characteristic blue intermediate stage; the Salkowsky reaction is negative; with antimony pentachloride a faint rose coloration is given, and similarly there is a faint Rosenheim reaction, but these may be due to traces of ergosterol. Fresh yeast which contains 0.1—0.15% of ergosterol contains 0.1% of zymosterol.
 E. W. WIGNALL.

Physical and biological study of the dextrorotatory sterol from yeast [zymosterol]. R. FABRE and H. SIMONNET (Compt. rend., 1929, 188, 1312—1315; cf. preceding abstract).—The ultra-violet absorption curves of zymosterol show no maximum from 4500 to 2500 Å., and the general absorption is very much weaker than that of ergosterol; no change in the absorption is produced by irradiation in an inert atmosphere. The antirachitic potency of the irradiated product is only about 1/100 that of irradiated ergosterol (this vol., 359) and may be due to contamination with the latter substance. E. W. WIGNALL.

Superheating of uniform organic compounds.

V. Aryl naphthenates and the mechanism of

their transformations. S. SKRAUP and O. BINDER (Ber., 1929, 62, [B], 1127—1138; cf. A., 1927, 659).—Thermal decomposition of the phenyl esters of cyclopentane-, cyclobutane-, and probably cyclopropane-carboxylic acids resembles that of cyclohexanecarboxylic esters in yielding the corresponding *o*-hydroxyphenyl ketones; the sensitiveness of the compounds to heat increases with diminishing size of the ring. Introduction of a methyl group in position 1 increases the thermostability and causes ultimate rupture into phenyl formate and unsaturated hydrocarbon. The primary fission of phenyl naphthenates into phenol and a cyclic keten which subsequently unite to an *o*-hydroxyphenyl ketone is possible for the unsubstituted compounds, but not for their 1-methyl derivatives. When gently warmed, diphenylketen and phenol afford phenyl diphenylacetate; at higher temperatures, however, nuclear substitution predominates. The intermediate formation of ketens is established by use of azobenzene which gives heterocyclic compounds decomposing at a higher temperature into benzophenoneanil and phenylcarbimide. The hypothesis that phenyl esters of fatty acids decompose primarily into phenyl formate and Δ^{α} -alkylenes which then yield acetylene and paraffins does not appear tenable, since hexadecene affords a dimeride and products of higher b. p., but not acetylene. Treatment of a phenyl ester of a naphthenic acid, $C_{10}H_{18}O_2$, from Galician petroleum causes loss of carbon dioxide and union of the residues with production of an alicyclically substituted benzene, the behaviour being neither that of a fatty ester nor that of a nuclear carboxylated naphthene.

The following observations appear new: cyclopentanecarboxylic acid, b. p. 112—113°/14 mm. (by hydrogenation of cyclopentenecarboxylic acid) and its phenyl ester, b. p. 137°/13 mm.; *o*-hydroxyphenyl cyclopentyl ketone, b. p. 125—135°/13 mm.; phenyl cyclobutanecarboxylate, b. p. 127°/13 mm.; *o*-hydroxyphenyl cyclobutyl ketone, b. p. 139—140°/15 mm.; methyl cyclobutanecarboxylate, b. p. 40°/13 mm.; phenyl cyclopropanecarboxylate, b. p. 117—118°/13 mm.; 1-methylcyclohexanecarboxylic acid, b. p. 127—130°/13 mm. (amide, m. p. 67°), conveniently prepared by oxidation of methylcyclohexylphenol by potassium permanganate in alkaline solution; phenyl 1-methylcyclohexanecarboxylate, b. p. 149—150°/13 mm.; phenyl 1-methylcyclopentanecarboxylate, b. p. 137°/14 mm.; phenyl naphthenate, $C_{16}H_{22}O_2$, b. p. 161—171°/13 mm.; *p*-anisyl naphthenate, $C_{17}H_{24}O_3$, b. p. 198—200°/13 mm.; benzyl *o*-hydroxyphenyl ketone, b. p. about 165°/23 mm.; m. p. 55°.

H. WREN.

Synthesis of chaulmoogric acid from hydnocarpic acid. W. M. STANLEY and R. ADAMS (J. Amer. Chem. Soc., 1929, 51, 1515—1518).—The following have been prepared by standard methods from natural hydnocarpic acid: ethyl hydnocarpate, b. p. 143—144°/2 mm., d_4^{25} 0.9087, $[\alpha]_D^{25}$ +70.5°; hydnocarpyl alcohol (λ - Δ^2 -cyclopentenylundecan- α -ol), m. p. 23°, b. p. 144—145°/2 mm., d_4^{25} 0.8022, $[\alpha]_D^{25}$ +75.2° in chloroform; hydnocarpyl bromide, b. p. 156—157°/2 mm., d_4^{25} 1.0763, $[\alpha]_D^{25}$ +27.4° in chloroform (cf. Sacks and Adams, A., 1926, 1137); ethyl hydnocarpylmalonate, b. p. 182—183°/2 mm., d_4^{25} 0.9519,

n_D^{25} 1.4601, $[\alpha]_D^{25}$ +25.6° in chloroform, and hydnocarpylacetic acid (u - Δ^2 -cyclopentenyltridecoic acid), which, after purification, is identical with natural chaulmoogric acid. H. E. F. NOTTON.

Phenols from chaulmoogric acid and resorcinol. W. S. HINEGARDNER and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 1503—1509).—Di-hydrochaulmoogric acid, resorcinol, and zinc chloride at 120° give dihydrochaulmoogrylresorcinol (4- μ -cyclopentyltridecoylresorcinol, (I) (50% of theory), m. p. 89.5° (oxime, m. p. 169—170°). Chaulmoogryl chloride (cf. Power and Gornall, J.C.S., 1904, 85, 855), resorcinol dimethyl ether, and aluminium chloride in carbon disulphide give 3-hydroxy-4-chaulmoogrylanisole (II), m. p. 65°, $[\alpha]_D^{25}$ +6.98°, and 1-chaulmoogryl-2:4-dimethoxybenzene (III), m. p. 46°, $[\alpha]_D^{25}$ +18.8°. Demethylation does not occur at 30—35°, or when ferric chloride is used in place of aluminium chloride. Chaulmoogryl chloride with potassium resorcinol in ether gives resorcinol dichaulmoograte, m. p. 51°, b. p. 270—281°/2—3 mm., $[\alpha]_D^{25}$ +45.93°, and with resorcinol in nitrobenzene in presence of aluminium chloride, 4-chaulmoogrylresorcinol (IV), m. p. 83°, $[\alpha]_D^{25}$ +1.38° (oxime, m. p. 161°), which is also formed in small yield from resorcinol, chaulmoogric acid, and zinc chloride. By amalgamated zinc and boiling dilute hydrochloric acid I is reduced to 4- ν -cyclopentyltridecylresorcinol, m. p. 73—74°; II to 3-hydroxy-4- ν - Δ^2 -cyclopentenyltridecylanisole, m. p. 47.5°, $[\alpha]_D^{25}$ +6.15°; III to 2:4-dimethoxy- ν - Δ^2 -cyclopentenyltridecylbenzene, b. p. 250—252°/2 mm., d_4^{25} 0.955, $[\alpha]_D^{25}$ +9.53, and IV to 4- ν - Δ^2 -cyclopentenyltridecylresorcinol, m. p. 68°, b. p. 245—247°/2—3 mm., optically inactive. The new phenols are only slightly toxic to animals and to *B. typhosum*.

H. E. F. NOTTON.

Chaulmoogryl-substituted phenols and ethyl-*m*-chaulmoogryloxybenzoate. I. DE SANTOS and A. P. WEST (Philippine J. Sci., 1929, 38, 293—298).—Treatment of 2:4-dichlorophenol, 2:4-dibromophenol, quinol, and ethyl *m*-hydroxybenzoate, respectively, with chaulmoogryl chloride (prepared from chaulmoogric acid) after subsequent heating and extraction yielded the following compounds: 2:4-dichlorophenyl chaulmoograte, m. p. 53—55°, 2:4-dibromophenyl chaulmoograte, m. p. 57—60°, quinol ester of chaulmoogric acid, m. p. 54—57°, and ethyl *m*-chaulmoogryloxybenzoate, m. p. 56—59°.

B. W. ANDERSON.

Hydrolysis of nitriles with orthophosphoric acid. S. C. J. OLIVIER (Rec. trav. chim., 1929, 48, 568—570; cf. Berger and Olivier, A., 1928, 44). Although 2:4-dibromobenzonitrile (Montagne, A., 1913, i, 55) is not hydrolysed by boiling 92.5% (crystalline) phosphoric acid, a 90% yield of 2:4-dibromobenzoic acid is obtained by heating the nitrile for 2 hrs. at 160—170° with phosphoric acid to which has been added sufficient phosphoric oxide to combine with the water present. J. W. BAKER.

Electrolytic reduction of benzoic acid. F. SOMLÓ.—See this vol., 776.

Action of sunlight on the cinnamic acids, and the salts of trans-cinnamic acid. Trimorphism of cis-cinnamic acid. A. W. K. DE JONG (Chem.

Weekblad, 1929, 26, 270—275).—An historical survey is used as the basis of a tentative explanation of the mechanism of formation of truxillic and truxinic acids from the cinnamic acids and the salts. The trimorphism of the *cis*-acid is discussed.

S. I. LEVY.

Preparation of active sandaraco-pimaric acid and its derivatives. F. BALAS and J. BRZAK (Coll. Czech. Chem. Comm., 1929, 1, 306—314).—By extraction of sandarac resin with warm 1% sodium hydroxide solution and subsequent fractionation, *l*-sandaraco-pimaric acid, $C_{20}H_{30}O_2$, m. p. 173°, is obtained in 0.7% yield. The substance resembles the inactive acid, m. p. 173°, isolated by Henry (J.C.S., 1901, 79, 1144) and Wolff (A., 1907, i, 145). It has $[\alpha]_D -18.8^\circ$ in alcohol, -13.0° in chloroform. Crystallographic data [F. ULRICH] are recorded. The sodium, potassium, ammonium, silver, di-*d*-amylamine, piperidine, and cinchonidine salts are described. From the silver salt is obtained the methyl ester, m. p. 69°, $[\alpha]_D -27.91^\circ$ in methyl alcohol, d_4^{20} 1.0318, n_D^{20} 1.5207, $[R]_D$ 93.29. Crystallographic data [R. NOVACEK] are recorded. The ethyl ester, b. p. 177°/0.5 mm., has $[\alpha]_D -24.37^\circ$ in alcohol, d_4^{20} 1.0167, n_D^{20} 1.5150, $[R]_D$ 97.97.

R. K. CALLOW.

Oxidation by air of abietic acid. G. DUPONT and J. DUBOURG (Bull. Inst. Pin, 1928, 205—207; Chem. Zentr., 1928, ii, 2355—2356).—Atmospheric oxidation of abietic acid appears to afford a mono-acid glycol with an acetylated hydroxyl group, the phenanthrene group being no longer present, i.e., $C_{14}H_{21}(OH)(OAc) \cdot CO_2H$. Distillation of the oxidised abietic acid with sulphur gave small quantities of retene (from the residual abietic acid) and oily substances containing neither phenanthrene nor methylphenanthrene. Formulæ are proposed.

A. A. ELDRIDGE.

Resin acids. G. ROUIN (Bull. Inst. Pin, 1928, 221—231; Chem. Zentr., 1928, ii, 2722).—When heated in a vacuum (20 mm.) at 190—200°, abietic acid forms dextrorotatory oily products containing *d*-pyroabietic acid, which appears to be an isomeride of abietic acid, and a hydrocarbon, $C_{19}H_{30}$, but no abietic anhydride. Abietic acid, m. p. 171—173°, is a hydrate, $4C_{20}H_{30}O_2 \cdot H_2O$; pyrogeneration in a vacuum affords the anhydrous acid.

A. A. ELDRIDGE.

Resin acids. G. ROUIN (Bull. Inst. Pin, 1928, 191—204; Chem. Zentr., 1928, ii, 2555).—Tetrahydroxyabietic acid, m. p. 243—245°, obtained by oxidation of abietic acid ($\alpha_i -100^\circ$) with permanganate [M. MANVILLE] $\alpha_i -43.7^\circ$, $\alpha_r -51.3^\circ$, $\alpha_i -81^\circ$. Formic, butyric, and valeric acids and acetone, but not propionic acid, were produced in the oxidation.

A. A. ELDRIDGE.

Mixed glycerides of salicylic acid. I, II. V. HUMNICKI (Bull. Soc. chim., 1929, [iv], 45, 275—283).—I. Salicyloyl chloride, from thionyl chloride and sodium salicylate, with $\alpha\alpha'$ -dichlorohydrin affords β -salicyldichlorohydrin, m. p. 46—48°, identical with the product obtained by Fritsch and Gottig (A., 1891, 707), the constitution of which is hereby confirmed. Attempts to convert the dichlorohydrin into the di-iodohydrin with aqueous or

alcoholic potassium iodide at 100—150° or with sodium iodide in 15% acetone solution (cf. Finkelstein, A., 1910, i, 453) failed. With lead iodide at 140° β -salicyldichlorohydrin yields an oil containing 33.83% of iodine. Esterification of $\alpha\alpha'$ -di-iodohydrin with salicylic acid in presence of hydrogen chloride gives an oily product containing excess of iodine. Salicylic acid and glycerol in a current of dry hydrogen iodide at 130°, or salicyloyl chloride and $\alpha\alpha'$ -di-iodohydrin, afford β -salicyldi-iodohydrin, d^{15} 2.61.

II. The following β -acyldichlorohydrins have been prepared by the action of fatty acids on glycerol in presence of hydrogen chloride (cf. Whitby, A., 1926, 819): β -isovaleryl-, b. p. 127—140°/36 mm., d^{20} 1.444, n_D^{20} 1.450; β -lauryl-, b. p. 204—206°/15 mm., d^{20} 1.032, n_D^{20} 1.4584; β -hexoyl-, b. p. 140—145°/15 mm., d^{20} 1.074, n_D^{20} 1.4403; β -myristic-, m. p. 27—29°; β -stearyl-, m. p. 36—37°, and oleyl-, b. p. 260—275°/15 mm., d^{20} 0.994, n_D^{20} 1.4754, -dichlorohydrins. Acetyl-salicylic acid and glycerol in the same way afford salicylic acid and $\alpha\alpha'$ -dichlorohydrin. β -Lauryl- and oleyl-dichlorohydrin were also obtained by the action of the acid chloride on $\alpha\alpha'$ -dichlorohydrin. β -Acetyl-dichlorohydrin, similarly prepared, has b. p. 193—195°, d^{20} 1.281, n_D^{20} 1.4542.

R. BRIGHTMAN.

Electrolytic reduction of salicylic acid. B. RUTOVSKI and A. KOROLEV (Trans. Sci. Chem.-pharm. Inst. Moscow, 1928, 177—180; Chem. Zentr., 1928, ii, 2353).—By Weil's method, electrolytic reduction of salicylic acid afforded salicylaldehyde in a yield of 33% of the theoretical. If magnesium butyrate is added in order to avoid sparking and explosion of the benzene, the chief product (45% of the theoretical) is saligenin. Tesh and Lowy's method gave unsatisfactory results.

A. A. ELDRIDGE.

Condensation of aromatic aldehydes with glycine and acetylglycine. H. D. DAKIN (J. Biol. Chem., 1929, 82, 439—446).—The reaction between glycine and an aromatic aldehyde in presence of acetic anhydride is complicated by the tendency to the formation of the *N*-arylidene derivative of glycine (for which an alternative ring structure is proposed). It is accordingly found that improved yields of the azlactones of α -acetamidocinnamic acid and homologues are obtained using acetylglycine. *Benzylidene-glycine*, from glycine with a large excess of benzaldehyde in presence of acetic anhydride, has m. p. 207° after darkening at 180°. Glycine is conveniently acetylated by warming in suspension in acetic acid with the theoretical amount of acetic anhydride. Acetylglycine was condensed with benzaldehyde to give the azlactone of α -acetamidocinnamic acid; with salicylaldehyde to give the azlactone of *o*-acetoxy- α -acetamidocinnamic acid, m. p. 203—205°, yielding on treatment with alkali and acidification α -acetamidocoumarin, m. p. 203—204°; with *p*-hydroxybenzaldehyde, yielding the azlactone and acid obtained by Bergmann and Stern (A., 1926, 743); with piperonal to give the azlactone of α -acetamidopiperonylic acid, m. p. 183—184° (acid, m. p. 220—221°); with *p*-nitrobenzaldehyde to give the azlactone of α -acetamido-*p*-nitrocinnamic acid, m. p. 185—186° (acid, m. p. 234—235°).

C. R. HARRINGTON.

Isomerism among 9-substituted fluorenes? A. KIEGL [with E. THOMAE] (Ber., 1929, 62, [B], 1327—1335).—Fluorenone is reduced by zinc dust and boiling acetic acid to a mixture of fluorenyl alcohol, m. p. 156°, and fluorenopinacol, m. p. 190—192° (cf. Gomberg and Bachmann, A., 1927, 245), with small amounts of 9-acetoxyfluorene, difluorenyl ether, and diphenylenepheneanthrone; indications of the formation of an isomeric form of fluorenyl alcohol are not obtained. 9-Methoxyfluorene, m. p. 43·5°, is prepared by the action of boiling methyl alcohol and powdered silver nitrate on 9-chlorofluorene.

Attempts to repeat the preparation of β -fluorene-9-carboxylic acid, m. p. 232°, according to the directions of Schlenk and Bergmann (A., 1928, 1034) resulted in the formation of an acid, m. p. 221—223° (slight decomp.), identical in m. p. with the ordinary α -acid but differing therefrom by crystallising in needles. The technical acid also separates in needles from benzene; this was the sole form in which the acid could be isolated from sodiofluorene prepared by a variety of methods. Similarly, endeavours to isolate Schlenk's β -9-methoxyfluorene-9-carboxylic acid, m. p. 172—173°, gave only the known acid, decomp. 184°, according to the rate of heating. Schlenk's "isomeric" benzhydrylfluorene, m. p. 187°, is recognised as a mixture of benzhydrylfluorene, m. p. 217°, with *s*-tetraphenylethane and little difluorenyl, m. p. 240°. The action of 9:9-dichlorofluorene on disodiobenzophenone yields, according to Schlenk and Bergmann, diphenyldiphenylene-ethylene oxide and two isomeric diphenyldiphenylene-ethylenes, m. p. 225° and 213°, respectively; the "isomeride" of m. p. 213° is considered to be an isomorphous mixture of the compound, m. p. 225°, and diphenyldiphenylene-ethylene oxide for the following reasons. The m. p. is depressed slightly by addition of an approximately equal quantity of the "ethylene," m. p. 225°, and raised by similar addition of the oxide. Fractional crystallisation from benzene permits the isolation of the "ethylene," m. p. 225°, or the oxide, according to the relative amount present in the original mixture. If approximately equal quantities of "ethylene," m. p. 225°, and oxide are mixed in hot light petroleum, b. p. 120—180°, and the solution is cooled, the product separates in a form indistinguishable from the "isomeride" except in being colourless. Treatment of the "isomeride" with acetyl chloride places beyond doubt the presence in it of the oxide which when homogeneous is converted by the reagent exclusively into benzoylphenylfluorene; from the "isomeride" a mixture of the last-named compound and the "ethylene," m. p. 225°, is produced. There appears, therefore, no present reason for abandoning the tried hypothesis of the uniplanar arrangement of the rings in fluorene.

H. WREN.

Hexahydrophthalic acids. G. VAVON and P. PEIGNIER (Bull. Soc. chim., 1929, [iv], 45, 293—299).—Hydrogenation of phthalic acid or of methyl phthalate in acetic acid in presence of platinum-black affords the *cis*-hexahydro-derivative, hydrogenation of the free acid being very slow. The 1-quinine salt of *cis*-methyl hexahydrophthalate, m. p. 141·5—142°, $[\alpha]_D -136\cdot5^\circ$, with alcoholic sodium

hydroxide yields 1-*cis*-methyl hydrogen hexahydrophthalate, m. p. 48—49°, $[\alpha]_D -6\cdot67^\circ$, which on cold hydrolysis loses its activity and yields inactive *cis*-acid, m. p. 190° (decomp.). Similarly, the *cis*-hexahydrophthalamide, obtained in 85% yield from the anhydride, on resolution with quinine affords the 1-*cis*-hexahydrophthalamide, m. p. 165° (decomp.), $[\alpha]_D -15\cdot4^\circ$ [quinine salt, m. p. 149—150° (decomp.), $[\alpha]_D -128^\circ$], which, like the racemic amide, when heated at 190—200° for 1 hr., gives the inactive imide, m. p. 134·5—135°. These results support the Bayer formula and not that of Sachse (A., 1890, 1386) if the formulæ are regarded as rigid. Since, however, the *trans*-acid affords an anhydride, m. p. 140°, differing from the *cis*-anhydride, m. p. 32°, and existing at least partly in the simple form $C_6H_{10} \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$ (mol. wt. in camphor 218), a result more readily interpreted by the Sachse formula, the authors regard cyclohexane as possessing a mobile non-planar structure, pure substances consisting of mixtures of molecules with different configurations, the mobility of which can be diminished or suppressed by the two substituent radicals (cf. Mohr, A., 1919, ii, 229; Boeseken, A., 1921, i, 843).

R. BRIGHTMAN.

***cis-trans*-Isomerism and steric hindrance.**

VIII. Methyl hydrogen hexahydrophthalates.

G. VAVON and P. PEIGNIER (Bull. Soc. chim., 1929, [iv], 45, 299—302).—At 39° *cis*-hexahydrophthalic acid is esterified with methyl alcohol in presence of hydrogen chloride about 1·4 times more slowly than the *trans*-isomeride, m. p. 213—218° (decomp.) (anhydride, m. p. 142°). Similarly, the *trans*-methyl hydrogen hexahydrophthalate, m. p. 95—96°, is hydrolysed by sodium or potassium hydroxide in 75% alcohol at 39°, five times, and by aqueous sodium hydroxide at 39° and at 0° six times and ten times, as rapidly as the *cis*-isomeride.

R. BRIGHTMAN.

Conjugated compounds. VII. Additive formation of cyclohexenes. E. H. FARMER and F. L. WARREN (J.C.S., 1929, 897—909).—The possibility of modifying the cyclohexene ring-forming tendencies of butadienoid hydrocarbons has been studied using maleic anhydride as an addendum.

The formula, $\begin{smallmatrix} CH-CH_2-CH-CO \\ CH-CH_2-CH-CO \end{smallmatrix} > O$, given by Diels and Alder (A., 1928, 1018) to the condensation product from butadiene and maleic anhydride is correct, since $\beta\beta'$ -dicarboxyadipic acid is obtained from it by the action of dilute aqueous potassium permanganate. Maleic anhydride and $\beta\gamma$ -dimethylbutadiene yield directly 4:5-dimethyl-*cis*- Δ^4 -tetrahydrophthalic anhydride, m. p. 78°, which, by heating with water, gives 4:5-dimethyl-*cis*- Δ^4 -tetrahydrophthalic acid, m. p. 180—192°. Ozonolysis of a chloroform solution of the anhydride leads to the ketonic acid $[COMe \cdot CH_2 \cdot CH(CO_2H)]_2$ (or its cyclised equivalent, 3-acetyl-4-methylcyclopentan-4-ol-1-carboxylic acid), m. p. 186°.

$\alpha\zeta$ -Dibromo- $\Delta^{8,8}$ -hexadiene, when heated with maleic anhydride in benzene solution, forms 3:6-*ab*-bromomethyl-*cis*- Δ^4 -tetrahydrophthalic anhydride, m. p. 98°. This compound, by boiling with aqueous

sodium carbonate, is converted into the *dilactone*, m. p. 159—163° after previous softening at 147°, of 3:6-dihydroxymethyl-*cis*- Δ^4 -tetrahydrophthalic acid. The dilactone, by catalytic reduction, gives the *lactone*, m. p. 119—120°, of 3:6-dihydroxymethyl-hexahydrophthalic acid. Attempts to oxidise the last-named acid to hexahydrophthalic acid failed, only oxalic acid being definitely isolated.

It is concluded that cyclohexene formation from open-chain butadienes is complete and remains unaffected (except as regards velocity) by variation of positions of alkyl substituents.

Maleic anhydride and ethyl *trans-trans*-muconate combine when heated to give 3:6-dicarboxy- Δ^3 -tetrahydrophthalic anhydride, m. p. 185—188°, converted by alcoholic hydrogen chloride into the corresponding tetraethyl ester, m. p. 75°; the last-named compound, by alternate addition of bromine and removal of hydrogen bromide with diethylamine or pyridine, gives, after two such series of operations, an acid, $C_{10}H_8O_8$ (dihydrophthalic acid?), m. p. 241° (decomp.). The above dicarboxy- Δ^3 -tetrahydrophthalic anhydride gives oxalic acid extensively on treatment with permanganate or ozone. The corresponding acid is reduced by hydrogen and colloidal palladium to 3:6-dicarboxyhexahydrophthalic acid (hexahydrophthalic acid) (monohydrate, m. p. 168°, tetraethyl ester, b. p. 238°/15 mm., dianhydride, m. p. 223—225°). Ethyl *cis-cis*-muconate does not react with maleic anhydride.

Sorbic acid and maleic anhydride in benzene solution at 100° yield 6-carboxy-3-methyl-*cis*- Δ^5 -tetrahydrophthalic anhydride, m. p. 174°; boiling with water gives the corresponding acid, m. p. 194°, with anhydride formation, catalytic hydrogenation (palladium) of which gives 6-carboxy-3-methyl-*cis*-hexahydrophthalic acid (monohydrate, m. p. 194—196°).

Permanganate oxidation of cyclopentadiene- and cyclohexadiene-maleic anhydride condensation products gives in the first case a tetrabasic acid (either cyclopentane-1:2:3:4-tetracarboxylic acid or cyclobutane-1:2:3-tricarboxy-4-acetic acid), m. p. 181—182° (with anhydride formation) (tetraethyl ester, b. p. 226°/14 mm.), and in the second case, 3:6-dicarboxy-hexahydrophthalic acid, m. p. 168° (above).

Addition of maleic anhydride to *trans*-hexatriene occurs in benzene solution at the ordinary temperature, giving 3-ethylidene-*cis*- Δ^4 -tetrahydrophthalic anhydride, m. p. 51.5°, b. p. 148°/6 mm. (anilic acid, m. p. 174°); the corresponding acid, obtained by boiling with water, has m. p. 164—166° (with anhydride formation). Ozonolysis of the above anhydride yields acetaldehyde and a strongly enolic aldehyde; oxidation of the above acid by permanganate yields finally only oxalic acid.

cis-Hexatriene and maleic acid combine to give an impure liquid anhydride, b. p. 120—150°, which yields an anilic acid and an ethylidene-*cis*-tetrahydrophthalic acid identical with those of the *trans*-series. After many distillations the same ethylidene-*cis*-tetrahydrophthalic anhydride was isolated in a crystalline condition. R. J. W. LE FEVRE.

Synthesis of an isomeride of thyroxine, and of related compounds. C. R. HARRINGTON and

W. MCCARTNEY (J.C.S., 1929, 892—897).—Di-(4-methoxyphenyl)methyl chloride (A., 1922, i, 148) condenses with ethyl potassiophthalimidomalonate in xylene at 145° to give a 75% yield of ethyl di-(4-methoxyphenyl)methylphthalimidomalonate, m. p. 106°, which by hydrolysis with potassium hydroxide and decarboxylation at 180—200°/13 mm. affords the anhydride of α -o-carboxybenzamido- $\beta\beta$ -di-(4-methoxyphenyl)propionic acid, m. p. 209—210°, hydrolysed by hydriodic acid (*d* 1.7) and acetic anhydride to α -amino- $\beta\beta$ -di-(4-hydroxyphenyl)propionic acid (I), m. p. 241° (decomp.) after softening at 190—200°; by treatment with iodine and ammonia I is converted into $\beta\beta$ -di-(3:5-di-iodo-4-hydroxyphenyl)- α -aminopropionic acid, m. p. 218°. Decarboxylation of I at 290—315°/2 mm. in portions of 0.5 g. furnishes $\beta\beta$ -di-(4-hydroxyphenyl)-ethylamine, m. p. 207—208° (hydrochloride, m. p. 275°; tribenzoyl derivative, m. p. 200°), which by treatment with iodine and ammonia affords $\beta\beta$ -di-(3:5-di-iodo-4-hydroxyphenyl)ethylamine (II), m. p. 232—233° (decomp. with liberation of iodine). Similarly, diphenylmethyl bromide (cf. A., 1925, i, 656) with ethyl potassiophthalimidomalonate gives ethyl diphenylmethylphthalimidomalonate, m. p. 117° (yield 57%), hydrolysed, decarboxylated, and dehydrated to the anhydride of α -o-carboxybenzamido- $\beta\beta$ -diphenylpropionic acid, m. p. 214—215°; the latter by hydrolysis with hydriodic acid (*d* 1.7) and acetic anhydride affords α -amino- $\beta\beta$ -diphenylpropionic acid, m. p. 236° (decomp.). Bromination of 3:5-di-iodothyronine in glacial acetic acid gives a 45% yield of 3':5'-dibromo-3:5-di-iodothyronine, m. p. 244.5°.

Although I is isomeric with and retains the characteristic o-di-iodophenolic group of thyroxine, it exhibits no trace of any type of physiological activity; II is similarly inactive. An improved preparation of $\beta\beta$ -diphenylethylamine, m. p. 39—40°, b. p. 180°/15 mm. (hydrochloride, m. p. 259°; picrate, m. p. 216—217°), is described. C. W. SHOPPEE.

Alkyl- and aralkyl-resorcinolcarboxylic acids. H. STENZL.—See B., 1929, 427.

Substances related to cochinellic and carminic acids. II. Synthesis of α -coccinic acid (*m*-oxyuvitic acid). A. N. MELDRUM and R. L. ALUMOHANDANI (J. Indian Chem. Soc., 1929, 6, 253—258).—Condensation of 3-methoxy-*p*-toluic acid with chloral hydrate in presence of sulphuric acid affords, in addition to 3-methoxy-6- $\beta\beta\beta$ -trichloro- α -hydroxyethyl-*p*-toluic acid (I) (A., 1925, i, 1272), small amounts of 3-methoxy-6- $\alpha\beta\beta$ -tetrachloroethyl-*p*-toluic acid (II), m. p. 200—201°, and the 2-sulpho-derivative (barium salt) of I. When I is heated with sulphuric acid for a short time or treated with hydrogen chloride in presence of sulphuric acid at the ordinary temperature, II results. Reduction of II with zinc dust and acetic acid gives 3-methoxy-6- $\beta\beta$ -dichloroethyl-*p*-toluic acid, converted by treatment with sulphuric acid at 70—80° into 2-methoxy-4-methyl-5-carboxymethylbenzoic acid, m. p. 164—165° (barium salt +1.5H₂O). Treatment of II with hot 20% potassium hydroxide solution affords $\omega\omega$ -trichloro-4-methoxy-6-methylstyrene-3-carboxylic acid, m. p. 185—187°. Hydrolysis of I with barium hydroxide solution yields 4-methoxy-5-carboxy-2-methylmandelic acid, +H₂O,

m. p. 105—110° with effervescence after sintering at 95—100°, m. p. (anhydrous) 162—163° (*barium salt* + 4H₂O), oxidised by potassium permanganate to 4-methoxy-5-carboxy-*o*-toluylformic acid, m. p. 211—212° (*barium salt* + 2H₂O), and converted by treatment with sulphuric acid at 80—100° into 3-methoxy-6-aldehydo-*p*-toluic acid, m. p. 176—177°. Oxidation of this with potassium permanganate affords 4-methoxy-6-methylisophthalic acid, m. p. 250—252°, obtained also by similar oxidation of I. Demethylation of this methoxy-derivative with 10% hydriodic acid yields 4-hydroxy-6-methylisophthalic acid [α -coccinic acid], m. p. 320—322° [(decomp.); (lit. 298° and 310°); *barium salt* + 2H₂O, loses 0.5H₂O at 110—125°; *calcium salt* + 4H₂O, loses 2.5H₂O at 110—115°]. The α -coccinic acid (*m*-oxyuvitic acid) of Oppenheim and Pfaff (A., 1874, 1161) is impure. H. BURTON.

[Attempted] syntheses of ψ -opianic acid. I. S. N. CHAKRAVARTI (J. Indian Chem. Soc., 1929, 6, 207—229).—Various unsuccessful synthetic schemes are described. Reduction of 6-nitro-2:3-dimethoxybenzaldehyde (I), m. p. 110°, obtained together with the 5-nitro-isomeride by nitration of *o*-veratraldehyde (cf. Perkin, Robinson, and Stoye, A., 1925, i, 39), with ferrous sulphate and ammonia gives 6-amino-2:3-dimethoxybenzaldehyde (*hydrochloride*; *benzoyl derivative*, m. p. 150°; *phenylhydrazone*, m. p. 133°), which readily eliminates water from 2 mols., forming an *azomethine*, m. p. 235°. Attempts to introduce a cyano-group in place of the amino-group failed. Attempts to oxidise ψ -meconine with various oxidising agents were either negative or resulted in complete degradation (cf. Salomon, A., 1887, 585; Edwards, Perkin, and Stoye, A., 1925, i, 404). Bromination of ψ -meconine at 150° in bright sunlight yields a small amount of a substance, m. p. above 280°, together with an acid (probably 6-bromo-2-aldehydo-3:4-dimethoxybenzoic acid), m. p. about 200°, and a compound, m. p. about 90°. Methyl ψ -meconinate, m. p. 72—73° (from the silver salt and methyl iodide), is converted by treatment with thionyl chloride in pyridine, phosphorus pentachloride in chloroform, hydrogen chloride in presence of ether and anhydrous sodium sulphate, or hydrobromic and acetic acids, into ψ -meconine. The last-named substance is unaffected by phosphorus pentachloride at 160°, or hydrobromic and acetic acids. 2-Aminoveratric acid is converted by the usual method into 2-cyanoveratric acid, (II), m. p. 208—209°, which is readily hydrolysed by dilute hydrochloric acid to hemipinic acid. Attempted conversion of II into 2-aldehydoveratric acid by Stephen's method (A., 1925, i, 1131) resulted in the formation of hemipinimide.

When 2:3-dimethoxycinnamic acid (improved method of preparation given) is treated with an excess of nitric acid (*d* 1.5) below 0°, a dinitro-2:3-dimethoxycinnamic acid, m. p. 198°, is formed. With nitric acid (*d* 1.42) at 10—20°, about 10% of 6-nitro-2:3-dimethoxycinnamic acid (III), m. p. 220° (*methyl ester*, m. p. 150°; *ethyl ester*, m. p. 90°), is obtained together with the 5-nitro-isomeride, m. p. 231° (*methyl ester*, m. p. 154—155°), separable through the solubility of the methyl esters in alcohol. Condensation of I with malonic acid in presence of pyridine and piperidine

affords III, oxidised by potassium permanganate in presence of aqueous sodium carbonate and benzene to I. Reduction of III with ferrous sulphate and ammonia gives 6-amino-2:3-dimethoxycinnamic acid, m. p. 179°, converted by the usual method into 6-cyano-2:3-dimethoxycinnamic acid, (IV), m. p. 238°. Hydrolysis of this with 10% sodium hydroxide solution yields 6-carboxy-2:3-dimethoxycinnamic acid (V), m. p. 194°. Oxidation of IV with potassium permanganate affords indefinite products, whilst V furnishes a substance, m. p. 202°. H. BURTON.

Tautomerism of *o*-nitro-compounds. F. ARNDT (Ber., 1929, 62, [B], 1167—1171; cf. A., 1928, 752, 759).—A reply to Tanasescu (A., 1928, 177, 178). H. WREN.

"Oxidising" action of alkalis. II. Aromatic hydroxyaldehydes. G. LOCK (Ber., 1929, 62, [B], 1177—1188; cf. this vol., 67).—Hydroxyaldehydes which contain a free hydroxyl group in the *ortho*- or *para*-position to the aldehyde group are not affected by solutions of potassium hydroxide, but react with the powdered alkali at about 110° with formation of molecular quantities of hydroxy-acid and hydrogen. This is true also of dihydroxybenzaldehydes which contain a hydroxyl group in the *meta*- as well as in the *para*-position; for example, protocatechualdehyde and its 3-methyl ether. Hydroxyaldehydes containing a hydroxyl group in the *meta*-position undergo the Cannizzaro reaction with cold potassium hydroxide solutions, whereas at a higher temperature the alkali reacts with the hydroxybenzyl alcohol thus produced, giving hydrogen and hydroxy-acid, so that the final products of the two types of change are ultimately identical quantitatively. The reaction may be expressed by the scheme $C_6H_4(OK) \cdot CHO + KOH = C_6H_4(OK) \cdot CO_2K + H_2$, but the possibility of the intermediate formation of potassium hydride is not excluded. The following new data are recorded: 6-bromo-3-hydroxybenzyl alcohol, m. p. 142°; 6-nitro-3-hydroxybenzyl alcohol, m. p. 120.5° after softening (*potassium and lead salts*); 4-nitro-3-hydroxybenzyl alcohol, m. p. 97°; isovanillyl alcohol, m. p. 132°. H. WREN.

Action of diazomethane on piperonal. II. E. MOSETTIG (Ber., 1929, 62, [B], 1271—1278; cf. A., 1928, 887).—Safrole oxide, b. p. 140—145°/9 mm., is little affected by distillation under ordinary pressure or by prolonged agitation with concentrated sodium hydrogen sulphite solution, but is isomerised when boiled with pumice fragments soaked in 50% sulphuric acid to 3:4-methylenedioxyphenylpropanaldehyde (semicarbazone, m. p. 192—193.5° when slowly heated). It is converted by cautious treatment with hydrogen chloride in light petroleum into the corresponding chlorohydrin, C₁₀H₁₁O₃Cl, m. p. 47—48.5 after softening at 46°. The oxide is transformed by aqueous piperidine into β (or α)-piperidino- γ -3':4'-methylenedioxyphenylpropan- α (or β)-ol, m. p. 42—44 (*hydrochloride*, m. p. 165—167° after softening at 163—165°; *chloroplatinate*). Similarly, with aqueous dimethylamine the oxide affords β -(or α)-dimethylamino- γ -3':4'-methylenedioxyphenylpropan- α (or β)-ol (*picrate*, m. p. 164—165° after softening at 163°; very hygroscopic *hydrochloride*).

Finely-divided piperonal is added to an ethereal methyl-alcoholic solution of diazomethane at -15° . The products formed are piperonylacetone, acetopiperone, and safrole oxide (identified as the corresponding chlorohydrin and as the additive products with piperidine and dimethylamine). The same compounds result when an ethereal methyl-alcoholic solution of diazomethane is poured into an ethereal solution of piperonal. Acetopiperone when subjected to the same conditions as piperonal does not appear to react with diazomethane. Piperonylacetone reacts slowly, very probably with production of an oxide.

H. WREN.

Synthesis of safrovanillin from isosafro-eugenol. K. KAFUKU and N. ISHIKAWA (Bull. Ind. Dep. Centr. Res. Lab. Formosa, 1928, 24, 24—27).—Oxidation of isosafro-eugenol with ozonised oxygen affords (60—80% yield) 3-hydroxy-4-ethoxybenzaldehyde, m. p. 125° (oxime, m. p. $181-183^{\circ}$; semicarbazone, m. p. $202-203^{\circ}$).

CHEMICAL ABSTRACTS.

Intermolecular condensation of styryl ketones.

III. Further examples of the ready formation of bis-(styryl ketones). I. M. HELLBRON and F. IRVING (J.C.S., 1929, 931—936).—The interaction of benzaldehyde and methyl *n*-alkyl ketones gives both the simple styryl ketone and its dimeride. The solvent appears to be one of the main factors determining the formation of the mono- or bis-form; in aqueous alcohol the styryl ketone is formed, probably owing to its ready separation and consequent removal from the action of the alkali; in absolute alcohol the dimeride is produced even at the same alkali concentration. The dimerides are more readily produced from the higher members of the series, and less easily with substituted benzaldehydes. Dimerides are formed from branched-chain ketones only when at least one methylene group separates the radical from the carbonyl group. The styryl ketones differ widely from their bis-forms in m. p. and crystallise well; the bis-forms usually separate in masses of felted needles. By condensing the appropriate reactants with alkali under given conditions are obtained: *bis(styryl n-propyl ketone)*, m. p. $194-195^{\circ}$ (cf. Vorländer, A., 1898, i, 27); *bis(styryl n-butyl ketone)*, m. p. $175-176^{\circ}$; *bis(styryl isobutyl ketone)*, m. p. 202° , also prepared from styryl isobutyl ketone (cf. Gheorghiu and Arventiev, A., 1928, 522); *bis(4-isopropylstyryl isobutyl ketone)*, m. p. $192-194^{\circ}$; *bis(styryl n-hexyl ketone)*, m. p. 152° ; *4-methoxystyryl n-hexyl ketone*, m. p. $145-146^{\circ}$; *bis(styryl isoheptyl ketone)*, m. p. 177° ; *bis(styryl n-heptyl ketone)*, m. p. 144° ; and *bis(styryl n-octyl ketone)*, m. p. $131-135^{\circ}$. Alkali condensation has also been employed to obtain the following styryl ketones: styryl *n*-hexyl ketone, m. p. $32-33^{\circ}$ (cf. A., 1905, i, 214); *4-methoxystyryl n-hexyl ketone*, m. p. 52° (cf. A., 1905, i, 14); and styryl *n*-octyl ketone. It is probable that the styryl γ -methylamyl ketones (active and inactive) described by Rupe and Wild (A., 1917, i, 538) are dimerides.

C. W. SHOPPEE.

Natural system for polymorphic forms of *p*-methylchalkone [*p*-tolyl styryl ketone]. Isomeric relationships in the chalkone series.

VII. C. WEYGAND and H. BAUMGARTEL (Annalen, 1929, 469, 225—256; cf. A., 1926, 1041; this vol., 564).—Instead of three modifications α , β , and γ , as previously recorded, *p*-tolyl styryl ketone has been prepared in 13 crystalline forms, 7 of which are termed principal as distinct from subsidiary forms. All three of the earlier modifications belong to the principal group. The following classification is made, the figures after the m. p. indicating the velocity of crystallisation from a fused mass at $18-20^{\circ}$ in 0.001 mm. per sec.: I, m. p. 74.5° ; 89; II, m. p. 56.5° ; 39; III, m. p. 55.5° ; 30; (1 subsidiary form); IV, m. p. 54.5° ; 114; V, m. p. 45.5° ; 19; VI, m. p. 48° ; 4; (1 subsidiary form); VII, m. p. 44.5° ; 20; (4 subsidiary forms). Details of preparation are given, together with the results of a study of the mechanism of transformation. R. A. MORTON.

Relative stability of isomerides according to absorption spectra. V. Dehydration of glycols; isomeric change of ethylene oxides. (MME.) P. RAMART-LUCAS and F. SALMON-LEGAGNEUR (Compt. rend., 1929, 188, 1301—1303; cf. A., 1928, 760, 881, 1000; this vol., 441).—By dehydration of $\alpha\alpha$ -diphenyl- $\beta\beta$ -dimethyl- or $\alpha\beta$ -diphenyl- $\alpha\beta$ -dimethylpinacols (I, II) or ethylene oxides (III, IV), only methyl $\alpha\alpha$ -diphenylethyl ketone (V) or phenyl phenylisopropyl ketone (VI) can be formed; from the glycols $\text{CRPh(OH)CH}_2\text{OH}$ (VII) (where R = Me or CH_2Ph), only the aldehydes CHPhCHO (VIII) and the ketones $\text{CH}_2\text{PhCO-R}$ (IX) and $\text{CH}_2\text{R-COPh}$ (X). The absorption spectra of the above compounds have been examined; that of VI is nearer the visible than that of V, and those of IX and X are nearer the visible than those of the aldehydes VIII. Accordingly, from the rules given (*loc. cit.*) the compounds I—IV would be expected to give at low temperatures V and at high temperatures VI, and the compounds VII to give at low temperatures VIII and at high temperatures IX and X, and it is found that, by distillation over infusorial earth at $200-300^{\circ}$ under reduced pressure, V and VIII are actually obtained. At $400-500^{\circ}$ the pinacols yield the hydrocarbon which is derived from V or VI by heating, and of which the absorption curve is very much nearer the visible; the glycols VII give ketones or hydrocarbons.

The following new rules are proposed: if isomerides are heated and yield several transposition products, the latter are formed in such a sequence that the ultra-violet absorption is displaced towards the visible, provided that no carbon radical is lost, and the formation of the various products depends less on the structure of the isomeride than on the temperature. Thus I, III, and the two stereoisomerides of each of II and IV give the same product; $\alpha\alpha$ - or $\alpha\beta$ -diphenylethylene glycol both give, at $200-300^{\circ}$, diphenylacetaldehyde, whilst at 500° these all give deoxybenzoin. These rules do not apply to transpositions brought about by reagents, in which case the latter may have a specific effect; thus, I and III are converted by acetic anhydride and a trace of sulphuric acid into VI, but by concentrated sulphuric acid into V, which is, however, the product when either reagent acts on II or IV. E. W. WIGNALL.

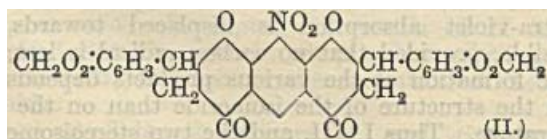
Spectrochemistry of α -diketones and ethylene oxides. K. VON AUWERS (Ber., 1929, 62, [B], 1317—1319; cf. Moureu, A., 1927, 246, 1173; 1928, 180, 419, 1334).—The data $d_{13}^{13.8}$ 1.0919, $n_D^{15.8}$ 1.52767, $n_D^{16.8}$ 1.53404, and $d_{14}^{14.4}$ 1.0756, $n_D^{18.4}$ 1.58698, $n_D^{19.4}$ 1.59953, are recorded for the diketonic and keto-enolic varieties of benzylmethylglyoxal, respectively, whereas acetylphenylethylene oxide has $d_{14}^{16.0}$ 1.0733, $n_D^{16.0}$ 1.51529, $n_D^{16.0}$ 1.52016. The diketone and keto-enol can be sharply differentiated spectroscopically, whereas discrimination between diketone and oxide appears impossible by this method. Comparison of Schlotterbeck's "trichloroacetone" (A., 1907, i, 185, 478; 1909, i, 553), $d_{13}^{19.0}$ 1.4962, $n_D^{19.0}$ 1.47310, $n_D^{19.0}$ 1.47729, with chloral, $d_{13}^{21.4}$ 1.5059, $n_D^{21.4}$ 1.44988, $n_D^{21.4}$ 1.45412, confirms the conclusion of Arndt and Eistert (A., 1928, 739) that the compound is $\alpha\alpha\alpha$ -trichloropropylene β -oxide.

H. WREN.

Oximes of unsaturated ketones. K. VON AUWERS (Ber., 1929, 62, [B], 1320—1323).—Phenyl *p*-ethoxystyryl ketone, m. p. 74—75°, is converted by hydroxylamine in alkaline solution into 5-phenyl-3:4'-ethoxyphenylisooxazoline, m. p. 107—108°, whereas in acidic solution it affords the corresponding oxime, m. p. 134—140°, converted by phosphorus pentachloride in ether into cinnam-*p*-phenetide, m. p. 143—144°. Phenyl α -bromostyryl ketone and hydroxylamine in alkaline solution yield 3:5-diphenylisooxazole, m. p. 140°, whereas in acid solution the oxime, m. p. 151°, is obtained; it is transformed in boiling alcoholic alkali hydroxide into 3:5-diphenylisooxazole.

H. WREN.

Condensation of aldehydes with nitrodiacetoresorcinol. J. ALGAR and (Miss) N. M. MACDONNELL (Proc. Roy. Irish Acad., 1929, 38, B, 171—174).—Nitration of 4:6-diacetoresorcinol with a mixture of nitric (*d* 1.5) and sulphuric acids in the cold affords 2-nitro-4:6-diacetoresorcinol (I), m. p. 235.5°, converted by an excess of fuming nitric acid into 2:4:6-trinitroresorcinol. Reduction of I with ferrous sulphate and sodium hydroxide yields a small amount of 2-amino-4:6-diacetoresorcinol, m. p. 185°, whilst condensation of I with benzaldehyde and furfuraldehyde in presence of aqueous methylalcoholic potassium hydroxide gives the corresponding dibenzylidene, m. p. 220°, and difurfurylidene derivatives, m. p. 262—265° (decomp.), respectively. With piperonal, a diflavanone (II), m. p. 262°, is

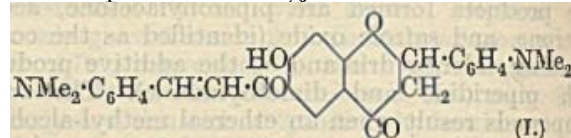


obtained: this does not give a coloration with ferric chloride solution, and dissolves in sulphuric acid to a violet-red solution.

H. BURTON.

Dichalkones derived from diacetoresorcinol. J. ALGAR and P. J. HANLON (Proc. Roy. Irish Acad., 1929, 38, B, 175—178).—Condensation of 4:6-diacetoresorcinol with *p*-dimethylaminobenzaldehyde in presence of alcohol and a small amount of piperidine yields the corresponding di-*p*-dimethylaminobenzylidene

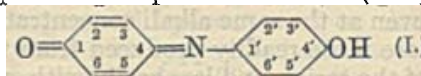
derivative (designated α -), scarlet, m. p. 240—241°, whilst in presence of 80% alcohol an isomeric (I)



(termed β -), orange-red, m. p. 262—263°, results. The lighter colour and smaller fusibility of the β -form indicates the flavanone structure. Difurfurylidene-4:6-diacetoresorcinol, m. p. 226—227°, is obtained using aqueous-alcoholic sodium hydroxide as the condensing agent.

H. BURTON.

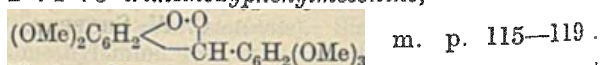
Oxidation-reduction. XIII. Indophenols used as oxidation-reduction indicators. H. D. GIBBS, W. L. HALL, and W. M. CLARK (U.S. Public Health Rep., Suppl. 69, 1928, 35 pp.).—Indophenols are best prepared by treating benzoquinonechloroimides with phenols and a slight excess of 3*N*-sodium hydroxide solution at about 0°, with subsequent purification of the sodium salts, which, however, is not easy, as their aqueous solutions are generally unstable. Reduction of the indophenols to the leuco-compounds (substituted diphenylamines) is carried out by treating a saturated aqueous solution of the salt with 20% potassium sulphide. The m. p. of the free indophenols vary considerably with the rate of heating, and have little significance. Various methods of analysis are quoted. The nomenclature is discussed and the name benzenoneindophenol (I) adopted for the parent substance (indophenol). The



following substituted benzenoneindophenols are described, many of which are new: 2-methyl, m. p. 162°; 3-methyl, m. p. 110—111° (decomp.); 2:6-dimethyl-; 3-methyl-6-isopropyl-, m. p. 134°, decomp. 151°; 2-methyl-*o*-isopropyl-, m. p. 121—125°; 2-methoxy-, m. p. 171°; 3-methoxy-; 2-chloro-; 2- and 3-bromo-; 2:6-dichloro-; 2:6-dichloro-3'-methyl-; 2:6-dichloro-2'-methyl-; 2:6:3'- and 2:6:2'-trichloro-; 2:6-dibromo-; 2:6-dibromo-3'-methyl-; 2:6-dibromo-2'-methyl-; 2:6-dibromo-2'-methyl-5'-isopropyl-; 2:6-dibromo-3'-methoxy-; 2:6:3'- and 2:6:2'-tribromo-; 3'-chloro-2:6-dibromo-, and 3'-methyl-. Sodium 2:6-dibromobenzenoneindophenol-2'- and -3'-sulphonates, benzenoneindophenol-*o*-phenol (I, OH in 2'-position; 3-methyl- and 2-bromo-derivatives), and 1-naphthanoneindophenol-2-sulphonic acid (3'-methyl-, 3':5'-dichloro-, and 3':5'-dibromo-derivatives), are also described.

H. BURTON.

Ready conversion of certain derivatives of hydroxyquinol trimethyl ether into quinone compounds. T. SZÉKI (Ber., 1929, 62, [B], 1373—1378).—Opianic acid and hydroxyquinol trimethyl ether are converted by 73% sulphuric acid into 3-2':4':5'-trimethoxyphenylmeconine,

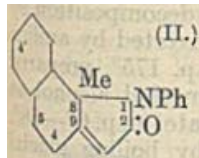


Under similar conditions, methyl opianate and 2 mols. of hydroxyquinol trimethyl ether give methyl 4:5:2':4':5':2'':4'':5'':octomethoxytriphenyl-

methane-6-carboxylate, m. p. 143°, whereas nitro-*opianic acid* affords 4-nitro-3-2':4':5'-trimethoxyphenylmeconine, m. p. 184°. Trimethoxyphenylmeconine is readily oxidised by nitric acid (*d* 1.48) in glacial acetic acid to 2-methoxy-5-meconyl-p-benzoquinone, m. p. about 220° after softening at 202—204°. 2-Methoxy-5-4'-nitromeconyl-p-benzoquinone, m. p. 199—200° (decomp.), is prepared by nitration of the last-named substance or by oxidation of 4-nitro-3-2':4':5'-trimethoxyphenylmeconine. 2-Methoxy-5-phthalidyl-p-benzoquinone has m. p. 152—154°. The following quinones are prepared by use of nitric acid in acetic acid: 2-methoxy-5-benzoyldiphenylmethyl-p-benzoquinone, m. p. 181°, from benzoyl-2:4:5-trimethoxytriphenylmethane; 2-methoxy- α - α -diphenylethyl-p-benzoquinone, m. p. 198°, from 2:4:5-trimethoxy- α - α -triphenylethane; 2-methoxy-6- α -diphenylisopropyl-p-benzoquinone, m. p. 183—184°. Reduction of the requisite quinones by sulphur dioxide yields 2-methoxy-5-meconylquinol, m. p. 210° (diacetyl compound, m. p. 158°), and 2-methoxy-5-phthalidylquinol, m. p. 204° (diacetate, m. p. 178°).

H. WREN.

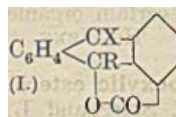
o-Quinamines of the naphthalene series and their rearrangement into homologues of β -naphthylacetic acid. K. FRIES and A. KUSTER (Annalen, 1929, 470, 20—37).—When 1-bromo-2-keto-1-methyl-1:2-dihydronaphthalene (Fries and Engel, A., 1924, i, 1187) is treated with alcoholic aniline, 1-anilino-2-keto-1-methyl-1:2-dihydronaphthalene, m. p. 141°, results. This is reduced by zinc dust and acetic acid, yielding 1-methyl- β -naphthol, and is brominated in alcoholic solution to the corresponding 1-2':4'-dibromoanilino-derivative, m. p. 174°. The following substituted -2-keto-1-methyl-1:2-dihydronaphthalenes are prepared by similar methods: 1-p-bromoanilino-, m. p. 148°; 6-bromo-1-anilino-, m. p. 149°; 6-bromo-1-p-bromoanilino-, m. p. 168°; 6-bromo-1-2':4'-dibromoanilino-, m. p. 185°, converted by treatment with zinc dust and acetic acid into 2:4-dibromoaniline and 6-bromo-1-methyl- β -naphthol, m. p. 152°; 4:6-dibromo-1-anilino- (I), m. p. 200°, converted by treatment with cold concentrated sulphuric acid into *p*-aminophenyl β :4:6-dibromo-1-methylnaphthyl ether, m. p. 137°. Bromination of I in alcoholic solution, or treatment of 1:4:6-tribromo-2-keto-1-methyl-1:2-dihydronaphthalene with an equimolecular quantity of alcoholic aniline, affords the *N*-bromo-derivative, m. p. 187°, of I, which when treated with hydrochloric, hydrobromic, or sulphurous acids passes into 4:6-dibromo-1-p-bromoanilino-2-keto-1-methyl-1:2-dihydronaphthalene, m. p. 201°. 1-Acetanilido-2-keto-1-methyl-1:2-dihydronaphthalene, m. p. 174°, when treated with sodium ethoxide undergoes an aldol-like condensation, yielding a mixture of 2-keto-1-phenyl-8-methyl-6:7-benzo-2:8-dihydroindole (II), m. p. 178°, and 9-hydroxy-2-keto-1-phenyl-8-methyl-6:7-benzo-2:3:8:9-tetrahydroindole (III), m. p. 174° (methyl ether, m. p. 184°). Treatment of III with sulphuric acid or alcoholic-hydrochloric acid gives II, whilst reduction with hydrogen in presence of palladised barium sulphate and acetic acid yields the



corresponding 2:3:4:5:8:9-hexahydro-derivative, m. p. 159° (acetyl derivative, m. p. 152°). Similar reduction of II affords the corresponding 2:3:4:5:8:9-hexahydro-derivative, m. p. 145°, but with stannous chloride and acetic acid the corresponding 2:3:5:8-tetrahydro-derivative, m. p. 189°, results. 3:4:5:9-Tetrabromo-2-keto-1-phenyl-8-methyl-6:7-benzo-2:3:4:5:8:9-hexahydroindole, m. p. 200° (decomp.), is obtained by bromination of II in chloroform solution. When II is reduced by Clemmensen's method aniline is eliminated and β -1-methylnaphthylacetic acid (IV), m. p. 166°, results: this is formed presumably through the intermediate β -1-anilino-1-methyl-1:2-dihydronaphthylacetic acid. Distillation of the sodium salt of IV with copper powder and soda-lime affords 1:2-dimethylnaphthalene. 1-Propionanilido-2-keto-1-methyl-1:2-dihydronaphthalene, m. p. 142°, when treated with sodium ethoxide yields 2-keto-1-phenyl-3:8-dimethyl-6:7-benzo-2:8-dihydroindole, m. p. 165°, reduced by Clemmensen's method to α -(β -1-methylnaphthyl)propionic acid, m. p. 128°. Similarly, 6-bromo-1-acetanilido-2-keto-1-methyl-1:2-dihydronaphthalene, m. p. 226°, affords a mixture of 9-hydroxy-2-keto-1-phenyl-8-methyl-6:7:4'-bromobenzo-2:3:8:9-tetrahydroindole, m. p. 201°, and 2-keto-1-phenyl-8-methyl-6:7:4'-bromobenzo-2:8-dihydroindole, m. p. 174°. The last-named compound is reduced by Clemmensen's method to 3-6-bromo-1-methylnaphthylacetic acid, m. p. 210°.

H. BURTON.

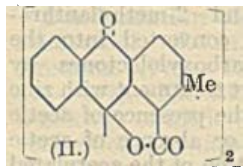
Anthraquinol- α -carboxylolactones. R. SCHOLL and F. RENNEN [with O. BOTTGER, S. HASS, and H. K. MEYER] (Ber., 1929, 62, [B], 1278—1295; cf. this vol., 567).—Anthraquinone- and 2-methylantraquinone-1-carboxylic acids are converted into the corresponding anthraquinol- α -carboxylolactones by the following methods. (1) Short treatment with zinc dust and glacial acetic acid in the presence of acetic anhydride; protracted heating or absence of acetic acid leads to quantitative formation of the acetylated lactones. (2) By treatment of the esters with alkaline or acid reducing agents: the aryl esters react readily with sodium hyposulphite, zinc dust and ammonia, or zinc dust and acetic acid. The alkyl esters of the 2-methyl acid but not those of the parent acid react to a slight extent in the same sense. (3) From the acid chloride or amide and sodium hyposulphite and sodium hydroxide. The anthraquinone-1-carboxylic acids, their esters, chlorides, and amides, are considered to belong to the normal type, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_3 \cdot CO_2H$, and not to the *pseudo*-series I ($X=O$), since the amide



is converted into a vat by sodium hyposulphite and sodium hydroxide from which it is precipitated by air, and the normal structure is established for the esters (following abstract). The constitution does not appear deducible from the colour. The most striking property of the lactones is the change from red to blue when they are brought into alkaline solution. In pyridine, anthraquinol-1-carboxylolactone dissolves at the ordinary temperature to a red solution from which the red pyridine compound, $C_{15}H_8O_3 \cdot C_5H_5N$, separates. If the pyridine solution is treated with water it be-

comes pure blue but red again when heated or treated with much pyridine. It is considered that the red, homopolar phenolic lactone ($I: N=H; X=H+OH$) with pyridine alone yields a homopolar pyridine compound ($I; R=H; X=H+OH, C_5H_5N$) which passes into the blue, heteropolar pyridinium salt ($I; R=H; X=H+O[(H_2O)_n, HC_5H_5N]$) of the hypothetical heteropolar acid.

The following substances are described: *anthraquinol-1-carboxylolactone* and its 10-*acetyl* derivative, m. p. 196°; *phenyl anthraquinone-1-carboxylate*, m. p. 213°; *methyl, ethyl, phenyl, and p-bromophenyl 2-methylanthraquinone-1-carboxylates*, m. p. 178—179°, 144°, 218—219°, and 226°, respectively; *2-methylpyridazoneanthrone*, m. p. 332°, from the phenyl ester and hydrazine hydrate in boiling benzene; *2-methylanthraquinol-1-carboxylic acid*; *2-methylanthraquinol-1-carboxylolactone*, m. p. about 265° (decomp.) after becoming lighter in colour at about 235°; *2-methylanthraquinone-1-carboxylamide*, gradual decomp. about 260° after softening at about 255°; *acetyl-2-methylanthraquinol-1-carboxylolactone*, m. p. 238°. *2-Methylanthraquinol-1-carboxylolactone* can be sharply titrated with potassium permanganate in acetone and acetic acid or with bromine in pyridine. The anthraquinol-1-carboxylolactones are highly sensitive to atmospheric oxidation in neutral, acid and alkaline solution and are readily oxidised by lead peroxide, ferric chloride, bromine, permanganate, etc. For preparative purposes the most suitable reagent is hot nitrobenzene, which transforms the 2-methyl derivative into 9:9'-*dihydroxy-2:2'-dimethyl-9'-di-anthranyl-1:1'-dicarboxylodilactone* (II), m. p. about 290° (decomp.) after darkening at about 270° when rapidly heated. The compound is also prepared by the action of finely-divided silver or dimethylaniline on the acid chloride in benzene. Con-



centrated sulphuric acid causes fission with oxidation to 2-methylanthraquinone-1-carboxylic acid. It is reduced by zinc dust and glacial acetic acid, very slowly by sodium hyposulphite and ammonia to the monomeric lactone. With aqueous or, preferably, alcoholic alkali the dilactone yields an olive-green solution apparently containing a quinhydrone-like compound of the salts of the anthraquinone- and anthraquinol-carboxylic acids. Sodium ethoxide appears to cause a radical dissociation into an anthroxyl with univalent oxygen; the same change is induced by exposing the dilactone in acetic acid to ultra-violet light and by heating its solution in certain organic media.

H. WREN.

Nature of anthraquinone- α -carboxylic esters. R. SCHOLL and J. DONAT [with H. SEMP and L. WANKA] (Ber., 1929, 62, [B], 1295—1301; cf. preceding abstract).—Esters of anthraquinone- and 2-methylanthraquinone-1-carboxylic acid are obtained (1) from the acid and alcohol in presence of hydrogen chloride or sulphuric acid, (2) from the acid chloride and alcohol or phenol, (3) from the silver salt and alkyl iodide, and (4) by oxidation of 2-methylanthracene-1-carboxylic esters. Method 1 is inapplicable to the 2-methyl

derivative on account of steric hindrance. The esters of anthraquinone-1-carboxylic acid prepared according to 1, 2, and 3 are identical with one another, as are those of 2-methylanthraquinone-1-carboxylic acid obtained according to 2, 3, and 4. The normal structure, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_2R \cdot CO_2R'$, is therefore assigned to them. Indications of the existence of isomeric acid chlorides are not obtained. The following compounds are described: *calcium anthracene-1-carboxylate*; *anthracene-1-carboxyl chloride*, which does not appear suitable for the Friedel-Crafts synthesis; *anthracene-1-carboxylic anhydride*, m. p. 206°; *ethyl anthraquinone-1-carboxylate*, m. p. 169°; *2-methylanthracene-1-carboxylic acid*, m. p. 212.5°, and the corresponding *acid chloride, ethyl ester*, m. p. 87—90°, and *phenyl ester*, m. p. 137—140°; *phenyl 2-methylanthraquinone-1-carboxylate*, m. p. 218—219°.

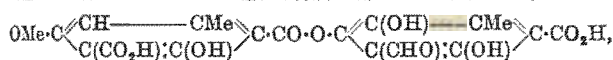
H. WREN.

Congo copal oil. L. WESTENBERG (Rec. trav. chim., 1929, 48, 580—582).—Catalytic dehydrogenation of Congo copal oil with sulphur yields a *hydrocarbon*, $C_{13}H_{14}$, m. p. 26°, b. p. 295° (corr.) (*picrate*, m. p. 139°), which is possibly identical with that obtained from Manila copal by Ruzicka and others (A., 1927, 60). Oxidation with chromic and acetic acids converts it into a monobasic *acid*, $C_{12}H_{12}O_4$, m. p. 204°, and a *substance* $(C_4H_4O)_n$, m. p. 69°.

J. W. BAKER.

Lichen substances. V. Constitution of thamnolic acid. Y. ASAHINA and S. IHARA (Ber., 1929, 62, [B], 1196—1207).—Thamnolic acid, isolated by Hesse from *Thamnolia vermicularis*, has been considered to have the composition $C_{20}H_{18}O_{11}$ and to be converted by barium hydroxide into thamnolinic acid, methyl alcohol, and carbon dioxide: $C_{20}H_{18}O_{11} + 3H_2O = C_{16}H_{20}O_9 + CH_3 \cdot OH + 3CO_2$. The acid has been isolated from *Cladonia flabelliformis*, Flk., var. *polydactyla*, and is shown by direct comparison to be identical with that from *Thamnolia vermicularis*. Analyses and titration with 0.1*N*-sodium hydroxide in the presence of hæmatoxylin indicate the molecular formula $C_{19}H_{16}O_{11}$ on the assumption that one methoxyl group is present. The *aniline salt*, m. p. 206—208°, *phenylhydrazone*, m. p. 173—174°, and *p-nitrophenylhydrazone*, m. p. 238—239°, are described. Warm potassium hydrogen carbonate solution or potassium or barium hydroxide converts thamnolic acid into orcinol monomethyl ether and evernic acid in addition to much dark-coloured resin. The formation of Hesse's thamnolinic acid could not be observed and his compound is probably evernic acid, for which the m. p. 172° is now found after crystallisation from light petroleum; specimens crystallised from water or alcohol have lower m. p., due to partial decomposition by heat and retention of products of decomposition by the crystals. Thamnolic acid is converted by aniline at 200° into the *evernanilide*, m. p. 175°, prepared also from its components, whilst methyl alcohol at 150° transforms it into methyl evernate, m. p. 67—68°. Thamnolic acid is little affected by boiling glacial acetic acid, which, at 150°, converts it into orcinol monomethyl ether, the monomethyl ether of *p*-orsellinic acid, and *thamnol*, $C_3H_8O_4$, m. p. 185° (more conveniently prepared by heating thamnolic acid with

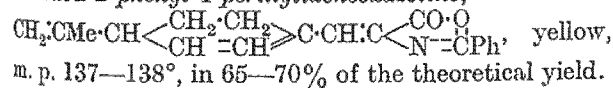
pelargonic acid in open vessels). The acidic and aldehydic nature of thamnol is established by its solubility in sodium hydrogen carbonate and sulphite and by the isolation of its *anil*, m. p. 128—129°, *phenylhydrazone*, m. p. 194° (decomp.), and *p*-nitro-*phenylhydrazone*, m. p. about 320° (decomp.). The *triacetate*, m. p. 133° (? corresponding *anil*, m. p. 129°), is described. Reduction of thamnol by Clemmensen's method yields *hydroxy-β-orcinol* [2 : 3 : 5-*trihydroxy-p-xylene*], m. p. 156° (*triacetate*, m. p. 107—108°), identified by comparison with the synthetic product (cf. Asahina and Ishibashi, this vol., 806). Thamnolic acid, when heated in potassium hydrogen carbonate solution with gradual addition of sodium sulphite, is converted into the *monomethyl ether of orcinoldicarboxylic acid*, m. p. 205—206° (decomp.), which is regarded as the parent of the monomethyl ethers of orcinolcarboxylic acid according as one or other of the carboxyl groups is eliminated as carbon dioxide. Thamnolic acid has therefore the constitution



in which the position of the depside linking is arbitrary. H. WREN.

New dihydroterpene. S. BLANCO (J. Amer. Pharm. Assoc., 1929, 18, 474—477).—Steam-distillation of the alcoholic extract of the fruits of *Pittosporum resiniferum* gave an oil having d_{20}^{20} 0.7692, n_D^{20} 1.435, $+20.02^\circ$ (100 mm. tube), 40.03° (200 mm. tube), saponif. value 0.67 (after acetylation 8.56). On fractionation it gave 26% of a fraction, b. p. 150—154° (mainly 152—153°), d_{20}^{20} 0.947, n_D^{20} 1.464, α_D^{20} $+39.34^\circ$, most of which was collected at 152—153°, which gave a *nitrobenzylamide*, m. p. 148—149° (cf. Bacon, A., 1909, i, 659). E. H. SHARPLES.

Derivatives of perillaldehyde. B. RUTOVSKI and A. KOROLEV (Trans. Sci. Chem.-pharm. Inst. Moscow, 1928, 153—156; Chem. Zentr., 1928, ii, 2355).—*Methyl*, *ethyl*, and *isoamyl* perillacrylates were prepared. By condensation of perillaldehyde with acetone or acetaldehyde in presence of sodium hydroxide, *perillylideneacetone*, *diperillylideneacetone*, and *perillylideneacetaldehyde* were obtained. Perillaldehyde, benzoylglycine, sodium acetate, and acetic anhydride afforded 2-*phenyl-4-perillylideneoxazoline*,



m. p. 137—138°, in 65—70% of the theoretical yield. A. A. ELDRIDGE.

Menthol. II. Menthyl esters of 2-nitro-4-carboxyphenylarsinic and -arsenious acids. K. L. MCCLUSKEY (J. Amer. Chem. Soc., 1929, 51, 1462—1465).—2-Nitro-4-carboxyphenylarsinic acid (Maschmann, A., 1924, i, 1357) is reduced by sulphur dioxide and concentrated hydrochloric acid to *dichloro-2-nitro-4-carboxyphenylarsine*, m. p. 173—174°. This is hydrolysed by water to 2-nitro-4-carboxyphenylarsenious acid (unchanged at 290°) and converted by thionyl chloride into the corresponding chloride, which with menthol yields 2-nitro-4-carbomenthyl-oxyphenylarsenious acid, decomp. above 100°. This is oxidised by 3% hydrogen peroxide in acetone to *menthyl 3-nitro-4-arsinobenzoate*, decomp. 210—211° [sodium salt (also $+4\text{H}_2\text{O}$)]. H. E. F. NOTTON.

Determination of configuration in the terpene series. III. J. VON BRAUN, H. KROPER, and W. REINHARDT (Ber., 1929, 62, [B], 1301—1307).—The replacement of the amino- by the hydroxyl group by means of nitrous acid is frequently accompanied by intramolecular transformation, whereas the structural relationship appears to be generally preserved if the amine is converted into its benzoyl derivative, which is decomposed by phosphorus pentachloride or pentabromide into benzonitrile, and the chloride or bromide which is readily transformed into the alcohol (cf. von Braun and Jostes, A., 1926, 825).

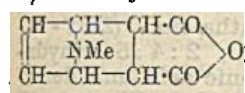
Menthonylamine hydrochloride is slowly but completely hydrogenated in aqueous solution in presence of palladised charcoal to *dihydromenthonylamine*, b. p. 85°/13 mm., $\alpha_D^{20} +2.5^\circ$ ($l=1$) [*hydrochloride*, m. p. 123—124°, $[\alpha]_D^{25} +5.74^\circ$ in water ($c=19.83$); *benzoyl derivative*, b. p. 201—202°/0.3 mm.]. The benzoyl compound is treated with phosphorus pentachloride and the product is distilled under atmospheric pressure, whereby *dihydromenthonyl chloride*, b. p. 80—87°/10 mm., d_{20}^{20} 0.8752, $[\alpha]_D^{25} -2.56^\circ$, is obtained. *Dihydromenthonyl iodide*, b. p. 108—112°/10 mm., d_{20}^{20} 1.1533, $[\alpha]_D^{25} -9.69^\circ$, from the chloride and sodium iodide in acetone, is converted by trimethylamine in benzene into the corresponding quaternary *iodide*, m. p. 235—236°, $[\alpha]_D^{25} +4.13^\circ$ in alcohol, identical with the product obtained by exhaustive methylation of dihydromenthonylamine with methyl iodide and sodium hydroxide.

Dihydro- α -campholenitrile is reduced by sodium and alcohol or by hydrogen in presence of nickel and decahydronaphthalene at 250° to *dihydrocamphylamine*, b. p. 88°/13 mm., d_{20}^{20} 0.8640, $[\alpha]_D^{25} +34.72^\circ$ [*hydrochloride*, m. p. 255° (decomp.); *picrate*, m. p. 197°; corresponding *phenylthiocarbamate*, m. p. 116°]. The *benzoyl* compound, b. p. 190°/0.2 mm., $[\alpha]_D^{25} +26.37^\circ$ in alcohol, is transformed into *dihydrocamphyl chloride*, b. p. 88°/13 mm., d_{20}^{20} 0.9983, $[\alpha]_D^{25} +46.65^\circ$. *Dihydrocamphyl iodide*, b. p. 115—120°/13 mm., d_{20}^{20} 1.0051, $[\alpha]_D^{25} +44.72^\circ$, is transformed into *dihydrocamphyltrimethylammonium iodide*, m. p. 277—278°, $[\alpha]_D^{25} +23.74^\circ$ in water, also obtained by exhaustive methylation of dihydrocamphylamine. H. WREN.

Oxidation of d - Δ^4 -carene with Beckmann's chromic acid mixture. C. S. GIBSON and J. L. SIMONSEN (J.C.S., 1929, 909—910).—Oxidation of d - Δ^4 -carene from *Andropogon Jwarancusa* with Beckmann's chromic acid mixture gave *l-trans*-caronic acid, m. p. 202—203°, $[\alpha]_{5461}^{20}$ in alcohol -11.85° , together with small quantities of terebic acid, m. p. 173—174°, dimethylmalonic acid, m. p. 185—186°, and a neutral oil yielding a semicarbazone, m. p. 205—207°, which was not further investigated. A. I. VOGEL.

Syntheses in the hydroaromatic series. III. Syntheses of terpenes, camphors, hydroaromatic and heterocyclic systems. O. DIELS and K. ALDER [with W. LUBBERT, E. NAUJOKS, F. QUERBERITZ, K. ROHL, and H. SEGEBERG] (Annalen, 1929, 470, 62—103).—When 2 : 5-*endomethylenehexahydrobenzaldehyde* (I) (semicarbazone, m. p. 160.5°; cf. A., 1928, 1018) is heated with acetic anhydride and sodium acetate, the enol *acetate* (II), b. p. 109—111°/

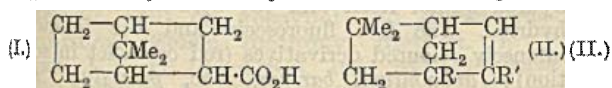
catalytically to β -methyl- Δ^8 -pentene. The dibromide, b. p. 94–95°/62 mm., of this substance affords $\alpha\gamma$ -dimethylbutadiene when heated with quinoline at 155°. This butadiene combines with maleic anhydride in benzene, forming 3 : 5-dimethyl- Δ^4 -tetrahydrophthalic anhydride (V), m. p. 56–57°. The three hydrocarbons, C_6H_{10} , described by Harries (A., 1901, i, 194), Saytzev (A., 1877, ii, 298), and Kyriakides (A., 1914, i, 506), are all $\alpha\gamma$ -dimethylbutadiene, since they react with maleic anhydride, yielding V. Isoprene, α -methyl-, $\beta\gamma$ -dimethyl-, and ω -dimethylbutadienes combine with maleic anhydride to give 5-methyl-, m. p. 63–64°, 6-methyl-, m. p. 62°, 4 : 5-dimethyl-, m. p. 78–79°, and 3 : 6-dimethyl- Δ^4 -tetrahydrophthalic anhydrides, m. p. 95–96°, respectively; $\alpha\gamma$ -trimethylbutadiene affords a compound, m. p. 49°.



Maleic anhydride and N -methylpyrrole react slowly at ordinary temperature, yielding the anhydride, m. p. 98–99°, possessing the annexed formula.

H. BURTON.

Fenchene series. I. Ozonisation and constitution of fenchenes. G. KOMPPA and R. H. ROSCHTER (Annalen, 1929, 470, 129–156).—Decomposition of an acetic acid solution of the ozonide from l - α -fenchene (A., 1917, i, 398), by warming on the water-bath, affords about 50% of d - α -fenchocamphorone, together with l - α -fenchenylic acid (I), m. p. 71.5–72° (anilide, m. p. 149.5–150°; various salts are described briefly), and the corresponding impure aldehyde. Dehydration of r -fenchyl alcohol



with potassium or sodium hydrogen sulphate at 180° gives a mixture of hydrocarbons, b. p. 145–160°, separated into the following fractions: (A) b. p. 151–153°, d_4^{20} 0.8598, n_D^{20} 1.46620 (nearly pure dl - β -fenchene), (B) b. p. 145–147°, d_4^{20} 0.8547, n_D^{20} 1.46072 (impure γ -fenchene (II; R=H, R'=Me)), and (C) b. p. 141–143°, d_4^{20} 0.8476, n_D^{20} 1.45424 [a mixture of δ - or ω -fenchene (II; R=Me, R'=H) and cyclofenchene]. Decomposition of the ozonide from A, in the above manner, yields dl - β -fenchocamphorone (semicarbazone, m. p. 193–195°), oxidised by alkaline potassium permanganate to dl - α -fenchocamphoric acid, p. 144–145° (various salts described). A small amount of cis -apocamphoric acid is obtained during the oxidation of an impure specimen of the ketone, showing that A contains some α -fenchene. β -Fenchocamphorone is identical with β -isocamphenilone (Nametkin and Chuchrikova, A., 1915, i, 701). Fraction B contains some β -fenchene, since decomposition of the ozonide gives β -fenchocamphorone in addition to 3-acetyl-5 : 5-dimethylcyclopentanecarboxylic acid (III), d_4^{20} 1.0924, n_D^{20} 1.4774 (semicarbazone, m. p. 220–221°; various salts described). Oxidation of III with sodium hypobromite yields $trans$ -apofenchocamphoric acid, m. p. 147–148° (cf. Nametkin, A., 1924, i, 1084). Ozonisation of fraction C affords small amounts of

III and a ketone, $C_9H_{14}O$ (semicarbazone, m. p. 209°), oxidised by alkaline potassium permanganate to a dicarboxylic acid, $C_9H_{14}O_4$, m. p. 117–118°, together with dl - cis -fenchocamphoric acid, m. p. 173–174°. This acid is obtained also by oxidation of C with potassium permanganate.

During the ozonisation of the hydrocarbon fractions, b. p. below 147°, cyclofenchene, b. p. 142–143°/752 mm., d_4^{165} 0.8624, n_D^{20} 1.45364 (hydrochloride, m. p. 26–28°; hydrobromide, b. p. 92–93°/12 mm., m. p. 4°), remains unchanged. Treatment of this with acetic and sulphuric acids gives the acetate, b. p. 89–90°/10 mm., d_4^{20} 0.9648, n_D^{20} 1.45810, of isofenchyl alcohol, b. p. 84.5–85°/10 mm., d_4^{20} 0.9543, n_D^{20} 1.47664 (phenylcarbimide derivative, m. p. 94–96°), oxidised by potassium permanganate at 60° to dl -isofenchone (Wallach, A., 1908, i, 809), and dl - cis -fenchocamphoric acid. cycloFenchene appears to be identical with β -pinolene (Aschan, A., 1912, i, 198). Physical constants for the five fenchenes are given.

H. BURTON.

Tricyclene series. G. KOMPPA (Ber., 1929, 62, [B], 1366–1370; cf. this vol., 192).—The following additional data are recorded: phenylurethane of tricyclenol, m. p. 86°; tricyclenyl chloride, b. p. 75–76°/6 mm., d_4^{20} 1.0348, n_D^{20} 1.49336; $\beta\omega$ -dichlorocamphane, m. p. 53–55°.

H. WREN.

Synthesis of coumarin derivatives. II. R. WEISS and A. KRATZ (Monatsh., 1929, 51, 386–396).—The synthesis of coumarin derivatives by the interaction of m -dihydroxybenzene derivatives with ethyl ethoxymethyleneacetoacetate (I) in the presence of sodium ethoxide (this vol., 73) is extended, and it is found that ethyl ethoxymethylenemalonate (II) may be used in a similar manner. Thus with resorcinol II yields ethyl 7-hydroxycoumarin-3-carboxylate, m. p. 165–170°, but with 2-nitroresorcinol is obtained 7-hydroxy-8-nitrocoumarin, $+0.5H_2O$, m. p. 228° [not identical with the 7-hydroxynitrocoumarin obtained by direct nitration (Clayton, J.C.S., 1910, 97, 1396)], together with a tetrahydro-(3 : 5 : 3' : 5' or 2 : 4 : 2' : 4')-dinitro-(4 : 4' or 3 : 3')-diphenyl, darkening at 270°. With I, however, 7-hydroxy-3-acetyl-8-nitrocoumarin, m. p. 230–231° (decomp.), is obtained. Similarly with I, 4-chlororesorcinol yields 6-chloro-7-hydroxy-3-acetylcoumarin, m. p. 241–242° (p-toluenesulphonyl derivative, m. p. 160–161°). Condensation of 4-ethylresorcinol with acetic acid in the presence of anhydrous zinc chloride at 140° yields 5-ethylresacetophenone (III), m. p. 115°, which is reduced with amalgamated zinc and hydrochloric acid to 4 : 6-diethylresorcinol (IV), m. p. 65–71°, identical with the product obtained by similar reduction of 2 : 4-dihydroxy-1 : 5-diacetylbenzene (Eijkman and others, A., 1905, i, 359). By condensation with I, IV yields 5-hydroxy-3-acetyl-6 : 8-diethylcoumarin, m. p. 192° (p-toluenesulphonyl derivative, m. p. 99°), which reacts with hydrazine hydrate to yield the azine, m. p. 214°, of the unknown 2 : 6-dihydroxy-3 : 5-diethylbenzaldehyde. Similar condensation of IV with II yields ethyl 5-hydroxy-6 : 8-diethylcoumarin-3-carboxylate, m. p. 156°, together with the corresponding free acid, m. p. 212°. Condensation of III with II yields ethyl 5-hydroxy-6(?8)-acetyl-8(?6)-ethyl-

coumarin-3-carboxylate, m. p. 180—185°, which is hydrolysed with alcoholic potassium hydroxide to the corresponding 5-hydroxy-6(8)-acetyl-8(6)-ethylcoumarin, m. p. 180°. 4:6-Dichlororesorcinol, m. p. 108—109°, is obtained pure by rechlorination with sulphuryl chloride of the product obtained by the method described in the literature, which yields an indefinite mixture of mono- and di-chloro-compounds. It condenses with I to yield 6:8-dichloro-5-hydroxy-3-acetylcoumarin, m. p. 235—236° (decomp.) (p-toluene-sulphonyl derivative, m. p. 150—151°).

J. W. BAKER.

Styrylpyrylium salts. XI. Determination of the reactive group in ketones of the type $\text{CH}_3\text{CO}\cdot\text{CH}_2\text{R}$ by the benzo- β -naphthaspiropyran colour change. I. M. HEILBRON and F. IRVING (J.C.S., 1929, 936—946).—The reaction whereby benzo- β -naphthaspiropyran substituted in the 3-position ionise on being heated in inert solvents giving coloured solutions, a reaction which is not observed with the isomeric 3'-substituted compounds, has been utilised in determining the mode of condensation of salicylaldehyde with ketones, $\text{CH}_3\text{CO}\cdot\text{CH}_2\text{R}$ (cf. Dickinson and Heilbron, A., 1927, 884). The compound I obtained by Dickinson (A., 1926, 1144) by condensing salicylaldehyde with benzyl methyl ketone and a little piperidine condenses with 2-naphthol-1-aldehyde in the presence of absolute alcohol and dry hydrogen chloride to give 3-phenylbenzo- β -naphthaspiropyran, m. p. 208—209°, which is identical with the spiropyran obtained from the condensation product of salicylaldehyde and benzyl methyl ketone in the presence of dry hydrogen chloride, and β -naphthol-1-aldehyde. This spiropyran gives a purple colour when heated in solvents of high b. p. and hence the condensation has taken place on the methylene group. The compound II, m. p. 145°, obtained by Dickinson (*loc. cit.*) from o-methoxybenzaldehyde, benzyl methyl ketone, and hydrogen chloride, and also a new isomeric compound, m. p. 180°, isolated in the same condensation, are bimolecular and are probably stereoisomeric cyclic compounds (cf. Japp and Maitland, J.C.S., 1904, 85, 1473). The structure of Gheorghiu and Arventiev's styryl isobutyl ketone III (A., 1928, 522) has been confirmed by synthesis from ethyl isopropylacetate; the latter condenses with benzaldehyde and 8% aqueous sodium hydroxide to γ -benzylidene- α -isopropylacetate, m. p. 134° (decomp.), decomposed by heating with copper powder to the ketone III, which was isolated as the semicarbazone, m. p. 167°. Methyl isobutyl ketone, salicylaldehyde, and 20% sodium hydroxide yielded 2-hydroxystyryl isobutyl ketone, m. p. 104°, which, with β -naphthol-1-aldehyde, gave 3'-isopropylbenzo- β -naphthaspiropyran, m. p. 118°; the last did not acquire colour when heated in solvents of high b. p. The same spiropyran is obtained by condensation of methyl isobutyl ketone and salicylaldehyde and hydrogen chloride, followed by reaction of the pyrylium salt with β -naphthol-1-aldehyde and hydrolysis. 3'-Octylbenzo- β -naphthaspiropyran, m. p. 101—102°, and 3-octyldi- β -naphthaspiropyran, m. p. 157°, were prepared from 2-hydroxystyryl nonyl ketone and methyl nonyl ketone, respectively.

A. I. VOGEL.

Styrylpyrylium salts. XII. spiroPyrans from 9-methyl and 9-ethylxanthylum salts. F. IRVING (J.C.S., 1929, 1093—1095).—Condensation of 9-methylxanthanol and β -naphthol-1-aldehyde in the presence of hydrogen chloride afforded xantho- β -naphthaspiropyran, m. p. 201°, which gave a red colour on heating in diphenyl ether (cf. preceding abstract). Benzoxanthaspiropyran, m. p. 154°, prepared from 9-methylxanthanol, salicylaldehyde, and hydrogen chloride, and 3'-methylxantho- β -naphthaspiropyran, m. p. 271°, prepared from 9-ethylxanthanol, β -naphthol-1-aldehyde, and dry hydrogen chloride, do not give colours when heated in solvents of high b. p. The three spiropyrans give xanthylum salt colorations with trichloroacetic but not with acetic acid.

A. I. VOGEL.

Hydroxyquinolsulphonephthalein (2:7-dihydroxysulphonefluorescein); 2:4:5-trihydroxybenzoylbenzene-o-sulphonic acid and derivatives. W. R. ORNDORFF and M. L. WILLARD (J. Amer. Chem. Soc., 1929, 51, 1466—1474).—Hydroxyquinol and o-sulphobenzoic anhydride (equal mols.) at 100° yield mainly 2:4:5-trihydroxybenzoylbenzene-o-sulphonic acid, m. p. 210° (optical properties; ammonium, barium, and zinc salts; also the tetrasodium salt and tetra-acetate of the tautomeric lactonic modification). When this is heated at 140°, with or without hydroxyquinol (1 mol.), it yields 2:7-dihydroxysulphonefluorescein (optical properties). This is best prepared from hydroxyquinol triacetate and o-sulphobenzoic anhydride at 140°; it is also formed from hydroxyquinol itself and the acid chloride or anhydride. The free fluorescein and the following intensely coloured derivatives (red or violet in solution): ammonium, barium, zinc, potassium, and aniline, m. p. above 300°, salts; trimethyl ether (sodium salt), and dimethyl ether, are assigned quinonoid formulæ. The colourless tetra-acetate and tetrabenzoate are derived from the corresponding lactone. The fluorescein is brominated in ethyl alcohol to a dibromo-derivative (triammonium salt, tetra-acetate) and condensed by sulphuric acid at 120° to violet "sulphone-violet," $\text{C}_{19}\text{H}_{19}\text{O}_7\text{S}$. Pale yellow 2:7-dihydroxysulphonefluorescein, obtained by reduction with zinc dust and formic acid, is readily oxidised and gives a tetra-acetate (silver salt).

H. E. F. NOTTON.

Brazilin and hæmatoxylin. IX. Compounds of the phenoxyacetone series. P. PFEIFFER and J. WILLEMS (Ber., 1929, 62, [B], 1242—1250).—The action of zinc on a mixture of ethyl phenoxyacetate and ethyl bromoacetate gives ethyl γ -phenoxyacetate in 2—3% yield; the copper compound, m. p. 155.5—156° (decomp.), and p-nitrophenylhydrazine, m. p. 136—137°, are described. Addition of hydrogen cyanide to the ester affords the corresponding hydroxynitrile. Phenoxyacetyl chloride is converted by a suspension of methyl sodiomalonate in benzene into methyl phenoxyacetylmalonate, m. p. 51.5—52.5 (sodium salt; copper compound, m. p. 154.5°). Ethyl bromoacetate, ethyl m-methoxyphenoxyacetate, and zinc yield ethyl γ -m-methoxyphenoxyacetate, b. p. 176°/0.2 mm. (copper salt, m. p. 121°), which, with hydrocyanic acid and aqueous potassium cyanide, affords the corresponding cyanohydrin (non-crystalline

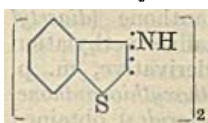
benzoyl derivative). Hydrolysis of the cyanohydrin with boiling, concentrated hydrochloric acid gives γ -*m*-methoxyphenoxycitramalic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (calcium salt). *m*-Methoxyphenoxycetyl chloride, b. p. 145—146.5°/15 mm., from the acid and phosphorus tri- and penta-chlorides, is converted by methyl sodio-malonate in benzene into methyl *m*-methoxyphenoxycetylmalonate, m. p. 55—56°. 2:3-Dimethoxyphenoxycetic acid, m. p. 102.5—103°, prepared from chloroacetic acid and pyrogallol 2:3-dimethyl ether in alkaline solution, is converted into the corresponding chloride, m. p. 162°/12 mm., which is condensed with methyl sodiocyanoacetate to methyl cyano-2:3-dimethoxyphenoxycetylacetate, m. p. 87—88°. A mixture of phenylacetonitrile and ethyl phenoxyacetate is converted by alcoholic sodium ethoxide into γ -phenoxy- α -phenylacetoacetonitrile, m. p. 126—127°, converted by methyl-alcoholic hydrogen chloride into methyl γ -phenoxy- α -phenylacetoacetate, m. p. 75.5—76°; the ester reacts as a homogeneous ketone, but is partly enolised when melted. Boiling, concentrated, aqueous hydrochloric acid transforms the keto-ester into γ -phenoxy- α -phenylacetone, m. p. 43—44°, which does not give a coloration with ferric chloride; the corresponding phenylhydrazone, m. p. about 94—96° after softening at about 65°, and semicarbazone, m. p. 151—152°, are described. The cyanohydrin has m. p. 94—95° after softening at about 83°. H. WREN.

Gossypol. V. Action of chromic acid on gossypol derivatives. VI. Action of boiling hydriodic acid on gossypol and derivatives; semi-micro Zeisel methoxyl method. E. P. CLARK (J. Amer. Chem. Soc., 1929, 51, 1475—1478, 1479—1483; cf. A., 1928, 208, 426, 1016).—Gossypol hexa-acetate in acetic acid is oxidised by aqueous chromic acid to bright yellow gossypolone tetra-acetate, $\text{C}_{25}\text{H}_{18}\text{O}_4(\text{OAc})_4$, darkening from 210°, charring at 230° [*dianil*, m. p. 255—256° (corr.), softening from 250°]. This corresponds with the removal of C_5H_8 from, and formation of two new quinonoid carbonyl groups in, the gossypol nucleus. *apo*Gossypol hexa-acetate is oxidised in acetic acid by Kiliani's chromic acid mixture (A., 1913, i, 381) to *apogossypolone tetra-acetate*, $\text{C}_{22}\text{H}_{16}\text{O}_2(\text{OAc})_4$, m. p. 230°, sintering from 220°, which does not condense with aniline. *apo*Gossypol hexamethyl ether is oxidised by this reagent to yellow *apo*gossypolone tetramethyl ether, $\text{C}_{28}\text{H}_{22}\text{O}_4(\text{OMe})_4$, m. p. 210° (corr.). This change involves the formation of four quinonoid carbonyl groups without loss of carbon from the *apogossypol* skeleton. The optical properties of the new compounds are described.

The high results obtained in the determination of methoxyl in methylated gossypol derivatives by the Weishut-Zeisel method (A., 1913, ii, 78) have been traced to the formation of a volatile iodide by the action of the hydriodic acid on part of the gossypol skeleton. This iodide, which has been shown to differ from methyl iodide (cf. Willstätter and Utzinger, A., 1911, i, 659), is also obtained from gossypol derivatives which contain no alkoxyl groups. Apparatus and methods are described suitable for the determination of methoxyl in 20 mg. samples, using an ordinary balance. H. E. F. NOTTON.

Conjugated unsaturated compounds. IX. Colouring matter from alkekengi (*Physalis alkekengi* and *P. franchetti*). R. KUHN and W. WIEGAND (Helv. Chim. Acta, 1929, 12, 499—506; cf. Kylin, A., 1927, 669).—Extraction of the dry sepals with benzene and subsequent purification gives 0.9—1.8% of *physalien* (I), $\text{C}_{60}\text{H}_{96}\text{O}_4$, m. p. 97° (uncorr. block), orange-red in transmitted light, also isolated from the skins of the berries (0.05% of wt. of fresh fruit). Treatment of I with iodine in ether gives a *di*-iodide, whilst the amount of hydrogen absorbed, during reduction in presence of platinum oxide and acetic acid, corresponds with eleven double linkings. *Perhydrophysalien* is colourless. Oxidation of I with potassium permanganate (cf. this vol., 425) gives 5 mols. of acetic acid showing the presence of five methyl groups. Colour reactions of I with various reagents are given. H. BURTON.

Thionaphthens. K. FRIES and E. HEMMECKE (Annalen, 1929, 470, 1—19).—Nitration of thionaphthen in acetic acid solution at 50—110° affords 2-nitrothionaphthen, m. p. 81°, reduced by stannous chloride and hydrochloric acid to 2-aminothionaphthen (I) (*acetyl* derivative, m. p. 168°). When I or its stannichloride (II) is heated with dilute mineral acid, 2-hydroxythionaphthen results (cf. Friedländer, A., 1907, i, 334), but when II is treated with 40% sodium hydroxide solution, or I is distilled in a vacuum, ammonia is evolved and 2:2'-*di*(thionaphthenyl)amine, m. p. 117°, is obtained. Reduction of 2-nitrothionaphthen with sodium disulphide in boiling alcohol affords the sodium salt (III) of the aci-form of 2:2'-dinitro-1:1':2:2'-tetrahydro-1:1'-*di*(thionaphthenyl) (IV), m. p. 126°. Oxidation of III with bromine water or alkaline potassium ferricyanide yields 2-nitrothionaphthen, whilst reduction with stannous chloride and hydrochloric acid gives 2:2'-diamino-1:1'-*di*(thionaphthenyl), m. p. 238° (decomp.) [*hydrochloride*; *diacetyl* derivative, m. p. 346° (decomp.)]. This is oxidised by alkaline potassium ferricyanide to *di*-iminothioindigo (annexed formula), m. p. 228° (decomp.) (*hydrochloride*; *diacetyl* derivative, m. p. 285°), prepared only by similar oxidation of the corresponding diacetamido-



derivative): reduction of these imino-compounds regenerates the original substances. Reduction of IV with stannous chloride and hydrochloric acid yields a mixture of 2:2'-diamino-1:1':2:2'-tetrahydro-1:1'-*di*(thionaphthenyl), m. p. 156° (*hydrochloride*, decomp. 338°; *acetyl* derivative, m. p. 365°), 2-amino-1:2-dihydro-1:1'-*di*(thionaphthenyl), m. p. 83.5° (*hydrochloride*; *acetyl* derivative, m. p. 231°), and 1:1'-*di*(thionaphthenyl) (V), m. p. 262°. Treatment of these two amines with nitrous acid affords V. Nitration of V with nitric acid (*d* 1.52) in acetic acid solution below 8° gives 2-nitro-1:2-dihydro-1:2'-*di*(thionaphthenyl), m. p. 161° (decomp.), which when reduced with stannous chloride and hydrochloric acid yields the corresponding amino-derivative, m. p. 271° [(decomp.); *acetyl* derivative, m. p. 225°; *hydrochloride*, m. p. 298° (decomp.)], together with 1:2'-*di*(thionaphthenyl), m. p. 76°, also formed from the amine by the action of nitrous acid. The production

of III from 2-nitrothionaphthen is postulated:
 $2\text{-CH}_3\text{C}\cdot\text{N}(\text{O})\text{:O} + 2\text{H} \longrightarrow 2\cdots\text{CH}\cdot\text{C}\cdot\text{N}(\text{O})\cdot\text{OH} \longrightarrow$
 $[\text{CH}\cdot\text{C}\cdot\text{N}(\text{O})\cdot\text{OH}].$

H. BURTON.

Methoxy-derivatives of thioxanthone. K. C. ROBERTS and S. SMILES (J.C.S., 1929, 863—872).—Condensation of 2-thiolbenzoic acid and 4-iodoanisole in the presence of amyl alcohol, potassium carbonate, and copper acetate yielded 2'-carboxy-4-methoxydiphenyl sulphide, I, m. p. 232°. 2'-Carboxy-3:4-dimethoxydiphenyl sulphide, m. p. 212—213°, and 2'-carboxy-5-methoxy-2-methyldiphenylsulphide, m. p. 176—177°, were similarly prepared by condensation of 2-thiolbenzoic acid with 4-aminoveratrole and 2-iodo-4-methoxytoluene, b. p. 252—253° (from 4-methoxy-*o*-toluidine), respectively. The by-product, m. p. 112°, formed in the reduction of 2-nitro-4-methoxytoluene with tin and hydrochloric acid is chloro-4-methoxy-*o*-toluidine, and not 4-methoxy-*o*-toluidine (Limpach, A., 1889, ii, 698). Sulphuric acid and I afforded 2-methoxythioxanthone (perchlorate), m. p. 129°. Treatment of a mixture of 2-thiolbenzoic acid and 4-chloroanisole with sulphuric acid gave 1-chloro-4-methoxythioxanthone, m. p. 196°, since further treatment with *p*-toluidine in the presence of potassium and copper acetates readily furnished 1-*p*-toluidino-4-methoxythioxanthone, m. p. 133°. 4-Methoxy-1-methylthioxanthone, m. p. 162°, was similarly prepared from 4-methoxytoluene. 1-Methoxy-4-methylthioxanthone, m. p. 128° (hydrochloride; perchlorate), was prepared by dehydration of 2'-carboxy-3-methoxy-6-methyldiphenyl sulphide with sulphuric acid. 1:4-Dimethoxythioxanthone (Clarke and Smiles, J.C.S., 1911, 99, 1539) yields a dihydrochloride, a chloroplatinate, a ferrichloride, and a perchlorate. Condensation of 2-bromoveratric acid and thiophenol in the presence of amyl alcohol, potassium carbonate, and copper acetate gave 6-carboxy-2:3-dimethoxydiphenyl sulphide, which furnished 3:4-dimethoxythioxanthone, m. p. 185° (perchlorate), with sulphuric acid. Reaction of pyrocatechol with 2-thiolbenzoic acid in sulphuric acid yielded a dihydrothioxanthone (diacetyl derivative, m. p. 191°), aqueous alkaline methylation of which yielded the dimethoxy-derivative, m. p. 172°, identical with 2:3-dimethoxythioxanthone, m. p. 172° (hydrochloride; two ferrichlorides), obtained by dehydrating 2'-carboxy-3:4-dimethoxydiphenyl sulphide with sulphuric acid or by condensing veratrole with 2-thiolbenzoic acid in sulphuric acid. Its structure was confirmed by treatment with boracetic anhydride and acetic anhydride, when the diacetyl derivative, m. p. 191°, and not a co-ordinated diacetate was obtained (cf. Dimroth, A., 1922, i, 155; 1926, 297). 1:2-Dimethoxythioxanthone, a by-product in the preparation of the 2:3-derivative, has m. p. 143—144° (hydrochloride; perchlorate). Interaction of 1:2:3-trimethoxybenzene and 2-thiolbenzoic acid in sulphuric acid afforded 2:3:4-trimethoxythioxanthone, m. p. 150°, identical with the product obtained from 1-iodo-2:3:4-trimethoxybenzene and 2-thiolbenzoic acid (cf. Ullmann and Sone, A., 1911, i, 739, who give m. p. 153—154°). The relative stabilities of the hydrochlorides derived from the thioxanthenes were investigated by a modification of Baeyer and Villiger's method (A., 1902, i,

769) and were shown to be in qualitative agreement with the tendency to salt-formation with dry hydrogen chloride at atmospheric pressure and temperature.

A. I. VOGEL.

Arylamides of lævulic acid. R. LUKES and V. PRELOG (Coll. Czech. Chem. Comm., 1929, 1, 282—287).—It has been concluded that the "lævulamide" formed by the interaction of ammonia with 2-methyl-5-keto-4:5-dihydrofuran ($\Delta^{\beta\gamma}$ -angelicalactone) (Wolff, A., 1885, 1123) cannot have a pyrrolidone structure (Beilstein, 4th ed., Vol. III, 676), since the product from methylamine and $\Delta^{\beta\gamma}$ -angelicalactone is not identical with the pyrrolidone obtained from magnesium methyl bromide and *N*-methylsuccinimide (A., 1928, 299; this vol., 576). This conclusion is supported by the non-identity of "lævulanilide," m. p. 102° (I), prepared from $\Delta^{\beta\gamma}$ -angelicalactone and aniline, or from γ -acetoxy- γ -valerolactone, aniline, and water, with 2-hydroxy-1-phenyl-2-methylpyrrolid-5-one, m. p. 101° (II), which is obtained (accompanied by 1-phenyl-2:5-dimethylpyrrole) by the interaction of magnesium methyl bromide with *N*-phenylsuccinimide. Aniline reacts with I in boiling toluene to yield lævulanilide anil, m. p. 145° (decomp.), which is readily hydrolysed to lævulanilide and aniline by water. Aniline does not condense with II. Hydrolysis of II by boiling, dilute sulphuric acid yields aniline and lævulic acid. The following "arylamides of lævulic acid" have also been prepared from $\Delta^{\beta\gamma}$ -angelicalactone or γ -acetoxy- γ -valerolactone: *p*-toluidide, m. p. 108—109°, α -naphthylamide, m. p. 105—106°, β -naphthylamide, m. p. 107—108°.

R. K. CALLOW.

Acridone derivatives. W. LÉSNIAŃSKI (Bull. Acad. Polonaise, 1929, A, 81—88).—Condensation of 2-chloro-5-nitrobenzoic acid with *p*-anisidine in glycerol in the presence of anhydrous potassium carbonate and copper-bronze gave 4-nitro-4'-methoxydiphenylamine-2-carboxylic acid, m. p. 230.5° (potassium salt), which was converted into 3-nitro-7-methoxyacridone, m. p. 395°, when heated with phosphorus oxychloride at 115° (sulphuric acid is unsatisfactory). The following compounds were similarly prepared: 4-nitro-4'-ethoxydiphenylamine-2-carboxylic acid (from chloronitrobenzoic acid and *p*-phenetidine; ammonium salt), m. p. 213—214°, and 3-nitro-7-ethoxyacridone, m. p. 378° [the corresponding hydroxy-compound (sublimes above 360°) was produced with sulphuric acid at 140°]; *N*-4-nitrophenyl- α -naphthylamine-2-carboxylic acid, m. p. 266° (from α -naphthylamine and chloronitrobenzoic acid) and 9-nitro- α -phen-naphthylacridone, m. p. 382°; *N*-4-nitrophenyl- β -naphthylamine-2-carboxylic acid, m. p. 284—285°, and 10-nitro- β -phen-naphthylacridone, m. p. 440°. A. I. VOGEL.

Constitution of Guareschi's cyano-butadiene acids. Attempt to synthesise β -isopropylglutaconic acid. C. S. GIBSON and J. L. SIMONSEN (J.C.S., 1929, 1074—1080).—Various cyano-acids described by Guareschi are in reality dihydroxypyridines. The condensation of isobutaldehyde and ethyl cyanoacetate gave the ammonium salt of 2:6-dihydroxy-3:5-dicyano-4-isopropylpyridine, hydrolysis of which by 60% sulphuric acid gave 2:6-dihydroxy-4-isopropylpyridine, m. p. 213—214° (hydro-

chloride; di-*p*-nitrobenzoyl derivative, m. p. 200—201°; oxime, m. p. 123—124°), accompanied by a little 2 : 6-dihydroxy-3-cyano-4-isopropylpyridine, m. p. 273° (monohydrate, lost H_2O at 110°). Similarly, the condensation of acetaldehyde and ethyl cyanoacetate led to the ammonium salt of 2 : 6-dihydroxy-3-*o*-dicyano-4-methylpyridine and, by hydrolysis of this, to 2 : 6-dihydroxy-4-methylpyridine (Rogerson and Thorpe, J.C.S., 1905, 87, 1685).

An attempt to remove hydrogen bromide from ethyl α -bromo- β -isopropylglutarate, b. p. 178°/30 mm., by boiling with diethylaniline led mainly to the ethyl ester of the lactone of *dl*- α -hydroxy- β -isopropylglutaric acid, b. p. 178°/26 mm., n_D^{20} 1.4466, from which *dl*-isopropylsuccinic acid was obtained by oxidation; small quantities of ethyl isopropylglutarate were also obtained.

R. J. W. LE FEVRE.

Nitration of *N*-2-pyridyl-*N'*-ethylcarbamide.

R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 545—547).—By heating 2-aminopyridine and ethyl carbimide in ether at 100°, 2-pyridyl-*N'*-ethylcarbamide, m. p. 119°, is obtained. Nitration of this with either absolute nitric acid or mixed acids probably yields *N*-nitro-*N'*-2-pyridyl-*N*-ethylcarbamide, but on pouring the nitration mixture into water it decomposes, yielding 2-aminopyridine, ethylnitroamine, and carbon dioxide.

J. W. BAKER.

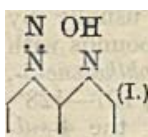
Indole halogeno-ketones. I. G. SANNA (Gazzetta, 1929, 59, 169—181).—The action of chloroacetyl chloride on 2-methylindolyl magnesium bromide in anhydrous ether furnishes 3- ω -chloroacetyl-2-methylindole, m. p. 220°, which gives a silver derivative, and a phenylhydrazone, m. p. 134°. With pyridine the chloride gives 2-methyl-3-indolacetylpyridinium chloride, m. p. 332° (hydroxide prepared), and with quinoline, a quinoline derivative. Similarly, bromoacetyl chloride yields 3- ω -bromoacetyl-2-methylindole, m. p. 204° (silver, pyridine, and quinoline derivatives). Either the chloride or the bromide may be oxidised by alkaline potassium permanganate to *o*-acetamidobenzoic acid, with a substance, m. p. 156°, and may be converted by fusion with potassium hydroxide to 2-methylindole-3-carboxylic acid. 3- ω -Iodoacetyl-2-methylindole has also been prepared.

E. W. WIGNALL.

Derivatives of 8-aminoquinoline. R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 517—544; cf. this vol., 452).—8-Aminoquinoline and ethylcarbimide heated in ethereal solution at 100° yield *N*-8-quinolyl-*N'*-ethylcarbamide (I), m. p. 176° (181° on remelting), which is nitrated by absolute nitric acid at -15° to *N*-nitro-*N'*-5-nitro-8-quinolyl-*N*-ethylcarbamide (II), 145°. This, when freshly prepared, is converted by

boiling with water into 5-nitro-8-aminoquinoline, m. p. 197° [the substance obtained by Claus and Hartmann (A., 1896, i, 391), not being this compound] (converted by elimination of the amino-group into 5-nitroquinoline), and *o*-nitroquinoline-8-carbamic acid, m. p. about 300°. Esterification of the latter with methyl or ethyl alcohol yields, respectively, methyl, m. p. 210°, and ethyl, m. p. 115° (121° on remelting) 5-nitroquinoline-8-carbamate. The same esters are obtained by the action of the appropriate alcohol on II or V (below), and by nitration with absolute nitric acid below 0° of, respectively, methyl, m. p. 46°, and ethyl, m. p. 66°, quinoline-

8-carbamate (III), which, in turn, are obtained by the action of the alkyl chloroformate on 8-aminoquinoline in the presence of powdered potassium carbonate. By the action of *N*-alcoholic ammonia on II at 100° is obtained *N*-5-nitro-8-quinolyl carbamide, m. p. 245° (decomp.). When I is nitrated with mixed acids below 0° and the product poured on to ice it is decomposed with the formation of 5 : 7-dinitroquinoline-8-carbamic acid, m. p. 230° (decomp.) (the presence of ethylnitroamine is proved by the isolation of its barium salt from the aqueous liquors). This is converted by 50% sulphuric acid at 100° into 5 : 7-dinitro-8-aminoquinoline (Claus and Dewitz, A., 1896, i, 654) and by boiling with methyl and ethyl alcohol into, respectively, methyl, m. p. 205°, and ethyl, m. p. 195°, 5 : 7-dinitroquinoline-8-carbamate. When the methyl and ethyl esters III are nitrated with mixed acids they also yield methyl and ethyl 5 : 7-dinitroquinoline-8-carbamates, but the specimens prepared in this manner have m. p. 190° and 166—167°, respectively. Evidence is given to prove that in these pairs of esters the orientation of the nitro- and carbamate groups is identical, and it is suggested that the isomerism may be due to the existence of a quinonoid form, the nitro-group existing in its *aci* form, and in agreement with this view it is possible to convert the higher into the lower m. p. forms by heating with the alcoholic hydrogen chloride at 100°. When 8-aminoquinoline reacts with potassium cyanate and dilute hydrochloric acid it yields 8-quinolylcarbamide (IV), m. p. 223—224°, together with 8-quinolylbiuret, m. p. 250—252°, the amount of the latter formed being negligible if acetic acid at low temperatures is used. Nitration of IV with absolute nitric acid under special conditions yields *N*-nitro-*N'*-5-nitro-8-quinolylcarbamide (V), decomp. 190°. When 8-aminoquinoline and its nitro-derivatives are diazotised in concentrated sulphuric acid and the solution of the diazonium sulphate is poured into water or cold, dilute potassium hydrogen carbonate solution, the diazohydroxide is immediately converted into a stable product which, the author suggests, is the *anti*-diazohydroxide (I).



Thus from the appropriate 8-aminoquinoline are obtained: quinoline-, decomp. 145°, 5-nitroquinoline-, decomp. 185°, and 5 : 7-dinitroquinoline-, decomp. (with spontaneous ignition) 155°, -8-*anti*-diazohydroxides. These compounds do not give the characteristic reactions of diazonium or *syn*-diazo-compounds, but the 5-nitro-compound is converted by 60% sulphuric acid into the reactive *syn*-form, which then couples with β -naphthol, whilst in 48% hydrobromic acid solution it yields 8-bromo-5-nitroquinoline by the Sandmeyer reaction.

J. W. BAKER.

Quinolyl-2 : 4-dinitronaphthylamines. R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 548—549).—8-Aminoquinoline condenses with 1-chloro-2 : 4-dinitronaphthalene in alcohol at 100° to yield *N*-8-quinolyl-2 : 4-dinitro- α -naphthylamine, m. p. 196°. The corresponding *N*-5-quinolyl-2 : 4-dinitro- α -naphthylamine, m. p. 195°, can be obtained only by fusing together the two reactants at 100—150°.

J. W. BAKER.

Halogenodinitroquinolines. R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 550—559).—In agreement

with the literature, nitration of 5- and 8-bromoquinoline (obtained by the Sandmeyer reaction from the corresponding aminoquinoline) yield, respectively, a mixture of 5-bromo-6- and -8-nitroquinolines and 8-bromo-5-nitroquinoline. Attempts to introduce a second nitro-group were unsuccessful. Thus 5-bromo-6-nitroquinoline, when warmed with mixed acids yields (probably) 3:5-dibromo-6-nitroquinoline, m. p. 186°, and 5-bromo-8-nitroquinoline similarly yields 3:5-dibromo-8-nitroquinoline, m. p. 195°, oxidation of a portion of the original material yielding quinolinic acid (isolated as its copper salt) and bromine, the latter attacking more of the original material to yield the dibromo-compound. The product obtained by nitration of 8-bromoquinoline (Claus and Howitz, A., 1893, i, 668), in agreement with these authors, is proved to be the 5-nitro-derivative, since the same product is obtained by the Sandmeyer reaction from 5-nitro-8-aminoquinoline (this vol., 825). 5:7-Dinitro-8-hydroxyquinoline, decomp. 325° (obtained pure by nitration of 8-hydroxyquinoline under prescribed conditions), is converted, in small yield, by the method of Ullmann and Nadai (A., 1908, i, 525), into 8-chloro-5:7-dinitroquinoline, m. p. 154°. J. W. BAKER.

Quinaldinic acid. T. W. J. TAYLOR (J.C.S., 1929, 1110—1111).—When copper quinaldinate (Reissert, A., 1905, i, 472) is boiled with sufficient 2*N*-sodium hydroxide to convert all copper present into copper oxide, and filtered, 85% of the product separates as sodium quinaldinate (hydrate with 1.5H₂O) on cooling. The salt can be recrystallised from dilute sodium hydroxide, or from 95% alcohol, and yields the acid by acidification. The hydrate is converted into the anhydrous salt at 140—150°, or in a vacuum over calcium chloride. C. W. SHOPPEE.

Synthetic drugs [quinoline and pyrazolone derivatives]. H. P. KAUFMANN.—See B., 1929, 452.

Arylamides of aromatic carboxylic and sulphonic acids. K. HELLER (J. pr. Chem., 1929, [ii], 121, 193—203).—[With H. STURM.]—The following amino-derivatives have been prepared, usually by reduction of the corresponding nitro-compounds with iron and dilute acetic acid: 1-aminonaphthalene-5-, -6-, -7-, and -8-sulphonanilides, m. p. 171°, 127—128°, 146—147°, and 139—140°, respectively; the 4-sulphonanilide, m. p. 190°, is obtained by hydrolysis of the corresponding acetyl derivative (Schroter, A., 1906, i, 415) with 0.5*N*-alcoholic potassium hydroxide solution; 2-amino-*p*-toluenesulphon-*p*-toluidide, m. p. 128°, -*o*-toluidide, m. p. 148°, and -*o*-anisidide, m. p. 128°. 2-Nitro-*p*-toluenesulphon-*o*-anisidine has m. p. 135°. When 2-acetoxynaphthalene-6-sulphonyl chloride, m. p. 107°, is treated with aniline, and the acetyl group eliminated by Zincke's method (A., 1918, i, 220), β -naphthol-6-sulphonanilide, m. p. 104°, results. α -Naphthol-5-sulphonanilide, m. p. 200°, is prepared similarly from 1-acetoxynaphthalene-5-sulphonyl chloride, m. p. 129°. *o*-Chlorobenz-*p*-nitroanilide and *p*-nitrobenz-*o*-chloroanilide, m. p. 160°, are obtained by a slightly modified Schopff's reaction (A., 1892, 1476). The former compound is reduced by iron and dilute acetic acid to the *p*-aminoanilide, m. p. 153°, and the latter by sodium hyposulphite to the amino-

derivative, m. p. 145°. 2-Amino-3-naphthanilide, m. p. 192° (β -naphthylamide, m. p. 110°), is also described. Diazotisation of the anilides containing a free amino-group and subsequent reduction with alkaline sodium pyrosulphite or sodium hydrogen sulphite affords the corresponding phenylhydrazine, isolated as the hydrochloride. Condensation of this with ethyl acetoacetate or benzoylacetate in presence of sodium acetate and acetic acid yields 1-substituted phenyl-3-methyl(or phenyl)-5-pyrazolones. Thus, 3-methylphenylhydrazine-6-sulphon-*o*-toluidide hydrochloride, m. p. 199°, gives 1-*m*-tolyl-3-methyl-5-pyrazolone-6'-sulphon-*o*-toluidide, m. p. 116° (the corresponding -*p*-toluidide derivatives have m. p. 168° and 129°, respectively); 3-*p*-toluenesulphonamidophenylhydrazine hydrochloride, m. p. 179—180°, furnishes 1-3'-*p*-toluenesulphonamidophenyl-3-methyl-5-pyrazolone, m. p. 147° (3-phenyl derivative, m. p. 168°); 3-methylphenylhydrazine-6-sulphon-*o*-anisidide hydrochloride, m. p. 196°, affords 1-*m*-tolyl-3-methyl-5-pyrazolone-6'-sulphon-*o*-anisidide, m. p. 118°; phenylhydrazine-4-carboxyanilide hydrochloride, m. p. 235°, yields 1-phenyl-3-methylpyrazolone-4'-carboxyanilide, m. p. 271°; *p*-benzamidophenylhydrazine hydrochloride, m. p. 273°, gives the corresponding 3-methyl-, m. p. 233°, and 3-phenyl-pyrazolones, m. p. 268°; phenylhydrazine-4-carboxy-*o*-chloroanilide hydrochloride, m. p. about 180°, furnishes 1-phenyl-3-methylpyrazolone-4'-carboxy-*o*-anilide, m. p. 231° (3-phenyl derivative, m. p. 238°); β -naphthylhydrazine-3-carboxyanilide hydrochloride, m. p. 110°, affords 1- β -naphthyl-3-methylpyrazolone-3'-carboxyanilide, m. p. 179° (3-phenyl derivative, m. p. 186°) (the corresponding β -naphthylamide derivatives have m. p. 145°, 129°, and 155°, respectively); *p*-(2-hydroxy-3-naphthamido)-phenylhydrazine hydrochloride, decomp. 295°, yields the corresponding methyl-, m. p. 310° (decomp.), and phenyl-pyrazolones, m. p. 195° (decomp.). *m*-(2-Hydroxy-3-naphthamido)phenylhydrazine hydrochloride, m. p. 175°, gives the corresponding methyl- and phenyl-pyrazolones, m. p. 203—205° and 194°, respectively. Many of the pyrazolone derivatives couple with diazo-compounds to give alkali-insoluble dyes.

H. BURTON.

Glyoxaline fission products. I. Benzoyl derivative of diaminoethylene and its conversion into a glyoxalone. P. RUGGLI, R. RATTI, and E. HENZI (Helv. Chim. Acta, 1929, 12, 332—361).—Contrary to the statement of Oddo and Mingoa (A., 1927, 260), Bamberger and Berlé's observation (A., 1893, i, 437) that Schotten-Baumann benzoylation of glyoxaline gives dibenzamidoethylene is confirmed. The α -form (I), m. p. 202—203°, of this is converted into the β -form (II), m. p. 280—290° (decomp.), by boiling with alcohol (cf. Bamberger and Berle, *loc. cit.*). Reduction of I with hydrogen in presence of palladium or a nickel catalyst and aqueous alcohol yields dibenzamidoethane, whilst treatment of I or II with bromine, directly or in chloroform or tetrachloroethane solution, affords a dibromide (III), decomp. 177° after sintering at 148°. This is converted by treatment with alcohol into two forms of *s*-dibenzamidodiethoxyethane, m. p. 190—191° (decomp.) and 219° (decomp.), respectively. With isobutyl alcohol a corresponding diisobutoxy-derivative, m. p. 214—215° with darken-

ing, and a small amount of a substance of lower m. p., result. Treatment of III with ethylene glycol gives 2 : 3-dibenzamido-1 : 4-dioxan, m. p. 247—248° (decomp.), whilst decomposition with aqueous acetone affords *s*-dibenzamidoethylene glycol, m. p. 169—170° (decomp.; diacetate, m. p. 153—154°; bisphenyl-carbimide derivative, m. p. 193—194°). This is decomposed by methyl-alcoholic potassium hydroxide. *s*-Dibenzamidodianilinoethane has m. p. 211—212°. When III is treated with cold pyridine an additive compound, $+3C_5H_5N$, m. p. 143—145° becoming yellow at 140°, is produced; with hot pyridine, 1-benzoyl-2-phenyl-4-glyoxalone (IV), m. p. 184° (picrate, m. p. 182—183°), results by loss of 2 mols. of hydrogen bromide. This is soluble in alkali hydroxide or carbonate, affords the double salt, $2C_{16}H_{12}O_2N_2 \cdot AgNO_3$, decomp. 171° after sintering at 167° and darkening at 140°, and yields a methiodide, m. p. 194° (decomp.). Hydrolysis of IV with cold concentrated sulphuric acid gives hippurbenzamide, m. p. 185° (lit. 179°), hippuric and benzoic acids. Bromination in chloroform solution furnishes 5-bromo-1-benzoyl-2-phenyl-4-glyoxalone, m. p. 163—164° (decomp.), and treatment of the sodium salt of IV with benzyl bromide in presence of benzene yields 1-benzoyl-2-phenyl-5-benzyl-4-glyoxalone (V), m. p. 176—177° [picrate, m. p. 128—135°; hydrochloride (VI), m. p. 180—181°; dibenzyl derivative, m. p. 111—112°]. Hydrolysis of V with 15% hydrochloric acid gives *N*-benzoylphenylalanine, m. p. 182—183°, and phenylalanine. 1-Benzoyl-2-phenyl-5-*p*-bromobenzyl-4-glyoxalone, m. p. 212—213°, is hydrolysed to *p*-bromophenylalanine, decomp. 245° after sintering at 225°. When IV is coupled with diazosulphanilic acid in presence of pyridine and sodium hydroxide an orange-red compound, $C_{22}H_{15}O_5N_5Na \cdot 4H_2O$ (free acid $+3H_2O$, m. p. 130° resolidifying with decomp. at 195°), results. Benzyl hippurate, m. p. 91—92° (lit. 85—86°), and benzyl aminoacetate hydrochloride are described. When VI is heated at 190—195° for a short time, acid vapours are evolved and a substance, m. p. 257—258°, isomeric with V, is produced. Formation of IV from III occurs presumably by loss of water from the hydroxyl and substituted amino-groups of the enol form, elimination of 1 mol. of hydrogen bromide, replacement of bromine by hydroxyl, and subsequent ketonisation.

H. BURTON.

Glyoxaline fission products. II. Production of a glyoxaline solution and glyoxaline fission product. P. RUGGLI and E. HENZI (Helv. Chim. Acta, 1929, 12, 362—364).—Glyoxal sulphate, prepared from tetrachloroethane and fuming sulphuric acid (A., 1923, i, 896), is treated with formaldehyde ammonia in aqueous solution below 55°. Schotten-Baumann benzoylation of this solution gives α -dibenzamidoethylene, m. p. 202°, showing initial formation of glyoxaline and subsequent fission.

H. BURTON.

New methylcytosine. F. H. CASE and A. J. (J. Amer. Chem. Soc., 1929, 51, 1590—1592).—Chloro-2-ethylthiolpyrimidine (Wheeler and Johnson, 1903, i, 526) and methylamine in absolute alcohol give at 50—60° the hydrochloride, m. p. 216°, *o*-methylamino-2-ethylthiolpyrimidine (I), m. p.

58°, and at 150° the hydrochloride, m. p. 262°, of 2 : 6-dimethyldiaminopyrimidine, m. p. 132°. The amine, I, is hydrolysed by concentrated hydrochloric acid to the hydrochloride, decomp. 320°, of 6-methylamino-2-hydroxypyrimidine, m. p. 270° (picrate, m. p. 220—225°), which gives a purple coloration with bromine water and barium hydroxide (cf. A., 1907, ii, 826).

H. E. F. NOTTON.

New aryliminoketo- γ -[1 : 3 : 5]-triazidine derivatives. A. OSTROGOVICH and V. BENA MEDIAN (Gazzetta, 1929, 59, 181—198, 198—200).—The condensation of benzaldehyde with guanylcabamide (A., 1909, i, 461) is repeated with substituted benzaldehydes, and the corresponding 4-imino-2-keto-6-aryl-1 : 3 : 5-triazidines (hexahydrotriazines) are obtained. Thus *o*-nitrobenzaldehyde and guanylcabamide sulphate yield the sulphate, m. p. 249—250° (decomp.), of the 6-*o*-nitrophenyl compound, m. p. 208—209°, which darkens in daylight, and gives the salts: hydrochloride, $[+H_2O]$, m. p. 235—236° (decomp.); abnormal chloroplatinate, $PtCl_4(C_6H_4O_3N_5 \cdot HCl)_4$ or $[PtCl_4](H \cdot C_6H_4O_3N_5)_4$, m. p. 233—234°; nitrate, m. p. 216—218° (decomp.); picrate, m. p. 213—215°; dipicrate; complex silver salt, $[Ag(C_6H_4O_3N_5)_2]NO_3$, m. p. 200° (decomp.) (obtained by treating the base with silver nitrate); and silver salt, $C_6H_4O_3N_5Ag$ (?) (obtained in the presence of ammonia). *m*-Nitrobenzaldehyde yields the sulphate, m. p. 257—258° (decomp.), of the 6-*m*-nitrophenyl compound, m. p. 222°, which is less sensitive to light, and gives: hydrochloride, m. p. 268°; normal chloroplatinate, m. p. 255—256° (decomp.); nitrate, m. p. 250° (decomp.); picrate, $[+H_2O]$, m. p. 210—211°; dipicrate; and silver salts, $[Ag(C_6H_4O_3N_5)_2]NO_3$ and $C_6H_4O_3N_5Ag$; and *p*-nitrobenzaldehyde the sulphate, m. p. 253—254° (decomp.), of the 6-*p*-nitrophenyl compound, m. p. 180° (decomp.), which gives: hydrochloride, m. p. 250° (decomp.); normal chloroplatinate, m. p. 230—231° (decomp.); picrate, m. p. 212—213°; dipicrate (?); and silver salts as above.

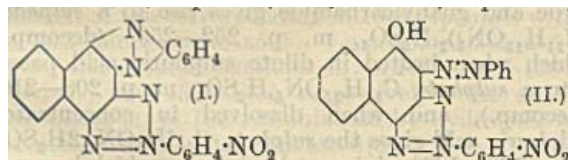
The reaction between *p*-dimethylaminobenzaldehyde and guanylcabamide gives rise to a sulphate, $(C_{11}H_{15}ON_5)_2 \cdot H_2SO_4$, m. p. 252—253° (decomp.), which when heated in dilute sulphuric acid passes into a sulphate, $C_{11}H_{15}ON_5 \cdot H_2SO_4$, m. p. 208—210° (decomp.), and when dissolved in concentrated sulphuric acid gives the sulphate, $C_{11}H_{15}ON_5 \cdot 2H_2SO_4$, m. p. 120—122°, giving a cloudy mass which becomes green at 180—190°, and then completely melts. The base, 4-imino-2-keto-6-*p*-dimethylaminophenyl-1 : 3 : 5-triazidine, $[+H_2O]$, m. p. 220—221° (decomp.), gives: hydrochloride, m. p. 212—214°; dihydrochloride, m. p. $[+H_2O]$ 222—223° (decomp.), $[+2H_2O]$ 200°; nitrate, m. p. 215° (decomp.); acetate, m. p. 202—203° (decomp.); formate, m. p. 213° (decomp.). According to conditions of preparation, a semipicrate, m. p. 205—206°, a monopicate, m. p. 220°, and a tripicrate, m. p. 190°, are formed; hydrolysis of the picromonohydrochloride, m. p. 190° (decomp.), obtained from the monopicate, gives also a dipicrate, m. p. 190° (decomp.). A picrodihydrochloride, m. p. about 176°, is formed from the picrotrihydrochloride, m. p. 153—155° (decomp.), obtained from the monopicate,

which also yields, in gaseous hydrogen chloride, a colourless *picrotetrahydrochloride*.

E. W. WIGNALL.

Three isomeric 1-tolyl-3:5-dimethyl-1:2:4-triazoles and their salts. F. HERNLER (Monatsh., 1929, 51, 267—276).—By condensation of the appropriate tolylhydrazine hydrochloride and diacetamide in the presence of crystalline sodium acetate, the three isomeric 1-tolyl-3:5-dimethyl-1:2:4-triazoles have been prepared, and characterised by the preparation of several of their salts. 1-o-Tolyl-3:5-dimethyl-1:2:4-triazole, m. p. 25°, b. p. 141—145°/11 mm. (*hydrochloride*, subliming, m. p. 214—216°, in a sealed tube; *picrate*, m. p. 192—193°; *chloroplatinate*, m. p. 158—162°; *mercurichloride*, m. p. 136—137°), is obtained in 40% yield. Similarly, from *m*-tolylhydrazine in acetic acid is obtained a 57% yield of 1-m-tolyl-3:5-dimethyl-1:2:4-triazole, b. p. 147—149°/11 mm. (*hydrochloride*, m. p. 206—207° in a sealed tube; *picrate*, m. p. 138—139.5°; *chloroplatinate*, +2H₂O and anhydrous, m. p. 220—223°; *mercurichloride*, m. p. 181°; *hydrochloride* of *mercurichloride*, m. p. 215—220°, with previous sintering at 180°). 1-p-Tolyl-3:5-dimethyl-1:2:4-triazole, m. p. 47—49°, b. p. 151—153°/11 mm. [*hydrochloride*, m. p. 233—235°; *picrate*, m. p. 128—129°; *chloroplatinate*, m. p. 223—225° (decomp.); *mercurichloride*, m. p. 150—152°; double salt, (C₁₁H₁₃N₃)₄.3HgCl₂, m. p. 144—147°], is obtained in 45% yield. J. W. BAKER.

2-Nitrophenyl- $\alpha\beta$ -naphtha-1:2:3-triazole-quinones. M. GALLOTTI [with A. ERCOLI] (Gazzetta, 1929, 59, 207—211).—Oxidation of 2-o-, 2-m-, and 2-p-nitrophenyl- $\alpha\beta$ -naphtha-1:2:3-triazoles (Meldola and Hughes, J.C.S., 1891, 59, 373: the 2-m-compound has new m. p. 226.5°) by chromic acid in acetic acid yields the corresponding *triazolequinones*, m. p. 267°, 237—238°, and 297°, respectively (cf. Charrier and others, A., 1926, 848), which react with *o*-phenylenediamine to give the *phenazines*, I, m. p. 277—278°, 328°, and 312°, respectively, with phenylhydrazine hydrochloride to give the *hydroxyazo-derivatives*, II, m. p. 229°, 255°, and 240°, respectively,



and with alkaline potassium permanganate solution, or with chromic acid in acetic acid, to give 2-o-, 2-m-, and 2-p-nitrophenyl-4-o-carboxyphenyl-1:2:3-triazole-5-carboxylic acids, m. p. 260°, 274°, and 267°, respectively, which are also obtained by oxidation of the corresponding *m*-nitrobenzeneazo- β -naphthylamines.

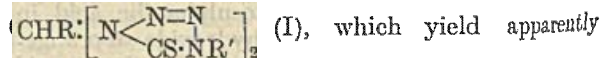
E. W. WIGNALL.

5-Aminotetrazole. R. STOLLE [with E. SCHICK, F. HENKE-STARK, and L. KRAUSS] (Ber., 1929, 62, 1119—1126).—5-Aminotetrazole monohydrate, m. p. 199°, is conveniently prepared by the action of azoimide on dicyanodiamide; the nitrate, decomp. 174° after softening, and *hydrobromide*, m. p. 118° after softening at 110°, decomp. about 150°, are described. Anhydrous 5-aminotetrazole is converted

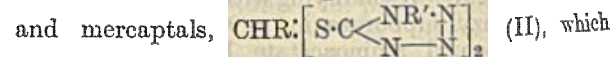
by phenylcarbimide at 100° into *N*-phenyl-*N'*-5-tetrazolylcarbamide, m. p. 245° (decomp.), and by ethyl chloroformate into 5-tetrazolylurethane, m. p. 256° (decomp.). Acetyl chloride transforms 5-amino-tetrazole into 5-acetamidotetrazole, m. p. 269° (decomp.), whereas boiling acetic anhydride affords 5-acetamido-2-methyl-1:3:4-furodiazole, m. p. 180°. Appropriate treatment of a diazotised solution of 5-aminotetrazole yields the following compounds: 5-hydroxytetrazole, m. p. 254°; tetrazole; 5-chlorotetrazole, m. p. 73° after softening, decomp. 120°, and the copper compound C₂N₈Cl₂Cu; 5-bromotetrazole, m. p. 156° (decomp.), and the corresponding copper salt; 5-iodotetrazole, decomp. about 190°, reduced by sulphurous acid or sodium sulphite to tetrazole and converted by 60% sodium hydroxide into 5-hydroxytetrazole. *N*¹-5-Tetrazolyl-*N*³-p-nitrophenyltriazine, decomp. about 169°, is derived from diazotised 5-aminotetrazole and *p*-nitroaniline or *p*-nitrophenyldiazonium chloride and 5-aminotetrazole. *N*¹-5-Tetrazolyl-*N*³-phenyltriazine, decomp. 97°, is described. Treatment of dicyanodiamide with azoimide in presence of nitric acid yields 5-guanylaminotetrazole nitrate, decomp. about 183° after softening. 5-Guanylaminotetrazole, not molten below 300°, is converted by water at 200° into 5-aminotetrazole.

H. WREN.

Action of diazo-compounds on tetrazolyl disulphides. R. STOLLE, F. HENKE-STARK, and H. PERREY (Ber., 1929, 62, [B], 1112—1118).—The action of diazomethane, diazoethane, and ethyl diazoacetate on 1-substituted di-5-tetrazolyl disulphides affords the methylene compounds,



non-uniform additive compounds with silver nitrate,



do not give precipitates with alcoholic silver nitrate. The mercaptals are also prepared from the requisite dihalogeno-derivatives and the sodium salts of the 5-thiolotetrazoles. The following compounds are described: *methylenedi-1-phenyl-4:5-dihydro-5-tetrazolyl disulphide* (I, R=H, R'=Ph), m. p. 124°, decomp. about 160°; *methylene di-1-phenyl-5-tetrazolyl disulphide* (II, R=H, R'=Ph), m. p. 136°, decomp. about 175°; *ethylene di-1-phenyl-5-tetrazolyl disulphide*, m. p. 150°; *methylenedi-1-p-tolyl-4:5-dihydro-5-tetrazolyl disulphide*, m. p. 108°, decomp. about 160°; *methylene di-1-p-tolyl-5-tetrazolyl disulphide*, m. p. 136°, decomp. 145°; *methylenedi-1-o-tolyl-4:5-dihydro-5-tetrazolyl disulphide*, m. p. 118°, decomp. 160°; *methylene di-1-o-tolyl-5-tetrazolyl disulphide*, decomp. 161°; *methylenedi-1-m-xylol-4:5-dihydro-5-tetrazolyl disulphide*, m. p. 106°; *methylene di-1-methyl-5-tetrazolyl disulphide*, m. p. 157°; *ethylenedi-1-phenyl-4:5-dihydro-5-tetrazolyl disulphide*, decomp. 177°; *ethylene di-1-phenyl-5-tetrazolyl disulphide*, m. p. 93°; *carbethoxymethylenedi-1-phenyl-4:5-dihydro-5-tetrazolyl disulphide*, m. p. 104°, decomp. about 150°; *carbethoxymethylenedi-1-phenyl-5-tetrazolyl disulphide*, m. p. 110°; *carbomethoxymethylenedi-1-phenyl-4:5-dihydro-5-tetrazolyl disulphide*, decomp. 139°. Di-1-phenyl-5-tetrazolyl disulphide is

converted by mercury into the mercury compound of 1-phenyl-5-thiotetrazole, decomp. 223°. Tetra-phenylthiocarbamide and alcoholic silver nitrate afford the compound, $C_{25}H_{20}N_2S, AgNO_3$, m. p. about 240° (decomp.). H. WREN.

Oxidation of uric acid in presence of hydrogen acceptors. S. DOBROWOLSKA (Compt. rend. Soc. Biol., 1928, 99, 1022—1023; Chem. Zentr., 1929, i, 102).—At p_H above 8, in presence of methylene-blue, uric acid (1 in 5000) at 37° decomposes to the extent of 50% in 6 days, with production of allantoin and carbon dioxide. Uric acid in dilute solution is oxidised by thioglycollic acid in presence of air. Small amounts of copper facilitate the reaction. Methylene-blue stimulates, whilst potassium cyanide depresses, the oxidative action of sulphur compounds. It is possible that thioglycollic acid is concerned in uricolysis *in vivo*. A. A. ELDRIDGE.

Chlorophyll group. L. MARCHLEWSKI and A. SZYMANSKI (Bull. Acad. Polonaise, 1929, A, 119—129).—Copper neochlorophyll, copper allochlorophyll, and copper prophyllotaonines were prepared by interaction of the chlorophyll with copper acetate in acetic acid. Copper neochlorophyll is decomposed by methyl-alcoholic potassium hydroxide into copper neo- β -prophyllotaonine (soluble in 10% disodium hydrogen phosphate solution) and copper neo- α -prophyllotaonine. The absorption spectra of phytol, copper allo- and copper neo-chlorophyll, copper allo- and copper neo- β -prophyllotaonine in alcohol-chloroform solution have been measured. A. I. VOGEL.

Structure of furazan oxides. II. C. R. KINNEY (J. Amer. Chem. Soc., 1929, 51, 1592—1600).—*p*-Methoxybenzoin, conveniently obtained by condensing benzaldehyde and *p*-anisaldehyde in presence of potassium cyanide in aqueous alcohol, is oxidised by copper sulphate and pyridine to *p*-methoxybenzil, m. p. 62—63°. This is converted by hydroxylamine hydrochloride and sodium hydroxide in boiling water into a mixture of dioximes which is oxidised by sodium hypochlorite (cf. Meisenheimer and others, A., 1925, i, 1073) to a mixture of furazan oxides (phenylanisylfuroxans) from which a pure α -isomeride (approx. 90% of the product), m. p. 108—109°, and a nearly pure β -isomeride, m. p. 104—105°, softening from 102°, were isolated by fractional crystallisation. The latter was also obtained by oxidising the *p*-methoxybenzil δ -monoxime, prepared from phenyl *p*-methoxybenzyl ketone, amyl nitrite, and sodium ethoxide. Ozonisation of the α -isomeride, followed by hydrolysis with cold 10% sodium hydroxide, gives anisic acid and a product which is hydrolysed by boiling alkali to benzoic acid. The β -isomeride gives the same acids in the reverse order. Diphenylfuroxan with ozone gives benzoic acid only, whilst diphenylfurazan reacts slowly and does not give acids. These results confirm the formulæ assigned by Meisenheimer to the oximes and furoxans derived from *p*-methoxybenzil (cf. A., 1927, 367). H. E. F. NOTTON.

Aminobenzthiazoles. XII. Mobility of amino-3 : 5-dimethylbenzthiazole. A case of complete reactivity in the aminothiazole form. F. HUNTER and W. E. PRIDE (J.C.S., 1929, 943—

946).—Interaction of stable acetyl-*m*-xylylthiocarbamide, m. p. 181—182°, with bromine in chloroform gave 1-acetamido-3 : 5-dimethylbenzthiazole hydrotribromide, m. p. 167° (decomp.), converted by sulphurous acid into acetamidobenzthiazole, m. p. 259—260°, also obtained from 3 : 5-dimethylbenzthiazole and acetic anhydride. Methyl iodide converts 1-amino-3 : 5-dimethylbenzthiazole into the hydriodide of the imino-methyl base I, m. p. 265° (decomp.), which with alkali yielded 1-imino-2 : 3 : 5-trimethyl-1 : 2-dihydrobenzthiazole, m. p. 105—106°, the hydriodide, m. p. 274° (decomp.), of which was identical with I. Methyl iodide in benzene solution converted 1-amino-3 : 5-dimethylbenzthiazole into a substance, m. p. 156—157°. 1-Methylamino-3 : 5-dimethylbenzthiazole, m. p. 124—125°, prepared by reducing the bromo-additive compound obtained from *s*-*n*-xylylmethylthiocarbamide (from *m*-xylylthiocarbimide and methylamine), m. p. 152°, and bromine in chloroform, furnished an acetyl derivative, m. p. 156—157°, and a hydriodide, m. p. 225—227° (decomp.). 1-Amino-3 : 5-dimethylbenzthiazole methosulphate, m. p. 216—217°, is obtained when 1-amino-3 : 5-dimethylbenzthiazole is heated with methyl sulphate in benzene solution. The intermediate bromo-additive compound obtained in the interaction of *m*-xylylthiocarbamide and bromine in chloroform has m. p. 273° (decomp.). A. I. VOGEL.

Ketosulphonic acids. I. Synthesis of 1 : 2 : 3-thiodiazole derivatives. P. MAZAK and J. SUSZKO (Bull. Acad. Polonaise, 1929, A, 131—142).—Interaction of equimolecular quantities of potassium sulphite and chloroacetone gave a 40—45% yield of potassium acetonesulphonate, m. p. 193—194° (corresponding sodium salt, m. p. 180—181°). This reacted with phenylhydrazine to give the phenylhydrazine of acetonesulphonic acid (sinters and decomposes above 260°), which yielded 4-methyl-2-phenyl-dihydro-1 : 2 : 3-thiodiazole-1 : 1-dioxide, $NPh \begin{smallmatrix} SO_2 \cdot CH_2 \\ N = CMe \end{smallmatrix}$ (I), m. p. 84—58°, when heated with phosphorus trichloride at 100°. I reacted with 1 mol. of bromine in acetic acid to give the 5(?) -bromo-derivative, whilst with 2 mols. of bromine I gave the 5 : 5(?) -dibromo-derivative, m. p. 95—96° (decomp.). Nitric acid (*d* 1.4) and I furnished the 5(?) -nitro-derivative, m. p. 170—172°. Attempts to prepare β -ketoprop-anesulphonic acid were unsuccessful. A. I. VOGEL.

Microchemical reactions of piperine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 405—406).—Crystallisation from dilute acetic acid and from acetone give characteristic forms. S. I. LEVY.

New reaction of hydrastine and papaverine. C. A. ROJAHN and F. STRUFFMANN (Pharm. Zentr., 1929, 70, 277).—Whilst hydrastine and papaverine separately give poorly characterised colour reactions with alkaloid reagents, mixtures of the two alkaloids give intense colorations, and this fact may be utilised in their identification. R. K. CALLOW.

Diastereoisomerism. I. Configuration of ephedrine. II. Steric rearrangement of ephedrine with hydrochloric acid. III. Chloro- and bromo-analogues of ephedrine. IV. Steric

rearrangement of ephedrine with sulphuric acid. H. EMDE (Helv. Chim. Acta, 1929, 12, 365—376, 377—384, 384—399, 399—405).—I. Natural (—)-ephedrine base (I), m. p. 39—40°, is a monohydrate (the anhydrous base is obtained only as an oil and has $[M]_D^{20} +18.5^\circ$ in water), whilst natural (+)- ψ -ephedrine base (II), m. p. 118°, $[M]_D^{20} +87.5^\circ$ in alcohol, is anhydrous. The higher m. p. of II suggests a betaine-like saturation of the residual valencies of the hydroxyl and methylamino-groups, indicating that these groups are in close spatial proximity (cf. Spath and Gohring, A., 1921, i, 45). The optical configuration of I,

OH·CHPh·CHMe·NHMe, is $-\alpha+\beta$, whilst that of II is $+\alpha+\beta$, where $\alpha>\beta$. (+)-Deoxyephedrine (β -methylamino- α -phenylpropane) (hydrochloride, m. p. 172°, $[M]_D^{20} +32^\circ$ in water) is obtained together with *dideoxyephedrine*, $C_{20}H_{28}N_2$, b. p. 165°/0.6 mm., m. p. 70°, $[M]_D^{20} +78.8^\circ$ in *N*-hydrochloric acid [*chloroplatinate*, m. p. 224—225° (decomp.)], by reducing α -bromo(chloro)- β -methylamino- α -phenylpropane hydrobromide (hydrochloride) with hydrogen in presence of palladised barium sulphate, acetic acid, and sodium acetate.

II. When either I or II is heated with 10 parts of 25% hydrochloric acid at 100°, the same end-product is obtained after 60 hrs. This contains a preponderance of (+)- ψ -ephedrine hydrochloride (cf. Schmidt, A., 1908, i, 452). With 38% hydrochloric acid replacement of the hydroxyl group by chlorine occurs. Equilibration of I and II with 25% hydrobromic acid at 100° is complete after about 300 hrs., II again predominates. (—)-*Ephedrine hydrobromide*, m. p. 204.5°, $[M]_D^{20} -77.5^\circ$ in water, and (+)- ψ -ephedrine hydrobromide, m. p. 179°, $[M]_D^{20} +148.1^\circ$ in water, are described.

III. Treatment of (—)-ephedrine hydrochloride (III) with phosphorus pentachloride in cold chloroform gives (+)- α -chloro- β -methylamino- α -phenylpropane hydrochloride, m. p. 201°, $[M]_D^{20} +266^\circ$ in water (free base [*chloroplatinate*, m. p. 188° (decomp.); *chloroaurate*, m. p. 128°]), also obtained from III and (+)- ψ -ephedrine hydrochloride (IV) and thionyl chloride. The α -chlorine atom is replaced by hydroxyl when heated at 100° with water, giving a mixture of 62% of IV and 38% of III. From IV and phosphorus pentachloride, or III and fuming hydrochloric acid, (—)- α -chloro- β -methylamino- α -phenylpropane hydrochloride, m. p. 197°, decomp. 199° with evolution of hydrogen chloride, $[M]_D^{20} -167^\circ$ in water, is obtained. Hydrolysis of this furnishes 51% of III and 49% of IV. Treatment of (—)-ephedrine hydrobromide (V) with phosphorus pentabromide yields (+)- α -bromo- β -methylamino- α -phenylpropane hydrobromide, m. p. 174—175° (decomp.), $[M]_D^{20} +385^\circ$ in water. This is converted by heating with chloroform almost entirely into (—)- α -bromo- β -methylamino- α -phenylpropane hydrobromide, m. p. 175.5°, $[M]_D^{20} -287^\circ$ in water, obtained also from (+)- ψ -ephedrine hydrobromide (VI) and phosphorus pentabromide. Both these bromides are hydrolysed by water, yielding mixtures of V and VI.

IV. When (—)-ephedrine hydrochloride is treated for a short time with cold concentrated sulphuric acid

(+)- ψ -ephedrine-*O*-sulphonic acid, m. p. 248—250° (decomp.), $+322^\circ$ in water (cf. Schmidt, A., 1914, i, 989), is obtained together with small amounts of ephedrine and ψ -ephedrine sulphates. Prolonged treatment with sulphuric acid gives *apoephedrine* (Schmidt, *loc. cit.*), which is not identical with *dideoxyephedrine*. This last substance is not formed from *dideoxyephedrine* and α -chloro- β -methylamino- α -phenylpropane hydrochloride in presence of acetic acid and sodium acetate solution, and is not, therefore, a *sec.-tert.*-amine formed by elimination of hydrogen chloride during catalytic reduction (Part I).

H. BURTON.

Belladonnine, bellatropine, and chlorotropan.

M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1929, [iv], 45, 304—311).—Belladonnine, obtained pure by decomposing the *chloroplatinate*, m. p. 252°, or *chloroaurate*, m. p. 168° (cf. Hesse, A., 1891, 228, 748; 1892, 1498; 1894, i, 153), is hydrolysed by boiling alcoholic potassium hydroxide into tropine, together with atropic acid and polymerised atropic acid. Sulphuric acid (0.2*N*) similarly yields tropine and traces of tropidine. Concentrated hydrochloric acid at 140° affords 3-chlorotropan, b. p. 163—165°/760 mm. (decomp.) (*hydrochloride*, m. p. 232—233°, *chloroplatinate*, m. p. 227—228°, *chloroaurate*, m. p. 215°, *picrate*, m. p. 216—217°). The *methiodide*, m. p. 305—306°, is reduced by zinc and sulphuric acid to tropan methiodide. Hydrogen peroxide (30%) in acetone converts 3-chlorotropan into the *N*-oxide (*hydrochloride*, m. p. 210°, *picrate*, m. p. 174—175°). *apo*-Atropine, atropine, hyoscyamine, and tropine and other tropeines are similarly converted into 3-chlorotropan (yields 75%), and with hydrobromic acid into 3-bromotropan (*hydrobromide*, m. p. 219°, *chloroaurate*, m. p. 158°, *chloroplatinate*, m. p. 211°, *picrate*, m. p. 205°). The supposed "bellatropine" of Hesse is a mixture of bases of which chlorotropan is the chief constituent.

R. BRIGHTMAN.

Sinomenine and disinomenine. VIII. Colour reactions of sinomenine and sinomenol. K. Goro (Bull. Chem. Soc. Japan, 1929, 4, 103—105; cf. A., 1926, 1160).—Colour reactions given by sinomenine with alkaline potassium ferricyanide in chloroform, and by sinomenol with ammoniacal silver in acetone closely resemble those given by thebainone and 3-methoxy-4:6-dihydroxyphenanthrene, respectively, and differ from those produced by morphothebaine and morphol, respectively. It is therefore assumed that the relative position of the hydroxy- and keto-groups in sinomenine is analogous to that in thebainone. The formula of sinomenine is discussed.

C. W. SHOPPEE.

Strychnine and brucine. VIII. Action of hydriodic acid on strychnidine. Dihydrostrychnidine (B) and substances derived therefrom. W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1929, 964—1000).—When strychnidine is reduced with hydriodic acid (*d* 1.94) and amorphous phosphorus for 24 hrs., *dihydrostrychnidine* (B) (I), $C_{21}H_{26}ON_2$, m. p. 151°, b. p. 225—230°/0.4 mm., is obtained; it does not yield an acetyl derivative, neither does it condense with hydroxylamine or with aldehydes, and is unaffected by sodium in boiling

alcohol, or by electrolytic reduction [cf. dihydrostrychnidine (A), A., 1927, 1208]. It is a strong base, giving with hydrochloric acid a *hydrochloride* [*trihydrate*, losing $2\text{H}_2\text{O}$ at 100° to yield the *monohydrate*, m. p. 123° (decomp.)] from which it is regenerated by treatment with ammonia. Solutions of I in dilute mineral acids afford colour reactions with dichromate, nitrite, and ferric chloride; the acetate combines with diazobenzenesulphonic acid. The sulphate of I when treated with potassium iodide yields the *dihydriodide*, converted by boiling methyl alcohol into the *monohydriodide*, m. p. $235\text{--}240^\circ$ (efferv.), which, when treated with silver chloride and water, affords the above hydrochloride. Treatment of I in dry benzene at 10° with methyl sulphate gives the *monomethosulphate* (a), converted by sodium iodide into the *monomethiodide* (a) (II), glistening needles becoming opaque at 100° , m. p. $340\text{--}345^\circ$ (decomp.) (compound $+\text{ICHCl}_3$), which when treated with silver chloride and water affords the *methochloride* (a), m. p. $335\text{--}340^\circ$ with loss of methyl chloride and conversion into I. Methylation of I with methyl sulphate in dry benzene at 30° for 24 hrs. gives the *dimethosulphate* (A), converted by sodium iodide into the *dimethiodide* (A) (III), m. p. $238\text{--}242^\circ$ (decomp.), which gives II with methyl-alcoholic potassium hydroxide, and when treated in aqueous solution with silver chloride or sodium bromide furnishes the *dimethochloride* (A) and the *dimethobromide* (A), m. p. 345° (efferv.), respectively. When I is treated with methyl iodide in the cold II is obtained, but on heating a second reaction occurs, giving a mixture of II, III, and the *dimethiodide* (B) of I, m. p. $260\text{--}265^\circ$ (efferv.). The dimethiodides (A) and (B) of I do not lose methyl iodide when digested with mesitylene (cf. A., 1927, 888), but elimination takes place by treatment with hot 25% methyl-alcoholic potassium hydroxide, yielding II and the *monomethiodide* (b) of I, needles, which do not become opaque at 100° , shrink about 250° , and melt gradually above this temperature. The latter when treated with water and silver chloride affords the *monomethochloride* (b), (*dihydrate*), for which colour reactions are described, converted by sodium bromide into the *monomethobromide* (b), which blackens at 330° and effervesces at $340\text{--}345^\circ$. The base I combines with benzyl chloride in hot toluene to yield *dihydrostrychnidine* (B) *benzyl chloride*, m. p. 325° with effervescence and regeneration of I, smoothly converted by mixing with 25% methyl-alcoholic potassium hydroxide and heating at 150° into *methoxybenzyltetrahydrostrychnidine* (B), $\text{C}_{29}\text{H}_{34}\text{O}_2\text{N}_2$, m. p. $126\text{--}127^\circ$, which does not combine with methyl iodide.

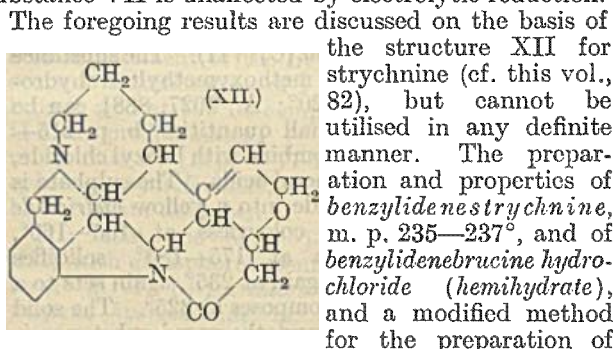
Oxidation of I with powdered permanganate in moist acetone at 15° yielded mainly *dihydrostrychnidine* (B) (IV), $\text{C}_{21}\text{H}_{24}\text{O}_2\text{N}_2$, m. p. 196° (*hydrochloride* converted by sodium iodide into the *hydriodide*, m. p. $350\text{--}355^\circ$), together with a small quantity of an acid, $\text{C}_{21}\text{H}_{24}\text{O}_7\text{N}_2$, m. p. 205° (decomp.), for which colour reactions are given. The base IV gives colour reactions reminiscent of those of strychnine; it does not couple with diazobenzenesulphonic acid, and is very readily soluble in dilute mineral acids and in dilute acetic acid. Treatment of IV with methyl iodide in boiling acetone yields a yellow *methiodide*, darkens about 220° , m. p. 365° (decomp.), converted by silver

chloride and sodium bromide into the *methochloride*, m. p. $370\text{--}375^\circ$ (efferv.) (colour reactions described), and the *methobromide*, m. p. 375° (decomp.), respectively. Benzaldehyde and IV condense readily in the presence of alcoholic sodium ethoxide to afford the *benzylidene* derivative, m. p. $270\text{--}275^\circ$ (colour reactions; *hydrochloride*; *sulphate*), but an oxime could not be obtained. Hydrolysis of IV with sodium ethoxide at 100° yielded *dihydrostrychnic acid* (B), $\text{C}_{21}\text{H}_{26}\text{O}_3\text{N}_2$, m. p. 285° with regeneration of IV, m. p. 203° , mixed m. p. $201\text{--}202^\circ$ (colour reactions; *hydrochloride*). Oxidation of I with hydrogen peroxide in the presence of methyl-alcoholic potassium hydroxide affords *dioxydihydrostrychnic acid* (B), $\text{C}_{21}\text{H}_{26}\text{O}_5\text{N}_2$, m. p. $300\text{--}305^\circ$ (decomp.). The isomeride of I, dihydrostrychnidine (A) (A., 1927, 1208), when oxidised with powdered permanganate in hot, moist acetone yields *oxydihydrostrychnidine* (A), $\text{C}_{21}\text{H}_{24}\text{O}_2\text{N}_2$, m. p. 345° (decomp.), isomeric but not identical with IV. The substance is a feeble base, and does not combine with methyl iodide or with benzaldehyde; its colour reactions are described.

When the mono- and di-methochlorides of I are heated with methyl-alcoholic potassium hydroxide, the main product is *methoxymethyltetrahydrostrychnidine* (B), (V), $\text{C}_{23}\text{H}_{32}\text{O}_2\text{N}_2$, m. p. $180\text{--}181^\circ$ (cf. the conversion of strychnidine methochloride into methoxymethyldihydrostrychnidine; A., 1927, 888), together with small quantities of *methyl- ψ -strychnidine* (B) (VI) and *dihydrostrychnidine* (C) (VII). The substance V [cf. the isomeride methoxymethyltetrahydrostrychnidine (A), m. p. 220° ; A., 1927, 888], can be distilled unchanged in small quantities, b. p. $215\text{--}225^\circ/1\text{ mm.}$; it does not combine with benzyl chloride, but dissolves in dilute mineral acids. The sulphate is converted by sodium iodide into a yellow *hydriodide* (VIII), which becomes colourless at $155\text{--}160^\circ$, softens and decomposes at $175\text{--}180^\circ$, solidifies immediately, effervesces again at 235° , again sets to a solid (IX), and finally decomposes at 325° . The solid IX was identified as II, and the same substance is produced more readily and completely when V is boiled with hydriodic acid ($d\ 1.94$) and amorphous phosphorus. Methyl iodide combines with V at 100° to yield a *methiodide*, m. p. $235\text{--}238^\circ$ with regeneration of V. The *methochloride*, obtained from the foregoing methiodide when treated with water and silver chloride, begins to decompose at 150° , and effervesces at 170° , regenerating V; its colour reactions are described. The *dimethosulphate* is prepared with methyl sulphate in benzene at 80° , and when treated with sodium iodide gives the *dimethiodide*, m. p. 210° , converted by methyl-alcoholic potassium hydroxide at 100° into the above methiodide, m. p. $235\text{--}238^\circ$. When V is oxidised with powdered permanganate in moist acetone at 12° *formylmethoxytetrahydrostrychnidine* (B) (X), $\text{C}_{23}\text{H}_{30}\text{O}_3\text{N}_2$, m. p. 154° , is obtained. This is not hydrolysed by sodium ethoxide at 100° , and does not combine with methyl iodide or benzaldehyde; its colour reactions are described. When boiled with dilute sulphuric acid X eliminates formic acid, or when distilled in a vacuum gives carbon monoxide and *methoxytetrahydrostrychnidine* (B) (XI), $\text{C}_{22}\text{H}_{30}\text{O}_2\text{N}_2$, m. p. $150\text{--}152^\circ$ (colour reactions; *nitroso-derivative*), which is not reducible electrolytic-

ally. Methyl iodide converts XI into the hydriodide VIII, identity being confirmed by conversion into V with ammonia. The mother-liquors from the permanganate oxidation of V, after evaporation and distillation, afford a fraction, b. p. 218—223°/1 mm., which consists of an inseparable mixture of X and XI, m. p. 137—138°, since it is completely converted into XI when boiled with dilute sulphuric acid.

The mother-liquors from the purification of V, after evaporation and distillation, yield a fraction, b. p. 220—225°/1 mm., from which, after removal of a quantity of V, the substances VI and VII were obtained by fractional crystallisation. *Methyl-ψ-strychnidine* (B) (VI), $C_{22}H_{26}ON_2$, m. p. 222—225° (colour reactions described), readily furnishes a *dimethiodide*, m. p. 275° effervescing at 280—285°, with methyl iodide in the cold; attempted preparation of the dimethochloride from the foregoing methiodide was unsuccessful and accompanied by characteristic colour phenomena. *Dihydrostrychnidine* (C) (VII), $C_{21}H_{26}ON_2$, m. p. 132—134, is a strong base and dissolves readily in dilute acetic acid; its colour reactions and crystallographic data are given. When heated with methyl iodide at 100°, it yields a *dimethiodide*, m. p. 265—270° (efferv.), converted by water and silver chloride into the *dimethochloride*, which with methyl-alcoholic potassium hydroxide regenerates VII. The substance VII is unaffected by electrolytic reduction.



strychnidine methosulphate (cf. A., 1927, 888) are given. *Strychnidine methochloride*, m. p. 370° leaving a residue containing strychnidine (*dihydrate*), is obtained from the methiodide (cf. Tafel, A., 1898, i, 703) with water and silver chloride at 100° for 3 hrs., and is dechlorinated by silver oxide to *strychnidine methohydroxide*. Methylation of strychnidine with methyl sulphate in benzene at 80° for 20 hrs., and treatment of the product with sodium iodide, affords *strychnidine dimethiodide*, converted by water and silver chloride into the *dimethochloride*, which when heated with 25% methyl-alcoholic potassium hydroxide up to 140° yields methoxymethylhydrostrychnidine (A., 1927, 888). Strychnidine combines with benzyl chloride in boiling toluene to give *strychnidine benzyl chloride*, m. p. 330—335° (efferv.) with production of strychnidine accompanied by other substances (colour reactions described), which when heated at 150° with 25% methyl-alcoholic potassium hydroxide yields *methoxybenzylidihydrostrychnidine*, m. p. 92—95° (cf. A., 1927, 888). C. W. SHOPPEE.

Structure of narceine. J. J. L. ZWIKKER (Pharm. Weekblad, 1929, 66, 461—464).—The

accepted formula of Freund, which postulates the existence of a $\cdot\text{CO}\cdot\text{CH}_2\cdot$ group in narceine, is improbable in view of the fact that the alkaloid does not give a coloration with alkaline nitroprusside solution. It is suggested that in alkaline solution the nitrogen becomes quinquivalent, one hydrogen atom going from the CH_2 group to the dimethylamino-group, with closing of the ring, whilst in acid solution the structure is represented by Freund's formula. S. I. LEVY.

Sensitive new reaction for ergotamine, ergot-oxin, and ergotinine, and its application to the investigation and colorimetric determination of ergot preparations. H. W. VAN URK (Pharm. Weekblad, 1929, 66, 473—481).—*p*-Dimethylaminobenzaldehyde gives sensitive colour reactions with the ergot alkaloids; the test is applied to ergot preparations by extracting with ether and ammonia, adding the reagent dissolved in ether, and a little sulphuric acid. The individual alkaloids cannot be differentiated. Approximate determination is possible.

S. I. LEVY.

Use of vanillin as an alkaloidal reagent. A. PORTNOV (Pharm. J. Russia, 1928, 89, 453; Chem. Zentr., 1928, ii, 2271).—When an alkaloid is warmed with 2 drops of 2*N*-sulphuric acid and 2 drops of a solution of vanillin in glycerol (0.1 g. in 10 c.c.), a reddish-violet, becoming raspberry-red, colour is obtained. The reagent is stable. A. A. ELDRIDGE.

Structure of Boyd's chloroanhydride. A. E. ARBUZOV and B. A. ARBUZOV (J. Russ. Phys. Chem. Soc., 1929, 61, 217—253; cf. J.C.S., 1923, 123, 813; A., 1924, i, 1121; 1926, 1161).—Boyd's researches on the reaction product of triphenylmethylcarbinol and phosphorus trichloride are reviewed and his theories as to its structure and the mechanism of its reactions with reagents critically examined.

In order to determine whether the chloroanhydride formed the structure $[\text{OCPh}_3]\text{PCl}_2$ or $\text{CPh}_3\cdot\text{P}\cdot\text{OCl}_2$, it was treated with the sodium derivatives of different alcohols, when di-esters of triphenylmethylphosphinic acid, which were identical with those from the products of reaction of the di-esters of phosphorous acid and triphenylbromomethane, were obtained. The *methyl* ester has m. p. 155—156°, the *ethyl* 120—121°, the *n*-propyl 119—120°. The *isopropyl* ester exists in three modifications, two colourless, m. p. 122.5—128, 216.5—217°, and one yellow, m. p. 119—120°. The *isobutyl* ester has m. p. 96—96.5°. By the action of the sodium derivatives of the primary alcohols on the chloroanhydride in the correct proportions, the corresponding chloro-esters are obtained. The *ethyl* chloro-ester has m. p. 125—126°, the *isopropyl*, 164—165°, and the *isobutyl*, 103—103.5°, and the *n*-propyl (by the action of the potassium derivative of propyl alcohol on the chloro-anhydride), m. p. 107—108°. The *methyl* chloro-esters could not be isolated in the pure condition.

The di-esters were hydrolysed by the action of hydrochloric acid in sealed tubes at 180°, triphenylmethylphosphinic acid being formed. The chloro-esters were easily hydrolysed even by water alone. The chloroanhydride itself is hydrolysed at normal pressure into triphenylmethylcarbinol, but in a sealed tube at 180° triphenylmethane is formed almost

quantitatively. By the action of phosphorus trichloride on triphenylmethylcarbinol a 95.2% yield of the chloroanhydride is obtained, together with a *compound*, which cannot be purified and which on hydrolysis yields triphenylmethylphosphinic acid. It is suggested that the *compound* is the triphenylmethyl chloro-ester of triphenylmethylphosphinic acid formed by the action of an excess of triphenylmethylcarbinol on the chloroanhydride.

M. ZVEGINTZOV.

Action of aromatic Grignard reagents on arsenious oxide. F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1929, 51, 1558—1565).—Magnesium phenyl bromide and arsenious oxide in ether and benzene at 0° give diphenylarsenious oxide, m. p. 95.5—96.5°, and triphenylarsine, the latter becoming practically the sole product when excess of Grignard reagent is used in boiling solution. The intermediate product in the formation of triphenylarsine is not the oxide (cf. Matsumiya and Nakai, A., 1925, i, 1339; Sachs and Kantorowicz, A., 1908, i, 1031), since this is not formed until the reaction mixture is decomposed with water, but is probably the derivative, $\text{AsPh}_3 \cdot \text{O} \cdot \text{MgBr}$. Magnesium *p*-tolyl bromide and magnesium *p*-anisyl iodide behave similarly, but magnesium α -naphthyl bromide gives only di- α -naphthylarsine oxide, m. p. 250—253° (decomp.), which has the normal formula (cf. *loc. cit.*), and magnesium 4-diphenyl bromide gives *bis*-4-phenylarsenious oxide, m. p. 150—152°. Phenylarsine and diphenylarsenious oxides are quantitatively converted by excess of magnesium phenyl bromide in boiling ether and benzene into triphenylarsine. The following are described: *bromo*-, m. p. 65—66°, and *iodo*-, m. p. 64—65°, di-*p*-tolylarsines; *chloro*-, m. p. 83—84°, *bromo*-, m. p. 60—62°, and *iodo*-, m. p. 40—42°, di-*p*-anisylarsines; *bromo*-, m. p. 172—173°, and *iodo*-, m. p. 140—141°, di- α -naphthylarsines; *chloro*-, m. p. 145—147°, *bromo*-, m. p. 147—149°, and *iodo*-, m. p. 140—141°, *bis*-4-diphenylarsines. H. E. F. NOTTON.

Chemotherapy of some bromine derivatives of phenylarsinic acids and arsenobenzenes. A. HAYTHORNTHWAIT (J.C.S., 1929, 1011—1014).—The chemotherapeutic indices of the following organic arsenicals are less than that of salvarsan. 2-Nitro-4-acetamidophenylarsinic acid, prepared from diazotised 3-nitro-4-aminoacetanilide and copper arsenite, gave *m*-nitroaniline when boiled with 50% sulphuric acid and 2-amino-4-acetamidophenylarsinic acid (I) when reduced with ferrous sulphate at 30°. The acid I was converted by the diazo-reaction into 2-bromo-4-acetamidophenylarsinic acid, hydrolysed by dilute hydrochloric acid to 2-bromo-4-aminophenylarsinic acid. 3-Bromo-4-hydroxyphenylarsinic acid and 5-bromo-3-acetamido-4-hydroxyphenylarsinic acid (hydrolysed to 5-bromo-3-amino-4-hydroxyphenylarsinic acid with alkali) were obtained from 3-amino-4-hydroxyphenylarsinic acid and 5-amino-3-acetamido-4-hydroxyphenylarsinic acid, respectively. The following arsenobenzenes were obtained from the respective phenylarsinic acids and sodium hyposulphite: 4:4'-dibromoarsenobenzene; 3:3'-dibromo-4:4'-diaminoarsenobenzene; 2:2'-dibromo-4:4'-diaminoarsenobenzene; 4:4'-diacetamidoarsenobenzene

and 2:2'-dibromo-4:4'-diacetamidoarsenobenzene; 3:3'-dibromo-4:4'-dihydroxyarsenobenzene; 5:5'-dibromo-3:3'-diamino-4:4'-dihydroxyarsenobenzene and 5:5'-dibromo-3:3'-diacetamido-4:4'-dihydroxyarsenobenzene. The first five of these arsenobenzenes are insoluble, the rest are soluble, in alkali.

A. I. VOGEL.

Thiolacetamide as a reagent for identifying arsenic acids. H. J. BARBER (J.C.S., 1929, 1024—1026).—Arsenic acids react with 4 mols. of thiolacetamide with the formation of di(carbamylmethyl)thioarsinites: $\text{AsAr}(\text{OH})_2 + 4\text{SH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2 = \text{AsAr}(\text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2 + (\text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2 + 3\text{H}_2\text{O}$.

These compounds generally have sharp m. p. and can be rapidly determined by direct titration with iodine in dilute acetic acid solution at about 40° (cf. preceding abstract). The m. p. of the *thioarsinites* of the following arsenic acids are: phenyl-, 129—130°; *o*-aminophenyl-, 140°; *p*-aminophenyl-, 145°; *o*-hydroxyphenyl-, 161—163°; *p*-hydroxyphenyl-, 160—162°; 3-amino-4-hydroxyphenyl-, 132—133°; 3-acetamido-4-hydroxyphenyl-, 176°; 5-acetamido-2-hydroxyphenyl-, 138°; 3-amino-4-methylaminophenyl-, 141—143°; 4-chlorophenyl-, 134—136°; 4-chloro-3-nitrophenyl-, 142—143°; 3:5-diamino-4-hydroxyphenyl-, 159—161°; 2:6-diacetamido-phenoxycetic-4-arsinic acid, 157°; 8-acetamido-3-hydroxy-1:4-benzisooxazine-6-arsinic acid, 233—235°.

A. I. VOGEL.

Derivatives of arylthioarsinous acids. H. J. BARBER (J.C.S., 1929, 1020—1024).—Aryl arsinoxides and aliphatic thiol compounds react with the formation of thiolarsinous acids, which are also obtained by condensation of the arsenic acids (1 mol.) with organic thiol compounds (4 mols.), the arsenic acid being immediately reduced to the tervalent state. The following compounds are described: *di*(carboxymethyl) 4-aminophenylthioarsinite, m. p. 142—143° (from thiolacetic acid and 4-aminophenylarsinic acid); *di*(carboxymethyl) 4-aminophenylthioarsinite (hydrochloride, m. p. 100—105°); *di*(carbamyl) 4-aminophenylthioarsinite, m. p. 145° (from preceding compound and aqueous ammonia but best prepared from 4-aminophenylarsinic acid and thiolacetamide); *di*(carboxymethyl) 3-amino-4-hydroxyphenylthioarsinite, m. p. 157—158° (from 3-amino-4-hydroxyphenylarsinic acid); *di*(carbamylmethyl) 3-amino-4-hydroxyphenylthioarsinite, m. p. 132—133°; *di*(β -carboxy-aminoethyl) 3-amino-4-hydroxyphenylthioarsinite (from 3-amino-4-hydroxyphenylarsinic acid and cysteine hydrochloride); *di*(carboxymethyl) 5-acetamido-2-hydroxyphenylthioarsinite, m. p. 172—174° (from 5-acetamido-2-hydroxyphenylarsinic acid and thiolacetic acid in benzene solution); *di*(carboxymethyl) 4-carbamylmethylaminophenylthioarsinite, m. p. 90° (from sodium *N*-phenylglycineamide-4-arsinate, thiolacetic acid, and 2*N*-sodium hydroxide followed by acidification); *di*(carboxymethyl) 8-acetamido-3-hydroxy-1:4-benzisooxazine-6-thioarsinite, m. p. 212°; *di*(carbamylmethyl) 8-acetamido-3-hydroxy-1:4-benzisooxazine-6-thioarsinite, m. p. 233—235° (from the arsenic acid and cysteine hydrochloride); *di*(β -hydroxyethyl) 8-acetamido-3-hydroxy-1:4-benzisooxazine-6-thioarsinite (from the arsenic acid in excess of aqueous ammonia and β -hydroxyethylmercaptan). The *di*(carboxy-

methyl) arylthioarsinites react quantitatively with iodine in acid or in hydrogen carbonate solution thus : $\text{AsAr}(\text{SR})_2 + 2\text{I}_2 + 3\text{H}_2\text{O} = \text{AsArO}(\text{OH})_2 + 4\text{HI} + \text{R}_2\text{S}_2$.

A. I. VOGEL.

3 : 4 - Methyleneedioxyphenylarsinic acid. I. E. BALABAN (J.C.S., 1929, 1088—1093).—By the diazo-method 4-aminopyrocatechol methylene ether hydrochloride gave a 42% yield of 3 : 4-methyleneedioxyphenylarsinic acid I, $0.75 \text{ H}_2\text{O}$, m. p. 270° (decomp.) (calcium, barium, and magnesium salts), reduced (sodium hyposulphite) to arsenopyrocatechol methylene ether (65% yield). Nitration of I at 0° yielded 6-nitro-3 : 4-methyleneedioxyphenylarsinic acid, m. p. 231° (decomp.) (magnesium, calcium, and barium salts), identical with the arsenic acid, m. p. 228° (decomp.), obtained (diazo-method: 74% yield) from 5-nitro-4-aminopyrocatechol methylene ether. This acid was converted by ferrous sulphate at 70° into 6-amino-3 : 4-methyleneedioxyphenylarsinic acid II (magnesium and calcium salts), reduced to 6 : 6'-diaminoarsenopyrocatechol methylene ether; II gave 6-acetamido-3 : 4-methyleneedioxyphenylarsinic acid (magnesium salt) when acetylated in alkaline solution. Treatment of 4-nitropyrocatechol with acetic anhydride and sulphuric acid afforded 4-nitro-1 : 2-diacetoxybenzene, m. p. 98° , reduced by iron and dilute acetic acid or by moist aluminium amalgam in ether to 4-amino-1 : 2-diacetoxybenzene, m. p. 114° (N-acetyl derivative, m. p. 144°). Benzylolation of 4-nitropyrocatechol yielded 4-nitropyrocatechol dibenzyl ether, m. p. 97° , reduced by moist aluminium amalgam to the amine, m. p. 92° (hydrochloride, m. p. 197° ; acetyl derivative, m. p. 150°).

A. I. VOGEL.

Merequinonoid derivatives of the phenarsazine series. II. G. A. RAZUBAIEV (Ber., 1929, 62, [B], 1208—1220; cf. this vol., 585).—Treatment of 10-chloro-3(1)-methyl-, 10-chloro-3 : 7(1 : 9)-dimethyl-, and 10-chloro-3 : 4-benzo-5 : 10-dihydrophenarsazine with formic acid causes addition of 1 atom of hydrogen per mol. of substance to intensely-coloured solutions which are decolorised by atmospheric oxygen. Warming the solution causes reappearance of the colour, which may be again discharged by air. The added hydrogen is determined by measurement of the carbon dioxide evolved, calculated according to the equation $\text{H}\cdot\text{CO}_2\text{H} = \text{CO}_2 + \text{H}_2$. Addition of halogen to the reduced solutions causes disappearance of the colour after reaction of 1 atom of halogen per mol. of substance. 10-Chloro-1 : 2 : 8 : 9-dibenzo-5 : 10-dihydrophenarsazine, 10-chloro-2 : 8-dinitro-5 : 10-dihydrophenarsazine, and 10-chlorophenoxarsine are not reduced by formic acid. The following are described : 10-bromo-3 : 4-benzo-5 : 10-dihydrophenarsazine, m. p. 209° , and the corresponding 10-iodo-compound, m. p. $202\text{—}203^\circ$; 10-chloro-3(1)-methyl-5 : 10-dihydrophenarsazine, m. p. $195\text{—}196^\circ$, from arsenic chloride and phenyl-*m*-tolylamine in *o*-dichlorobenzene; 10-bromo-3(1)-methyl-5 : 10-dihydrophenarsazine, m. p. about 220° (decomp.), and the 10-iodo-compound, m. p. 188° ; 10-chloro-3 : 7(1 : 9)-dimethyl-5 : 10-dihydrophenarsazine, m. p. $250\text{—}252^\circ$, from arsenic trichloride and di-*m*-tolylamine; 10-iodo-3 : 7(1 : 9)-dimethyl-5 : 10-dihydrophenarsazine, m. p. $241\text{—}244^\circ$.

H. WREN.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. VIII. Bromination of 10-chloro-5 : 10-dihydrophenarsazine and its derivatives. L. A. ELSON, C. S. GIBSON, and J. D. A. JOHNSON (J.C.S., 1929, 1080—1088).—Treatment of 10-chloro- and also of 10-bromo-5 : 10-dihydrophenarsazine (1 mol.) with bromine (4 mols.) in hot glacial acetic acid and other solvents in the cold (10-chloro-derivative) gave 2 : 4 : 2' : 4' (?)-tetrabromodiphenylamine, m. p. 186° , also obtained by brominating diphenylamine under similar conditions. Diphenylamine yields a hexabromodiphenylamine, m. p. $221\text{—}222^\circ$ (lit. 218°), with 6 mols. of bromine in boiling glacial acetic acid. Similarly, 10-chloro-2 : 8-dimethyl-5 : 10-dihydrophenarsazine afforded tetrabromodi-*p*-tolylamine, m. p. $161\text{—}162^\circ$, or 166° (from di-*p*-tolylamine); 7-chloro-12 : 7-dihydrobenzophenarsazine gave tetrabromophenyl- α -naphthylamine, m. p. 150° ; 12-chloro-7 : 12-dihydrobenzophenarsazine gave a tetrabromophenyl- β -naphthylamine, m. p. 205° (lit. $202\text{—}203^\circ$); 7-chloro-9-methyl-7 : 12-dihydrophenarsazine gave tetrabromo-*p*-tolyl- β -naphthylamine, m. p. $167\text{—}170^\circ$, identical with the compound obtained from *p*-tolyl- β -naphthylamine. Phenarsazinic acid and 4 mols. of bromine in boiling glacial acetic acid afforded chiefly tetrabromodiphenylamine together with small quantities of 2 : 4 : 6 : 8 : 10-pentabromo-5 : 10-dihydrophenarsazine (I), m. p. 275° , and 2 : 4 : 6 : 8-tetrabromophenarsazinic acid, m. p. 294° (decomp.). The last-named was also obtained from I and hydrogen peroxide.

A. I. VOGEL.

Heterocyclic systems containing selenium. I. **cycloSelenobutane** (tetrahydroselenophen). G. T. MORGAN and F. H. BURSTALL (J.C.S., 1929, 1096—1103).— α -Dibromobutane and sodium selenide react when heated at 80° in a current of hydrogen to give cycloselenobutane, purified by conversion into the dibromide and regenerated by treatment with sodium metabisulphite, b. p. $90\text{—}91^\circ/172 \text{ mm.}$, $135\text{—}136^\circ/770 \text{ mm.}$, d^{20}_4 1.493, 1.452, γ^{20} 41.28, parachor (mean)=229.5. It is decomposed by aqueous permanganate or fuming nitric acid, but moderately concentrated nitric acid gave cycloselenobutane-1.1-dinitrate. cycloSelenobutane and mercuric chloride in alcoholic solution yielded cycloselenobutane mercurichloride, m. p. 146° ; chlorine in carbon tetrachloride solution gave cycloselenobutane-1 : 1-dichloride, m. p. $88\text{—}89^\circ$; bromine yielded the corresponding 1 : 1-dibromide, m. p. 92° (interaction of a concentrated chloroform solution of the latter and of bromine gave a perbromide, $\text{C}_4\text{H}_8\text{SeBr}_2\cdot\text{Br}_5$, 5 atoms of bromine being removed by acetone), whilst interaction with iodine in carbon tetrachloride solution gave the diiodide, m. p. $99\text{—}100^\circ$. Treatment of the dibromide with 0.5 mol. of silver oxide furnished cycloselenobutane-1-hydroxy-1-bromide, m. p. $99\text{—}100^\circ$ (decomp.); the corresponding hydroxy-chloride, similarly prepared, had m. p. 116° (decomp.); the 1 : 1-dihydroxide was produced in aqueous solution with excess of silver oxide. cycloSelenobutane 1-chloroplatinate, m. p. 230° (decomp.), is formed in dilute solution from the 1 : 1-dichloride, whereas in warm concentrated solution containing excess of the 1 : 1-dichloride bis-1-chloro-cycloselenobutane 1-chloroplatinate, m. p. 179° (decomp.), is produced. cycloSelenobutane and excess

of $\alpha\delta$ -dibromobutane react at the ordinary temperature to give 1- δ -bromobutylcycloselenibutane 1-bromide, m. p. 65—66°; if the mixture be heated in the presence of water at 90° tetramethylene- $\alpha\delta$ -biscycloselenibutane 1:1-dibromide, m. p. 95—96°, is obtained.

Tetramethylene- $\alpha\delta$ -diselenocyanate, m. p. 40°, is produced by heating $\alpha\delta$ -dibromobutane and potassium selenocyanate in acetone solution for several hours, and is converted by alcoholic sodium hydroxide followed by atmospheric oxidation into cyclotetramethylene diselenide (cyclodiselenobutane) (I), m. p. 41—42°, the structure of which was established by its quantitative conversion with excess of nitric acid into $\alpha\delta$ -tetramethylenediseleninic acid dinitrate, m. p. 136° (decomp.), identical with the substance obtained by treatment of tetramethylenediselenocyanate under similar conditions. When heated, I afforded cycloselenobutane and selenium, whilst bromine in chloroform solution gave cycloselenibutane-1:1-dibromide.

A. I. VOGEL.

Interaction of tellurium tetrachloride and dimethylaniline. G. T. MORGAN and H. BURGESS (J.C.S., 1929, 1103—1106).—Tellurium tetrachloride and dimethylaniline react in dry ethereal solution to give bisdimethylaniline tellurium tetrachloride (I), m. p. 144—145° (decomp.), together with a small quantity of 4:4'-tetramethyldiaminodiphenyl telluridichloride (II), m. p. 188—189°, more conveniently prepared by digesting the tetrachloride I with boiling water and oriented by conversion into *p*-nitrosodimethylaniline and tellurium dioxide on treatment with cold nitrous acid. 4:4'-Tetramethyldiaminodiphenyl telluridiodide, m. p. 158—159° (decomp.), is obtained by refluxing the dichloride II with sodium iodide in acetone, whilst 4:4'-tetramethyldiaminodiphenyl telluride is produced by reduction of II in dilute acetone solution with potassium metabisulphite. Trisdimethylaniline hydrochloride tellurium tetrachloride, (NPhMe₂,HCl)₃.TeCl₄.EtOH, m. p. 119—121°, is obtained as a by-product in the preparation of the dichloride II from the tetrachloride I. Interaction of tellurium tetrachloride and *N*-methyldiphenylamine yielded 4:4'-diphenyldimethyldiaminodiphenyl telluridichloride, m. p. 170—172°. A. I. VOGEL.

Mechanism of the abnormal salt formation of chromium pentaphenyl hydroxide and a peculiar hydrogen union with chromium tetraphenyl salts. F. HEIN [with O. SCHWARTZKOPFF, K. HOYER, K. KLAR, W. EISSNER, W. CLAUS, and W. JUST] (Ber., 1929, 62, [B], 1151—1167; cf. A., 1928, 55).—In the majority of instances, chromium pentaphenyl hydroxide is converted by acids and salts into chromium tetraphenyl salts, whereby the fifth phenyl group appears as phenol and diphenyl. The yields of phenol depend to some extent on the previous history of the base, but homogeneous chromium pentaphenyl hydroxide (as hydrate) yields with salts such as potassium bromide in presence of chloroform almost 100% of phenol and only traces of diphenyl. The base hydrate in absolute alcohol in complete absence of air affords 1 mol. of phenol from each mol. of base when acted on by potassium iodide. Production of phenol is therefore not due to oxidation, but occurs according to the scheme: $\text{CrPh}_5\cdot\text{OH} + \text{KX} + \text{H}_2\text{O}$

$\longrightarrow \text{CrPh}_4\text{X} + \text{Ph}\cdot\text{OH} + \text{KOH} + (\text{H})$. In complete absence of water the anhydrous base yields, therefore, as expected, not more than 50% of phenol: $2\text{CrPh}_5\cdot\text{OH} + 2\text{RX} \longrightarrow 2\text{CrPh}_4\text{X} + \text{R}_2\text{O} + \text{PhOH} + (\text{H})' + \text{Ph}\cdot\text{Ph}$. The anhydrous base does not react with gaseous or liquid ammonia and, when suspended in the last-named medium, is converted by potassium iodide or ammonium bromide into the chromium tetraphenyl salt and phenol but not aniline. The fifth phenyl group can therefore react only with a similar group or with a molecule of solvent which is united by solvation to the base. The intramolecular activity of the group explains its inability to form tetraphenylmethane with triphenylmethyl. The schemes proposed to explain the reaction indicate the production of hydrogen, the formation of which is established by decomposing the base with ammonium chloride in presence of methylene-blue, which is thereby decolorised. Addition of palladised calcium carbonate or barium sulphate or slight rise of temperature accelerates the change. Under the most favourable conditions (illumination of the solutions and presence of an excess of dye) about 33% of the theoretical quantity of methylene-blue is hydrogenated within 3 days. [Excess of dye is determined by titration with ferrous ammonium sulphate in presence of alkali tartrate and ammonia.] Chromium tetraphenyl salts therefore appear to have the ability to combine with hydrogen. Exact measurements show that chromium tetraphenyl chloride, without particular pre-treatment, absorbs 8.5—11.5% of hydrogen and that the product, after being partly dehydrogenated with methylene-blue, absorbs more active hydrogen than otherwise. Since the properties of the chromium tetraphenyl salts (colour, m. p., analytical behaviour) are not appreciably influenced by such addition, an unusual form of union is postulated. This union is so feeble that a portion of the hydrogen is lost during the isolation of the salts; the gas appears present in a form similar to that in certain metallic hydrides, notably palladium hydride. H. WREN.

Mass and size of protein molecules. T. SVEDBERG (Nature, 1929, 123, 871).—All stable native proteins so far studied may be classed, as regards molecular mass, as haemocyanins (M of the order 10^6) and others (M about $35\text{--}210 \times 10^3$), the latter being divisible into four sub-groups. The molecules of the first and fourth sub-groups are spherical (r 2.2 and 4.0 $\mu\mu$, respectively), whilst those of the other sub-groups are not. The molecules of most of the members of the fourth sub-group are easily disaggregated by increasing p_H . The close relations existing between the various proteins is exemplified by the fact that a protein may, according to the p_H to which it is brought, appear with the molecular mass, size, and shape of another protein.

A. A. ELDRIDGE.

Identity of proteins. S. PEROV (Arb. staatl. Timirjasev Inst., 1925, 29 pp.; Chem. Zentr., 1929, i, 92).—Proteins, insoluble in water or 10% sodium chloride solution, functioning as "protein acids" and having the properties of animal proteins have been prepared from oats, wheat, peas, and almonds by extraction with alkali and coagulation with acetic acid.

Proteins are classified according to their ionic function, and hence their equivalent weight. A. A. ELDRIDGE.

Physico-chemical properties of protein. M. LISSIZYN (Arb. staatl. Timirjasev Inst., 1925, 5 pp.; Chem. Zentr., 1929, i, 92—93).—Extraction of plant proteins is normally incomplete; it is considered that a portion of the protein is combined as insoluble calcium proteate. The whole of the protein is extracted by 0.05*N*-sodium hydroxide following treatment with 2% acetic acid. A. A. ELDRIDGE.

Structure of protein materials. W. BERGMANN (Naturwiss., 1929, 17, 314—316).—The relation of arginine and its derivatives to proteins is discussed. R. A. MORTON.

Colorimetric micro-determination of chloroform. K. YODOMIGAWA (Bul. Hokuetsu Med. Soc., 1928, 43, 355—363).—The liquid to be tested is added to a heated mixture of sodium hydroxide and pyridine; the mixture is shaken and the colour compared with standards prepared from solutions containing phenol and phosphate. CHEMICAL ABSTRACTS.

Determination of citric and tartaric acids. F. PIRRONE (Riv. Ital. Ess. Prof., 1928, 10, 101—102; Chem. Zentr., 1928, ii, 2491—2492).—Tartaric acid (0.05 g.) or citric acid (0.0388 g.) is boiled with 0.1*N*-potassium iodate solution (50 c.c.), and concentrated sulphuric acid (25 c.c.) until the volume is reduced to 30 c.c.; after cooling, 100 c.c. of water are added and evaporation to 30 c.c. is repeated. To the cold solution 100 c.c. of water and 10 c.c. of 30% potassium iodide solution are added; excess of 0.1*N*-sodium thiosulphate is added and the excess titrated with 0.1*N*-iodine solution.

A. A. ELDRIDGE.

Detection and determination of methylpentose. T. FUKAI (Bul. Ferm. Tokyo, 1928, No. 100, 106—129).—The distillate obtained from methylpentose and hydrochloric acid gives a violet-red coloration with vanillin in 0.5% sulphuric acid. Solubility differences of the phloroglucides of furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde are applied to their separation. CHEMICAL ABSTRACTS.

Volumetric determination of hexamethylenetetramine. C. V. BORDEIANU (Ann. sci. Univ. Jassy, 1929, 15, 380—383).—The method proposed by Kollo and Angelescu (A., 1927, 786) gives erroneous results, mainly because of the solubility of hexamethylenetetramine picrate in water. With increasing amounts of picric acid in excess, a large negative error decreases to a minimum and finally increases to large positive errors. With hexamethylenetetramine in excess, some picric acid always remains in solution and can be titrated by sodium hydroxide owing to the solubility of the picrate in water.

L. S. THEOBALD.

Diphenylamine and diphenylamine-blue. A. THIEL (Z. Elektrochem., 1929, 35, 274—278).—A method whereby diphenylamine may be determined colorimetrically with an accuracy of 1% is described. The comparison solution is made up by taking 1 c.c. of a 50 vol.-% solution of sulphuric acid containing 40 mg. of diphenylamine per litre, oxidising it with ferric sulphate in sufficient excess, about 100—200 mols. per mol. of diphenylamine, boiling for 5 min., making up to 10 c.c., and viewing the resulting blue solution through a layer 30 mm. thick. The colour of a solution of unknown concentration produced by oxidation with a sufficiently large excess of ferric sulphate is then matched in a colorimeter, and, assuming the validity of Beer's law, the amount of diphenylamine present is calculated.

The basic dissociation constant of diphenylamine, K_b , was found to be 7.6×10^{-14} at 15° by saturating acid solutions of known p_H with the base, and determining colorimetrically the amounts dissolved. The absorption of light by diphenylamine-blue is maximal at 5870 Å., when the molar extinction coefficient is 4.46×10^3 . The oxidation of diphenylamine is a time-reaction, but the precise order of the reaction depends on both the concentrations of diphenylamine and of ferric sulphate. The change corresponds approximately with the expression: $dx/dt = k [\text{diphenylamine}][\text{ferric sulphate}]^{0.8}$, where x is the proportion changed and t is the time in min.

H. T. S. BRITTON.

Biochemistry.

Respiration in excess of oxygen. BOUNHIOL (Compt. rend., 1929, 188, 1340—1342).—Guinea-pigs in 80% oxygen died within two or three days; death is accompanied by increase in the soluble nitrogen compounds of the blood. The ease of obtaining oxygen retards circulation, so that the metabolic products accumulate and cause death. E. BOYLAND.

Influence of carbon dioxide tension on the oxygen dissociation curve [of hæmoglobin]. V. MENKIN and M. F. MENKIN (Science, 1928, 68, 518—519).—The lowering of the oxygen dissociation by an increase in pressure of carbon dioxide is explained by assuming a double dissociation of oxyhæmoglobin represented by $\text{HHbO}_2 \rightleftharpoons \text{HHb} + \text{O}_2$ and $\text{HHbO}_2 \rightleftharpoons \text{H}^+ + \text{HbO}_2^-$. L. S. THEOBALD.

Solubility of gases in blood. A. GROLLMAN (J. Biol. Chem., 1929, 82, 317—325).—Figures are given for the solubilities of ethylene and acetylene at different temperatures in water, whole blood, blood-plasma, and solutions of hæmoglobin. Henry's law is followed by ethylene at 25° for all these fluids. The greater solubility of these gases in blood than in water is due to the lipoidal constituents of the former. C. R. HARRINGTON.

Manganese as a factor in hæmoglobin formation. R. W. TITUS and H. W. CAVE (Science, 1929, 68, 410).—Manganese has a beneficial effect on the formation of hæmoglobin by rabbits and rats fed on a milk-iron diet freed from copper.

L. S. THEOBALD.

Preparation of crystalline potassium salts of oxyhæmin. A. HAMSÍK (Z. physiol. Chem., 1929, 182, 117—124).—A crystalline tripotassium salt was prepared by the action of 20% methyl-alcoholic potassium hydroxide on α -oxyhæmin. It was washed with a mixture of methyl alcohol and ether. The β - and ψ -modifications do not give well-crystallised salts.

J. H. BIRKINSHAW.

Bile pigment content in local hæmorrhage in man. KURISHITA (Klin. Woch., 1928, 7, 1914; Chem. Zentr., 1928, ii, 2376).—Shed blood contains more bilirubin than circulating blood; it is therefore supposed that most of the bilirubin found is formed outside the liver.

A. A. ELDRIDGE.

Adsorption of bilirubin by protein. O. WELTMANN and F. JOST (Deut. Arch. klin. Med., 1928, 161, 203—226; Chem. Zentr., 1928, ii, 2493).—Of the total serum-bilirubin, 0—10% is normally adsorbable; in icterus 5—100% is adsorbable. Adsorbable bilirubin is apparently excreted only through the liver; non-adsorbable bilirubin is concerned in bilirubinuria.

A. A. ELDRIDGE.

Colorimetric determination of proteins of blood-serum. D. M. GREENBERG (J. Biol. Chem., 1929, 82, 545—550).—Blood-serum is treated with sodium sulphate solution; the precipitated globulin is redissolved in dilute sodium hydroxide solution and determined colorimetrically with the phenol reagent of Folin and Ciocalteu (A., 1927, 892); the albumin in the filtrate is determined similarly.

C. R. HARRINGTON.

Determination of protein and residual nitrogen in blood and urine. FISCHER (Süddeut. Apoth.-Ztg., 1928, 68, 693—695; Chem. Zentr., 1929, i, 115).—A discussion of the degradation of protein, the formation of urea, and of analytical methods.

A. A. ELDRIDGE.

Isolation of a carbohydrate derivative from serum-proteins. C. RIMINGTON (Biochem. J., 1929, 23, 430—443).—The albumin and globulin fractions were prepared from the serum by the usual method of precipitation with ammonium sulphate. The proteins were hydrolysed with baryta and the hydrolysate was treated with lead acetate and ammonia. The precipitate after being dissolved in acetic acid was reprecipitated several times with ammonia and decomposed with carbon dioxide. After clearing the solution with mercuric chloride the compound $C_{12}H_{21}O_{10}N$ was finally precipitated and reprecipitated with methyl alcohol and ether. The compound is a structural unit of these proteins. Glucosamine and mannose are the constituent sugars. The same product is obtained from serum-proteins when trypsin is employed as the hydrolytic agent. A structure is suggested for the compound.

S. S. ZILVA.

Sources of error in the determination of blood-sugar by Bang's micro-method. E. RAITH (Biochem. Z., 1929, 208, 357—360).—The filter-papers used for determining blood-sugar by Bang's method reduce Fehling's solution sufficiently to cause an appreciably high result. Washing removes the reducing substance, but also decreases the absorbent power of the paper so that it is no longer of any use for this type of

determination. Blank determinations on a number of papers are therefore essential.

P. W. CLUTTERBUCK.

Distribution of reducing substances between plasma and corpuscles; a comparison of various blood-sugar methods. F. K. HERBERT and J. GROEN (Biochem. J., 1929, 23, 339—351).—Various methods for the determination of blood-sugar give widely different results for the distribution of "sugar" between plasma and corpuscles. The average discrepancies between methods are not great for determinations on plasma, but are considerable for those on corpuscles. Tungstic filtrates of whole blood or corpuscles produce a reduction of the Folin-Wu copper reagent in the cold, whereas filtrates from plasma give no such reaction. The reaction is not given by iron filtrates or zinc filtrates. This is most probably due to the presence of a non-dextrose-reducing substance in corpuscles which is present in tungstic but not in iron and zinc filtrates. Such substances may also be responsible for the residual reduction after fermentation of blood by yeast. Uric acid, creatine, creatinine, and ergothioneine in the small amounts in which they occur in human blood have not, whilst glutathione has, an important effect on blood-sugar methods.

S. S. ZILVA.

Determination of blood-sugar. I. Benedict's alkaline copper solution. M. R. EVERETT (J. Biol. Chem., 1929, 82, 369—376).—The lower values for blood-sugar obtained with alkaline copper reagents containing sulphite (e.g., the reagent employed by Benedict, A., 1925, i, 994; 1926, 984) are due to an unequal fading of the colour of the standard and unknown solution rather than to an increased specificity of the reagent for dextrose. The use of the acid molybdate reagent of Folin (A., 1926, 648, 1282) is therefore recommended for the determination of the true blood-sugar.

C. R. HARRINGTON.

Comparison of gravimetric and colorimetric methods of cholesterol determination in blood-serum. W. N. NEKLUDOV and S. S. CHALATOV (Biochem. Z., 1929, 208, 60—72).—The best gravimetric method for total cholesterol consists in heating the serum to 100° with 20 or 45% sodium hydroxide for 8 hrs. The cholesterol is extracted with ether and after removal of the ether dissolved in alcohol and precipitated and weighed as the digitonin complex. Fox's method (A., 1920, i, 697) gives 97% of the total cholesterol and offers the possibility of determining free and esterified cholesterol. Of the colorimetric methods Grigaut's gives high results and has other disadvantages; Krastelevski's method (A., 1924, ii, 127) gives 95—98% of the cholesterol present and is recommended.

J. H. BIRKINSHAW.

Effect of the use of a [mercury] silica lamp on the blood-cholesterol. S. MALCZYNSKI (Compt. rend. Soc. Biol., 1928, 99, 922—925; Chem. Zentr., 1929, ii, 255).—Irradiation of the whole body raises the blood-cholesterol by 50%, normal values being attained in 4 days.

A. A. ELDRIDGE.

Oxidative determination of phospholipin in blood and tissues. W. R. BLOOR (J. Biol. Chem., 1929, 82, 273—286).—The blood or finely divided

tissue is extracted with alcohol; aliquot portions of the extract are evaporated and the lipins taken up in light petroleum; the concentrated solution is treated with acetone and alcoholic magnesium chloride. The precipitated phospholipins are dissolved in moist (peroxide-free) ether; after removal of the latter by evaporation the residue is subjected to the quantitative oxidation of Bang as modified by the present author (A., 1928, 662). C. R. HARRINGTON.

Phosphoaminolipins and sterols of blood-serum and plasma. II. Physical chemistry of the protein fraction richest in phospholipins and sterols. M. MACHEBŒUF (Bull. Soc. Chim. biol., 1929, 11, 485—503; cf. this vol., 206).—The phosphoaminolipin-protein is soluble in water in either alkaline or neutral media. Extraction with ether of aqueous solutions at varying p_H yields only traces of a substance which consists of 50% cholesterol and 45% fatty acids, moreover addition of neutral salts to the aqueous solutions does not increase the amount of the ethereal extract. Small quantities of alcohol in neutral or more concentrated solutions yield a precipitate which is rich in phosphorus, fatty acids, and cholesterol and dissolves if treated at once in excess of alcohol or water. Prolonged treatment with alcohol of a neutral solution at 12° yields a precipitate consisting of a protein coagulum and crystalline cholesteryl esters, but in alkaline media the precipitation is incomplete. Precipitation of the protein in any solution is obtained on treatment with alcohol at 70° for 10 min.

The protein fraction forms a stable gel when the precipitate is converted into a faintly alkaline paste with 3*N*-ammonia. Treatment with 2*N*-ammonia yields a viscous mass which corresponds in all its properties with the gliode of Bottazzi (Arch. Sci. Biol., 1923, 4, 3), an independent phase intermediate between a sol and a gel. It is suggested that the protein fraction under examination is an entity and that the linkings between the constituents modify the physical properties of the individual constituents.

C. C. N. VASS.

Calcium and potassium contents of the blood-serum of fasting dogs. S. MORGULIS (Biochem. Z., 1929, 208, 257—258).—The serum-calcium for fasting dogs is 11.0 mg.-% and remains constant during rest for a long time. When the body-weight has decreased by 20% the calcium content is 10.6 mg.-%, and when the body-weight has decreased by 35—40% the serum-calcium is 9.6 mg.-%. The potassium:calcium ratio during prolonged fasting is almost unchanged, the normal value of 2.0 increasing only to 2.1.

P. W. CLUTTERBUCK.

Dispersoidal properties of some salts of the plasma. B. DOGADKIN (Russ. fisiol. Zhur., 1925, 10 pp.; Chem. Zentr., 1929, i, 210).—Sol systems (protected by sodium chloride or sulphate) are formed between the following concentrations: calcium monohydrogen phosphate $N/130$ — $N/250$; tricalcium phosphate $N/700$ — $N/1100$; calcium carbonate $N/100$ — $N/180$; calcium oxalate $N/600$ — $N/1200$; calcium formate, citrate, and lactate do not form colloidal solutions.

A. A. ELDRIDGE.

Physico-chemical behaviour of magnesium in serum. Z. STARY and R. WINTERNITZ (Z. physiol.

Chem., 1929, 182, 107—116).—The non-dialysable fraction of magnesium in serum amounts to 28%. In spite of the fact that cerebrospinal fluid shows a higher magnesium content than serum, it is shown by compensation dialysis at varying p_H values that the magnesium in serum follows the Donnan law.

J. H. BIRKINSHAW.

Determination of inorganic phosphate of blood-serum. L. GUNTHER and D. M. GREENBERG (J. Biol. Chem., 1929, 82, 551—553).—The calcium-free filtrate obtained in the determination of calcium by the method of Tisdall (A., 1923, ii, 656) is freed from protein with trichloroacetic acid; phosphate is then determined by the method of Fiske and Subbarow (A., 1926, 443), excess of oxalate being oxidised with permanganate.

C. R. HARRINGTON.

Determination of phosphorus in small amounts of serum and cerebrospinal fluid. K. SAMSON (Biochem. Z., 1929, 208, 230—236).—Slight modifications in Neumann's volumetric method which enable 0.01—0.15 mg. of phosphorus to be determined to 0.001—0.002 mg are described. J. H. BIRKINSHAW.

Micro-determination of chlorides in serum and cerebrospinal fluid by the method of electrical conductivities. M. DUBOUX and L. PARCET (Bull. Soc. Chim. biol., 1929, 11, 504—516).—A conductance titration whereby the chloride content of 0.4 c.c. of serum can be determined to an accuracy of 0.05 g. per litre is described. Prolonged contact of the serum with the blood clot lowered its chloride content by adsorption. The average chloride content expressed as g. sodium chloride per litre is 5.65—5.90 in normal human serum and 6.70—7.20 in cerebrospinal fluid.

C. C. N. VASS.

Determination of small amounts of iodine [in blood]. E. GLIMM and J. ISENBRUCH (Biochem. Z., 1929, 207, 368—376).—When proper care is taken, the amount of iodine contained in human blood is found to be 20—30 γ -%, a figure much higher than that usually accepted (10 γ -%).

P. W. CLUTTERBUCK.

Anticoagulant action of antithrombin. J. O. W. BARRATT (Biochem. J., 1929, 23, 422—424).—The anticoagulant action of antithrombin on a mixture of fibrinogen and thrombin *in vitro* is exerted on thrombin alone, which becomes diminished in amount.

S. S. ZILVA.

Urobilin in organs. M. ROYER (Compt. rend. Soc. Biol., 1928, 99, 1006—1007; Chem. Zentr., 1929, i, 419—420).—The liver and kidneys contain the largest, and the musculature, pancreas, and lung contain the smallest amount of urobilin.

A. A. ELDRIDGE.

Preparation of glycogen. Glycogen of the abalone, *Haliotis rufescens*, Swainson. L. G. PETREE and C. L. ALSBERG (J. Biol. Chem., 1929, 82, 385—395).—Glycogen was prepared from the flesh of the abalone (an edible mollusc), without the use of alkali, as follows. The finely-divided flesh was extracted with boiling water, the extract being kept neutral to litmus by addition of sodium hydroxide, and then slightly acidified with acetic acid; proteins were removed with picric acid, and the glycogen was precipitated from the filtrate by addition of alcohol.

Purification was accomplished by repeated re-dissolution in water and precipitation with alcohol, addition of a trace of ammonium acetate being necessary in the final precipitations. Glycogen prepared in this way retained small amounts of ash which could not be removed by electrodialysis, nor did the latter process separate the glycogen into fractions containing different proportions of phosphoric acid. The ash of the electrodialysed preparations contained small amounts of calcium and iron in addition to phosphoric acid.

C. R. HARRINGTON.

Keratohyalin. L. NURNBERGER (Klin. Woch., 1928, 7, 1961—1962; Chem. Zentr., 1928, ii, 2373).—Keratohyalin is not identical with nucleochromatin.

A. A. ELDRIDGE.

Cholesterol content of the human intestinal wall. M. BURGER and H. D. OETER (Z. physiol. Chem., 1929, 182, 141—147).—The sigmoid contains considerably more cholesterol than any other section of the intestinal tract. It was shown by bromination that coprosterol was absent, indicating that the high sterol content is due to excretion rather than resorption.

J. H. BIRKINSHAW.

Phosphatide content of different kinds of muscle. K. SORG (Z. physiol. Chem., 1929, 182, 97—106).—A method involving methyl-alcoholic extraction is described whereby the phosphatide content of small amounts of tissue (0.5—2 g.) may be determined to $\pm 1\%$. The phosphatide content of the heart muscle of the rabbit may amount to 0.430%; that of red and white muscle is much less, 0.173% and respectively, representing maximum values.

The total acid-insoluble phosphoric acid of heart muscle and nearly all of that contained in the red and white muscle is present as phosphatides.

J. H. BIRKINSHAW.

Tyramine and tyrosine content of the salivary glands of cephalopods; micro-determination of these two substances. M. HENZE (Z. physiol. Chem., 1929, 182, 227—240).—Tyramine and tyrosine determinations on the salivary glands of *Octopus vulgaris* were made using the apparatus of Widmark (Stand. Arch. Physiol., 1927, 48, 61) for micro-extraction of organic acids. The amounts present in the right and left glands from the same animal are approximately the same; the tyramine content is two to six times that of the tyrosine.

J. H. BIRKINSHAW.

Iodine-containing compounds of the thyroid gland. Isolation of *dl*-3:5-di-iodotyrosine. C. R. HARRINGTON and S. S. RANDALL (Biochem. J., 1929, 23, 373—383).—The desiccated thyroid gland was hydrolysed with baryta and the hydrolysate precipitated with sulphuric acid at p_H 5.0. The precipitate after having the acid-soluble iodine extracted with alkali was worked up for thyroxine. The filtrate to which the alkaline extract from the acid-insoluble fraction was added in the isolation process was treated as follows. It was precipitated with basic lead acetate, the precipitate hydrolysed again with baryta and precipitated twice with silver nitrate. The filtrate from the decomposed silver salts was then extracted with butyl alcohol. This extract was cleared with uranium acetate and after final

treatment with lead acetate yielded a crystalline compound which was recrystallised from 50% acetic acid and was identical with *dl*-3:5-di-iodotyrosine. The iodine content of the various fractions was followed up. Evidence is adduced that the whole of the acid-soluble iodine is present as di-iodotyrosine, whilst the whole of the acid-insoluble iodine belongs in all probability to thyroxine.

S. S. ZILVA.

Occurrence of methylguanidine in the animal organism. III. Use of benzenesulphonyl chloride for separation of methylguanidine. I. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1929, 182, 259—264; cf. this vol., 589).—The amount of methylguanidine precipitated as the benzenesulphonate by excess of benzenesulphonyl chloride is only 9—30% of the theoretical, depending on the conditions. The yield is diminished in presence of creatinine.

J. H. BIRKINSHAW.

Tetradecenoic acid from *Tetradenia glauca*, Motsum. M. TSUJIMOTO (Bull. Inst. Tokyo Ind. Res. Lab., 1928, 23, No. 3, 53—60).—“Tsuzuic acid,” from the oil of *Tetradenia glauca*, is Δ^3 -tetradecenoic acid; Δ^5 -tetradecenoic acid, from the oil of the whale *Physeter macrocephalus* is named physeteric acid.

CHEMICAL ABSTRACTS.

Rufin, the epidermal pigment of *Arion Rufus*. C. DHERÉ and C. BAUMEIER (Compt. rend. Soc. Biol., 1928, 99, 492—496; Chem. Zentr., 1928, ii, 2479—2480).

Histochemical detection of urea. W. LAVES (Wien. klin. Woch., 1928, 41, 1403—1404; Chem. Zentr., 1928, ii, 2493).—The section is immersed for 6 hrs. in a 6% solution of xanthhydrol in acetic acid, whereby crystals of dixanthylcarbamide are formed.

A. A. ELDRIDGE.

Use of mercurochrome and modified mercurochrome as biological stains. J. D. HERRMANN, W. DENNIS, and D. D. DEDRICK (Univ. Oklahoma Bull., 1928, [ii], No. 409, Studies ser. 29, 132—133).

Adrenaline and choline in lymph. G. VIALE (Compt. rend. Soc. Biol., 1928, 99, 1009—1010; Chem. Zentr., 1929, i, 96).—10—35 Mg. of choline per g. of lymph, and adrenaline, were detected.

A. A. ELDRIDGE.

Excretion of nucleoproteins in the bile. P. CARNOT and Z. GRUZEWSKA (Compt. rend. Soc. Biol., 1928, 99, 598—600; Chem. Zentr., 1929, i, 103).—The cholenucleins are obtained by treating the bile with an equal volume of alcoholic chloroform and washing the precipitate with ether. The moist substance is readily soluble in dilute alkali solutions. The cholenuclein content of dog's bile is reduced by large doses of sodium hydrogen carbonate from 1 to 0.3%.

A. A. ELDRIDGE.

Absorption and secretion in the small intestine. I. Secretion of electrolytes. S. KUCZKOWSKI (Acta Biol. Exp., Warsaw, 1929, 3, 57—80).—The fluid found in an intestinal loop after the introduction of water, neutral salts, acids, or alkalis has the same mineral content, viz., sodium 32.5, potassium 2.4, calcium 1.1, magnesium 0.15, chlorine 26.7, and phosphorus 0.3 mg.-%. A comparison of this fluid

with that normally found indicates that the mineral constituents of the latter are secreted by intestinal glands. Sodium and potassium salts, phosphates, and above all hydrogen carbonates are absorbed freely, whilst calcium and magnesium undergo resorption relatively very slowly. R. TRUSZKOWSKI.

Simultaneous determination of pepsin and lipase in gastric juice. L. GÓZONY and F. HOFFENREICH (Biochem. Z., 1929, 208, 259—261).—The gastric juice is brought to p_H 5.6 and a saturated solution of monobutyrin in physiological saline added to a series of dilutions. After keeping, sodium caseinogenate is added; the amount of caseinogen precipitated by the freed fatty acids is determined nephelometrically and forms a measure of the activity of the lipase. The caseinogen is then completely precipitated by addition of a drop of 0.1*N*-hydrochloric acid, and, after keeping, the activity of the pepsin is determined by the decrease in the amount of caseinogen precipitated. P. W. CLUTTERBUCK.

Urea and chlorine in the cerebrospinal fluid in retention of both substances. P. SAVY and H. THIERS (Compt. rend. Soc. Biol., 1928, 99, 516—518; Chem. Zentr., 1928, ii, 2376).—Determination of urea and chlorine in cerebrospinal fluid does not suffice for a decision concerning their retention. Both substances take at least 53 hrs. to reach equilibrium with the blood-chlorine and -urea.

A. A. ELDRIDGE.

Ch'an Su, the dried venom of the Chinese toad. Isolation of adrenaline. H. JENSEN and K. K. CHEN (J. Biol. Chem., 1929, 82, 397—401).—Finely-powdered Ch'an Su was extracted with dilute acetic acid, the extract was cleared by addition of alcohol and centrifuging, and then concentrated; it was further cleared with lead acetate and extracted with chloroform; the residual aqueous solution, on concentration and treatment with ammonia, yielded adrenaline (0.35 g. from 150 g.).

C. R. HARRINGTON.

Determination of amino-acids in urine. L. TIXIER (Bull. Sci. pharmacol., 1928, 35, 570—571; Chem. Zentr., 1929, i, 419).—Use is made of the sensitivity of phenolphthalein, and the insensitivity of litmus, towards amino-acids. A. A. ELDRIDGE.

Detection of alcohol in urine. P. LIEBESNY (Klin. Woch., 1928, 7, 1959—1960; Chem. Zentr., 1928, ii, 2388).—With the chromic acid method, 0.5 c.c. of alcohol ingested per kg. body-weight can be detected within 6 hrs.; 3 c.c. per kg. can still be detected after the seventh hour. A. A. ELDRIDGE.

Citric acid content of normal urine. O. ÖSTBERG (Biochem. Z., 1929, 208, 352—353).—The presence of citric acid is detected and its amount determined in normal urine in terms of the increased velocity of decolorisation of methylene-blue in presence of the citric acid dehydrogenase of cucumber seeds. The total amount of citric acid excreted daily by a man varies from 0.23 to 1.85 g.

P. W. CLUTTERBUCK.

Effect of the blood-serum of the healthy and alcaptonuric individual on homogentisic acid. F. LANYAR and H. LIEB (Z. physiol. Chem., 1929, 182, 218—226).—Free homogentisic acid in aqueous

solution is not oxidised by air at 37°; if the acid is neutralised or the solution contains free alkali oxidation occurs. When mixed with healthy serum there is a small loss of acid due to adsorption by the protein. Oxidation occurs when the acid is brought to the p_H of serum. The same phenomena were observed with alcaptonuric serum. J. H. BIRKINSHAW.

Changes of cholesterol content of serum in anaphylaxis. J. M. GOLDBERG and W. N. NEKLUDOV (Biochem. Z., 1929, 208, 285—287).—In experiments with sensitised rabbits and guinea-pigs, the serum-cholesterol content during the period of anaphylactic shock increased, fell, and then increased again, remaining high when the shock was greatest. P. W. CLUTTERBUCK.

Reaction of the blood in cancer. H. MILLET (J. Biol. Chem., 1929, 82, 263—267).—No change from the normal was observed in the p_H of the blood of patients suffering from cancer. C. R. HARRINGTON.

Carbohydrate metabolism of tumours. H. G. CRABTREE (Biochem. J., 1929, 23, 536—545).—Determinations of the carbohydrate metabolism of several strains of mouse tumours are recorded. In many cases there were great deviations from the standard value found for tumours of rat, fowl, and a limited series of human tumours. There were also variations between tumours of different strains and also between those of the same strain. There was a number of cases of high respiration both in its absolute value and in its relation to the aerobic and anaerobic glycolysis. This respiration is ineffective in checking the aerobic glycolysis. The respiratory quotients with one exception were found to be below unity. Xylose was not metabolised by tumour tissue. Evidence is brought forward which suggests that the glycolytic activity of tumours exerts a checking effect on their respiration. The carbohydrate metabolism of tumours is to some extent influenced by the environment in which they grow. The respiration of the subcutaneous growths was on the average 50% higher than that of the intraperitoneal growths. The majority of these subcutaneous tumours do not exhibit a positive value for the excess fermentation.

S. S. ZILVA.

Reaction of neutral-red in cancerous sera and its relation to other dyes. A. ROFFO and H. DEGIORGI (Z. Krebsforsch., 1927, 25, 136—140; Chem. Zentr., 1929, i, 272).—Cresol-red and rosaniline also react. Since the three dyes belong to different groups, the constitution of the dye appears to be unconcerned in the reaction. A. A. ELDRIDGE.

A peculiar disturbance of carbohydrate metabolism. R. SCHONHEIMER (Z. physiol. Chem., 1929, 182, 148—150).—The liver and kidney of a child which, having shown curious symptoms from birth, succumbed to influenza, were found to be enormously enlarged and contained about 35% of glycogen (on dry weight). The liver was incapable of metabolising its own glycogen. J. H. BIRKINSHAW.

Potassium : calcium ratio and magnesium content of cerebrospinal fluid. B. EISLER (Z. ges. exp. Med., 1928, 61, 549—559; Chem. Zentr., 1928, ii, 2660).—A study of pathological conditions.

A. A. ELDRIDGE.

Behaviour of the lactic acid of the cerebrospinal fluid in normal and pathological conditions. G. MARGRETH (*Folia Clinica*, 1929, 3, 397—405).—In normal individuals the proportion of lactic acid in the cerebrospinal fluid is 16—18 mg. per 100 c.c., that in the blood being 10—14 mg. per 100 c.c. In cases of tubercular meningitis the proportion is 41—60, in those of meningo-myelitis and tabes it is slightly above the normal, and in a case of *lues cerebri* normal. The leucocytes doubtless play a considerable part in the transformation of sugar into lactic acid during the course of meningitis, and bacteria possibly help in the glycolysis in the inflammatory processes of the meninges. T. H. POPE.

Action of insulin and pituitrin on the elimination of urine and especially on carbonuria in diabetes insipidus. G. MARINESCO, O. KAUFFMAN-COSLA, and S. DRAGANESCU (*Compt. rend. Soc. Biol.*, 1928, 99, 911—913; *Chem. Zentr.*, 1929, i, 97).—Pituitrin reduces to normal the quantity of urine, but does not affect the carbonuria. Insulin does not reduce the quantity of urine, but abolishes deoxidative carbonuria. A. A. ELDRIDGE.

Action of guanidine derivatives in diabetes. M. R. CASTEX and M. SCHTEINGART (*Compt. rend. Soc. Biol.*, 1928, 99, 999—1000; *Chem. Zentr.*, 1929, i, 101).—Glycosuria is influenced more strongly than glycaemia by synthalin or "glukhorment." In combination with insulin a greater effect is produced than by either type alone. In normal subjects "glukhorment" causes hyperglycaemia. A. A. ELDRIDGE.

Decreased diastatic action of the urine in kidney diseases and in diabetes. F. SCHMEREL (*Biochem. Z.*, 1929, 208, 415—427).—The small diastatic action of diabetic urine is not due to decreased diastase content of blood and cannot be accounted for solely in terms of the medium (since bringing back the urine to optimal conditions of pH and salt content for diastase action does not bring back the diastatic value to normal), but is in part due to the lowered permeability of the kidney to diastase. P. W. CLUTTERBUCK.

Cutaneous and venous blood-sugar curves.
II. **Benign glycosuria and diabetes.** M. FRIEDENSON, M. K. ROSENBAUM, E. J. THALHEIMER, and J. P. PETERS (*Arch. Int. Med.*, 1929, 43, 633—652).—The cutaneous and venous blood-sugar curves have been studied in cases of benign glycosuria and diabetes after the administration of dextrose or mixed meals both with and without insulin therapy. In 14 cases of benign glycosuria all the patients developed distinct positive arterial-venous differences. The differences may be so great that the venous curves fail to show hyperglycaemia. In 15 studies on diabetic patients, all but the two least severe cases showed large differences after meals; consequently such differences cannot be taken as a measure of the severity of the disease nor can much guidance be obtained from a study of the arterial-venous curves in differentiating benign from diabetic glycosuria. In extreme hyperglycaemic reactions the ability of the tissues to remove sugars is not entirely lost, but it is limited, rapidly exhausted, and occurs at a higher blood-sugar

level. Insulin-treated patients with diabetes of variable severity gave arterial-venous differences during fasting with far greater frequency than normal persons, and after meals at a reduced blood-sugar level. F. C. HAPFOLD.

Inorganic salts and the acid-base equilibrium of the blood in fever. M. AKIYA (*Z. klin. Med.*, 1928, 109, 312—341; *Chem. Zentr.*, 1929, i, 253).—Determinations on rabbits and man are recorded.

A. A. ELDRIDGE.

Lacticæmia, spontaneous and induced, as a test of hepatic function. G. MARGRETH (*Folia Clinica*, 1929, 3, 381—396).—The liver plays the principal part in the re-synthesis of lactic acid to glycogen and dextrose, although the muscles also appear to participate in these changes. Experiments made by administering lactic acid to healthy individuals and patients with liver disease kept without food and in a state of complete rest for the previous 12 hrs. show that only very serious alterations of the hepatic cells are accompanied by marked increase in the lactic acid content of the blood. With healthy subjects this lactic acid content increases slightly 1—2 hrs. after ingestion of the acid, but reverts to the normal value after 3 hrs., whereas with those suffering from diseased livers the increase still persists after 3 hrs. and usually becomes more marked. T. H. POPE.

Fat metabolism. II. Character of blood-lipins in hepatic disorders, including migraine. C. W. MCCLURE and M. E. HUNTSINGER (*Arch. Int. Med.*, 1929, 43, 715—730).—The blood of normal subjects and patients suffering from migraine, gallstones, cirrhosis of the liver, toxic jaundice, hæmochromatosis, and cancer of the liver has been examined both in the fasting state and after ingestion of olive oil, oleic acid, egg-white, and dextrose. The lecithin-phosphorus, cholesterol, total fatty acids, and the iodine number of the two latter have been determined. The variations in cholesterol concentrations from the fasting level after ingestion of food were not great, but changes in the iodine numbers and in the concentrations of the blood-lipins followed. In particular an increased iodine number of the blood-cholesterol in these pathological conditions was fairly general, and suggests differences in the chemical constitution of the cholesterol in disease and that of normals. The lecithin-phosphorus concentration was not demonstrably influenced. F. C. HAPFOLD.

Distribution of lipins in normal and abnormal liver. III. Effect of disease on human liver. E. R. THEIS (*J. Biol. Chem.*, 1929, 82, 327—334).—The lipins of normal human liver are closely similar in the proportion of phospholipins (60% of the total) and in the distribution of fatty acids to the lipins of ox and rabbit liver (*A.*, 1928, 319, 676). In pathological degeneration of the liver the proportion of phospholipins shows a progressive decrease.

C. R. HARRINGTON.

Blood-bilirubin in catarrhal and salvarsan icterus. D. SANCER and M. POPESCO (*Compt. rend. Soc. Biol.*, 1928, 99, 1084—1085; *Chem. Zentr.*, 1929, i, 97).—In icterus the maximal blood-bilirubin is 0.4 g. per litre (normally 1 in 3500—7000); in salvarsan icterus bilirubinæmia is more prolonged.

Insulin has a favourable effect in reducing the value.

A. A. ELDRIDGE.

Action of iron on the resting metabolism of rachitic rats. H. SEEL (Biochem. Z., 1929, 208, 295—298).—The decreased oxygen utilisation in rachitic rats may be increased almost to normal by administration of ferrous sulphate or better of ferrous hydrogen carbonate, but this has no beneficial effect on the rachitic condition of the bone.

P. W. CLUTTERBUCK.

Hexosediphosphatase in hens with leg weakness. M. SCHECHTER (Biochem. Z., 1929, 208, 443—444).—Hens kept in a small darkened cage for several months became unable to walk or stand. In this condition, the plasma-calcium content is slightly lower (mean for 4 hens, 11.1, for 6 normals 16.8 mg.-%) whilst the inorganic phosphorus content is somewhat increased (mean 5.0, in controls 3.9 mg.-%). The hydrolysis of hexosediphosphate is investigated with material from the limiting cartilage of the distal joint of the phalanx of the second and third toes. The tissue from hens in the above condition hydrolysed hexosediphosphate more strongly than tissue from normal hens.

P. W. CLUTTERBUCK.

Prevention of tetany in parathyroidectomised dogs. I. Cod-liver oil; effect on calcium assimilation. II. Lactose. I. GREENWALD and J. GROSS (J. Biol. Chem., 1929, 82, 505—530, 531—544).—I. The power of cod-liver oil to protect parathyroidectomised dogs against the development of tetany is not so regular or so considerable as has been claimed by other workers; the effect of cod-liver oil is increased if it be administered in conjunction with a source of calcium. The variability of the results is explained on the assumption that most animals possess more or less accessory parathyroid tissue which escapes removal at operation, and that it is through the stimulation of parathyroid tissue that cod-liver oil exercises its effect. The development of tetany is due not only to the final degree of reduction of the blood-calcium, but also to the rapidity with which this reduction is brought about. Irradiated ergosterol was without effect, even in conjunction with calcium. The theory that the parathyroids are stimulated by cod-liver oil is supported by the increased excretion of calcium following the substitution of cod-liver oil for maize oil in the diet of a dog on normal diet.

II. Administration of lactose prevents the development of tetany in parathyroidectomised dogs only when the diet contains large amounts of calcium (cf. Dragstedt and Peacock, Amer. J. Physiol., 1923, 64, 424).

C. R. HARRINGTON.

Tuberculous pus. R. ZANOLI (La Chir. Org. Mov., 1927, 11, 26 pp.; Chem. Zentr., 1929, i, 419).—Organic and inorganic constituents, and the enzyme content, of tuberculous pus have been determined.

A. A. ELDRIDGE.

Chloride metabolism and alkalosis in alkali treatment of peptic ulcer. H. A. WILDMAN (Arch. Int. Med., 1929, 43, 615—632).—The alkali treatment of cases of peptic ulcer is studied and its effect on chloride metabolism and alkalosis discussed. Hypochloræmia is accompanied by a marked decrease in

the urinary chlorides, an early sign of approaching alkalosis; when decreased gastric secretion is concurrent the ratio of cell to plasma-chlorides is reduced. A normal carbon dioxide capacity of the plasma may occur in hypochloræmia with symptoms of alkalosis, consequently such capacity cannot be taken as a trustworthy index of alkalosis.

F. C. HAPFOLD.

Course of [biological] oxidation processes. H. WIELAND (Anal. Eis. Quim., 1929, 27, 181—191).—A lecture.

R. K. CALLOW.

Respiratory quotient of nerve at rest and during activity. O. MEYERHOF and F. O. SCHMITT (Biochem. Z., 1929, 208, 440—455).—The mean respiratory quotient for frog's resting nerve is 0.69 (varying from 0.64 to 0.73) and the resting respiration (mm.³ of oxygen per g. moist wt. per hr.) 14.5 (varying from 14.4 to 18.0). During stimulation the respiratory quotient is 0.79 (0.71—0.85) and the mean respiration 28 (21—39.6). The respiratory quotient of resting nerve therefore corresponds with the oxidation of fat and on stimulation is increased to a small extent, whilst the respiration is doubled.

P. W. CLUTTERBUCK.

Chemistry of the micelle and its application to biochemical and biological problems. K. H. MEYER (Biochem. Z., 1929, 208, 1—31).—A general discussion of the reactions of colloids from the point of view of micellar structure.

J. H. BIRKINSHAW.

Iodine metabolism. III. Iodine metabolism of the thyroidectomised dog. A. STURM. IV. Iodine distribution in the human and animal organism in relation to the thyroid gland. A. STURM and B. BUCHHOLZ (Deut. Arch. klin. Med., 1928, 161, 129—142, 227; Chem. Zentr., 1928, ii, 2484—2485).—III. After thyroidectomy in dogs the blood-iodine falls from 12—17 γ -% to 3—10 γ -%; the urinary elimination of iodine markedly increases, becoming normal again after 10 days. During hunger the iodine elimination falls only slightly in the normal dog, but disappears almost completely in the thyroidectomised dog. The thyroid gland is regarded as the centre of the mechanism of iodine regulation.

IV. The iodine contents of the more important organs of man, dogs, and guinea-pigs have been determined. Iodine was always detected; the endocrine organs, skin, and hair are richest in iodine, but in the testicles and pancreas the iodine content does not exceed that of the general tissue. The human spleen contained in 7 cases 14.4—129 γ -%, and the skeletal muscle 8—111.5 γ -%. The total iodine content markedly rises in the spring; this cannot be ascribed to increased consumption of green vegetables. Only active ovaries have a high iodine content (30—160 γ -%); in the menopause ovarian iodine is frequently not observed. The musculature contains 0.33—0.5 of the total iodine of the organism, and the thyroid gland 0.2—0.1. Removal of the thyroid gland causes the iodine content of the endocrine organs to fall whilst the iodine of the other tissue remains unaltered; hence only the "endocrine iodine" is regulated by the thyroid gland. The thyroid gland of tuberculous guinea-pigs was very

poor in iodine. Infective diseases appear to cause a diminution of iodine in almost all organs.

A. A. ELDRIDGE.

Influence of ration of salts on nitrogen retention during growth. E. F. TERROINE and T. REICHERT (Compt. rend., 1929, 188, 1268—1271).—In continuation of previous work (Terroine and Mahler-Mendler, Arch. int. Physiol., 1927, 28, 101), in which a mixture of salts containing the elements chlorine, sulphur, phosphorus, sodium, potassium, calcium, magnesium, and iron was found to promote nitrogen retention and growth of young pigs, the effect of certain single salts has been investigated. Sodium or potassium chloride, dipotassium hydrogen phosphate, or calcium citrate separately have no promoting effect. The reality of the better utilisation of nitrogen with the complex salt mixture is shown by the persistence of better nitrogen retention when the ration is discontinued.

R. K. CALLOW.

Does feeding with cabbage increase the calcium of rabbit's blood-serum. R. KAPSINOW and F. P. UNDERHILL (J. Biol. Chem., 1929, 82, 377—384).—In experiments on variations in the calcium of the blood-serum of rabbits, the effect of frequent withdrawal of blood cannot be neglected. Definite support could not be obtained for the suggestion of Culhane (A., 1927, 904) that feeding with cabbage produces a rise in the serum-calcium of rabbits.

C. R. HARRINGTON.

Copper content of plant and animal foods. C. W. LINDOW, C. A. ELVEHJEM, and W. H. PETERSON [with H. E. HOWE]. Copper content of feeding stuffs. C. A. ELVEHJEM and E. B. HART [with H. E. HOWE] (J. Biol. Chem., 1929, 82, 465—471, —477).—Figures are given for the copper content of 160 human foods of vegetable and animal origin, and of 47 vegetable feeding stuffs commonly given to domestic animals. In no case was copper absent.

C. R. HARRINGTON.

Physico-chemical phenomena during regeneration. III. Determination of the hydrogen-ion concentration of the regenerating extremity of the crab (*Paralithodes camtschatica*). N. OKUNEV (Biochem. Z., 1929, 208, 328—333).—During regeneration of the crab's extremity, a shift of p_H to the acid side is obtained, similar to that obtained during regeneration of the extremity of the axolotl (A., 1928, 916), the displacement in the two cases being almost identical (0.24 and 0.28 p_H).

P. W. CLUTTERBUCK.

Metabolism of sulphur. XV. Relation of protein and cystine content of diet to growth of hair in the white rat. H. D. LIGHTBODY and H. B. LEWIS (J. Biol. Chem., 1929, 82, 485—497).—Rats which show deficiency of growth on diets containing inadequate amounts of protein and particularly of cystine exhibit also a deficiency in the production of hair of a still greater magnitude. This indicates that the demand for cystine for the growth of hair is secondary to the demand for this amino-acid for other more essential tissue formation.

C. R. HARRINGTON.

Tryptophan and growth. I. Growth on a tryptophan-deficient basal diet supplemented at

intervals with tryptophan. C. P. BERG and W. C. ROSE (J. Biol. Chem., 1929, 82, 479—484).—In order satisfactorily to supplement a tryptophan-deficient diet for growing rats by separate administration of tryptophan, the doses of the latter must be given at least as frequently as every 12 hrs.

C. R. HARRINGTON.

Formation of creatine from proteins [in diet]. E. F. TERROINE and P. DANMANVILLE (Compt. rend., 1929, 188, 1439—1441).—By simultaneous determinations of excreted creatine and the amount of nitrogen retained by young, growing pigs fed on diets in which only the protein constituent was varied it is shown that during growth the larger was the amount of nitrogenous material retained by the animal the smaller was the amount of creatine excreted. Thus the order of creatine formation of proteins is exactly the reverse of that of their nutritive value.

J. W. BAKER.

Origin of creatine. E. ABDERHALDEN (Naturwiss., 1929, 17, 293—294).—Creatine can be formed from arginine and choline in the presence of arginase. Adenine and guanine, hydantoin, methylhydantoin, and histidine are likewise bases from which creatine may arise. The processes involved in the Abderhalden reaction for pregnancy are shown to be fermentation reactions. Investigations on the nature of fermentation lead to the view that an enzyme-substrate compound is formed at a definite hydrogen-ion concentration, the nature of the entire molecule being by this time so changed that a hydrogen-ion concentration, which results in negligible hydrolysis for the substrate as such, is now quite effective.

R. A. MORTON.

Benzoylated amino-acids in the animal organism. IV. Origin of glycine. W. H. GRIFFITH (J. Biol. Chem., 1929, 82, 415—427).—After administration of benzoic acid to rats, 66—95% was excreted in the urine in the form of hippuric acid. A satisfactory basal diet for the growth of rats could be impaired by addition of 3% of sodium benzoate, the limiting factor being the supply of glycine, since addition of the latter neutralised the effect of the benzoate. This effect of benzoic acid on the rate of growth of rats affords therefore a method for the investigation of the presence or absence of glycine or its precursors in the diet.

C. R. HARRINGTON.

Behaviour of aromatic amines in the organism. H. WEBER and C. HEIDEPRIEM (Zentr. Gewerbehyg. Unfallverh., 1928, 15, 269—272; Chem. Zentr., 1928, ii, 2662).—Naphthylamine and dimethylaniline, when injected subcutaneously into dogs, are partly eliminated unchanged in the urine, partly hydroxylated. Benzidine is eliminated unchanged. Dimethylaniline poisoning produced methæmoglobin.

A. A. ELDRIDGE.

Decomposition of creatinephosphoric acid in relation to the activity of muscle. II. D. NACHMANSOHN (Biochem. Z., 1929, 208, 237—256; cf. A., 1928, 917).—The isometric coefficient K_m (kg. tension \times cm. muscle-length/mg. phosphoric acid split off) and the isometric time-coefficient K_t (kg. tension \times cm. muscle-length \times sec. tetanus/mg. phosphoric acid split off) were determined. K_t is about 15 for 2 sec. tetanus, 32 for 5 sec., 50 for 10 sec. The anaerobic resynthesis for periods of varying length is about 30% of the

amount hydrolysed. In curarised muscle K_m is relatively high for 2 sec., and changes little with number or length of period. It falls with submaximal and increases with excessive stimulation. Muscle in phosphate solution resynthesises creatine-phosphoric acid up to 95% of the creatine present. The K_m value at 4° is 70—100, at 24° 40—60.

J. H. BIRKINSHAW.

Significance of guanidinephosphoric acids (phosphagens) for muscle activity. O. MEYERHOF (Naturwiss., 1929, 17, 283—287).—Creatinine-phosphoric acid (phosphagen) is decomposed to a measurable extent as a result of a muscular contraction lasting 5 sec. The phosphagen is resynthesised anaerobically to the extent of 30% during the first 30 sec. after the contraction. The process has been studied with normal muscle and curarised muscle in relation to the time of contraction. The decomposition of phosphagen bears a very close relationship to the velocity of response to stimulus.

R. A. MORTON.

Muscular contraction. III. Change in glycogen during contraction produced by tetanus toxin. H. A. DAVENPORT, H. K. DAVENPORT, and S. W. RANSON (J. Biol. Chem., 1929, 82, 499—504).—Contraction of rabbit and guinea-pig muscles under the influence of tetanus toxin was accompanied by reduction of the glycogen content; this was not the case in the rat, nor did contraction caused by section of the dorsal roots of the spinal nerves influence the glycogen content. Tetanus toxin had no effect on the glycogen of denervated muscles.

C. R. HARINGTON.

Lactic acid excretion in urine and sweat in various sports. I. SNAPPER and A. GRUNBAUM (Biochem. Z., 1929, 208, 212—220).—After football on cold days and rowing, more than 60 mg. of lactic acid was found in the urine of the majority of contestants. Football on warm days led to high lactic acid and chlorine excretion (468 and 846 mg.) in the sweat. After long-distance running there was little lactic acid excretion in the urine, the "steady state" is reached after 9 min. After swimming (5 and 20 min.) there was much lactic acid in the urine (maximum 1.76 g.). Albuminuria frequently occurs after swimming, glucosuria occasionally after football and swimming.

J. H. BIRKINSHAW.

Relation between phosphoric acid and carbohydrate metabolism in isolated liver. W. A. ENGELHARDT and A. N. PARSHIN (Biochem. Z., 1929, 208, 221—229).—Surviving isolated rabbit's liver was perfused with Ringer's solution. With well-fed animals the phosphoric acid eliminated shows a steady increase, with fasting animals a constant value or slight decrease. Addition of dextrose to the perfusion liquid decreases the phosphoric acid excretion. Fluoride and calcium nullify the effect of dextrose, although inactive in its absence.

J. H. BIRKINSHAW.

Carbohydrate metabolism. IV. Action of hydroxymethylglyoxal on normal and hypoglycaemic animals. W. O. KERMACK, C. G. LAMBIE, and R. H. SLATER (Biochem. J., 1929, 23, 410—415).—Hydroxymethylglyoxal in its dimeric

form is highly toxic to mice and rabbits, and in sublethal doses produces symptoms similar to those of insulin hypoglycaemia. In its monomeric form the toxicity is reduced by 75% and the same train of symptoms is not produced. Hydroxymethylglyoxal in either the dimeric or monomeric form is unable to cause recovery from insulin hypoglycaemia.

S. S. ZILVA.

Carbohydrate metabolism. V. Effect of administration of dextrose and of dihydroxyacetone on glycogen content of muscle in depancreatized cats. W. O. KERMACK, C. G. LAMBIE, and R. H. SLATER (Biochem. J., 1929, 23, 416—421).—Small quantities of dihydroxyacetone administered intravenously to decerebrated cats from which the pancreas has been removed tend to increase, whilst large quantities tend to decrease, the muscle-glycogen. Similar results are obtained with dextrose except that the relation between the amount of dextrose administered and the change in glycogen may not be so great. High initial blood-sugars before pancreatectomy appear to cause an increase in muscle-glycogen. Muscle-glycogen is not more readily formed from dihydroxyacetone than from dextrose in presence of the liver.

S. S. ZILVA.

Action of acid on glycogen in the cell. H. ELLAS and S. WEISS (Wien. med. Woch., 1928, 78, 1351—1352; Chem. Zentr., 1928, ii, 2571).—With increasing hydrogen-ion concentration of the surrounding liquid, the glycogen content of frog-spawn gradually diminishes.

A. A. ELDRIDGE.

Inhibiting action of polysaccharides on dextrose hyperglycaemia. G. SOLARINO (Boll. Soc. Ital. Biol. sper., 1927, 2, 1039—1042; Chem. 1928, ii, 2375).—Soluble rice or cereal starch (25 g.) in warm water causes in fasting dogs a hyperglycaemia of 0.012—0.048%. Soluble starch, when administered after dextrose, inhibits the hyperglycaemia, the values being between those for dextrose alone and those for starch alone.

A. A. ELDRIDGE.

Changes in metabolism during irradiation. V. Changes in carbohydrate metabolism. II. L. PINCUSSEN and T. KAWAKAMI (Biochem. Z., 1929, 208, 185—190; cf. A., 1928, 918).—Rats exposed to the light of a mercury lamp for 30 min. showed an increase in glycogen in the liver and muscle and a decrease in lactic acid content; the heart showed no change. The effect is compared with that of insulin.

J. H. BIRKINSHAW.

Pentose metabolism. III. Rates of disposal of *d*- and *l*-arabinose in the rabbit. R. C. CORLEY (J. Biol. Chem., 1929, 82, 269—272).—Following intravenous administration of *d*- and *l*-arabinose to rabbits the rates of disappearance of the two sugars from the blood are closely similar, that of the *d*-isomeride being possibly slightly more rapid; the conclusion of Neuberg and Wohlgenuth (A., 1902, ii, 336) is therefore not confirmed.

C. R. HARINGTON.

Scyllitol in selachian ontogeny. J. NEEDHAM (Biochem. J., 1929, 23, 319—323).—The yolks of the undeveloped eggs of *Acanthias vulgaris* contain only insignificant quantities of scyllitol, whilst the embryo contain greater amounts. The dogfish therefore

synthesises most of its scyllitol. The yolk and jelly of *Scyllium canicula* egg, also contain only traces of scyllitol. S. S. ZILVA.

Influence of work on the fat content of frog muscle. W. NIEMIĘKO (Acta Biol. Exp., Warsaw, 1929, 3, 143—164).—The fat contents of symmetrical gastrocnemius muscles are identical; individual values for different animals vary by 300%. During the winter the fat content declines progressively from an average value of 0.74% in the autumn to 0.30% in June. The destruction of cell structure, as well as heat tetanus, does not affect the fat content of muscle-tissue. The fats present in frog muscle are not utilised until glycogen reserves have been considerably exhausted. R. TRUSZKOWSKI.

Body fats. Physiology of fat deposition. W. SPRANGER (Biochem. Z., 1929, 208, 164—178).—The viscosity of a number of emulsions was determined as a measure of the dispersion. The viscosity of Ringer solution is scarcely changed by sodium or calcium oleate, lecithin, cholesterol, and cholesteryl ester present in physiological amounts. Albumin, lecithin, and sodium oleate act as oil-in-water emulsifiers. The effect is increased by cholesterol, cholesteryl ester, and calcium oleate at low concentrations and diminished at higher concentrations: these substances cause phase inversion when the amount of fat is increased. Cholesterol and its ester when present together (optimum ratio 1:2), however, favour an oil-in-water emulsion. The phase-inverting action of cholesterol, but not of the ester, depends on the amount of the water phase. A water-in-oil emulsion exists in fatty deposits. J. H. BIRKINSHAW.

Phosphatide content of organs after administration of large amounts of phosphatide. II. B. REWALD (Biochem. Z., 1929, 208, 179—184; cf. A., 1928, 1154).—A dog receiving 30 g. of phosphatides per day for 15 months showed practically the same increase in the lipin content of various organs as occurred in a previous experiment lasting 6 months. The glands—ovaries, thyroid, pancreas, etc.—showed very large increases, two to three times normal. J. H. BIRKINSHAW.

Asymmetric utilisation of *p*-isobutylphenol in the animal body. C. FROMAGEOT (Biochem. Z., 1929, 208, 490—492).—When optically inactive *p*-isobutylphenol is fed to rabbits and the urine hydrolysed, isobutylphenol is obtained. P. W. CLUTTERBUCK.

Parenteral absorption of colloids. II. S. HAYASHI (Biochem. Z., 1929, 208, 361—367).—By intravenous injection of urease, a considerable concentration of the enzyme is obtained in the serum and is maintained for several hours. Intraperitoneal injection of larger amounts also causes urease to accumulate in the serum, but more slowly. Subcutaneous injection results in the appearance gradually of traces of urease in the serum. Intraperitoneal absorption of the enzyme is dependent on the medium, on its p_H , on the ions present, and their concentration. P. W. CLUTTERBUCK.

Increase in the calcium content of the organs of rabbits on feeding with naphthalene. A. CADE BARRAL (Compt. rend. Soc. Biol., 1928, 99, 520—522; Chem. Zentr., 1928, ii, 2479).

Effect of ethyl alcohol on dehydrogenation and on the oxygen demand of muscle. G. DI MACCO and P. FORMICOLA (Riv. Pat. sper., 1928, 3, 44—51; Chem. Zentr., 1929, i, 410).—Small doses of alcohol, on injection into frog's muscle, have an inhibitory, and large doses an activating, action. The decomposition of alcohol in the tissue is accomplished by an enzyme. A. A. ELDRIDGE.

Blood anti-coagulant in peptone. B. E. BRUDA (Klin. Woch., 1928, 7, 1742; Chem. Zentr., 1928, ii, 2482).—Witte's peptone, on precipitation with acetone, extraction with methyl alcohol, taking up with water, filtering, and evaporating, affords a substance which renders blood non-coagulable, and is similar to Howell's heparin. A. A. ELDRIDGE.

Neutralising power of soaps for cobra venom. M. RENAUD (Compt. rend. Soc. Biol., 1928, 99, 496—498; Chem. Zentr., 1928, ii, 2480).—Detoxication of cobra venom by soaps is slower than that of tetanus, diphtheria, or *B. coli* toxins. A. A. ELDRIDGE.

[Electrostatics in biochemistry.] K. SPIRO (Koll.-chem. Beih., 1929, 28, 208—219).—A lecture on the relations between electrical phenomena and the phenomena of life. E. S. HEDGES.

Cell- and tissue-potentials. K. UMRATH (Koll.-chem. Beih., 1929, 28, 259—262).—The relation between electrical potential and susceptibility to staining in tissue is discussed, and also the variation in potential according to whether the cell is living or dead. E. S. HEDGES.

Electrostatics as a special domain in biochemistry. R. KELLER (Koll.-chem. Beih., 1929, 28, 219—234).—A lecture, in which qualitative and quantitative methods of determining electrical potential in living cells are discussed. E. S. HEDGES.

Physical foundations of electrical potential in the organism and direct methods of measurement. R. FURTH (Koll.-chem. Beih., 1929, 28, 235—245).—The measurement of electrical potential in organisms is discussed and a practical potentiometric method is described in detail. E. S. HEDGES.

Comparative cardiovascular action of two stereoisomerides, tropanol and ψ -tropanol. M. POLONOVSKI and R. HAZARD (Compt. rend., 1929, 188, 1441—1443).—Whilst intravenous injection of tropanol (*cis*) into a dog lowers the blood-pressure, large doses causing a decrease in the regularity and amplitude of the contractions of the heart, the *trans*-isomeride, ψ -tropanol, similarly injected, raises the blood-pressure, seemingly due to peripheral vascular contraction. The action is complex (closely resembling that produced by nicotine) and consists of two phases: (1) one of inhibition which is suppressed by atropine; (2) one of relative acceleration and increased blood-pressure. Normal conditions are subsequently restored and the effects produced diminish with each successive injection. J. W. BAKER.

Biological assay of ergot preparations. G. L. PATTEE and E. E. NELSON (J. Pharm. Exp. Ther., 1929, 36, 85—105).—The assay of ergot by the cock's comb method and the adrenaline reversal method

of Brown and Clark have been compared. The results are practically identical. Ergotoxin is found to be slightly but distinctly stronger than ergotamine.

F. C. HAPFOLD.

Reagent for detection and determination of quinine. E. G. STERKIN and G. I. HELFGAT (Biochem. Z., 1929, 207, 8—24).—The reagent consists of a mixture of equal volumes of 0.12% sodium arsenate solution, 2% ammonium molybdate solution, and 2% hydrochloric acid. It can be preserved in the dark for 4—5 months and under certain conditions it will detect quinine hydrochloride at a dilution of 1 in 2×10^6 . For the determination 1 c.c. of the reagent is added to 5 c.c. of a slightly acid, suitably diluted portion of the liquid to be tested and after a certain time a nephelometric measurement is made. A method for the extraction of quinine from blood is described. At a dilution of 1 in 1.5×10^5 quinine hydrochloride can be determined in such extracts with an error not exceeding 5%. At higher dilutions the error is greater. Caffeine, morphine, apomorphine, cocaine, atropine, and plasmoguin are precipitated by the reagent, but their presence in sufficient quantity to interfere with the determination of quinine is not likely to occur. Potassium mercuric iodide cannot be used for the nephelometric determination of quinine.

W. MCCARTNEY.

Regulation of the hydrogen-ion concentration of the blood. III. Effect of strychnine on the acid-base equilibrium. IV. Action of strychnine on the blood. VI. Effect of synthalin on the acid-base equilibrium. VII. Respiratory regulation. S. K. LIU and R. KRUGER. VIII. Effect of acids, bases, and other toxic substances on the acid-base equilibrium of the blood. S. K. LIU (Z. ges. exp. Med., 1928, 61, 757—766, 767—774, 780—786, 787—793, 794—807; Chem. Zentr., 1929, i, 97—99).—With rabbits, intravenous or intramuscular administration of large doses of strychnine causes acidosis which can be suppressed by chloral hydrate. Strychnine and lactic acid accelerate the reduction by hydrogen of oxalated whole blood, and retard its oxidation in air. Intravenous, but not intramuscular or subcutaneous, administration of small doses of synthalin often causes a temporary rise in p_H , whilst large intravenous doses cause a fall in p_H . The acidosis is ascribed to increased combustion of sugar and considerable formation of acid. The effect of synthalin is very similar to that of insulin. Small quantities of lactic acid momentarily reduce the p_H of the blood, but the acid is rapidly neutralised and the acid-base equilibrium readjusted. Large quantities of lactic acid momentarily reduce the p_H of the blood; after some time the blood may have an alkaline reaction. Small quantities of sodium hydroxide raise the p_H only momentarily. A study of the relation between the acid, sodium hydroxide, or other toxic substance administered and the buffer mixture of the blood shows that the change in p_H of the blood is directly proportional to the administered hydrogen-ion concentration, and inversely proportional to the total buffering. The toxic reactions (oxidation, reduction) between the substance administered (quinhydrone, salvarsan, neosalvarsan) and the

blood appear to be retarded or diminished by the buffer mixture of the blood. A. A. ELDRIDGE.

Quantitative micro-detection of morphine.

I. Determination of morphine in pure solution. II. Determination of morphine in serum and in whole blood. P. FLEISCHMANN (Biochem. Z., 1929, 208, 368—391, 392—414).—I. A method for the determination of morphine, which depends on the precipitation of the alkaloid with phosphomolybdic acid with colorimetric determination in terms of the colour formed on solution in concentrated sulphuric acid, is described. 0.02—2 Mg. of morphine hydrochloride in 5 c.c. of water may then be determined, the error with amounts over 0.6 mg. being less than 1%, with amounts between 0.2 and 0.5 mg. up to 3%, and with smaller amounts as much as 10%.

II. Morphine hydrochloride (up to 0.01 mg. per 5—7 c.c. of blood) in the whole blood of sheep, rabbits, and guinea-pigs may be determined without extraction and purification by deproteinising with 14.5% uranyl acetate, eliminating the excess of uranium with concentrated phosphate solution, and applying the colorimetric method above. With serum of these animals and of man, much smaller concentrations of uranyl salts can be used, and elimination of the excess is unnecessary. The error in the determinations in blood and serum are the same as in pure solution. P. W. CLUTTERBUCK.

Opium addiction. IV. Blood of the addict during morphine administration. W. G. KARR, A. B. LIGHT, and E. G. TORRANCE (Arch. Int. Med., 1929, 43, 684—690).—A comprehensive study of the blood of addicts receiving morphine sulphate hypodermically has been made. There is a tendency for a low red and a high white cell count. The cholesterol content was usually increased and the phosphates were diminished; the lactic acid content was uniformly high. F. C. HAPFOLD.

[Toxicity of] arsenic. F. WASMUTH (Arch. exp. Path. Pharm., 1929, 142, 17—40).—Small quantities of arsenious oxide reduce the power of suitably prepared extracts of animal tissues to oxidise reduced phenolphthalein. It is concluded from this and other observations that the toxic action of arsenic on the animal organism is a result of its inhibitory action on the oxidative enzyme.

W. O. KERMACK.

Toxicity of arsenic. Comparative study of injections of solutions of sodium arsenate and of arsenical mineral waters of the Bourboule. J. GODONNECHE (Bull. Soc. Chim. biol., 1929, 1, 477—484).—Intraperitoneal injections of guinea-pigs with synthetic Bourboule water, or with the bottled natural water, or with the natural water direct from the spring, showed that whilst the first two possessed the same toxicity, the water obtained direct from the spring possessed a much greater toxicity.

C. C. N. VASS.

Mercury poisoning and its chemical detection. FRIEDERICH and BUHR.—See this vol., 784.

Buffer antiseptics. III. Silver ion buffers. J. K. GJALDBAEC (Dansk Tidsskr. Farm., 1929, 133—172).—Solutions of simple silver salts have all

their silver in a therapeutically active form, but they injure the tissue and tend to produce merely local effects. The optimum concentration of silver nitrate to obtain a deep effect below the surface of the tissue is 0.01—0.02%. Diffusible silver complexes are effective at greater depths. Sodium citrate does not form complexes with silver ions, and does not depress ionisation more than any other salts. Colloidal silver preparations produce very few silver ions, even in the presence of iodide. Ammoniacal silver nitrate solutions and silver nitrate solutions with hexamethylenetetramine contain 97—98% of their silver in a complex form. These solutions should be valuable for the therapeutic administration of silver.

E. BOYLAND.

Fermentative formation of allantoinic acid from allantoin. R. FOSSE and A. BRUNEL (Compt. rend., 1929, 188, 1067—1069).—The occurrence of an enzyme capable of converting allantoin into allantoinic acid is reported in the following: frog, eel, pike, carp, conger-eel, herring, dab, whiting, plaice, thorn-back, dog-fish, salmon, crab, shrimp, lobster, cray-fish, star-fish, and sea-urchin.

E. A. LUNT.

Biochemical determination of allantoin in presence of carbamide. R. FOSSE, A. BRUNEL, and P. DE GRAEVE (Compt. rend., 1929, 188, 1418—1421).—The determination of allantoin as xanthylcarbamide (A., 1927, 891) in the presence of carbamide (or substances generating it such as ureides etc.) may be effected if *Saja hispida* is used as a hydrolysing agent in place of alkali. The urease present destroys the carbamide and creates the correct degree of alkalinity required by a second enzyme, allantoinase, which converts allantoin into allantoinic acid. The latter is then determined as xanthylcarbamide as in the previous process.

J. W. BAKER.

Influence of formaldehyde on dilute malt extracts. O. MULLNER (Biochem. Z., 1929, 208, 354—356).—When formaldehyde is added to dilute (2%) solutions of malt extract, the diastatic power is considerably decreased.

P. W. CLUTTERBUCK.

Activation of certain oxidase preparations. C. E. M. PUGH (Biochem. J., 1929, 23, 456—471).—The apparent activation by peroxidases of a constituent of the oxidase of the fungus *Lactarius vellereus* separable from it by 40% alcohol observed by Bach and Chodat (A., 1902, ii, 344, 522; 1903, i, 377) has been confirmed. Peroxidase from horseradish and various species of *Lactarius* fungi were employed. No evidence was, however, obtained to support Bach and Chodat's view of the dual constitution of oxidases. The most probable interpretation of the phenomenon is the presence in the fungus of an autoxidisable substance. The phenomenon is not due to the formation of hydrogen peroxide or to the presence of an inhibitory substance (cf. Szent-Gyorgyi, this vol., 98). The addition of boiled peroxidase or of glycine does not produce the activation. Dialysed peroxidase activates. Unless excess of substrate be present the rate of action cannot be assumed to be a measure of activity of the enzyme. Preparations from potatoes were not activated by peroxidase. The action of tyrosinase on tyrosine and on *p*-cresol is shown to be autocatalytic, the lag being eliminated by addition of a

small amount of pyrocatechol or of dihydroxyphenylalanine. The lag can also be eliminated by boiled tyrosinase preparations.

S. S. ZILVA.

Peroxidase of phanerogams. D. MICHLIN and P. KOPELOVITSCH (Biochem. Z., 1929, 208, 288—294).—A peroxidase is prepared from the bark of fir trees which is thermolabile and sensitive to cyanide but contains no iron and does not give an aldehyde reaction. The optimum p_H for its action is from 3.8 to 5.6.

P. W. CLUTTERBUCK.

Specificity of intracellular dehydrogenases.

II. Effect of poisons on dehydrogenase systems of frog and fish muscle. M. E. COLLETT and M. F. CLARKE. III. Dehydrogenases of frog muscle. M. E. COLLETT, M. F. CLARKE, and J. MCGAVRAN (J. Biol. Chem., 1929, 82, 429—434, 435—437).—II. Selenite, arsenite, phenol, and benzoate show similar degrees of toxicity towards the dehydrogenase of fish muscle regardless of the nature of the hydrogen donor; in the case of frog muscle, however, the relative toxicity varies with the donor, from which it appears that frog muscle must possess at least three specific dehydrogenases.

III. Five different donors exhibit mutually accelerating effects on the rate of dehydrogenation by frog's muscle; the latter therefore contains a specific dehydrogenase for each of the donors (succinic, citric, malic, lactic, and glycerophosphoric acids).

C. R. HARRINGTON.

Influence of p_H on glycerophosphatase. K. INOUE (J. Biochem. Japan, 1928, 10, 133—145).—The preparation of glycerophosphatase from taka-diastase is described. Purification with kaolin shifts the point of optimal activity from p_H 5.6 to p_H 2.7—3.0. The activity- p_H curve is a typical dissociation curve, pK 4.8. The X-substance affects only that portion of the curve which corresponds with the dissociation curve of a base. The unit of X-substance is the quantity necessary to shift the optimum p_H of the reaction from 3.0 to 5.6, 0.5 unit to 5.0, and 0.25 unit to 4.5, the enzyme activities of these optima being 60, 30, and 20%, respectively, of that of the purified enzyme at p_H 3.0.

CHEMICAL ABSTRACTS.

Cataphoresis of glycerophosphatase. H. KOBAYASHI (J. Biochem. Japan, 1928, 10, 147—155).—Glycerophosphatase from taka-diastase contaminated with the X-substance migrated to the anode on the alkaline side of its optimum reaction (p_H 5.56), and to the cathode on the acid side. The enzyme, when free from X-substance, has its optimum reaction at p_H 3—4, but migrates to the anode over the entire p_H range 3.8—6.7. The difference is due to the greater protein content of the crude enzyme.

CHEMICAL ABSTRACTS.

Kidney glycerophosphatase. K. ASAKAWA (J. Biochem. Japan, 1928, 10, 157—175).—The preparation of glycerophosphatase from pig's kidney is described. At p_H 8.9 the kidney phosphatase has the same activity as the phosphatase of taka-diastase at p_H 2.8—3.0. The kidney glycerophosphatase has a basic dissociation constant pK_b 4.8; for the acid dissociation constant the values of pK_a are 10.8 and 9.0, respectively.

CHEMICAL ABSTRACTS.

Sulphatase. XI. Stereochemical specificity of sulphatase. C. FROMAGEOT (Biochem. Z., 1929, 208, 482—489).—The sulphatase of the mould *Aspergillus oryzae* and that of pig's liver hydrolyse potassium *p*-isobutylphenyl sulphate, giving in both cases *d*-*p*-isobutylphenol, the highest rotation obtained being $[\alpha]_D^{20} +13.3^\circ$. In both cases the portion of the sulphate not attacked was hydrolysed with hydrochloric acid and gave a phenol with the opposite rotation.
P. W. CLUTTERBUCK.

Effect of various substances of the quinine group on the enzymic functions of the organism. XI. Comparison of the influence of potassium, sodium, and quinine chlorides on the peptic digestion of protein. J. A. SMORODINCEV and E. A. SVESCHNIKOVA (Biochem. Z., 1929, 208, 151—163; cf. this vol., 97).—The chlorides of sodium and potassium and quinine hydrochloride in 0.025 molar concentration inhibit the peptic digestion of egg-albumin. Lower concentrations have no effect. The effect of quinine hydrochloride is due to the reduced acidity of the medium which it produces; there is no inhibition when the p_H is kept constant.

J. H. BIRKINSHAW.

Factors influencing tryptic digestion in the intestine. H. J. VONK and H. P. WOLFEKAMP (Z. physiol. Chem., 1929, 182, 175—200).—Since the average p_H of the intestinal contents is about 7 (not 8 as stated in the earlier literature), tryptic digestion does not take place at the optimum reaction (about p_H 8). However, two factors were found either of which would nullify the disadvantage due to the displacement of the p_H . (1) The movement of the intestinal contents. The digestion of fibrin *in vitro* is about twice as fast when the substrate is stirred. (2) The activation of tryptic digestion by the bile (or bile salts). To compensate for a displacement of p_H from 8 to 6 would require only 5% of bile in the intestinal contents. Digestion of peptone is not activated in this way, but here the p_H optimum is very broad.

J. H. BIRKINSHAW.

Formation of urocanic acid in the tryptic digestion of edestin. E. ABDERHALDEN, W. IRION, and H. SICKEL (Z. physiol. Chem., 1929, 182, 201—204).—A small amount of urocanic acid was isolated from the products of a 50 days' tryptic digestion of edestin. This may have arisen by bacterial action, although the usual precautions were taken to avoid contamination.

J. H. BIRKINSHAW.

Enzymatic fission of proline peptides. W. GRASSMANN, H. DYCKERHOFF, and O. VON SCHOENE-BECK (Ber., 1929, 62, [B], 1307—1310).—Prolylglycine and prolylglycylglycine, like the peptides of other amino-acids, are rapidly hydrolysed by the glycerol extracts of intestinal mucous membrane, less readily by pancreas extract or crude yeast autolysate. Solutions of intestinal erepsin, freed from trypsin by adsorption with aluminium hydroxide, decompose both peptides rapidly, frequently at a greater rate than the corresponding leucyl peptides. Unexpectedly, dry, purified preparations of dipeptidase and polypeptidase from yeast or intestine, preparations of pancreas trypsin, yeast proteinase, or activated papain are completely or nearly inactive

towards both peptides. The enzyme responsible for the hydrolysis of prolyl peptides is therefore not identical with any of the previously described peptidases of yeast or intestine.
H. WREN.

Intestinal erepsin. K. LINDERSTROM-LANG (Z. physiol. Chem., 1929, 182, 151—174).—Erepsin from the intestinal mucosa of the pig contains two dipeptidases. For one the optimum p_H is 7.3, it hydrolyses leucylglycine and glycylglycine at about the same rate. The other has optimum p_H 8.1; it hydrolyses leucylglycine some 20 times as fast as glycylglycine. A partial separation can be effected by fractional extraction or adsorption by aluminium hydroxide.

J. H. BIRKINSHAW.

Influence of hydrogen-ion concentration on the inactivation of urease by some heavy metal salts. M. KITAGAWA (J. Biochem. Japan, 1928, 10, 197—205).—In the presence of acetate buffer mixtures the action of urease is partly inhibited at p_H 7.3 by small quantities of zinc ions, but this inhibition becomes less as the p_H is decreased and has almost disappeared at p_H 6.0. Practically complete inhibition of urease activity is effected at p_H 7.0—7.5 by small quantities of cupric or mercuric ions. In the case of cupric ions the inhibition becomes less as the p_H is decreased, but in the case of the mercuric ions it is still almost complete at p_H 6.0. The quantities of sodium chloride, potassium chloride, or potassium iodide necessary to effect appreciable inactivation are considerably greater than those of the heavy metal salts. The inhibiting action of sodium or potassium chloride does not change much when the p_H is varied, whereas that of potassium iodide increases as the p_H decreases.

W. O. KERMACK.

Auxo-substances in the urease reaction. M. KITAGAWA (J. Biochem. Japan, 1928, 9, 347—35).—The activating action of glycine, starch, or fibrin (auxo-substances) on pure urease solutions is apparently due to their removing from combination with the urease some inhibitory substance present even in ordinary distilled water. Treatment of urease solutions by insoluble fibrin followed by removal of the fibrin is sufficient to effect activation. From adsorption experiments with alumina it appears that the activating mechanism does not consist of combination of the enzyme with the activator.

W. O. KERMACK.

[Biochemical factors in] heredity. H. VON EULER, H. HELLSTROM, and D. RUNEHJELM (Z. physiol. Chem., 1929, 182, 205—217).—In the first 6—16 days of germination, the catalase content of chlorophyll-defective and chlorophyll-normal strains of barley representing Mendelian mutants was in the ratio 1:2 to 1:3. No marked difference was observed in the peroxidase action.

J. H. BIRKINSHAW.

Quantitative enzyme studies with respect to Mendelian factors. H. VON EULER and H. NILSSON (Naturwiss., 1929, 17, 289—290).—Studies on the crosses of chlorophyll-defective and chlorophyll-normal barley in respect of the action of catalase for 6—14 days at 18° show that the green is a dominant and the white a recessive Mendelian factor. The green and white barley differ definitely in respect of the action

of catalase and of xanthophyll content. The Mendelian effect has been experimentally detected for the first time for a concentration of enzyme.

R. A. MORTON.

Mechanism of alcoholic fermentation. A. J. KLUYVER (Bull. Soc. chim., 1929, [iv], 45, 311—312; cf. A., 1925, ii, 1173).—A claim for priority over Kostytschev (A., 1926, 756) and others in reply to a statement by Favorski (*ibid.*, 500).

R. BRIGHTMAN.

Interchange of ions between yeast-cells and ammonium chloride solutions. P. GENAUD (Compt. rend., 1929, 188, 1513—1514).—If brewer's yeast is immersed in a solution of ammonium chloride (p_H 7), whilst the concentration of the chloride ion remains unchanged, the initial concentration (n_0) of the ammonium ions decreases to a value n_1 which is approximately independent of the amount of yeast. Simultaneously potassium and calcium ions are found in the ammonium chloride solution, their total concentration being approximately equal to that of the ammonium ions which have disappeared ($n_0 - n_1$), whilst an equal quantity of potassium and calcium disappears from the yeast. These results confirm the conclusions of Devaux (A., 1916, i, 457), the living yeast-cell acting like an insoluble salt of which the anion is always insoluble, but with which a partial and reciprocal interchange of cations with those of the saline solution occurs. The ratio n_1/n_0 is independent of the initial concentration of the saline solution when the interchanging ions are of the same valency, but it increases with concentration when the ion of the saline solution has a lower valency than that of the ion replaced, the equilibrium being governed by the law of mass action. J. W. BAKER.

Species of yeast stable towards boiling. J. RENNING (Ber., 1929, 62, [B], 1267—1270).—Technical "Südwein" yeasts (yeasts which are capable of producing at least 15% of alcohol) or their spores resist the temperature necessary to expel the alcohol formed by them in a sugar solution since fermentation occurs when the residue from the distillation, including the yeast, is mixed with a boiled 20% sugar solution so as to give about a 10% sugar solution, which is covered with a layer of oil. The new fermentation begins after 4—6 days and hence cannot be due to enzymes but must be attributed to the spores, since its incidence occurs after precisely the necessary period of incubation. Under similar conditions, the yield of alcohol by the second fermentation is of the same order of magnitude as by the first. Similar resistant spores appear to be derived from various fruits. H. WREN.

Co-enzyme. H. VON EULER and K. MYRBACK (Naturwiss., 1929, 17, 291—293; cf. this vol., 472).—A stage has been reached in the purification of co-enzyme in which the activity appears to have reached a maximum (0.01 mg. gives a fermentation velocity of 0.8 c.c. carbon dioxide per hour). The preparation appears to consist of an adenine nucleotide a special type. A carbohydrate is present in the molecule and the phosphorus content corresponds with one atom in a mol. wt. of 400—500. Inactivation by means of a pancreas preparation discloses a

33% decrease in activity when the phosphate is set free to the extent of 31%, from which it would seem that the phosphorus is an essential constituent of the co-enzyme molecule. The yeast preparations used in the determination of co-enzyme activity are described. R. A. MORTON.

Growth and fermentative power of wine yeasts at low temperatures. K. KROEMER and KRUMBHOLZ (Landw. Jahrb., 1928, 68, Suppl. I, 445—446; Chem. Zentr., 1929, i, 159).—A selective study of wine yeasts for fermentation at 7—8°.

A. A. ELDRIDGE.

Effect of alcohol and sulphur dioxide on the fermentability of wine yeasts. KRUMBHOLZ and Soós (Landw. Jahrb., 1928, 68, Suppl. I, 451—452; Chem. Zentr., 1929, i, 159).—An examination of wine yeasts for resistance to alcohol and carbon dioxide.

A. A. ELDRIDGE.

Influence of iodine on the growth and metabolism of yeasts. J. E. GREAVES, C. E. ZOBELL, and J. D. GREAVES (J. Bact., 1928, 16, 409—430).—Iodine (1 in 10^6) as the element or combined with sodium, potassium, or calcium accelerates the growth of yeast; iodine appears to be essential for yeast growth. Iodine compounds may possibly be the cause of the phenomena attributed to Wildier's bios.

CHEMICAL ABSTRACTS.

Accelerating action of very small quantities of lanthanum salts on fermentation. C. RICHERT and L. BRAUMANN (Compt. rend., 1929, 188, 1198—1199).—In presence of 10^{-7} to 10^{-8} g. per litre of lanthanum sulphate the production of acid in lactic fermentation after 48 hrs. was increased by about 30%.

R. K. CALLOW.

Enzymes secreted by *Hymenomyces*; alkaloids and the anti-oxygenic function. L. LUTZ (Compt. rend., 1929, 188, 1342—1344).—Alkaloids with free phenol or quinol groups inhibited slightly the oxidation of guaiacol and α -naphthol, and the reduction of methylene-blue, by *Hymenomyces*. Other alkaloids, particularly those with an esterified phenolic group, are inactive in these respects.

E. BOYLAND.

Action of colloidal calcium fluoride and mercurous chloride on *Aspergillus niger*. E. WEDEKIND and E. BRUCH (Biochem. Z., 1929, 208, 279—284).—Calcium fluoride and mercurous chloride in colloidal solution inhibit the growth of *Aspergillus niger*, the latter more strongly than the former. Increasing the concentration especially with calcium fluoride increases the fungicidal action, but the increase is not in proportion to the concentration. Addition of a solution containing calcium fluoride and mercurous chloride in equal proportions gave the same inhibition as the mercurous chloride alone. The inhibition is due solely to the ionised portion of the solutions of these substances.

P. W. CLUTTERBUCK.

Allelocatalytic substances in cultures of *Colpidium colpoda*, Ehrbg. E. GRINWALD (Acta Biol. Exp. Warsaw, 1929, 3, 81—100).—The rate of multiplication of *Colpidium* is greater when a single individual is placed in the same volume of culture medium (1—90 c.mm.) than when several are intro-

duced. The velocity of division is less in small drops ($<12.5 \text{ mm.}^3$) than in large ones; above 12.5 mm.^3 the volume of the culture medium is immaterial. Washing members of depressed cultures with fresh hay infusion does not affect the rate of division. The presence of Robertson's allelocatalyst cannot be demonstrated for the above infusorium, the rate of multiplication of which depends on the nutritive value of the medium, its volume, and its liquid-air interface.

R. TRUSZKOWSKI.

Biological decomposition of pectin. A. G. NORMAN (Ann. Bot., 1929, 43, 233—243).—The rate of decomposition of pectin and its degradation products by various bacteria is determined in suitable media, containing peptone, potassium dihydrogen phosphate, magnesium sulphate, and precipitated chalk. The most convenient concentration of pectin was 1%, and its destruction was followed by determinations of furfuraldehyde and calcium pectate. The former, which is determined as its insoluble phloroglucinol compound, gives the amount of pectin and its degradation products; the latter gives pectin alone. The author considers that, if the two values are close together, the organism in question utilises the degradation products more readily than pectin itself, and if, on the other hand, the difference is large, the organism contains an enzyme which decomposes pectin. *B. carotovorus*, *B. atrosepticus*, *B. solanisaprus*, and *B. subtilis* were shown to contain such an enzyme.

P. G. MARSHALL.

Enzymes in *B. coli communis* which act on fumaric acid. B. WOOLF (Biochem. J.), 1929, 23, 472—482).—*B. coli* contains a considerable quantity of fumarase. In the presence of propyl alcohol the same equilibrium between fumaric acid and *l*-malic acid is attained as that given by muscle-fumarase. In the absence of inhibitors such as propyl alcohol the action of this enzyme is masked by an irreversible anaerobic destruction of malic acid. The equilibrium between aspartic acid, fumaric acid, and ammonia (cf. Quastel and Woolf, A., 1926, 868) is really a complex malic-fumaric-aspartic acid equilibrium. When the fumarase of the organism is destroyed by treating it with cyclohexanol the true aspartic-fumaric acid equilibrium is obtained. The change of fumaric acid to aspartic acid is catalysed by a distinct enzyme for which the name *aspartase* is suggested.

S. S. ZILVA.

Participation of micro-organisms in the dissolution of insoluble phosphates. K. DREWES (Zentr. Bakt. Par., 1928, II, 76, 102—113; Chem. Zentr., 1929, i, 432).—*Bacillus coli aerogenes*, *B. amylobacter*, *B. prodigiosus*, *Torula*, and *Penicillium* are most active in dissolving tricalcium phosphate. The quantity of phosphoric acid dissolved is parallel with that of the acid formed by the organism from dextrose.

A. A. ELDRIDGE.

Diphtheria toxin. Biological and chemical analysis. A. LEULIER, P. SEDALLIAN, and (MME.) CLAVEL (Bull. Soc. Chim. biol., 1929, 11, 413—436).—Diphtheria toxin is precipitated as an amorphous substance from filtered Martin's broth at p_H 4.7. Rapid centrifuging within 4 hrs. of precipitation enables a toxin to be obtained possessing 95—100%

of its original toxicity. It can be dissolved in slightly alkaline solutions and from its phosphorus content is considered to be of the nucleoprotein type. Pepsin causes incomplete decomposition. Dialysis of the toxin removes the inorganic salts and destroys the toxicity. After 2 days' growth the amount of toxin produced is strictly proportional to the weight of the bacteria, up to 6 days' growth. Formaldehyde at 37° causes inactivation of the toxin, whether it is dissolved in a faintly alkaline solution, in peptone solution, in aqueous gelatin solution, or in Martin's broth.

C. C. N. VASS.

Purification of vaccine virus by adsorption on kaolin. H. YAO and H. KASAI (Proc. Imp. Acad. Tokyo, 1929, 5, 179—181).—Vaccine virus was purified by adsorption on kaolin in slightly acid solution. The sediment containing the virus is washed with distilled water, suspended in 0.04*N*-ammonia, shaken for 10 min., and centrifuged. The supernatant fluid which contains the virus is neutralised to phenolphthalein with acetic acid and the preparation made up to its original volume. The resultant preparation when concentrated gives a weak biuret, but no Molisch, reaction.

F. C. HARPOLD.

Interrelationship between hormones and immune bodies. Y. TOKUMITSU (Acta Med. Keijo, 1929, 12, 34—50).—Immunised rabbits at the stage of constant immune titre were injected intravenously with hormones, kidney extract, muscle extract, bovine serum, peptone, pilocarpine, and physiological salt solution, and the variation of the agglutinin titre was recorded during 24—48 hrs. after the injection. Increase of the agglutinin titre was observed with the extracts of the suprarenal cortex, testicle, thyroid, liver, ovary, corpus luteum, and insulin, whilst adrenaline, thymus, pituitary, parathyroid, and renal extract showed a decrease. Injection of pilocarpine always gave a temporary increase even on removal of endocrine organs. The effect on the agglutinin titre of the extirpation of endocrine organs either singly or in various combinations, or their transplantation, or the blockade of the reticulo-endothelial system, in injected animal was measured. The decrease in agglutinin titre caused by peptone and also by the renal extract was shown to be non-hormonal by extirpation experiments. Muscle extract, bovine serum, and physiological salt solution caused no variation in agglutinin titre.

C. C. N. VASS.

Heart hormone. G. KATZ and E. LEIBENSON (Compt. rend. Soc. Biol., 1928, 99, 695—696; Chem. Zentr., 1929, i, 96).—An active solution was obtained by emulsifying mixed alcoholic and aqueous extracts of secretory glands, heart, blood-vessels, liver, and kidneys with physiological salt solution.

A. A. ELDRIDGE.

Female sexual hormone, Menoformon. X. E. LAQUEUR and S. E. DE JONGH (Klin. Woch., 1928, 7, 1851—1853; Chem. Zentr., 1928, ii, 2480).—Experiments with rabbits and mice are described.

A. A. ELDRIDGE.

Effect of ovarian hormone on the blood-sugar of the normal dog. F. RATHERY, R. KOURILSKY, and S. GIBERT (Compt. rend. Soc. Biol., 1928, 529—532; Chem. Zentr., 1929, i, 96).—In the

fasting dog injection of ovarian hormone causes a rise in blood-sugar. Rise of blood-sugar on oral administration of dextrose is intensified or prolonged if the hormone is simultaneously administered.

A. A. ELDRIDGE.

Action of folliculin on the blood-sugar of de-pancreatized bitches. F. RATHEEY, R. KOURILSKY, and Y. LAURENT (*Compt. rend. Soc. Biol.*, 1928, 99, 679—682; *Chem. Zentr.*, 1929, i, 96).—A considerable rise in blood-sugar follows injection of ovarian hormone.

A. A. ELDRIDGE.

Physiology of the isolated pancreas. I. External secretion. B. GOLDSTEIN (*Z. ges. exp. Med.*, 1928, 61, 694—699; *Chem. Zentr.*, 1928, ii, 2660—2661).—Secretin in large, but not in small, concentrations increased the quantity and enzyme content of the secretion. Pilocarpine was less effective in increasing the amount of secretion, which contained much trypsin.

A. A. ELDRIDGE.

Crystalline insulin. VIII. Isolation of crystalline insulin from fish islets and pig's pancreas. Activity of crystalline insulin. H. JENSEN, O. WINTERSTERNER, and E. M. K. GEILING (*J. Pharm. Exp. Ther.*, 1929, 36, 115—128).—Crystalline insulin from the islets of the cod and pollock is identical in shape, in physiological activity, and in its sulphur and nitrogen content with crystals prepared from bovine insulin. Difficulties have been encountered in the preparation of crystalline pig's insulin, and such material differs in physiological activity and sulphur content from bovine and fish insulin, probably because it is not quite pure. The physiological activity of bovine and fish insulin is about 24 international units per mg.

F. C. HAPFOLD.

Insulin. I. Chemical observations. C. R. HARRINGTON and D. A. SCOTT. II. Physiological assay. K. CULHANE, H. P. MARKS, D. A. SCOTT, and J. W. TREVAN (*Biochem. J.*, 1929, 23, 384—409).—Active crystals were obtained from crude preparations of insulin by a modified Abel's method (A., 1926, 1063) and by a method devised by the authors. In the latter method an acetic acid solution of insulin treated with saponin and ammonia, centrifuged, adjusted to pH 5.6, and the insulin allowed to separate as a micro-crystalline precipitate on keeping. The hamolytic index of saponin is a better indication of its efficiency of promoting crystallisation than is its fothing power. By the use of digitonin active crystals may also be obtained by a procedure similar to the above. Although the addition of butyl alcohol yields a further crop of crystalline material from the saponin-containing mother-liquors the preparation of active crystals by the application of this reagent and of bile salts did not meet with success. Potentially crystalline material inactivated by alkali could not be regenerated or making the reaction acid. Four batches of crystals prepared by the two methods and assayed by four different workers showed no significant difference of activity, which was 23.3 international units per mg.

S. S. ZILVA.

Comparison of the effects of sodium hydrogen carbonate and insulin on the excretion of ketonic substances in the urine of dogs on a water diet. F. MAGNON and E. KNTTHAKIS (*Compt. rend. Soc.*

Biol., 1928, 99, 604—606; *Chem. Zentr.*, 1929, i, 97).—A water diet does not lead to ketosuria in dogs; the β -hydroxybutyric acid is so much reduced that in spite of the appearance of a small amount of acetone the total quantity of ketonic substances falls. Administration of sodium hydrogen carbonate or acetone reduces the elimination of acetone and usually also of β -hydroxybutyric acid.

A. A. ELDRIDGE.

Effect of insulin and synthalin on the glycogen content of the liver and muscle. P. RUBINO, B. VARELA, and I. A. COLLAZO (*Klin. Woch.*, 1928, 7, 2186—2190; *Chem. Zentr.*, 1929, i, 405).—When administered subcutaneously to rabbits, small doses of synthalin prevent the accumulation of glycogen in the liver, and diminish that already present, whilst the glycogen content of muscle is not markedly changed.

A. A. ELDRIDGE.

Effect of thyroid feeding on protein and fat metabolism. B. KOMMERELL (*Biochem. Z.*, 1929, 208, 112—126).—Two fasting experiments were carried out on a dog at an interval of 5 weeks; during the second experiment 5 g. of thyroid-gland powder were administered daily. Thyroid produced a 30.5% increase in the basal metabolism; this was covered by an increase in protein combustion of 31.3% and in fat combustion of 68.7%. Feeding of thyroid during fasting about doubles the nitrogen excretion. Certain improvements in the technique of the Haldane method of gas analysis are described.

J. H. BIRKINSHAW.

Specific dynamic action of meat on animals receiving thyroid gland. F. MEYER (*Biochem. Z.*, 1929, 208, 127—150).—Thyroid preparation administered to dogs considerably lowers the specific dynamic action of a protein diet; the oxidation curve rises more sharply but the level is much lower than normal. The view is held that the specific dynamic calories are placed at the service of the increased metabolism due to thyroid. The specific dynamic action is evidence of a chemical change involving loss of energy in the food materials.

J. H. BIRKINSHAW.

Role of the iodo-components in the thyroxine molecule. B. ZAVADOVSKI, N. RASPOPOVA, T. ROLITSCH, and E. UMANOVA-ZAVADOVSKAJA (*Z. ges. exp. Med.*, 1928, 61, 526—538; *Chem. Zentr.*, 1928, ii, 2662).—Metamorphosis of axolotls is brought about by iodine, which is one eightieth as effective as thyroxine. Di-iodotyrosine had an even smaller effect, and is probably not an intermediate product in the formation of thyroxine from iodine and tyrosine.

A. A. ELDRIDGE.

Antimony trichloride reaction of fish oils. H. VON EULER, M. RYDBOM, and H. HELLSTROM (*Biochem. Z.*, 1929, 208, 73—78).—The vitamin-A content as measured by the antimony trichloride reaction of a 96% alcohol extract of cod-liver oil after removal of the alcohol is greater than that of the extracted oil. The difference between the two is more marked at the second extraction of the same oil. The extract, treated with antimony trichloride, gives an absorption band at 322—317 $m\mu$, maximum 320

J. H. BIRKINSHAW.

Oryzatoxin theory. M. MIURA (*Bull. Inst. Phys. Chem. Res.*, 1929, 8, 311—318).—Using nervous

symptoms, particularly the convulsions and the rapid fall of body temperature, as a criterion of the onset of polyneuritis, and the effect of subsequent vitamin-B administration as a check, a large number of dietetic experiments have been carried out on pigeons, *Uroloncha domestica*, and albino-rats. Typical polyneuritis can be caused by a diet of alcohol-extracted polished rice or alcohol-extracted potato-starch, and can be cured or prevented by administration of vitamin-B. With Simonnet's diet pigeons suffered from convulsions, the onset of which was remarkably delayed in some cases, and death from marasmus was occasioned by removal of fats and alcohol-soluble matter from the diet; the incubation period of polyneuritis in *U. domestica* was similarly affected. Although the addition of a very minute amount of vitamin-B, vitamin-A, irradiated or non-irradiated ergosterol in a vitamin-B-free diet, did not affect the onset of polyneuritis, the possible presence of some specific non-toxic substance (or substances), in alcoholic extract of polished rice, which increases the requirement of vitamin-B, is admitted. The alcoholic extract of polished rice shows slight protein reactions, and contains a little vitamin-B and a large amount of fats; potato-starch extract contains much less vitamin-B. These results are not in agreement with those of Teruuchi on chickens, and the existence of oryzatoxin in alcoholic extract of polished rice is considered unproved. An excessive dosage of irradiated ergosterol is poisonous for *U. domestica*.

C. W. SHOPPEE.

Purification of the antineuritic water-soluble vitamin-B by fractional precipitation. A. DE CUGNAC (Bull. Soc. Chim. biol., 1929, 11, 443—465).—The vitamin-B concentrates obtained by the method of Seidell (A., 1926, 644) from brewer's yeast after absorption on fuller's earth with subsequent liberation by sodium hydroxide and immediate neutralisation with dilute sulphuric or acetic acids were used. Assay of vitamin-B content was carried out on pigeons as described by Seidell. Aqueous solutions of vitamin-B, both "acetate" and "sulphate" concentrates, were precipitated successively with 70%, 80%, 87% alcohol and with acetone. In every experiment the activities of the precipitates, which contained decreasing amounts of inorganic substances, were approximately equal to that of the original product, whereas the residue obtained on removal of the solvents had lost the greater portion of its activity. Acetic acid solutions of the "sulphate" concentrates on successive treatment with acetic acid and ether gave precipitates the activities of which equalled that of the original, but the residue, contrary to the findings of Levine, McCollum, and Simmonds (A., 1922, i, 975), showed no activity. Anhydrous or aqueous ethyl acetate did not dissolve the active constituent of the vitamin-B concentrates, but they dissolved in the cold in pure formic acid, and less readily in dilute formic acid. Treatment of the formic acid solution successively with acetone and ether yielded a white and a brown precipitate of almost equal activity; the residue contained none of the active principle.

C. C. N. VASS.

Water-soluble vitamins and their relation to each other. W. KOLLATH (Arch. exp. Path. Pharm.,

1929, 142, 86—110).—Rats fed on a diet deficient in the vitamins-B die of symptoms which are characteristic of the absence of both the pellagra-preventive and the anti-beriberi factors, whereas when alkaline hæmatin is added to the diet in sufficient quantities the symptoms are those of beriberi only. It therefore appears that alkaline hæmatin can function as the pellagra-preventive factor.

W. O. KERMACK.

Sparing action of fat on the antineuritic vitamin. H. M. EVANS and S. LEFKOVSKY (Science, 1928, 68, 298).—The presence of fat appears to favour the action of the antineuritic vitamin.

L. S. THEOBALD.

Vitamin requirements of nursing young. VI. Anhydraemia of rats suffering from deficiency of vitamin-B. B. SURE, M. C. KIK, and D. J. WALKER (J. Biol. Chem., 1929, 82, 287—306).—A marked concentration of the blood was observed in nursing rats the mothers of which were kept on a diet deficient in the vitamin-B complex.

C. R. HARRINGTON.

Effect of vitamin deficiencies on carbohydrate metabolism. I. Hypoglycæmia associated with anhydraemia in young rats suffering from deficiency of vitamin-B. B. SURE and M. E. SMITH (J. Biol. Chem., 1929, 82, 307—315).—Coincidentally with the anhydraemia already described (cf. preceding abstract) young rats suffering from vitamin-B deficiency develop marked hypoglycæmia; both conditions are immediately relieved by administration of vitamin-B.

C. R. HARRINGTON.

Nutrition. IX. Comparative vitamin-B values of pulses and nuts. R. H. A. PLIMMER, W. H. RAYMOND, and J. LOWNDES (Biochem. J., 1929, 23, 546—557).—Taking the vitamin-B value of dried yeast to be 100, the following are the relative activities: split peas 13, whole dried green peas 13, lentils 13, haricot beans 10, soya beans 13, peanuts 20, ground almonds 10, whole almonds 10, hazel nuts 20, dried chestnuts 10, coconut 0, green coffee less than 13, roasted coffee 0. The tests were carried out on pigeons. More vitamin is required for hatching and rearing of young pigeons than for maintenance.

S. S. ZILVA.

Assay of the antineuritic vitamin-B₁ in which the growth of young rats is used as a criterion. H. CHICK and M. H. ROSCOE (Biochem. J., 1929, 23, 498—503).—The unit is the minimum dose necessary to restore normal growth when growth has failed in a diet deficient only in this vitamin. Vitamin-B₁ is supplied in the basal diet in the form of fresh egg-white or of yeast autoclaved at 120° for 5 hrs. Although by using autoclaved yeast there is a risk of traces of vitamin-B₁ escaping destruction, it is preferable to egg-white, because when the latter is used normal growth is frequently maintained for only a few weeks after weaning; after this period growth is subnormal. This is possibly due to the absence of a third hypothetical dietary factor in the vitamin-B complex.

S. S. ZILVA.

Attempt to separate vitamin-B₂ from vitamin-B₁ in yeast and a comparison of its properties with those of the antineuritic vitamin-B₁. H. CHICK and M. H. ROSCOE (Biochem. J., 1929,

504—513).—About one half to three quarters of the vitamin- B_2 present in the original yeast is carried down in the precipitation with lead acetate at p_H 4.7 in Peter's scheme of fractionation (Kinnersley and Peters, A., 1925, i, 1516; A., 1927, 904). The vitamin- B_2 can be recovered from the lead fraction (maintenance dose = 0.03 g., equivalent to 0.5 g. of the original yeast). This preparation contains more or less vitamin- B_1 depending on the reaction at which precipitation took place and probably on the amount contained in the original yeast. Vitamin- B_2 is insoluble and vitamin- B_1 is soluble in 92 wt.-% alcohol. Concentrated alcohol destroys vitamin- B_2 in the process of fractionation. Both vitamins dialyse freely through cellophan. Ultra-violet light exerts a destructive action on both vitamins, vitamin- B_2 being destroyed at a quicker rate than vitamin- B_1 (cf. Hogan and Hunter, A., 1928, 1059).

S. S. ZILVA.

Distribution of vitamin- B_2 in certain foods. W. R. AYKROYD and M. H. ROSCOE (Biochem. J., 1929, 23, 483—497).—The vitamin- B_2 value of wheat and maize is poor, that of maize being on the whole lower. The vitamin content of germ and bran of wheat is about equal and is lower than that of the endosperm. In maize the germ is not so rich a source, but whole maize is better than maize endosperm. Dried peas have a low vitamin- B_2 content, whilst dried ox liver, yeast, and fresh whole milk are excellent sources of this vitamin. Dried meat and egg yolk are not as good as the preceding substances, but are richer than cereals. The distribution of vitamin- B_2 , Goldberger's "P.P." factor, and the factor preventing black-tongue in dogs is identical. Chick and Roscoe's method (A., 1928, 800) was employed for determining vitamin- B_2 .

S. S. ZILVA.

Effect on vitamin- B_2 of treatment with nitrous acid. H. CHICK (Biochem. J., 1929, 23, 514—516).—Levene's observation (A., 1928, 1405) that the activity of vitamin- B_2 is destroyed by the action of nitrous acid is not confirmed.

S. S. ZILVA.

Antirachitic potency of biosterin. S. HAMANO (Bull. Inst. Phys. Chem. Res., 1929, 8, 293—296).—Albino-rats were made to suffer from rickets after having been fed on Steenbock's diet No. 2965 for 4–5 weeks. The regular daily dose, 0.1, 0.05, 0.01, 0.001 mg., respectively, of biosterin dissolved in linseed oil was given to each rat *per os* for 3 weeks, and then animals were examined by radiograph. Six series of observations on 88 rats showed that a daily dose of 0.01–0.05 mg. of biosterin was necessary to produce healing or curative effects.

C. W. SHOPPEE.

Effects [on animals] of large doses of irradiated ergosterol. J. C. HOYLE and H. BUCKLAND (Biochem. J., 1929, 23, 558—565).—The incorporation of 1% of ergosterol, irradiated in oil, in the diet had no lethal effect on rats subsisting on this diet for a period of more than 50 days. There was a persistent or marked loss in weight and urinary calculi were found *post mortem*. There was also persistent diuresis without any increase in the total phosphate and chloride passed per day and without any significant change in the reaction of the urine. This confirms

Dixon and Hoyle's previous observations (cf. Brit. Med. J., 1928, ii, 832).

S. S. ZILVA.

Growth of rats on fat-free diets. A. J. MCAMIS, W. E. ANDERSON, and L. B. MENDEL (J. Biol. Chem., 1929, 82, 247—262).—Good, but not optimal, growth was obtained in rats kept on a diet freed as far as possible from fat; addition of a small amount of fat produced a definite improvement, but it is not certain whether this was due to the fat as such or to the vitamins associated with it.

C. R. HARRINGTON.

Deficiency disease due to exclusion of fat from the diet. G. O. BURR and M. M. BURR (J. Biol. Chem., 1929, 82, 345—367).—Rats kept on a diet almost completely free from fat, but containing all vitamins except vitamin- E , developed a deficiency disease chiefly characterised by caudal necrosis but involving lesions on other parts of the body also. The condition is relieved by addition of 2% of fatty acids to the diet, but not by addition of glycerol or of the unsaponifiable fraction from cod-liver oil.

C. R. HARRINGTON.

A. Relation between maximum rate of photosynthesis and concentration of chlorophyll. B. Photosynthesis as a function of light intensity and of temperature with different concentrations of chlorophyll. R. EMERSON (J. Gen. Physiol., 1929, 12, 609—622, 623—639).—(A) By growing *Chlorella vulgaris* in media containing various quantities of ferric sulphate, cells were obtained differing in the content of chlorophyll per unit volume of cell. The maximum rate of photosynthesis with suspensions of such cells is a smooth function of the chlorophyll content provided uniform conditions are observed. (B) The depressing effect of hydrogen cyanide on the rate of photosynthesis increases as the chlorophyll content of the cells decreases, but the effect of temperature on the reaction and also the light intensity at which the maximum rate is attained are independent of the chlorophyll content.

W. O. KERMACK.

Energetic metabolism of germination (*Helianthus annuus*). Z. KRASINSKA (Acta Biol. Exp., Warsaw, 1929, 3, 101—141).—Sunflower seeds germinating in the dark at 25° lose during the first 6 days 0.362 g. of fat per g. of dry substance, the original fat content being 58.2%. Over the same period the heat of combustion of 1 g. of dry substance falls from 7330 to 5275 g.-cal., corresponding with a loss of 60% of the calorific value of the fats utilised. The respiratory quotient is 0.523, pointing to the retention of the greater part of the oxygen by the organism. 93% of the energy requirements of the processes of germination are covered by fats, and the remainder by proteins and carbohydrates. About 44% of the fats undergoes complete combustion, 56% being converted into carbohydrates, whence it follows that 23% of the energy supplied by fats is due to the latter reaction and 77% to the former. Respiration attains a maximum on the fourth day of germination, by which day the value of the respiratory quotient has fallen from 0.928 to 0.488, to rise again to 0.644 on the seventh day.

R. TRUSZKOWSKI.

Variations in the intensity of respiration and fermentation in the tissues of peas. L. GENEVOIS

(Compt. rend., 1929, **188**, 1338—1340).—Sterile anaerobic soaking of peas increased their power to ferment; this was reduced by mincing the material. On the other hand, mincing increased the respiration, which could be inhibited with potassium cyanide, without effect on the fermentation. E. BOYLAND.

Respiration and geotropism in *Vicia faba*. I. A. E. NAVEZ (J. Gen. Physiol., 1929, **12**, 641—667).—The rate of excretion of carbon dioxide by a single seedling of *Vicia faba* (brown Windsor bean) is constant over a considerable range of time provided the temperature and other conditions remain uniform. When the seedling is rotated so as to excite the geotropic response an increase in the rate of excretion of carbon dioxide occurs which is a measure of the geotropic activity. Observations have been made on the basic rate of respiration as well as on the geotropic response at various temperatures.

W. O. KERMACK.

Changes in chemical composition of pears stored at different temperatures (with special reference to pectic changes). A. M. EMMETT (Ann. Bot., 1929, **43**, 269—307).—Determinations of total pectic substances, and acidity, viscosity, and pectic substances of the juice of Conference pears were made on pears stored at 12° and 1°. In a further series of experiments at 4°, 5°, and 1° the same determinations were made together with the following determinations: (a) hardness of fruit, (b) dry weight, (c) residue after alcoholic extraction, (d) total sugars, (e) reducing sugars, (f) acidity, and (g) specific gravity of juice.

Carre's method of determination of pectic compounds was used, whilst the pectin plus protopectin were determined by the calcium pectate method after extraction of the pulp with *N*/75-hydrochloric acid. It was found necessary, for the determination of soluble pectin, to centrifuge the extracts, as otherwise results nearly 100% too high were obtained. Pectin of the juice was determined as calcium pectate, and its viscosity was measured by the Ostwald method at 25°. The alcohol-insoluble residue was determined by extraction with 95% alcohol. Archbold's method of determination of the "dry weight" of the juice was employed for the later determinations and was more accurate than the high temperature method originally employed. Determinations of sugars were carried out by Evans' methods and of the acidity by titration with *N*/10-sodium hydroxide, using phenolphthalein as indicator. Errors of sampling were estimated on the individual pears and, except in the case of the acidity, errors of weight were found to be not more than 2%. The changes occurring during storage were determined, the loss of weight being due almost entirely to transpiration.

Whereas fruit stored at 5° ripened in 3 weeks, that stored at 1° showed only slight signs of ripening in 6 months as determined by penetration of the skin by methylene-blue. The different rates of ripening at different temperatures were accompanied by differences in the rate of change in pectic content; in nearly all cases, however, the protopectin was converted into soluble pectin according to the exponential law, and the rate of decomposition of the soluble

pectin after the period of full ripeness followed the same law. During the early stages of ripening, the viscosity increased according to the amount of soluble pectin present, but later decreased more rapidly than the soluble pectin disappeared, possibly owing to demethoxylation of the pectin. Evidence was obtained showing that the "hardness" depended on the amount of soluble pectin present.

The inversion of sucrose took place at a greater rate than the utilisation of sugars in respiration. Unsound pears appeared to have a smaller content of all constituents except acid and reducing sugars than sound pears. In pears and apples of low acidity the pectic changes are considered to be controlled mainly by the enzymes present.

P. G. MARSHALL.

Transport of nitrogenous substances in the cotton plant. I. Downward transport of nitrogen in the stem. E. J. MASKELL and T. G. MASON (Ann. Bot., 1929, **43**, 205—231).—A preliminary examination of the variations in total nitrogen content of the tissues of the cotton plant is undertaken using the salicylic-thiosulphate method of determination as modified by Ranker (Ann. Miss. Bot. Gard., 1925, **12**, 367—380). The diurnal variations in total nitrogen of leaf and bark are determined, the results being expressed in most cases as g. of nitrogen per 100 g. residual dry weight (dry weight less total carbohydrates). In the case of the leaf there is a fall in total nitrogen during the night, organic nitrogen being presumably drawn from it during that period. The deviation (expressed as a percentage of the mean) is about 3.9%. In the case of the bark there is no evidence of any real change of nitrogen content.

The effect of ringing the stem is to cause accumulation of nitrogen in the wood and bark above the ring. The transport of nitrates to the leaves is not obstructed, thus showing that they travel by way of the wood and not the bark. Separation of the bark and wood produces no variation in the mean nitrogen content of the bark, thus showing that contact between wood and bark is unnecessary for normal transport of organic nitrogen from leaf to root.

The effect of a constriction (produced by partial removal of the bark) is to reduce the rate of transport, although not in proportion to the cross-sectional area. The increase in rate per unit area is not as great as in the transport of carbohydrate, a fact which suggests variable diffusibility of the nitrogen compounds. The deviation for nitrogen is 36% of the mean rate of transport, compared with 71% for carbohydrate. The bark and wood contain approximately equal amounts of nitrogen, but the wood is more sensitive to changes than the bark (average change is 8.48% of the mean content for the wood and only 4.74% for the bark).

The rate of transport of organic nitrogen compounds downwards is greatly in excess of that due to diffusion.

P. G. MARSHALL.

Influence of a complete [inorganic] fertiliser on the osmotic pressure in cultivated plants. Special action of potassium fertilisers. BLANCHARD and J. CHAUSSIN (Compt. rend., 1929, **188**, 1515—1517).—The effect of a complete inorganic fertiliser on growing oats and beetroot, and of a

potassium fertiliser on wheat, has been investigated by methods similar to those used for wheat (A., 1925, i, 623) grown in the same plot. The results are similar to those previously obtained, the extracts of the various portions of the fertilised plant having a larger proportion of ash of smaller mean mol. wt. than those of the unfertilised plant. The results support the earlier conclusion that the increase in growth promoted by the fertiliser coincides with an increased internal osmotic pressure in the plant, this effect being due largely to the potassium salts in the fertiliser. J. W. BAKER.

Effects on *Pisum sativum* of a lack of calcium in the nutrient solution. D. DAY (Science, 1928, 68, 426—427).—Plants deprived of calcium show less growth, chlorotic lower leaves, and tough curled upper leaves; death occurs in 9—10 weeks. The anatomical structures of stem and root remain practically constant except for a change in elongation. Rapid recovery to normal accompanies the addition of calcium after 5 weeks' growth. Calcium stored in seed is used for early growth. L. S. THEOBALD.

Titanium in phanerogamic plants. G. BERTRAND and C. VORONCA-SPIRT (Compt. rend., 1929, 188, 1199—1202).—The titanium content of a variety of phanerogamic plants, mostly foodstuffs, has been determined after careful removal of dust. All the plants examined have been found to contain titanium up to a maximum of 6 mg. per kg. of fresh material. As in the case of zinc (this vol., 362), the amount of titanium increases, in general, with the chlorophyll content of the part examined. Grains of cereals contain 0.7—1.5 mg. per kg., almost entirely in the husks, whilst leguminous seeds contain about 3 mg. per kg. Reserve material such as the flesh of fruits and potato tubers is poor in titanium. The aerial portions of flowering annuals contain about 1 mg. per kg. R. K. CALLOW.

Tobacco. I. Water in tobacco. N. J. GAVRILOV and B. B. EVSLINA (Biochem. Z., 1929, 208, 79—90).—Water in tobacco was determined by various methods. The methods of Marcusson (distillation in toluene) and of Tausz and Rumm (distillation in tetrachloroethane) gave concordant results somewhat lower than the figure obtained by drying at 95°. Drying in a current of dry air at the ordinary temperature gave results about 30% lower. It is suggested that this method gives the true "hygroscopic water," rest is chemically bound. Zerevitinov's method gives only a small fraction of the "hygroscopic" J. H. BIRKINSHAW.

Effects of the absence of boron and of some other essential elements on the cell and tissue structure of the root tips of *Pisum sativum*. L. SOMMER and H. SOROKIN (Plant Physiol., 1928, 237—254).—Experiments with culture solutions containing or lacking boron, magnesium, sulphur, manganese, potassium, nitrogen, iron, phosphorus, and calcium are described.

CHEMICAL ABSTRACTS.

Effect of boron deficiency on the growth of tobacco plants in aerated and unaerated solutions. J. E. McMURTRY (J. Agric. Res., 1929, 38,

371—380).—Tobacco plants do not develop to maturity in the usual nutrients in the absence of boron. Addition of 0.5 part per million of boron to the culture solutions is sufficient to produce normal growth. In the absence of boron the growth of the stem is restricted and there is a well-marked injury to the bases of the young leaves forming the terminal bud. The improved root development and subsequent top growth due to aeration of the culture solution is not merely the result of mechanical mixing of the nutrient. A. G. POLLARD.

Seeds of *Euphorbia Paralias*, L. P. GILLOT (Bull. Sci. pharmacol., 1928, 35, 561—564; Chem. Zentr., 1929, i, 402).—The seeds contained: water 7.08, fat 38.05, protein 22.43, sugar 2.58, mineral substances 5.39, cellulose 24.47%. The oil showed an absorption band at 675 μ , complete absorption below 520 μ ; $\alpha + 4^\circ 30'$, $d_{20}^{25} 0.9368$, $n_D^{25} 1.4819$, $n_D^{15} 1.4845$; Crismer value 62° , f. p. -25° ; Chemical constants of the oil are recorded. A. A. ELDRIDGE.

Water-soluble phosphatide and the Nadi oxidase reactions. M. GUTSTEIN (Biochem. Z., 1929, 207, 177—185).—The water-soluble iron-free phosphatide prepared from peas and from yeast according to the method of Cranner (cf. Grafe and Magistris, A., 1926, 1280) in amounts as small as 0.00004 g. gives a positive oxidase reaction *in vitro* and also reduces dyes and permanganate, being, in these respects, twenty times as active as an equal weight of yeast. The oxidase action, which is entirely specific, is not inhibited by heat or by cyanide. W. MCCARTNEY.

Composition of spinach fat. J. H. SPEER, E. C. WISE, and M. C. HART. **Unsaponifiable fraction of spinach fat.** F. W. HEYL, E. C. WISE, and J. H. SPEER (J. Biol. Chem., 1929, 82, 105—110, 111—116).—From 68 kg. of spinach there were obtained 550 g. of fatty acids of which 47% were present in the form of neutral fat. The solid acids, forming a small proportion of the total, consisted of palmitic and stearic acids with a small amount of cerotic acid. The liquid fraction contained 12.7% of linolenic, 34.7% of linoleic, and 26.3% of oleic acids; volatile acids were practically absent. The unsaponifiable fraction of the spinach fat yielded a hydrocarbon, $C_{20}H_{42}$, m. p. 67.5—68.5°, a sterol, $C_{27}H_{46}O \cdot H_2O$, m. p. 165—167°, $[\alpha]_D^{25} + 1.7^\circ$ in chloroform, two alcohols, (a) $C_{22}H_{46}O$, m. p. 76—77°, (b) $C_{24}H_{50}O_2$, m. p. 87—88°, and an unsaturated compound, $C_{27}H_{54}O$, b. p. 172—188°/0.85 mm., which gave a dibromide. C. R. HARRINGTON.

Seed fats of the Umbelliferae. II. Seed fats of some cultivated species. B. C. CHRISTIAN and T. P. HILDITCH (Biochem. J., 1929, 23, 327—338; cf. A., 1928, 560, 1059).—The seeds of fennel (*Foeniculum capillaceum*, Gilib.), carrot (*Daucus Carota*, Linn.), coriander (*Coriandrum sativum*, Linn.), celery (*Apium graveolens*, Linn.), parsnip (*Pastinaca sativa*, Linn.), chervil (*Chaerophyllum sativum*, Gartn.), and caraway (*Carum Carvi*, Linn.) have been examined and it has been found that Δ^6 -octadecenoic (petroselinic) acid is present in quantity in all cases. The other components of the mixed fatty acids are palmitic acid in small quantity (1—8%) together

with Δ^9 -octadecenoic (oleic) acid and linoleic acid in somewhat varying proportions. The fatty oils are accompanied in all cases by considerable amounts of unsaponifiable and resinous matter. S. S. ZILVA.

Sterols from vegetables. M. SUMI (Bull. Inst. Phys. Chem. Res., 1929, 8, 228—233).—Sitosterol has been isolated from *Enteromorpha compressa*, *Cytophyllus fusiforme*, Harv., *Digena simplex*, C., *Osmunda regalis*, L., spores of *Lycopodium clavatum*, pollen of *Typha japonica*, Miq., seeds of *Ginkgo biloba*, L., and oil of rice-bran. Stigmasterol was not obtained in any case. The uncrystallisable portion of the unsaponifiable matter from the first three, after precipitation with digitonin, has antirachitic properties. H. BURTON.

Pine-wood lignin. E. HAGGLUND and H. URBAN (Biochem. Z., 1929, 207, 1—7).—Lignin obtained from resin-free pine wood by the action, for a short time, of hydrochloric acid still contains carbohydrates which can be removed without damage to the material by boiling for 1—2 days with 4—5% mineral acid. Continued hydrolysis with such acid and with periodical washing out of the lignin produces gradual rise of the methoxyl content to 17% without important loss of material. Simultaneously the amount of formaldehyde which can be eliminated by the Tollens method falls to 0.4%. Lignosulphonic acids, according to the method of preparation, give, in the Tollens distillations, varying amounts of substances which condense with barbituric acid. In these distillations no formaldehyde is eliminated from naphthylamine compounds, from lignin produced by the action of amyl or propyl alcohol containing 0.4—0.5% of hydrogen chloride on wood or on lignin prepared by the hydrochloric acid method, or from lignin derived from the action of glacial acetic acid containing 0.4% of hydrogen chloride on lignin. Piperonylic acid yields no formaldehyde when treated with amyl alcohol or glacial acetic acid under the conditions used in the preparation of lignin. Paraformaldehyde, when boiled with amyl alcohol and hydrogen chloride is converted into diamylmethylal. W. MCCARTNEY.

Nature of the sugars in liquorice root (*Glycyrrhiza glabra*). A. GIAMMONA (Annali Chim. Appl., 1929, 19, 110—127).—Fresh liquorice root contains 1.38% of dextrose and 3.183% of sucrose, the same root, air-dried and after 3 months, containing 2.373% and 5.40%, respectively, of these sugars. Thus, the dextrose of the fresh root is co-existent with the sucrose, which does not undergo scission during its natural drying. Possibly, as in the barley embryo, dextrose is converted into sucrose by enzyme action. T. H. POPE.

Preparation of gentianose from gentian root dried in the air without fermentation. M. BRIDEL and M. DESMAREST (J. Pharm. Chim., 1929, [viii], 9, 465—479).—By the authors' percolation process (cf. B., 1928, 491) 95–95% of the total gentianose is extracted by 90% alcohol and 36.5% by 95% alcohol from air-dried gentian powder containing 24% of gentianose. Cold percolation gives supersaturated solutions from which the gentianose crystallises on keeping. This may be due to the presence of

an unstable complex in the root which is more soluble than the gentianose and on decomposition the gentianose crystallises. By this method 5 g. of pure gentianose can be easily extracted from 100 g. of dry gentian powder. E. H. SHARPLES.

Nature of the carbohydrates found in the Jerusalem artichoke. A. C. THAYSEN, W. E. BAKES, and B. M. GREEN (Biochem. J., 1929, 23, 444—455).—Autumn-gathered tubers and the unripe pith of the Jerusalem artichoke contain considerable proportions of an insoluble non-fermentable carbohydrate apparently identical with inulin. This carbohydrate disappears almost completely from the tubers towards the spring with the formation of the more soluble carbohydrates which are already present in the autumn tubers. At the same time there is an increase in the dextrorotatory compounds, part of this being most probably due to the formation of sucrose. Comparatively mild autoclaving without acid hydrolysis renders inulin fermentable. The observation that inulin may be fermented by yeast when present in a solution of already fermenting carbohydrates has been confirmed. S. S. ZILVA.

Sweetening components of astringent "kaki" (varieties of *Dispyros Kaki*, L.). M. IWATA (Bull. Inst. Phys. Chem. Res., 1929, 8, 220—222).—*d*-Mannitol is shown to be a constituent of "kaki," in addition to dextrose, levulose, sucrose, and a small amount of pentose. H. BURTON.

Carrageen (*Chondrus Crispus*). IV. The hydrolysis of carrageen mucilage. P. HAAS and B. RUSSELL-WELLS (Biochem. J., 1929, 23, 425—429).—The loss of gelatinising power resulting from mild hydrolysis of carrageen is not accompanied by production of free sugars although reducing properties are developed. The products of hydrolysis contain two etheral sulphates. One of these is retained in dialysis and possesses reducing properties, the other dialyses and does not reduce. Alkaline hydrolysis of an aqueous extract breaks down completely the carbohydrate complex. Quantitative separation of the sulphate could not be effected by this means. Carrageen mucilage contains dextrose. S. S. ZILVA.

Chemical constitution of the gums. I. Nature of gum arabic and the biochemical classification of the gums. A. G. NORMAN (Biochem. J., 1929, 23, 524—535).—The acid group of gum arabic is the "uronic" type. The presence of galactose and arabinose as the only sugars in the molecule is confirmed and analytical figures for these are given for the untreated gum and for its products of hydrolysis. Gum arabic is not a substance of definite empirical formula. It is most probably composed of a nucleic acid consisting of galactose and a uronic acid, probably galacturonic acid, to which is attached arabinose by glucosidic linking. S. S. ZILVA.

Properties of laminarin from *Laminaria*. H. COLIN and P. RICARD (Compt. rend., 1929, 28, 1449—1451).—The isolation of laminarin (cf. K., 1915, i, 931). $[\alpha]_D -11.5^\circ$ (solubility 21 g. 100 g. of water at 15°; 16.5 g./100 g. 60% alcohol) (optical data by GAUDEYBOY) from *Laminaria flexilis*.

successive precipitation with alcohol from the aqueous extract previously boiled with barium hydroxide and purified by means of lead, is described (yield, 400 g. from 38 kg.). On hydrolysis, in confirmation of earlier results, it yields only dextrose in almost quantitative yield in accordance with the equation $(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$, cryoscopic measurements showing that $n=6$ or 7. J. W. BAKER.

Variation of colour of plants during desiccation. Glucoside of *Lathraea clandestina*, L., is aucubin. M. BRIDEL (Compt. rend., 1929, 188, 1182—1184).—The crystalline glucoside extracted by 86% alcohol from *L. clandestina* L. (yield, 1.66 g. per kg. fresh plant), is not, contrary to the conclusion of Goris (A., 1924, i, 815), meliatin, but is proved by direct comparison of its crystalline form, optical rotation, reducing power, and quantitative enzymolysis to be identical with aucubin isolated from *Aucuba japonica*, L. (A., 1921, i, 840).

J. W. BAKER.

Presence of monotropitin in *Gaultheria procumbens*, L., after drying. M. BRIDEL and S. GRILLON (Bull. Soc. Chim. biol., 1929, 11, 466—474).—See this vol., 613.

Methyl salicylate glucoside of *Gaultheria procumbens*, L., identical with monotropitin. M. BRIDEL and S. GRILLON (J. Pharm. Chim., 1929, viii], 9, 5—16).—See A., 1928, 1224.

Constituents of corn-cockle seed. II. Githagenin and githagenic acid. E. WEDEKIND and W. SCHICKE (Z. physiol. Chem., 1929, 182, 72—81; cf. A., 1926, 882).—The acid obtained by chromic acid oxidation of githagenin in glacial acetic acid and formulated as $C_{28}H_{42}O_5$ is now, from an analysis of its methyl ester, m. p. 206—207° [dioxime, m. p. 200° (decomp.)], shown to be $C_{29}H_{42}O_6$, a diketo-monobasic acid containing a lactone ring. Pure githagenin can be sublimed at 0.01 mm. at temperatures below 260° and is now formulated as $C_{29}H_{44}O_4$, a hydroxy-ketolactone. C. C. N. VASS.

Reproductive organs of plants. III. Constituents of the pollen-grains of the sugar-beet. A. KIESEL and B. RUBIN (Z. physiol. Chem., 1929, 182, 241—250; cf. A., 1926, 440).—A quantitative analysis of pollen grains from the sugar-beet gave figures differing considerably from analyses made some years ago. The ether extract yielded 5.38% "crude fat" which contained phosphorus equivalent to 12.6% of lecithin and about 30% of a hydrocarbon corresponding closely with heptacosane. The alcohol extract following the ether extraction was treated with light petroleum and gave 5.54% of a material containing 40% of lecithin. The phosphotungstic acid precipitate of the aqueous extract of the residue gave adenine and betaine (0.04% and 2.96% on original pollen) and traces of choline.

J. H. BIRKINSHAW.

Alkaloidal constituent of *Artabotrys suaveolens*, Blume. J. M. MARANON (Philippine J. Sci., 1929, 8, 259—265).—A physiologically active alkaloid, *arbotrine*, $C_{36}H_{55}NO_6$, m. p. 187°, was isolated from an extract of the bark of the stem and root of *A. suaveolens*. The alkaloid is soluble in chloroform,

alcohol, ether, and acetone; it is precipitated by the usual alkaloid reagents, and gives colour reactions with nitric acid and Froehde's reagent.

B. W. ANDERSON.

Histology and microchemistry of the bark and leaf of *Artabotrys suaveolens*, Blume. J. K. SANTOS (Philippine J. Sci., 1929, 38, 269—280).—A detailed description of the structure of *A. suaveolens* is given. Microchemical tests with gold chloride, palladium chloride, and other reagents showed that the alkaloid is located in the bark of the stem and root, and is absent from the wood and leaf.

B. W. ANDERSON.

Glutelins. V. Glutelins of rye (*Secale cereale*) and of barley (*Hordeum vulgare*). F. A. CSONKA and D. B. JONES (J. Biol. Chem., 1929, 82, 17—21).—Rye and barley flour respectively were extracted with 50% alcohol containing 0.2% of sodium hydroxide, and the filtered solutions adjusted to pH 6.8 with hydrochloric acid; after subjection to a second similar treatment the precipitated proteins were dissolved in 0.2% aqueous sodium hydroxide and treated with ammonium sulphate; the rye extract yielded a single glutelin and the barley extract an α -glutelin precipitating at 1—3% saturation with ammonium sulphate followed by a β -glutelin at 18% saturation. Figures are given for the nitrogen distribution of the rye glutelin and of the α -glutelin from barley, both of which resemble the α -glutelin of wheat.

C. R. HARRINGTON.

Symbiotic fungi of cereal seeds and their relation to cereal proteins. S. L. JODIDI and J. PEKLO (J. Agric. Res., 1929, 38, 69—91).—A prolamine has been isolated both from English ryegrass and from the symbiotic fungus identified as "smuts" which occurs on it. The percentages of prolamine-nitrogen in the seed are 0.52 and 28.35 of the dry weight and total nitrogen, respectively. The corresponding percentages in the fungi are 0.43 and 9.51, respectively.

E. A. LUNT.

Method for making aceto-carminc smears permanent. B. MCCLINTOCK (Stain Tech., 1929, 4, 53—56).—Anthers are placed in a mixture of 1 part acetic acid and 3 parts alcohol. The contents of the anther are squeezed out on a slide in a drop of Belling's iron-aceto-carminc solution and a cover-slip is placed over the drop. The slide is heated for a second in a flame, this is repeated four or five times. The slide is then placed in 10% acetic acid and the cover-slip removed. The slide and the cover-slip are then passed through the following liquids: 1 part acetic acid+1 part alcohol; 1 part acetic acid+3 parts alcohol; 1 part acetic acid+9 parts alcohol; absolute alcohol; 1 part xylene+1 part alcohol. The cover-slip is then replaced on the slide in xylene-balsam.

H. W. DUDLEY.

Staining fungal mycelium in wood sections. K. ST. G. CARTWRIGHT (Ann. Bot., 1929, 43, 412—413).—A combination of safranin and picro-aniline-blue was found to be satisfactory for differentiation of the lignified walls and the fungus mycelium which are stained red and blue, respectively.

P. G. MARSHALL.

Effect of partial decay on the alkali solubility of wood. W. G. CAMPBELL and J. BOOTH (Biochem. J., 1929, 23, 566—572).—The effect of partial decay caused by *Trameetes serialis*, Fr., on the wood of Sitka spruce is typical of the "brown rot" type. The effect of partial decay on the alkali solubility of the wood of Sitka is of the same order as that produced in the same species of wood by acid hydrolysis and consequently it should be regarded as an acid hydrolysis. S. S. ZILVA.

Plant hæmagglutinins; the navy bean. V. R. GODDARD and L. B. MENDEL (J. Biol. Chem., 1929, 82, 447—463).—The defatted meal prepared from the navy bean (*Phaseolus communis*) was extracted with 3% sodium chloride solution; the dialysed and filtered extract was salted out with ammonium sulphate and the solution of the precipitate again dialysed and evaporated. The albumin so obtained was non-toxic, and produced agglutination of rabbit's red blood-corpuscles (in 2.5% suspension in 0.89% sodium chloride solution) at a dilution of 1 : 6,000,000. The agglutinating activity was reduced by the presence of traces of egg-albumin and of blood-serum, or by exposure of the protein to dilute hydrochloric acid or to pepsin; it was increased by the presence of sodium chloride. The general behaviour of the plant agglutinin therefore resembles that of agglutinating blood-sera, and suggests that the protein is itself the agglutinating factor. C. R. HARRINGTON.

Acetone as a control substance for respiration and gas analysis apparatus. T. M. CARPENTER, E. L. FOX, and A. F. SEREQUE (J. Biol. Chem., 1929, 82, 335—343).—Acetone is recommended as an alternative to alcohol as a test substance for gas analysis apparatus, and the technique of its employment is described. C. R. HARRINGTON.

Anaerobiosis and the use of alkaline solutions of pyrogallol. H. NICOL (Biochem. J., 1929, 23, 324—326).—A study of the absorption by Rockwell's solution containing pyrogallol of oxygen from commercial oxygen and from the atmosphere with the production of carbon dioxide and carbon monoxide. S. S. ZILVA.

[Dialysis and extraction] apparatus. III. H. J. FUCHS (Biochem. Z., 1929, 207, 405—409).—The apparatus of Gutbier and Ottenstein (A., 1926, 647) is modified for rapid dialysis of physiological solutions. In a second apparatus by attaching a vacuum pump to a Soxhlet extraction apparatus, the extraction is carried out at temperatures below the b. p. of the extraction fluid. P. W. CLUTTERBUCK.

Micro-apparatus for conductivity measurements in small volumes of liquid. I. REMESOV (Biochem. Z., 1929, 207, 66—79).—The apparatus described enables accurate conductivity measurements at constant temperature to be carried out on volumes of liquid (including biological fluids) as small as 0.05 c.c. The method employed is a modification of that of Kohlrausch. W. MCCARTNEY.

Preparation of micro-electrodes for measurement of potential. J. GICKLHORN (Koll.-chem. Beih., 1929, 28, 252—258).—The essential features of micro-electrodes suitable for measurements of electrical potential in biochemical systems are discussed, and a method of preparing such electrodes is given. E. S. HEDGES.

Potential measurements. K. UMRATH (Koll.-chem. Beih., 1929, 28, 245—251).—A discussion of the practical methods of measuring potential as applied to biochemical systems, especially when the potential varies with time. E. S. HEDGES.

Foundations and limitations of biological p_H determinations. F. LEUTHARDT (Koll.-chem. Beih., 1929, 28, 262—280).—Methods of measuring the hydrogen-ion concentration of cells and tissues are summarised and the results discussed in connexion with the influence of neutral salts and of buffer mixtures. E. S. HEDGES.

Dielectric constants. R. FÜRTH (Koll.-chem. Beih., 1929, 28, 322—328).—Theoretical. E. S. HEDGES.

Relations of dielectric constants to physiology. J. GICKLHORN (Koll.-chem. Beih., 1929, 28, 328—332).—Some relations between dielectric constant and other properties of molecular and colloidal solutions are summarised. E. S. HEDGES.

Methods of measuring dielectric constants applicable to biology. R. FÜRTH (Koll.-chem. Beih., 1929, 28, 314—322).—Whereas measurements of dielectric constants are usually carried out on insulating materials, the measurements required in biology are on substances of relatively good electrical conductivity. Only certain methods of measurement are therefore applicable and a description of these methods is given. Results are given for a number of substances present in animal and plant organisms. E. S. HEDGES.

Application of the iodometric method to the determination of small amounts of aldoses. M. MACLEOD and R. ROBISON (Biochem. J., 1929, 23, 517—523).—Satisfactory results are obtained using three to four times the theoretical quantity of iodine with sodium carbonate as the alkali and allowing the oxidation to proceed during 30 min. at 21°. Under these conditions, the oxidation of dextrose is complete, whilst laevulose and sucrose are oxidised only to a very small extent. Values obtained for galactose, maltose, lactose, barium dextrosemonophosphate, barium laevulosemonophosphate, and barium laevulosediphosphate are also given. The extent to which laevulose is oxidised by iodine in presence of excess of sodium hydroxide is much greater than can be explained by the Lobry de Bruyn and van Ekenstein transformation, unless it is assumed that the change from ketose to aldose is largely increased owing to the rapid and continuous removal of the latter by oxidation. S. S. ZILVA.

Determination of halogens in organic substances. W. ROMAN.—See this vol., 713.

BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

AUGUST, 1929.

General, Physical, and Inorganic Chemistry.

Continuous spectrum of the hydrogen atom. P. S. EPSTEIN and M. MUSKAT (Proc. Nat. Acad. Sci., 1929, **15**, 405—411).—Expressions are obtained suitable for numerical calculations of the intensities in the continuous spectrum of atomic hydrogen by means of a new integral representation for the wave function in this special case. The results are applied to the calculation of the absorption spectra of hydrogen beyond the limits of the Balmer and Lyman series, as well as certain limiting values of the absorption.

N. M. BLIGH.

Helium band spectrum. II. S. IMANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 237—252; cf. *ibid.*, 193—209).—The green and orange regions of the helium band spectrum have been photographed in the first order of a 15-ft. concave grating. Two new bands, parhelium $2S(n=1)-3P(n=1)$ and $2S(n=2)-3P(n=2)$, were found and analysed. The band $2S(n=1)-3P(n=0)$ of Weizel and Fichtbauer is completed and the band $2S(n=0)-3P(n=0)$ much extended. Orthohelium $2s(n=2)-5p(n=2)$ were found in the ultra-violet. The Merton-Pilley-Fujioka bands at 4950 and 5350 Å. were re-investigated and are discussed. W. E. DOWNEY.

Band spectrum of helium. W. WEIZEL and E. PESTEL (Naturwiss., 1929, **17**, 390).—A preliminary communication. A series of hitherto unarranged bands has been analysed and arranged in series form.

J. W. SMITH.

Series in the arc spectrum of chlorine. T. L. DE BRUIN and C. C. KIESS (Science, 1928, **68**, 356—357).—The arc spectrum of chlorine from 2300 to 7000 Å. has been photographed, and the new lines are classified as members of the doublet and quadruplet systems. The lowest term 2P arises from the electron configuration s^2p^5 , and other terms which have been established are 2P and 4P arising from $^2s^4p \times 4s$, together with two sets of doublet and quadruplet S, P , and D terms from $s^2p^4 \times 4p$ and $s^2p^4 \times 5p$, respectively. Details will be communicated in a later paper.

L. S. THEOBALD.

Spectrum of doubly-ionised magnesium. J. E. JACK and R. A. SAWYER (Science, 1928, **68**, 306).—The levels of the most stable three configurations of the doubly-ionised magnesium atom, isoelectronic with neon, have been revealed by an investigation of the condensed spark discharge in a vacuum using electrodes of pure magnesium. The relative values of the terms arising from the configurations $2p^6$, $2p^63s$, and $2p^53p$ are tabulated. The ionisation potential of Mg III—Mg IV is 80 ± 2 volts. L. S. THEOBALD.

3 K

Arc spectrum of germanium. K. R. RAO (Proc. Roy Soc., 1929, **A**, 124, 465—477; cf. Rao and Narayan, A., 1928, 929).—Observations of the arc spectrum of germanium have been extended to 1630 Å., and the wave-lengths, intensities, wave-numbers, and classification of the lines from the visible region to 1630 Å. are tabulated. About 50 new lines are recorded. Gartlein's analysis (A., 1928, 679) is slightly modified to bring it into better agreement with that of Cr, Si I, and Sn I. The absolute values of the terms have been calculated. From the largest term, $4p^3P_0=65558.0$, the ionisation potential of Ge I is found to be 8.09 volts, approximately.

L. L. BIRUMSHAW.

Emission lines on the absorption bands of H and K. J. EVERSLED (Month. Not. Roy. Astron. Soc., 1929, **89**, 566—567).—Under favourable conditions close to the limb of the sun four emission lines can be detected near K and H: 1, 3931.54 (0); K 3933.684 (1000); 2, 3934.80 (2); 3, 3967.04 (0); H, 3968.494 (700); 4, 3969.40 X. (3); the figures in parentheses denoting intensity. The values for the emission lines are derived from solar iron lines in the limb spectra and are subject to a small positive correction for limb effect not exceeding 0.002—0.003 Å. The absorption line at 3931.590 (1) in the revised table of Rowland does not appear, nor does the 3967.057 (0) line attributed to Ce⁺. A line at 3969.407 coinciding with emission 4 appears as a very faint absorption line in one of the spectra of the centre of the disc.

R. A. MORTON.

Stark effect in the second order for the Balmer series of hydrogen. H. R. VON TRAUBENBERG and R. GEBAUER (Naturwiss., 1929, **17**, 442—443).—In recent papers (this vol., 224, 734) the authors record deviations from the Schrodinger theory for the higher components of H_γ. The theoretical values have been re-calculated and the discrepancies now disappear.

R. A. MORTON.

Intensities of the Stark effect components of the Balmer series. W. GORDON and R. MINKOVSKI (Naturwiss., 1929, **17**, 368).—Theoretical.

Spectra of Zn II, Cd II, In III, and Sn IV. R. J. LANG (Proc. Nat. Acad. Sci., 1929, **15**, 414—418).—In the spectrum of Zn II six new combinations between known terms are located. In Cd II three new combinations are given, and the 7S term is found. In In III one new multiplet 5P—6D, based on known term values, is given and possible values for the 6P^o terms are obtained. In Sn IV four multiplets

are located, all based on previously known term values. N. M. BLIGH.

Fine structure of the high series doublets of caesium. D. A. JACKSON (*Naturwiss.*, 1929, 17, 364; cf. this vol., 1).—In reply to the criticisms of Filippov and Gross (this vol., 365) it is pointed out that the fine-structure doublets of caesium previously reported were not due to reversal, since by variation of temperature and pressure conditions this spectrum could be obtained in the reversed state.

J. W. SMITH.

[**Fine structure of the high series doublets of caesium.**] A. FILIPPOV and E. GROSS (*Naturwiss.*, 1929, 17, 364).—A reply to Jackson (preceding abstract). J. W. SMITH.

Intensity relations in the spectra of titanium. II. Relative intensities of the stronger multiplets of Ti I. G. R. HARRISON and H. ENGWIGHT (*J. Opt. Soc. Amer.*, 1929, 18, 287—301).—The relative intensities of sixteen of the more important multiplets of the normal titanium spectrum have been measured with a 10-metre concave grating and using a low-tension vacuum arc. The agreement between the relative intensities and those predicted by Kronig's formulæ is best when an effective temperature of 10,000° is assigned to the arc. The data are thought to support the view that the real ultimate of titanium is 3653.49 Å. R. W. LUNT.

Spectrum of trebly-ionised thallium. K. R. RAO (*Proc. Physical Soc.*, 1929, 41, 361—365).—Using Carroll's measurements (cf. A., 1926, 214) of the vacuum spark spectrum of thallium, combinations of the triad of triplet and singlet *F*, *D*, *P* terms of the d^3p configuration of Tl IV with the deeper 3D and 1D of the d^3s state are found and tabulated. The scheme is supported by comparison with similarly constituted spectra. N. M. BLIGH.

Arc spectra in the region 1600—2100 Å. E. W. H. SELWYN (*Proc. Physical Soc.*, 1929, 41, 392—403).—A simple method, taking advantage of the transparency of nitrogen, of photographing ordinary arc spectra down to about 1600 Å. is described. Measurements were made and tabulated, together with the classification of lines between 1600 and 2100 Å., for the elements copper, gold, silver, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, boron, and aluminium. Impurity lines and their origins are also tabulated. A number of lines hitherto unobserved is recorded and additions are made to the analysis of the spectra of Mg I, Be I, and B I. N. M. BLIGH.

Hg II spectrum in the infra-red. E. RASMUSSEN (*Naturwiss.*, 1929, 17, 389—390).—The first spark spectrum of mercury in the near infra-red has been investigated over the range 6000—10,600 Å. The results of Paschen (this vol., 365) have been confirmed and extended, about 100 new lines having been measured and classified. J. W. SMITH.

Structure and significance of the mercury-inert gas bands. O. OLDENBERG (*Z. Physik*, 1929, 55, 1—15; cf. A., 1928, 346).—The fluorescence spectra obtained in mixtures of mercury vapour with argon and krypton show band series in the region

2540—2560 Å. which converge towards the long-wave side. These new bands are attributed to molecules HgA and HgKr. The energy of dissociation of these molecules in the normal state is calculated as 0.025 and 0.035 volt, respectively. It is pointed out, however, that these bands may bear other interpretations.

By correlating the data obtained with previous observations it is found that the lighter the inert gas atom the further does the resonance spectrum extend towards the short-wave side, the limit varying from 2513 Å. with helium to 2532 Å. for xenon. In the case of xenon only a diffuse maximum is observed at 2533 Å., corresponding with the maximum 2529 of HgKr. The previously reported observation that the extinguishing action of argon is strongly increased by heating is now explained as being due to increased pressure of mercury vapour. J. W. SMITH.

Fluorescence bands and heat of dissociation of the mercury molecule. S. MROZOWSKI (*Z. Physik*, 1929, 55, 338—357).—The intensities of the bands in the fluorescence spectrum of mercury vapour, and their dependence on temperature and density of the vapour, are investigated. It is shown that the fluorescence bands are emitted from the excited molecules which collide with atoms of a higher energy level. The effectiveness of the collision increases if the relative kinetic energy increases. Further, both the 3300 Å. and the 4850 Å. fluorescence bands have a common molecular origin, and apparently the first is due to spontaneous emission and the second to collisions of the second kind. The heat of vaporisation of the mercury molecule is derived from the relative change of the absorption coefficients of the bands of the saturated vapour with the temperature. It has the value 11 kg.-cal./mol. The heat of dissociation of the mercury molecule is about 17 kg.-cal./mol. This value agrees with the arrangement of absorption bands for the 2*P* state of the atom. An explanation of the intensity distribution in the mercury bands on the ground of Condon's theory is attempted, and a possible scheme of levels for the mercury molecule is derived. A. J. MEE.

Dependence of the intensity distribution in spectral lines broadened by gas pressure on the nature of the gas employed. R. MINKOVSKI (*Z. Physik*, 1929, 55, 16—27).—At small pressures of foreign gas the intensity distribution in the *D*-lines of sodium agrees with that calculated from the theory of collision damping. With increasing pressure of foreign gas deviations appear; in the case of gases of low mol. wt. such as hydrogen and helium the deviation is greater towards the short-wave side of the line, whilst with heavier molecules such as nitrogen and argon it is more pronounced on the long-wave side. These deviations are accounted for by the combined effect of radiation and collision.

J. W. SMITH.

Effect of gases and vapours on sparking voltage of small tubular electrodes. K. HONDA and K. OTSUKA (*Bull. Inst. Phys. Chem. Tokyo*, 1929, 8, 319—334).—When gases or vapours other than air flow from a jet into the gap between a tubular and a disc electrode, the sparking potential is lower

than when the gas is stationary. The lowering effect increases with the molecular complexity of the gas, except for nitrogen compounds, which are irregular. A theory is advanced to explain the characteristics of glow and striated discharges, according to which the positive ions in the gap are in the molecular state in the glow discharge and in the atomic state in the striated discharge. The theory explains the appearance of pulsations in the striated discharge and leads to the conclusion that the frequency of the pulsations should be expressed by the formula v/g , where v is the velocity of the positive ions and g the length of gap in cm. The calculated values agree well with the observed frequencies. The vapours of anti-knocking materials such as carbon tetrachloride never lower the sparking potential, but always raise it.

E. S. HEDGES.

Absorption of Hertzian waves by ionised gases. H. DANZER (Ann. Physik, 1929, [v], 2, 27—62).—A new sensitive detector for Hertzian waves of any wave-length and resembling the bolometer in principle is described. The absorption and reflexion of wave-lengths near 4 cm. have been studied for intensely ionised neon, argon, nitrogen, hydrogen, oxygen, and air. The time between excitation and the complete disappearance of absorption is considered to correspond with the life period T of the electrons set free in the gases. The following values were obtained: argon, $2 \times 10^{-3} < T < 10^{-1}$; hydrogen, 3×10^{-4} ; nitrogen, 3×10^{-4} ; oxygen, 1×10^{-4} ; air, 1×10^{-4} sec. The experimental results are considered theoretically.

R. A. MORTON.

External photo-electric effects of silver halides and silver sulphide. F. KRUGER and A. BALL (Z. Physik, 1929, 55, 28—43).—The external photo-electric effects of silver chloride, bromide, iodide, and sulphide have been measured at different wave-lengths. As the wave-length increases, the magnitude of the effect becomes asymptotic with the wave-length axis, the limiting values at which any effect could be measured being 407 m μ for silver iodide, 332 for silver bromide, and 312 for silver chloride. In each case this point lies at a wave-length rather below the maximum of the internal photo-electric effect, which coincides with the maximum photo-chemical action. It is concluded that in the external photo-electric effect the electron emitted from the surface does known work against an arresting surface film or against electrical forces. Similar observations are made in the case of silver sulphide, for which the absorption head in the infra-red lies at about 1.3 μ and the maximum internal photo-electric effect at 1.3—1.4 μ , whilst the external photo-electric effect can be detected only at 407 m μ .

J. W. SMITH.

Ratio of the mass of the proton to that of the electron. V. ROJANSKY (Nature, 1929, 123, 911—912).—In view of Eddington's conclusion (this vol., 231) that $ch/2\pi e^2 = 136$, it is thought that the relation $M/m = (136)^2/10 = 1849.6$ (observed, approx. 1840) may not be a coincidence.

A. A. ELDRIDGE.

Diffraction of electrons by a copper crystal. H. E. FARNSWORTH (Nature, 1929, 123, 941—942).—The total secondary emission from a single copper crystal has been measured under the same conditions

as the angular distribution of scattered electrons for bombarding potentials between 1 and 150 volts. The curve shows maxima at 3 and 10.5 volts, and several changes in slope between 10.5 and 150 volts. The results are discussed.

A. A. ELDRIDGE.

Scattering of fast electrons by atomic nuclei. N. F. MOTT (Proc. Roy. Soc., 1929, A, 124, 425—442).—Mathematical. A scattering formula is obtained by using the wave equation of Dirac, and it is found that the scattered beam is polarised. A method for detecting the polarisation is discussed.

L. L. BIRCUMSHAW.

Recombination of ions in atmospheric air. I. Investigation of the decay coefficient by Schweidler's method. P. J. NOLAN and C. O'BROLCHAIN (Proc. Roy. Irish Acad., 1929, 38A, 40—48; cf. Schweidler, Wien Ber., 1918, 127, 953; 1919, 128, 947, etc.).—The linear recombination law, $i + iH/E - S$ (i being the current in an ionisation chamber, E the P.D. between the electrodes, S the saturation current, and H the P.D. for $S/2$), for small ions in atmospheric air has been shown to be approximately true. The value of η_2 , the recombination coefficient between charged nuclei and small ions, is not constant; the variation does not appear to be associated with variation in the dust content measured by an Owens dust-counter.

R. A. MORTON.

Recombination of ions in atmospheric air. II. Law of recombination of ions and nuclei. P. J. NOLAN (Proc. Roy. Irish Acad., 1929, 38A, 49—59).—Experiments with air in a closed vessel show that the recombination coefficient between small ions and nuclei increases as the concentration of nuclei decreases. The coefficient varies inversely as the square root of the nucleus concentration. The equation $q - \alpha n^2 + \zeta n(N)^{1/2}$ (n being the number of positive or negative ions per c.c., q the number of pairs of ions formed per c.c. per sec., N the sum of the numbers of the oppositely-charged large ions and the uncharged nuclei, α is given by $dn/dt = q - \alpha n^2$, and the probable value of ζ is 55×10^{-5} cm.^{3/2}/sec.) represents the relation between the rate of production of ions in atmospheric air and the equilibrium concentrations of ions and nuclei. The equation has been tested with good results by measurements of ionic concentrations at different places and of the equilibrium of ionisation over the sea (assuming a nucleus concentration for sea air based on Aitken's observations).

R. A. MORTON.

"Mechanical" ionisation of gases under extreme pressure at any low temperature. W. ANDERSON (Physikal. Z., 1929, 30, 360—364).—Any gas can be ionised at low temperatures by means of pressure alone, provided only that the pressure is sufficiently great (cf. Bridgman, A., 1927, 183; Frenkel, Z. Physik, 1924, 29, 214). Under such conditions atomic hydrogen can be regarded as a mixture of electron-gas and proton-gas. The complete breakdown of ordinary ideas concerning ionisation potentials is demonstrated by calculations based on the ordinary Bohr theory of the hydrogen atom (and not requiring the Bose quantum statistics or the Pauli principle). The behaviour of mechanically ionised hydrogen at 0° Abs. is calculated in terms of density,

pressure, and electron velocity. Eddington's views ("Internal Constitution of the Stars," p. 172) are criticised. The density inside some stars must be extraordinarily great and Eddington's paradoxical result is arrived at by omitting from consideration the possibility of mechanical ionisation.

R. A. MORTON.

New regularities in the series of the elementary ionic radii. V. M. GOLDSCHMIDT (Z. physikal. Chem., 1929, 141, 451—452; cf. this vol., 487).—The attempt by Berkenheim to establish numerical relations between the ionic radii of the elements, or a proportionality between the latter and certain simple whole numbers, on the basis of similar relationships among at. wts., is not justified in view of the fact that these have no simple physical meaning. Neither is it appropriate to make use of ionic radii calculated in this manner to maintain the accuracy of the author's empirical values in preference to those derived by Pauling on the principles of wave mechanics.

F. L. USHER.

Transmission and reflexion of slow-moving electrons by metals. E. RUPP (Naturwiss., 1929, 17, 365).—Characteristic absorption maxima have been found for the transmission of slow-moving electrons (4—40 volts) through thin metallic films, transmitted electrons being here defined as such as pass through the film without considerable loss of velocity. Similar metallic surfaces show maxima at the same voltage for absorption and reflexion, the small differences observed (up to 1 volt) being explained by the difference in the contact potential in the two cases. Calculation of the maximum from known atomic magnitudes has not yet been found possible.

J. W. SMITH.

Dependence of the mobility of ions in air on the relative humidity. E. GRIFFITHS and J. H. AWBERRY (Proc. Physical Soc., 1929, 41, 240—247).—The relationship between relative humidity and the mobility of negative ions in air at atmospheric pressure was examined in order to provide a means of following fairly rapid changes of humidity. The principle of the method was to balance the movement of the ions under an electric field by an opposing air stream of definite humidity, the mobility being deduced from the critical potential required to produce a balance. Ionisation was obtained by a small quantity of polonium on a gauze sheet in the air stream. The relative humidity plotted against potential gradient is approximately linear.

N. M. BLIGH.

Mobility of gaseous ions. A. M. TYNDALL (Proc. Physical Soc., 1929, 41, 248—257).—There is no satisfactory quantitative theory of the motion of an ion through a gaseous medium. The ion may, however, be regarded as a charged core surrounded by a cluster of neutral molecules which may be treated as a dynamic or as a static cluster, as by Langevin (cf. Hasse, A., 1926, 219). The difference between positive and negative mobilities is discussed on these two theories. The effect of vapours with a marked dipole in lowering the mobility of the negative ion is found to be a direct result of the dynamic cluster theory (cf. A., 1926, 877). In pure gases, in absence of polar impurities, many negative ions do

not take on a cluster, but remain in the electronic state. Various explanations of the transformation with age of positive ions from the initial to the final type found by Erikson are discussed.

N. M. BLIGH.

Elastic scattering of electrons in argon and the Ramsauer effect. J. HOLTSMARK (Naturwiss., 1929, 20, 365—366).—The effective target area in argon may be calculated as a function of the velocity of the colliding electrons of the mean potential field if the argon atoms and the polarisation produced by the colliding electron are known. The curve calculated in this way gives values about 15% too high, but the agreement between the actual and predicted positions of the minimum at $0.7\sqrt{\text{volt}}$ and of the maximum at $3.6\sqrt{\text{volt}}$ is good.

R. W. LUNT.

Recombination of gaseous ions. L. B. LOEB (Amer. Electrochem. Soc., May, 1929. Advance copy. 16 pp.).—Previous work is reviewed and preliminary results of unpublished experimental work by Marshall are discussed in relation to the theoretical conclusions of Sommerfeld and the author. It is shown that the recombination is primarily a process of random drifting together of the ions, the attractive forces playing a part only in the last free path or two between the ions. The coefficient of recombination, α , depends on the duration of the ionising X-ray flash period as well as of the recombination period, and apparent variations in α are due to the non-random distribution of ions following their generation in pairs close together. The true value of α for air is probably about 0.9×10^{-6} instead of 1.6×10^{-6} as usually assumed. From a comparison of results with air and argon it is concluded that free electrons play no direct role in the recombination of ions and can act only by first attaching themselves to neutral molecules. With argon this attachment does not occur readily, but negative ions may be formed by attachment of electrons to molecules of an impurity. In such cases the apparent value of α is determined essentially by this rate of ion formation and depends on the molecules of impurity present. The fact that the velocity of thermal agitation determines the recombination prevents satisfactory comparison between theory and observation as to the relative values of α for different gases until the true masses of the ions in a given gas are known, as well as their mean free paths.

H. J. T. ELLINGHAM.

Different magnetic states of an ion. G. FOEX (Amer. Electrochem. Soc., May, 1929. Advance copy. 7 pp.).—Previously determined values of the constant θ in the Weiss equation $\kappa(T-\theta)=C$, where κ is the magnetic susceptibility and C a constant, and of the magnetic moment, μ , for the ferrous and nickelous ions are discussed. For the cobaltous ion varying values of θ and μ are obtained under different conditions and it is concluded that the ion in solution is not the same as the ion in a crystal. The possible nature of these differences is discussed.

H. J. T. ELLINGHAM.

[Optical] concentration determination of atoms and ions. W. DE GROOT (Z. Physik, 1929, 55, 52—55; cf. A., 1928, 1294).—Mathematical. The broadening of emission lines by self-absorption may have quite a

considerable effect on optical concentration measurements. Such complications cause the curve of $\log I/I_0$ against concentration never to reach an inflexion point.
J. W. SMITH.

At. wt. of arsenic. H. KREPELKA (Nature, 1929, 123, 944).—Analysis of arsenic trichloride gives the value 74.937 for the at. wt. of arsenic.

A. A. ELDRIDGE.

At. wt. of nitrogen occluded in fergusonite. H. P. CADY and H. U. BEECHER (Science, 1928, 68, 594—596).—Nitrogen was removed from the crude gas obtained from Norwegian fergusonite by hot metallic calcium, converted into ammonia by careful addition of water, and then absorbed in hydrochloric acid. The chlorine in the ammonium chloride was determined gravimetrically and the at. wt. of the nitrogen calculated to be only 0.02% greater than the value obtained for a control sample of nitrogen from liquid ammonia. The existence of an isotope of nitrogen of at. wt. 15, a possible decomposition product of potassium, is therefore negatived. The crude gas from the fergusonite contained 12.67% He.

L. S. THEOBALD.

At. wts. of terrestrial and meteoric nickel.
III. Analysis of nickelous bromide. G. P. BAXTER and S. ISHIMARU (J. Amer. Chem. Soc., 1929, 51, 1729—1735).—Terrestrial and meteoric nickel have identical isotopic compositions. The value found for the at. wt. of nickel was 58.694.

S. K. TWEEDY.

Fine structure of the magnetic spectrum of α -rays. S. ROSENBLUM (Compt. rend., 1929, 188, 1549—1550; cf. this vol., 738).—An α -ray of radium-A and a new ray (α_1 -ray) were obtained on the same plate as the α -rays of thorium-C, equidistant from the strongest of the latter and having a difference in velocity of about ± 0.003 . With the α -ray of radium-C', slowed down to the extent of 10% by a gold screen, the focalisation method produces a large band with maximum blackening in the middle. Sources of radium-A and radium-C' are conveniently prepared without loss of radon by introducing glass or platinum threads into a capillary tube containing a gaseous mixture rich in radon, and sealed at atmospheric pressure by a column of mercury. An activation yield of 50% is obtained with 500 millicuries of radon.

J. GRANT.

Speed of volatilisation of tungsten in presence of salt vapours. H. ALTERTHUM (Z. tech. Physik, 1928, 9, 285—288; Chem. Zentr., 1929, i, 27).—The volatility of tungsten in a vacuum lamp is increased by spraying the metal with various salts, particularly halogen compounds. Skaupy's view, that with sufficiently volatile addenda reaction takes place in the space between the filament and the wall, as well as at the filament itself, is supported. Interaction at the wall also occurs.

A. A. ELDRIDGE.

Penetrating radiation and de Broglie waves. F. T. HOLMES (Nature, 1929, 123, 943).

Active nitrogen. Z. BAY and W. STEINER (Naturwiss., 1929, 17, 442).—Active nitrogen, apart from the complications arising from the nature of the walls, is not properly described unless the con-

ditions of excitation are accurately specified. Generally, it consists of a mixture of ordinary and metastable (8-volt) nitrogen molecules, with ordinary and metastable (2.37- and 3.56-volt) nitrogen atoms. Its properties are determined by the mixture ratio. The presence of atoms is essential for the afterglow.

R. A. MORTON.

Reflexion of molecular rays by the lattice of a crystal cleavage plane. O. STERN (Naturwiss., 1929, 17, 391).—Improvements have been made on the apparatus previously described (this vol., 490), permitting the rotation of the reflecting plane during the progress of the experiment. Using this modification further experiments have been carried out on the reflexion of molecular streams from hydrogen and helium.

J. W. SMITH.

Paths of charged particles in electric and magnetic fields. W. BARTKY and A. J. DEMPSTER (Physical Rev., 1929, [ii], 33, 1019—1022).

Interpretation of the relativity wave equation for two electrons. N. F. MOTT (Proc. Roy. Soc., 1929, A, 124, 422—425).—Mathematical. Although two times (one for each electron) occur in the relativity wave equation for two electrons, all results of physical importance can be obtained by using one time only, putting $t_1 - t_2$ in the wave equation.

L. L. BIRCUMSHAW.

Collision problem in the wave mechanics. C. G. DARWIN (Proc. Roy. Soc., 1929, A, 124, 375—394).—With the object of determining whether a sharper line of demarcation could be drawn between the particle-like and the wave-like properties of matter, a problem is discussed which is at first sight irreconcilable with a pure wave theory but typical of the behaviour of particles, and it is shown how the correct result does in fact arise naturally from the consideration of waves alone. Certain fundamental questions of the quantum theory are discussed.

L. L. BIRCUMSHAW.

Velocity in Dirac's theory of electrons. V. FOCK (Z. Physik, 1929, 55, 127—140).—Mathematical.

W. E. DOWNEY.

Velocity in quantum mechanics. D. IWANENKO (Z. Physik, 1929, 55, 141—144).—The author comments on the views of Fock (cf. preceding abstract).

W. E. DOWNEY.

Quantity allowing a new classification of atoms. G. FOURNIER (Compt. rend., 1929, 188, 1553—1555).—From a consideration of the α - and β -transformations corresponding with a change in atomic number (N), at. wt. (A), and Harkins' isotopic number ($A - 2N$), it is suggested that an atom may be defined by its "filiation capacity" $U = (3A/4 - N)$ which decreases by unity with the passage from a radioactive atom to its direct descendant by α - or β -emission. U , which is the sum of the α - and β -transformation capacities, i.e., $A/4$ and $(A/2 - N)$, respectively, has the same value for those radioactive atoms produced from the same parent atom, and also for an isotope of zinc and one of krypton. J. GRANT.

Quantum mechanics of the molecule. H. LUDLOFF (Z. Physik, 1929, 55, 304—326).—Mathematical.

A. J. MEE.

Displacement of spectra of praseodymium compounds. V. F. EPHRAIM and P. RAY (Ber., 1929, 62, [B], 1509—1519; cf. A., 1927, 121; 1928, 217).—The displacement of the spectra of praseodymium compounds, previously explained on the basis of the volume factor of the metallic atom, is also interpreted by consideration of the energy relationships of the shared electrons. If a negative atom by attraction of electrons can render strongly positive the atom of a rare-earth metal with which it is combined, the removal of further electrons from its 4_f zone which conditions the absorption spectrum is rendered more difficult and the greater energy required corresponds with the shorter wave-length of the absorbed light. The violet displacement of the spectra of the rare-earths is the more pronounced as the metallic atom becomes more positive relative to its partner. The hypothesis is considered in detail with respect to a large series of praseodymium salts. The following praseodymium compounds are described: anhydrous ammonium nitrate, $(\text{NH}_4)_3\text{Pr}(\text{NO}_3)_5$, decomp. 160° ; nitrate ammonate, $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{NH}_3$; phosphite trihydrate; anhydrous hypophosphite; naphthalene-2-sulphonate pentahydrate; acetylacetonate; succinate pentahydrate, dihydrate, and anhydrous; perchlorate; chlorate; iodate tetrahydrate; periodate, $2\text{Pr}_2\text{O}_3 \cdot 3\text{I}_2\text{O}_7 \cdot 24\text{H}_2\text{O}$; bromide nona-ammonate and sesquiammonate.

H. WREN.

Displacement of spectra of neodymium compounds. F. EPHRAIM and P. RAY (Ber., 1929, 62, [B], 1520—1525).—The displacement of the spectra of neodymium compounds is analogous to that of praseodymium salts, but the spectra are so much more complex that the selection of comparison lines is rendered more difficult. The band at about $430 \text{ m}\mu$ is most suitable. The following observations are new: neodymium fluoride, in reddish-blue and pink varieties which give almost identical spectra, by precipitation of the chloride with hydrofluoric acid; the nitrate, $(\text{NH}_4)_2\text{Nd}(\text{NO}_3)_5 \cdot 4\text{H}_2\text{O}$ (also anhydrous); phosphite, $\text{Nd}_2(\text{HPO}_3)_3 \cdot 4 \cdot 5\text{H}_2\text{O}$; iodide; bromide octa-, hexa-, tri-, and nona-ammonate.

H. WREN.

Lanthanide contraction and spectrum displacement during formation of compounds. Alterations of the samarium spectrum. F. EPHRAIM and P. RAY (Ber., 1929, 62, [B], 1639—1650; cf. preceding abstracts).—The volume of the equivalent ions of the rare-earth metals diminishes with increasing atomic number, so that in the later members the electrons are more firmly retained by the nuclear charge and consequently their displacement towards the acid residue becomes more difficult. Since the displacement of the spectrum in salts of the rare earths is due to change in the energy of the anion of the electrons of the 4_f group with the metallic atom, the effect of the change of anion must be less marked with increasing firmness of retention of the electrons to the nucleus. Observations with samarium salts appear to confirm this conclusion. The spectra of praseodymium and, particularly, of samarium salts are unexpectedly sensitive to external influences. Thus very marked lines in the bromide spectrum are found at about $430 \text{ m}\mu$ which find no analogy in the chloride or other compound and cannot

be regarded as due to displacement of the chloride line. Cooling of samarium sulphate octahydrate from the ordinary temperature to -180° alters the spectrum "almost beyond recognition." Most certain comparison is afforded by use of the lines between 400 and $410 \text{ m}\mu$ and the band in the ultra-violet between 360 and $370 \text{ m}\mu$. The course of the displacement with samarium compounds is very similar to that of praseodymium and neodymium compounds.

The stability of the ammonates of the rare-earth metals may be expected to increase with increasing atomic number. This is fulfilled by samarium chloride decammine, which, unlike the amines of the other rare earths, is stable below 31.5° .

Contrary to Klemm and Rockstroh (this vol., 38) samarium chloride and bromide are colourless or yellowish-white. Samarium iodide nonahydrate has been prepared. The degradation of the amines of samarium chloride and bromide is described in detail.

H. WREN.

New ultra-violet band spectrum of hydrogen chloride. B. A. BRICE and F. A. JENKINS (Nature, 1929, 123, 944).—An extended band system observed in the region 2830 — 3966 \AA . from a low-pressure discharge in hydrogen chloride with platinum electrodes, or a discharge in hydrogen with electrodes carrying silver chloride or cuprous chloride, is probably emitted by the HCl^+ ion. The intensity distribution is unusual.

A. A. ELDRIDGE.

Absorption spectrum and decomposition of hydrogen peroxide by light. H. C. UREY, L. H. DAWSEY, and F. O. RICE (J. Amer. Chem. Soc., 1929, 51, 1371—1383).—The absorption spectrum of hydrogen peroxide in the ultra-violet is continuous, possibly because, as in the case of the alkali and hydrogen halides, the main intensity of absorption lies towards the violet side of a limiting wave-length separating the continuous and discontinuous spectra. The absorption coefficients appear to be the same for hydrogen peroxide in solution and in the gaseous state. The continuous spectrum shows that the molecule is broken up into two parts; the most probable reaction is $\text{H}_2\text{O}_2 + h\nu = \text{OH}(^2P_{1/2}) + \text{OH}(^2P_{3/2})$, indicating that hydrogen peroxide is a pseudohalogen. This is supported by the fact that water bands due to hydroxyl predominate in the emission spectrum of hydrogen peroxide streaming rapidly through a cool discharge tube. Illumination by the zinc spark spectrum causes water bands to appear in the fluorescence of hydrogen peroxide, indicating that under these conditions the molecules $\text{OH}(^2P)$ and $\text{OH}(^2S)$ are formed.

S. K. TWEEDY.

Near infra-red absorption spectra of some aldehydes, ketones, esters, and ethers. J. W. ELLIS (J. Amer. Chem. Soc., 1929, 51, 1384—1394).—Absorption curves for light below 2.5μ are recorded for a series of carbonyl compounds (cf. A., 1928, 1071). The band at 5.8μ due to the carbonyl group exhibits a second overtone at 1.9 — 2μ ; indications of the existence of other overtones up to the fifth were obtained.

S. K. TWEEDY.

Shift in the 1.14μ absorption band of some benzene derivatives. J. BARNES and W. FULWEILER (J. Amer. Chem. Soc., 1929, 51, 1750

1752).—The wave-lengths of the benzene absorption band at 1.14μ are shifted towards higher values with the progressive introduction of methyl groups into the molecule. Absorption curves are given for toluene, *p*-xylene, and mesitylene in the neighbourhood of 1.14μ (cf. A., 1927, 918). S. K. TWEEDY.

Infra-red investigations of molecular structure.

I. Apparatus and technique. C. P. SNOW and A. M. TAYLOR. II. Molecule of nitric oxide. C. P. SNOW, F. I. G. RAWLINS, and E. K. RIDEAL (Proc. Roy. Soc., 1929, A, 124, 442–452, 453–464).—I. Full details are given of the construction and use of a grating spectrometer (a modified form of that used by Slesator and Imes; Astrophys. J., 1919, 50, 251), designed to give dispersion and resolution sufficient to analyse a fine structure with a frequency difference of one or two wave-numbers. The apparatus is efficient from 2 to 6μ , and gives accurate results when used for the determination of absolute coefficients of absorption (cf. Robertson and Fox, A., 1928, 1073).

II. The vibration-rotation band spectrum of nitric oxide proves to be a fundamental, the transition being $n''=0 \rightarrow n'=1$, with a definite *Q* branch with its head at the wave-number 1882.9, and at least 42 rotation bands in each of the *P* and *R* branches. No overtone, which should fall in the region of 2.7μ , has yet been detected. The molecular constants, $I=1.64 \times 10^{-39}$ g.-cm.², $r_0=1.15 \times 10^{-8}$ cm., and $\omega=1882.9$, derived from the separation of the fine-structure bands (3.35 cm.⁻¹), correspond almost exactly with those obtained from electronic band spectral data (cf. Jenkins, Barton, and Mulliken, A., 1927, 916). The presence of a *Q* branch is to be attributed to the gyroscopic motion of the molecule, which is the only common diatomic molecule with an odd number of electrons, and the absence of alternating intensities in bands of low rotational quantum number is also in accordance with theoretical predictions for the gyroscopic diatomic molecule. L. L. BIRCUMSHAW.

Third positive carbon and associated bands.

R. K. ASUNDI (Proc. Roy. Soc., 1929, A, 124, 277–296).—The third positive carbon bands, the 3*A* bands (cf. Duffendack and Fox, A., 1926, 777), and the so-called Wolter spurious bands (Z. wiss. Phot., 1911, 9, 361), now regarded as forming a new system of bands “5*B*’’, have been photographed in the first order of a 21-foot grating. In addition, a second new system consisting of bands degraded towards the red has been photographed under small dispersion. A vibrational analysis of these four systems is given, showing that they all have the same final electronic level and that the initial state of the last system is identical with the new level at $\nu=58927$ found by Hopfield and Birge (A., 1928, 1307). The fine structure analysis of the 0–0 and 0–1 bands of the third positive system is given and the usual molecular constants are evaluated. Each band consists of five sub-bands, each with a *P*, *Q*, and *R* branch; the transition involved is $^5S \rightarrow ^5P$, and for the 3*A* bands it is probably $5P \rightarrow 5P$. L. L. BIRCUMSHAW.

Formation of absorption lines [in stellar spectra]. A. S. EDDINGTON (Month. Not. Roy. Astron. Soc., 1929, 89, 620–636).—Theoretical.

Effect of temperature of radiation on its photographic action. R. A. HOUSTON (Phil. Mag., 1929, 7, [vii], 1139–1143).—Negative results were obtained in attempts to detect differences in the photographic action of radiation of different temperatures on photographic plates of different types.

F. G. TRYHORN.

Raman effect. A. PETRIKALN and J. HOCHBERG (Z. Physikal. Chem., 1929, B, 3, 405; cf. this vol., 741).—A correction for the previously determined wave-lengths of the Raman lines of some compounds is given. The reference line should be 4046.6 \AA . instead of 4358.3 \AA ., and for five compounds it should be 4077.8 \AA .

A. J. MEE.

Importance of Raman spectra in the structure [and linking] problems in organic substances.

A. PETRIKALN (Z. physikal. Chem., 1929, B, 3, 360–366).—From experimental work on 24 organic compounds of various types it is shown that the linking of hydrogen to carbon can be determined from the Raman spectrum of the compound. The presence of a triple nitrogen linking can be found in the same way. It is easy to separate the compounds into two types according as the carbon is linked to the hydrogen by a single or a double linking. In the case of a —C—H linking the wave-length of the Raman lines is $3.25\text{—}3.27 \mu$; for a —C=H linking there are two types: (a) giving a wave-length of $3.32\text{—}3.43 \mu$, and (b) giving a wave-length of $3.48\text{—}3.49 \mu$ for the Raman lines. Compounds with triply-linked nitrogen ($\text{—C}\equiv\text{N}$) give a wave-length of $4.41\text{—}4.48 \mu$. In the case of a compound with a double linking, the binding force of the hydrogen atoms must be greater than one with single linkings. It is supposed that for a triple linking the hydrogen atom would be still more strongly bound. By means of the theory of linear oscillators the binding force and maximum amplitude for single quantum excitation of hydrogen and nitrogen (triply-linked) atoms are calculated. A. J. MEE.

Comparative study of the Raman spectra of some hydrogen compounds. P. DAURE (Compt. rend., 1929, 188, 1492–1494).—Comparison of the Raman spectra of 40 liquids shows that compounds of the type M—H (where M is a metalloid) are characterised only by lines of λ 278–340 mm.⁻¹ (*h*-lines). Compounds containing M—M or C—C linkings may produce lines of 20–196 mm.⁻¹, of which the lines 143–146 and 158–162 mm.⁻¹ (*l*-lines) are characteristic of single and double linkings, respectively. Lines of λ 166–174 mm.⁻¹ obtained in addition to the former type of *l*-lines indicate a $\text{C}\equiv\text{O}$ group.

J. GRANT.

Raman effect in gases. E. L. HILL and E. C. KEMBLE (Proc. Nat. Acad. Sci., 1929, 15, 387–392).—The results of a study of the Raman effect for diatomic molecules in the case of gaseous hydrogen chloride by Wood, and liquid hydrogen by McLennan and McLeod (cf. this vol., 378) are analysed theoretically, and it is shown that they can be interpreted by assuming new selection rules for the rotational quantum number *j*, from $\Delta j = \pm 1$ to $\Delta j = 0, \pm 2$, giving rise to a *Q*, a double *R*-form, and a double *P*-form

branch, respectively. It is shown that this rule can be derived from quantum mechanics. N. M. BLIGH.

Raman effect in acetone. J. W. WILLIAMS and A. HOLLAENDER (Proc. Nat. Acad. Sci., 1929, **15**, 421—423).—The Raman effect indicates a means of detecting compound formation in solution. Photographs for acetone were taken and the wave-lengths of the lines determined, the results tabulated, and their theoretical significance was discussed. The positions of a number of infra-red absorption bands were calculated and shown to correspond, as demanded by theory, with absorption bands observed in investigations of infra-red spectra. N. M. BLIGH.

Intensity of the secondary scattered radiation (Raman lines). C. MANNEBACK (Naturwiss., 1929, **17**, 364—365).—Theoretical. J. W. SMITH.

Raman effect with isomeric organic substances. A. DADIEU and K. W. F. KOHLRAUSCH (Naturwiss., 1929, **17**, 366—367).—The Raman effect has been investigated with series of isomerides and with series of compounds of the same homologous series. Analogy in the spectra is more noticeable in the cases of homologues than with isomerides with different chemical characters. In the case of the xylenes, however, the differences in the relative positions of the methyl groups produce very considerable differences in the spectra. The spectrum of *o*-xylene is very similar to that of toluene. The observations in general agree with the results of infra-red spectroscopy, but the lines which would be anticipated in the region 1800—2800 cm^{-1} do not appear. J. W. SMITH.

Photometric study of the Raman effect. P. DAURE (Compt. rend., 1929, **188**, 1605—1606).—The Raman formula for the ratio of the intensities of the positive and corresponding negative Raman lines produced by the same excitation (the mercury line 4358 Å.) has been confirmed within experimental error for the chlorides of arsenic, phosphorus, and carbon, although the results indicate that the value $N = 6.6 \times 10^{23}$ gives better agreement. Revision of previous results (A., 1928, 813) has led to the conclusion that the intensity of a Raman line of given characteristic frequency is proportional to the fourth power of the exciting frequency, the energy emitted by the Raman effect attaining in certain cases one tenth of that emitted by molecular diffusion. The majority of the characteristic frequencies of cyclohexane coincide with infra-red absorption frequencies (this vol., 865) although the relative intensities differ for the two phenomena. J. GRANT.

Perturbations in band spectra. I. (Miss) J. E. ROSENTHAL and F. A. JENKINS (Proc. Nat. Acad. Sci., 1929, **15**, 381—387).—Curves are given showing the deviations of lines from the regular formula for the *P* branches of the (11, 11) and (12, 12) violet CN bands (cf. A., 1928, 566). The perturbations in the α -S state occur in the normal, instead of as usual in the excited state of the molecule. The observed and calculated frequencies of the Q_1 branch are tabulated in order to detect perturbations. Results are shown to be in accordance with the predictions of Kronig (cf. A., 1928, 1067).

N. M. BLIGH.

Fluorescence spectrum of oxygen. F. RASETTI (Proc. Nat. Acad. Sci., 1929, **15**, 411—414).—The spectrum of the light from a mercury arc scattered by oxygen at atmospheric pressure and photographed with a quartz spectrograph was found to show, on long exposure, a series of doublets extending from the ultra-violet to the visible region. This appears as a fluorescence spectrum, observed for the first time, excited by the resonance line 1849 Å. of mercury. The relationship of the fluorescence spectrum with the known oxygen bands is determined, and reasons are given for regarding it as a transition case between Raman effect and fluorescence. N. M. BLIGH.

Ultra-violet bands of sulphur. J. GILLES (Compt. rend., 1929, **188**, 1607—1608).—A number of unrecorded bands in the ultra-violet spectrum of sulphur vapour (32715—45651), attributed to S_2 molecules, are tabulated (cf. Rosen, A., 1928, 687).

J. GRANT.

Flame fluorescence and the extinction of fluorescence in gas mixtures at high pressure. R. M. BADGER (Z. Physik, 1929, **55**, 56—64).—With the exception of the alkali metals the fluorescence of metal vapours in the Bunsen flame appears to be a general phenomenon. Attempts to produce sensitised fluorescence in the flame were unsuccessful. The extinguishing action of mixtures of nitrogen and hydrogen on the mercury fluorescence at high pressures and low temperatures was found to be qualitatively equal to the sum of the effects of the separate gases. J. W. SMITH.

Electric moments of some substitution products of benzene and diphenyl. A. WEISSBERGER and J. W. WILLIAMS (Z. physikal. Chem., 1929, **B**, 3, 367—376).—The electric moments of a number of *p*-disubstitution products of benzene were found on the basis of Debye's theory, and analogous compounds of diphenyl were tested to see if similar moments were found for these. Two derivatives of benzene and diphenyl were used in addition, in which the substituents were adjacent. The methods employed were those formerly used by Williams and Krichma (A., 1927, 819) and Williams and Weissberger (A., 1928, 1180). Diphenyl, 4:4'-dinitrophenyl, and 4:4'-dichlorodiphenyl have no electric moment. The usual formulae for these compounds will explain this result as well as the arrangements with co-axial, twisted rings. In contrast with these, other *p*-disubstitution products have considerable electric moments. These compounds contain oxygen linkings in which the valency linkings are mutually inclined. Formulae which would explain this are discussed, and some light is thrown on the structure of diphenyl compounds by this method of investigation. A. J. MEE.

Relation between the electric moment and the *P.D.* at an interface. A. FRUMKIN and J. W. WILLIAMS (Proc. Nat. Acad. Sci., 1929, **15**, 400—405).—Electric moments of molecules calculated from *P.D.* data at interfaces are shown to be approximate only, and a number of reasons for this fact are suggested and discussed. The Gans theory being unsound leads to inaccurate values of the electric moments, which can, however, now be determined by a method depending on the Debye modification of the Clausius-

Mosotti relation. It is concluded that in spite of a striking similarity between inferences drawn from electric moment data and interfacial *P.D.* data, any comparisons between the two can be qualitative only.

N. M. BLIGH.

Electric moment of ethylene chloride and ethylidene chloride. P. N. GHOSH, P. C. MAHANTI, and D. N. S. GUPTA (*Z. Physik*, 1929, 54, 711—714).—The permanent dipole moments of ethylene chloride and ethylidene chloride were determined by a null method. The values for the dipole moment obtained were 1.567×10^{-18} c.s.u. for ethylene chloride and 2.045×10^{-18} c.s.u. for ethylidene chloride. The results are discussed with reference to the structure of organic compounds examined previously (cf. Mahanti and Gupta, this vol., 243) and compared with results for methyl iodide, ethyl bromide, ethyl iodide, dichloromethane, and dibromomethane.

J. J. FOX.

Generalisation of stereochemistry. P. GOLDFINGER (*Naturwiss.*, 1929, 17, 388).—It is claimed that the conception of chemical stability as the structures in which the packing is densest (cf. this vol., 870) can be applied to general problems of stereochemistry and explains why only a few of the theoretically possible spacial configurations are experimentally realised. This view also explains such phenomena as steric hindrance and the enantiomorphy of *o*-substituted diphenyl derivatives.

J. W. SMITH.

Chemical combination as an electrostatic phenomenon. VII. A. E. VAN ARKEL and J. H. DE BOER (*Chem. Weekblad*, 1929, 26, 282—286).—The decrease of ionisation potential with increasing atomic volume in the same sub-group, and the relations of these quantities in the main groups of the periodic table, are discussed, and the theoretical work of Born and Grimm is further examined.

S. I. LEVY.

Chemical combination as an electrostatic phenomenon. VIII. A. E. VAN ARKEL and J. H. DE BOER (*Chem. Weekblad*, 1929, 26, 326—330).—A discussion of molecular stability in terms of the electrical properties of atoms.

S. I. LEVY.

Naphthalene ring and Sugden's parachors. III. S. S. BHATNAGAR and B. SINGH (*J. Indian Chem. Soc.*, 1929, 6, 263—266).—The surface tensions of 1-bromonaphthalene, α - and β -naphthols, and α - and β -naphthylamines have been determined by the maximum bubble pressure method. The parachor of the naphthalene ring, calculated from these and previously recorded data, is in better agreement with the value 12.2 (twice the value of the benzene ring) than the previously obtained value 9.2 (*A.*, 1928, 355).

H. BURTON.

Effects of pressure on the properties of matter. P. W. BRIDGMAN (*Proc. Physical Soc.*, 1929, 41, 341—360).—The effects of hydrostatic pressures of the same order of intensity as the atomic or molecular forces themselves is considered in the case of gases, liquids, and solids and illustrated graphically for compressibility, thermal expansion, electrical resistance, thermal conductivity, and thermal *E.M.F.*, and by phase diagrams for change of state. The anomaly of compressibility increasing with increasing pressure

is shown by certain quartz glasses and by the element cerium.

N. M. BLIGH.

X-Ray examination of the system anhydrous sodium sulphate-aluminium sulphate. F. A. STEELE (*Science*, 1928, 68, 156—157).—X-Ray examination of the solid obtained by evaporating equimolecular quantities of sodium and aluminium sulphates to dryness near the b. p. and heating at 400° showed a new diffraction pattern which contained no lines characteristic of the individual constituents. Samples richer in aluminium sulphate showed lines due to this substance superimposed on those of the new compound, *sodium aluminium sulphate*; those richer in sodium sulphate also showed these lines together with some new ones due not to sodium sulphate, but to another new compound containing more sodium sulphate than is represented by the formula $\text{Na}_3\text{Al}(\text{SO}_4)_3$. The position of the pattern due to sodium aluminium sulphate remained unchanged in both cases, eliminating the possibility of the formation of a solid solution.

L. S. THEOBALD.

Soft X-ray emission from various elements after oxidation. L. P. DAVIES (*Proc. Roy. Soc.*, 1929, A, 124, 268—277).—By means of the apparatus previously described (*ibid.*, 1927, A, 115, 280), a study has been made of the effect of oxidation on the total soft X-ray emission from silicon, manganese, iron, cobalt, nickel, copper, molybdenum, palladium, and tungsten. In each case the emission from the oxidised targets was measured before and after bombardment to red heat, and the results are expressed by a series of curves plotting the ratio i_p/i_i against the atomic number of the element at 600, 500, 400, and 300 volts. The effect of oxidation is to level up the efficiencies of the elements, and on the assumption that the oxygen atom simply introduces a common factor into the emitting targets the mean values of i_p/i_i for oxygen are calculated to be 3.61, 3.15, 2.82, and 2.06×10^{-6} at 600, 500, 400, and 300 volts, respectively.

L. L. BIRCUMSHAW.

Analysis by X-ray spectroscopy. C. E. EDDY, T. H. LABY, and A. H. TURNER (*Proc. Roy. Soc.*, 1929, A, 124, 249—268).—X-Ray spectral analysis has the great advantage that it uses a very simple spectrum, the interpretation of which is greatly facilitated by the Moseley relationship. It has the disadvantages that elements of low at. wt. require a vacuum spectrometer, that the excitation of the *K* spectra of elements of high atomic number requires high potentials and highly evacuated X-ray tubes, that the technique is difficult, and the apparatus complicated and expensive. It is believed that these difficulties can be considerably diminished. The possibilities of the method have been investigated, and the results obtained in a systematic analysis of the impurities occurring in several samples of zinc and one of manganese are described. The method is found to be sensitive to amounts as small as 0.0001%—i.e., much more sensitive than was indicated by Noddack, Tacke, and Berg (*A.*, 1925, ii, 939), who showed that impurities amounting to about 0.1% could be detected. It is sufficient for the identification of an element to record the α_2 , α_1 , and β lines

of its *K* spectrum, or about five lines of its *L* spectrum, and the known relative intensities of the lines are an additional aid to identification. The optical method (raies ultimes), on the other hand, is capable of detecting impurities down to 0.001%. In this method the number of observable lines from an element tends to diminish as the proportion of the element diminishes, so that the identification of an element may depend on observations of a couple of lines or even only one line in a crowded spectrum. In comparison with analysis by optical spectroscopy, therefore, the X-ray method has the advantages that it is more sensitive, that the sensitivity is independent of the elements sought and of the impurities present, and that there is greater certainty in identifying the lines observed. The technique of the construction of an X-ray tube and spectrometer to eliminate lines of elements not in the sample under examination is described.

L. L. BIRCUMSEAW.

X-Ray investigation of copper-magnesium alloys. G. GRIME and W. MORRIS-JONES (Phil. Mag., 1929, [vii], 7, 1113—1134).—The structure of eight copper-magnesium alloys has been determined by the powder method. Sahmen's equilibrium diagram (A., 1908, ii, 187) was confirmed generally. Two new regions of solid solution were detected, viz., the α -phase, a solution of magnesium in the copper lattice up to approximately 3% of magnesium, and the β -phase, a range of solution extending not more than 2—3% on either side of the composition represented by Cu_2Mg . The α -phase has a face-centred structure with a base varying from 3.610 Å. in copper to 3.634 Å. at the limit of solution. The β -phase has the face-centred spinel structure with eight molecules in the unit cell and a base increasing with the magnesium content from 7.003 to 7.059 Å. The phase Mg_2Cu possesses a hexagonal lattice of invariable dimensions. The unit cell, with $a = 5.281$ Å., has an axial ratio of 3.464 and contains eight molecules. Sahmen's diagram was verified in all other details. Solid solution was not found at the maximum end of the diagram. The lattice constants of copper and magnesium were found to be respectively, $a = 3.610$ and 3.206 Å., with an axial ratio of 1.624.

The results of this investigation agree with those of Westgren and others (A., 1928, 1175) except in the structure assigned to the phase Mg_2Cu .

F. G. TRYHORN.

Determination of the density and shape of sub-microscopic [standard] substances. G. PLACZEK (Z. Physik, 1929, 55, 81—118).—The behaviour of uncharged metallic particles in heterogeneous electric fields can be used to determine the shape and compact structure of the particles.

W. E. DOWNEY.

Multiple absorption and secondary *K*-absorption limits in the Röntgen region. B. B. RAY (Z. Physik, 1929, 55, 119—126).—The secondary absorption edges observed by Nuttall, Lindsay, and Van Dyke can be quantitatively explained on the assumption that a single quantum of radiation can be simultaneously absorbed by two or more electrons. It is further shown that on the hypothesis of free electrons in metals the fine structure absorption

edges observed by Kossel should not appear, at least in pure metals.

W. E. DOWNEY.

Röntgenographic detection of lattice disturbances in metals. J. HENGSTENBERG and H. MARK (Naturwiss., 1929, 17, 443).—Deformation can be detected by the measurement of the decrease in intensity of Debye-Scherrer lines with increasing angle of deflexion. The intensity ratio of two lines with different angles of deflexion differs for normal and deformed lattices. Taking the ratio J_{200}/J_{400} , the values for rolled tantalum, tungsten, and molybdenum are all definitely greater than for the unworked metals. Strongly hammered molybdenum shows further increase.

R. A. MORTON.

Production of the continuous X-ray spectrum. A. SOMMERFELD (Proc. Nat. Acad. Sci., 1929, 15, 393—400).—The original classical treatment of the angular intensity distribution of the general X-radiation of an anticathode was given when observations with solid anticathodes only were available. Following work on mercury vapour and thin foils, data are now available on the stopping process in the single atom. The conditions under which the classical formulæ hold are examined and a method is considered for treating the production of general X-radiation by wave mechanics. It is shown that the shift of the intensity maximum will be larger for the longer wavelengths of the continuous spectrum than for the short wave-length limit and that this is confirmed by the experiments of Kulenkampff (cf. this vol., 14).

N. M. BUGH.

Polarisation of the tungsten *L* radiations. P. KIRKPATRICK and I. MIYAKE (Proc. Nat. Acad. Sci., 1929, 15, 418—431).—The L_{α_1} , L_{β_1} , and L_{γ_1} radiations of tungsten were examined with an accuracy of 1% by a method using integrated reflected energy measurements, and no polarisation was found for any line.

N. M. BUGH.

Absolute intensity measurements with X-rays. O. GAERTNER (Ann. Physik, 1929, [v], 2, 94—122).—The intensity of filtered radiation (mean wave-length 1.38 Å.) from a tube with a copper anode has been measured by means of an electrically calibrated thermo-element, and compared with the ionisation of gases by the rays. The pressure of gas in the ionisation chamber was so high (for all gases except hydrogen) that the unabsorbing fraction (also measured) was merely a correction factor. The results are expressed in volts per ion-pair: nitrogen, 40.8; air, 36.4; oxygen, 34.4; argon, 29.6. Molybdenum radiation (0.714 Å.) was also used for argon, 29.3 volts per ion-pair being required. Oxygen has a higher saturation potential than nitrogen.

R. A. MORTON.

X-Ray method for determining the size and shape of crystalline ultramicroscopic particles. M. VON LAUE (Sitzungsber. preuss. Akad. Wiss., 1929, 227—228).—The breadth of the rings in Debye-Scherrer photographs can be used to determine the size and shape of ultra-microscopic crystalline particles (cf. Brill, this vol., 746; Hengstenberg and Mark, Z. Krist., 1929, 69, 271).

R. A. MORTON.

Methods for obtaining X-ray spectra of gases. A. BJORKESON (Z. Physik, 1929, 55, 327—377).—

Different methods for the production of the X-ray spectra of gases were investigated. The principle of the methods consists of the collision in a vacuum of cathode rays and a ray from the gas concerned. The first experiments were with sodium. A stream of electrons in an ionisation tube was directed against the opening of a space containing sodium, the whole having been thoroughly outgassed. It was shown that it was possible to obtain X-rays from a gas. In later experiments potassium vapour was used, a tube with a hot cathode being employed. It was possible to photograph the X-ray spectrum of potassium, but there was only one line of measurable intensity, viz., the $K\alpha$ line. Further experiments were carried out with sulphur in an improved apparatus. The photograph of the X-ray spectrum of sulphur had five measurable lines. This was compared with the photograph obtained for copper sulphide. In this case only three lines were obtained, which corresponded with the stronger lines of the sulphur vapour spectrum.

A. J. MEE.

Demonstration of polarisation of X-rays in a Lilienfeld X-ray tube. H. SEEMANN (Z. Physik, 1929, 55, 371—374).—Although the blue light of the Lilienfeld tube which gives a continuous spectrum is practically completely polarised, the major part of the decelerated spectrum is not polarised.

A. J. MEE.

Magnetic and crystallographic investigations. Ferric oxide hydrates. W. H. ALBRECHT (Ber., 1929, 62, [B], 1475—1482; cf. Wedekind and Albrecht, A., 1926, 1196; 1928, 9).—The α -hydrate, identical with goethite, is prepared by oxidation of ferrous hydrogen carbonate solution by (1) hydrogen peroxide, (2) a current of air or oxygen, and (3) prolonged exposure of the solution to air at 37°; substances obtained by method 3 contain ferrous iron. The γ -hydrate, identical with lepidocrocite, is obtained by the oxidation of very dilute ferrous solutions by the equivalent amount of sodium iodate in presence of sodium thiosulphate. Both hydrates are crystalline. The temperature of decomposition of the synthetic hydrates is markedly lower than that of the natural substances. The ratio $H_2O : Fe_2O_3$ is not constant, the water content being usually higher than the theoretical. The magnetic properties show a distinct change with the age of the specimens, whereas determination of water content and Röntgenographic examination indicate stability. Ageing under water causes a diminution of the susceptibility of both hydrates, whereas desiccation at 100° in a current of air diminishes the susceptibility of the α -hydrate but increases greatly that of the γ -hydrate. The natural or synthetic α -hydrate is more stable than the γ -hydrate; dehydration of the α -hydrate affords the α -oxide, whereas the γ -hydrate gives the γ -oxide which passes at a higher temperature into the α -oxide.

H. WREN.

Periodic and spiral forms of crystallisation. E. S. HEDGES (Nature, 1929, 123, 837—838).—Spiral crystal growth has been observed with potassium dichromate solution and camphorsulphonic acid (cf. Hughes, this vol., 495).

A. A. ELDRIDGE.

Crystal structure of nickel films. G. P. THOMSON (Nature, 1929, 123, 912).—Films of nickel deposited by sputtering on rock salt in residual gas or argon exhibit a hexagonal structure, c 4.06, a 2.474 Å., d 8.86, differing from that obtained by Bredig and Allolio (A., 1927, 502) by sputtering in hydrogen.

A. A. ELDRIDGE.

Crystal structure of barium. A. J. KING and G. L. CLARK (J. Amer. Chem. Soc., 1929, 51, 1709—1711).—The structure is a body-centred lattice, each unit cell containing 2 atoms and having an edge of 5.015 ± 0.003 Å. The calculated atomic radius of barium is 2.171 Å.

S. K. TWEEDY.

Connexion between the zig-zag structure of the hydrocarbon chain and the alternations in the properties of odd- and even-numbered chain compounds. A. MÜLLER (Proc. Roy. Soc., 1929, A, 124, 317—321).—X-Ray investigation of a number of carbon chain compounds has shown that the CH_2 groups of the chain molecule lie equally spaced on two parallel rows, the lines between successive centres thus forming a zig-zag (A., 1928, 1176). Whereas in an even-numbered member of a series the lines connecting the two end groups are parallel, this does not hold for the odd members. A number of diagrams are given to show the structural difference between odd and even chain compounds, and the alternations in physical properties (e.g., m. p., molecular volume, and heat of crystallisation of fatty acids, etc.) are readily explained on this basis. Considering molecules in which the two end groups are chemically identical, it is shown that in the actual crystal two molecules should lie along the c axis when the crystal is built up of odd-numbered chains, and only one molecule in a crystal composed of even-numbered chains.

L. L. BIRCHMUNSHAW.

Constitution and density of particles in precipitated smokes. H. P. WALMSLEY (Phil. Mag., 1929, [vii], 7, 1097—1112).—X-Ray analyses have been made by the powder method of the particles electrically precipitated from smokes produced from arcs burning in air between electrodes of various common metals. With the exception of silica particles dispersed from carborundum, the precipitated smokes were found to be crystalline. Readily oxidisable metals gave oxides, whilst gold, silver, and platinum gave metallic smokes. Particles from magnesium, cobalt, nickel, and cadmium arcs were of the simple face-centred cubic monoxides. The dispersion of calcium in the crater of a carbon arc gave calcium monoxide and hydroxide; thallium and chromium gave sesquioxides. Zinc gave the hexagonal monoxide. Other substances may be divided into two classes, those giving more than one substance in the disperse phase (silver, iron, and copper) and those giving polymorphous crystalline modifications (aluminium, arsenic, antimony, lead, and carborundum). Smokes consisting of oxides which are polymorphous usually give the form which is stable at high temperatures. The formation of mixed oxides by copper and iron arcs is attributed to dissociation in the former case, and to low-temperature oxidation in the latter. These results indicate that the formation of the smoke particles is completed at a high temperature and in the immediate neighbourhood of the hot electrodes.

The results for iron are shown to complete the explanation offered by Elihu Thomson of a magneto-optical effect observed with the fume from an iron arc. The densities of the precipitated smoke particles were calculated from the lattice measurements, and shown to be normal. Abnormally low values found by other workers using different methods are attributed to varying modes of aggregation of the particles.

F. G. TRYHORN.

Mesophases (intermediate states of aggregation). I. Nature of mesophases. H. ZOCHER and V. BIRSTEIN (*Z. physikal. Chem.*, 1929, **141**, 413—423).—Theoretical. A general discussion of the nature of states of aggregation. Mesophases occupy an intermediate position between crystals and purely amorphous substances and are characterised by their molecular movements having complete statistical equivalence in certain directions and a definite periodicity in others. The elastic behaviour of nematic and smectic phases (cf. Friedel, A., 1923, ii, 223) is discussed, as well as the X-ray interference patterns to be expected in substances in which there is incomplete symmetry of molecular movement. F. L. USHER.

Space lattice of the trigonal modification of acetamide. O. HASSEL and N. LUZANSKI (*Z. physikal. Chem.*, 1929, **B**, 3, 282—288).—The crystal structure of the trigonal form of acetamide is investigated. The form was obtained by cooling a saturated solution of acetamide in ethyl acetate at 50° to the ordinary temperature over a period of a fortnight. The elementary rhombohedron has an angle of 91° 17'. The length of the edge, r , is 8.05 Å. The number of (CH₃·CO·NH₂) groupings in the crystal is six, and the "calculated molecular weight" of the substance will be three times the value indicated by the formula. The substance is thus polymerised in the sense of the term as used by Weissenberg (cf. this vol., 247). In many organic solvents (but not in water) and in the vapour state, acetamide is known to be associated.

A. J. MEE.

Crystal structure of covellite. H. S. ROBERTS and C. J. KSANDA (*Amer. J. Sci.*, 1929, [v], **17**, 489—503).—X-Ray analyses have been made of covellite from Summitville, Colorado, and of synthetic covellite prepared by prolonged heating of copper and sulphur at 500°. A hexagonal unit cell was deduced; $a=3.802$ Å., $c=16.43$ Å., and $c/a=4.321$. It contains six copper and six sulphur atoms in Wyckoff's special position (d) and (f), and (a) and (e), respectively, of space-group $R\bar{3}m$, where $U_{Ca}=0.093$ and $U_{S}=0.126$. The structure assigned offers a satisfactory explanation for the perfect basal cleavage, and for the possibility of gliding parallel to the base. F. G. TRYHORN.

Possible reflecting planes in cubic crystals. L. W. MCKEEHAN (*Amer. J. Sci.*, 1929, [v], **17**, 548—556).—A table has been constructed giving the indices, hkl , of possible reflecting planes in cubic crystals, for values of $Q=h^2+k^2+l^2$ between 1 and 360. Besides values of Q , $\log(1/Q)$ to five places of decimals, and (hkl), a value is given for z , the relative number of planes of each form in holohedral crystals, and those values of Q^2 are also indicated which remain of account in body-centred, face-centred, and diamond-like arrangements. F. G. TRYHORN.

X-Ray analysis of cathode-deposited platinum in presence of helium. R. SALVIA (*Anal. Fis. Quim.*, 1929, **27**, 285—289).—The X-ray diagram of platinum, deposited in presence of helium, shows the existence of a face-centred cubic lattice. Calculations show that there is insufficient space for the entry of the helium atom into the lattice.

H. F. GILLBE.

Spinel of bivalent cobalt. Cobaltous aluminate, chromite, ferrite, and cobaltite. G. NATTA and L. PASSERINI (*Gazzetta*, 1929, **59**, 280—288).—An X-ray investigation has been made of the compounds of cobaltous oxide with the oxides of tervalent aluminium, chromium, and iron, obtained by calcining one molecule of cobaltous nitrate with two molecules of the nitrate of the corresponding tervalent metal. These compounds are isomorphous with cobaltous cobaltite previously described (Natta and Strada, A., 1928, 1079) and crystallise in the cubic system with a lattice of the spinel type. The following data have been obtained for the four compounds CoAl₂O₄, CoCo₂O₄, CoCr₂O₄, and CoFe₂O₄, respectively: length of unit cell, a , 8.06, 8.06, 8.31, and 8.36 Å.; volume of unit cell, 524, 524, 574, and 584 × 10⁻²⁴ c.c.; d 4.50, 6.11, 5.26, and 5.34; d_{obs} 4.57, 6.07, 5.14, and 5.19. O. J. WALKER.

Stability of atomic space configurations. P. GOLDFINGER (*Naturwiss.*, 1929, **17**, 387).—It is claimed that the relative stabilities of compounds with different spacial configurations can be predicted from a knowledge of the ionic radii involved, those involving the closest packing being supposed to be the most stable. The theory is supported by several examples of analogous compounds. J. W. SMITH.

Examination of the micro-crystals of calcium carbonate in molluscan shells by means of X-rays. III. J. TSUTSUMI (*Mem. Coll. Sci. Kyoto*, 1929, **12**, 199—202).—Shells of a number of Japanese molluscs have been examined by means of X-rays. In the porcelaneous and nacreous layers the calcium carbonate is in the form of aragonite, and in the prismatic layers generally in the form of calcite. The axis of the fibrous arrangement of the micro-crystals is always nearly perpendicular to the surface of the shell, and coincides with the principal axis of calcite or the orthorhombic c axis of aragonite.

C. W. GIBBY.

Crystal faces developed by etching metallic crystals of aluminium and zinc. B. FUJITA (*Mem. Coll. Sci. Kyoto*, 1929, **12**, 159—163).—The crystallographic indices of the crystal faces produced by etching strained samples of aluminium and of zinc have been measured. The facets of the aluminium crystals are (100) and (110), and of the zinc crystals (0001) and (1010).

C. W. GIBBY.

Determination of the edge of the lattice of the compound K₂[PtBr₆]. M. MATHIEU (*Compt. rend.*, 1929, **188**, 1611—1612).—The compounds K₂[PtBr₆] and K₂[PtCl₆] were shown by X-ray methods to have the same crystalline structure, and a for the former (10.35 ± 0.05) was therefore obtainable from that of the latter and from the mean of the differences in $\sin \theta$ for the various planes. There are 4 molecules per unit cell. J. GRANT.

Crystal properties and conditions of crystallisation. A. SMEKAL (Z. Physik, 1929, 55, 289—303).—Crystal properties can be divided into two classes according to whether alteration of the crystal structure through impurities or any other cause leaves the property unchanged or greatly alters it. The former may be called "structure-insensitive" properties, and the latter "structure-sensitive" properties. The "structure-insensitive" properties are governed by the lattice theory of ideal crystals, whereas the others cannot be described by this theory. The "structure-sensitive" properties are wholly or partly "loose-space" properties. "Structure-sensitive" properties are markedly influenced by the conditions of crystallisation, whereas the insensitive are not. The properties of rock salt crystals are taken as examples. Crystals formed from solution, and those formed by the solidification of molten salt at a much higher temperature, show different properties in some respects. Especially is this so with the ionic conductivity of the crystals. The conductivity of crystals from molten salt is almost a thousand times as great as that of crystals deposited from solution. The effect of the crystallisation temperature on the "loose-space" formation is discussed. A. J. MEE.

Distribution of recrystallisation centres in stretched tin strips. P. BECK (Z. Physik, 1929, 55, 374—377).—The distribution of the first recrystallisation centres in stretched quasi-isotropic polycrystalline tin strips was followed. The number of centres agrees with the Luders-Hartmann curve. The consequences of this dependence of the number of centres on the deformation are considered. A. J. MEE.

Property of superconducting metals. J. H. BARTLETT, jun. (Nature, 1929, 123, 869—870).—Polemical against Kapitza (Proc. Roy. Soc., 1929, A, 122, 342). A view which gives a qualitative picture of most of the facts is advanced. A. A. ELDRIDGE.

[Property of superconducting metals.] P. KAPITZA (Nature, 1929, 123, 870—871).—A reply to Bartlett (preceding abstract). A. A. ELDRIDGE.

Diamagnetism and crystal structure. C. V. RAMAN (Nature, 1929, 123, 945).—The abnormal susceptibility of graphite is intelligible in terms of the peculiar structure of the substance and its electrical conductivity if it is assumed (Ehrenfest) that there are electron orbits circulating round the plane hexagonal rings of carbon in the crystal lattice. Sugar charcoal and lamp-black are not crystalline, and, as anticipated, the susceptibility of amorphous carbon is normal. A. A. ELDRIDGE.

Magnetic properties of isolated atoms of cobalt. L. W. CONSTANT (Nature, 1929, 123, 943—944).—Platinum containing 5% or 10% of cobalt is ferromagnetic. Determinations of the magnetisation give values corresponding with a magnetic moment per cobalt atom 60% and 25%, respectively, greater than that calculated from the saturation magnetisation of pure cobalt, on the assumption that the platinum atoms do not contribute to the magnetisation. The relation between I and H varies with the heat treatment. A. A. ELDRIDGE.

Magnetic susceptibilities of some inorganic and organic electronic isomerides. S. S. BHATNAGAR and S. L. LUTHER (J. Indian Chem. Soc., 1929, 6, 303—307).—The value of k in the equation $\chi_m = -2.85 \times 10^{10} k r_1^2$, where χ_m is the molecular susceptibility and r_1 the mean radius of the molecule, increases with the number of atoms in the molecule; thus with 5 atoms $k=4$, with 13 atoms $k=7.54$, and with 24 atoms $k=11.26$. In the case of groups of isomerides having the same number of atoms in the molecule the values of k increase with the atomic numbers of the groups. A. R. POWELL.

Superconductivity of thorium. W. MEISSNER (Naturwiss., 1929, 17, 390—391).—Superconductivity has been established in the case of metallic thorium, commencing at about 1.4° Abs. Even slightly above this temperature the resistance is only about 0.017 of that at 0° C., but it drops sharply within 0.2° until at 1.3° Abs. it is less than 0.0001 of that at 0°. It is considered possible that some of the other elements with which superconductivity has not yet been observed (this vol., 250) may show similar effects at temperatures lower than those so far attained. J. W. SMITH.

Triboelectricity of quartz and mercury. L. H. DAWSON (J. Opt. Soc. Amer., 1929, 18, 344—348).—Experiments are described on the electrification produced when the contact between a plane quartz surface and mercury is severed in an atmosphere of air. The electrification is variable unless precautions are taken to exclude water vapour; under these conditions a $P.D.$ of about 350 volts is set up corresponding with a charge of about 1 e.s.u. per cm.² of quartz surface. R. W. LUNT.

Quantum theory of dispersion in metallic conductors. R. DE L. KRONIG (Proc. Roy. Soc., 1929, A, 124, 409—422).—Mathematical.

Photodichroism and photoanisotropy. I. Fundamental phenomena and definitions. II. Fundamental effects of induced photodichroism and experimental method. F. WEIGERT (Z. physikal. Chem., 1929, B, 3, 377—388, 389—404).—I. When layers of light-sensitive material are illuminated with linearly polarised light they become anisotropic and exhibit the phenomenon of dichroism. The old and new experimental data on these phenomena are discussed. They can be classed together as "photodichroism" and "photoanisotropy"; the effects are very complex. Three different effects appear to be present—primary, secondary, and induced photodichroism (photoanisotropy). Induced photodichroism is a new phenomenon which consists of the presence in a primary photoanisotropic system of new coloured particles which exhibit photodichroism.

II. The phenomenon of induced photodichroism is discussed, and it is stated that it can be obtained pure, and without distortion, in a photographic layer exposed to polarised light with the simultaneous occurrence of primary and secondary photodichroism, if, after exposure, it is fixed and the coloured silver particles are produced by physical development. The experimental method for this new phenomenon is, with few modifications, that previously used for the investigation of primary photodichroism. The applic-

ation of the new effect to photographic and other problems is given. A. J. MEE.

Kerr effect and molecular structure. H. A. STUART (Z. Physik, 1929, 55, 358—370).—The importance of the Kerr effect in the question of molecular structure is shown. An accurate formula for the gaseous state is considered together with a formula for molecular diffraction due to Debye, and discussed from the point of view of its analysis into terms corresponding with certain physical quantities. One term in the Kerr constant is due to the asymmetry of optical and electrostatic polarisation, and the other is due to the dipole moment of the substance concerned. They can be separated by a knowledge of the effect of temperature on the value of the Kerr effect. The possibility of obtaining the amount and direction of the maximum polarisation by means of the Kerr effect is discussed. For dipole-less molecules the agreement between the Kerr constant calculated from the degree of depolarisation and that observed is good. For hydrogen chloride, sulphur dioxide, and ammonia the degree of polarisation is calculated for all three axes. In the case of ammonia there is apparently no axis of symmetry as regards polarisation.

A. J. MEE.

Molecular lengths measured by an optical lever. W. N. BOND (Phil. Mag., 1929, 7, [vii], 1163—1182).—The construction and technique of optical levers are described. The use of such an optical lever enables changes in the thickness of a sheet of mica to be measured with an accuracy of about 1.5×10^{-8} cm. On tilting the lever and letting it return gently on to the mica surface apparent changes in the thickness are observed. These changes have been analysed for periodicity. The periodicity, $(10 \pm 0.3) \times 10^{-8}$ cm., found for muscovite mica is concluded to correspond with the length of the unit cell of muscovite, which by X-ray measurements is found to be 9.95×10^{-8} cm. For steel a periodicity of $(6.8 \pm 0.2) \times 10^{-8}$ cm. was obtained, agreeing with the X-ray value of 6.737×10^{-8} cm. for the cementite cell. It is shown that in each of four experiments described the probability of so marked a periodicity so close to a possible X-ray value is about 1 in 100. The results seem best explained by assuming that the needle tip of the lever ruptures a certain number of the surface layers of the crystal, which flow radially outward until the needle reposes on the first intact layer. If flow did not occur it is estimated that pressures of from 3000 to 180,000 atm. would have occurred at the contact. It is found necessary to conclude that a more or less ordered return flow of a small number of the surface layers occurs when the needle tip is withdrawn. The return flow is attributed to surface tension or cohesion forces. No periodicity was found with selenite, possibly owing to the plastic nature of this substance. F. G. TRYHORN.

Intensive drying of liquids. S. LENHER (Nature, 1929, 123, 907—908).—The rise of b. p. observed by Baker (J.C.S., 1922, 121, 568; 1923, 123, 1223) and Smits (J.C.S., 1924, 125, 1068) with intensively dried liquids can be observed in a similar apparatus with undried benzene, carbon tetrachloride, and water; hence the effect is attributed to superheating. Con-

ditions favourable to the apparent rise in b. p. have been determined. The b. p. of benzene subjected to a direct-current potential of 450 volts was unchanged (cf. Baker, J.C.S., 1928, 1054). A. A. ELDRIDGE.

cycloHexanol and the third law of thermodynamics. K. K. KELLEY (J. Amer. Chem. Soc., 1929, 51, 1400—1406).—The true specific heats of both crystalline forms of cyclohexanol have been determined down to about 15° Abs. The transition of the two crystalline forms occurs at 263.5° Abs.; the heat of transition was determined. The following thermal data are recorded for cyclohexanol: m. p. 297° Abs.; molar heat of fusion at m. p., 406 g.-cal.; molal entropy, 47.5—47.8 g.-cal./1°; molal free energy, —37,500 g.-cal. Both crystalline forms have the same entropy at 0° Abs. S. K. TWEEDY.

B. p. of hydrocarbons. B. NEKRASSOV (Z. physikal. Chem., 1929, 141, 378—387).—Theoretical. The b. p. of a number of hydrocarbons of various types can be calculated by means of an empirical equation $T = \text{const.} (M - \Sigma) / \sqrt{\Sigma}$ (where $T = \text{b. p. Abs.}$, $M = \text{mol. wt.}$, $\Sigma = \text{sum of various atomic and structural constants}$) based solely on the structural formula of the compound. Direct comparison of the b. p. is unsatisfactory in discussing the important question of the connexion between b. p. and molecular constitution, since the latter exerts a progressively weaker influence as the mol. wt. increases. For this reason the regularities hitherto found are qualitative. To overcome the difficulty of taking account of the combined effects due to several structural units, the influence of mol. wt. on the b. p. is eliminated by adapting a formula previously deduced (cf. this vol., 497). The influence exerted by different types of structure is represented by numbers, the value for each structure being chosen so as to give the best average result for all compounds in which it occurs. F. L. USHER.

Relation between the b. p. and molecular structure of cis-trans ethylenic, saturated, and acetylenic acids. BOURGUEL (Compt. rend., 1929, 188, 1494—1496).—The author's values for the b. p./15 mm. of five pairs of these acids are related to the number of carbon atoms they contain (C_4 to C_9) by two straight lines. The ethylenic acids are classified accordingly into those produced by catalytic reduction (e.g., isocrotonic acid), and those which undergo isomeric transformation in the presence of iodine (e.g., crotonic acid). The lines for the saturated and acetylenic acids coincide with those for the cis- and trans-ethylenic acids, respectively. The b. p. and other physical constants depend on the structure as well as on the mol. wt. J. GRANT.

Calorimetric absolute measurement of electrolytic conductivity for high-frequency alternating current. E. JUSTI (Ann. Physik, 1929, [v], 2, 65—93).—The theory of inductive heating advanced by Fischer and Wever (Mitt. K. W. Inst. Eisenforschung, 69) is confirmed. Encasing the metal in an insulator appears to enhance the skin effect in proportion to an increase in dielectric constant or wall-strength. This implies that the increase in resistance of an insulated wire when carrying high-

frequency current must be ascribed to the high dielectric constant rather than to dielectric loss. When the heating of a body in a high-frequency furnace varies as its conductivity, the role of coil length can be treated as a constant factor. In the range of frequencies used in wireless telegraphy no change of electrolytic conduction occurs on a sufficient scale to have any decisive influence on the mode of operation of underground and underwater antennæ.

R. A. MORTON.

Derivation of the chemical equilibrium constant. H. LUDLOFF (Naturwiss., 1929, 17, 367—368).—Mathematical. J. W. SMITH.

Heat balance in crystals in the light of quantum mechanics. T. VON KÁRMÁN (Naturwiss., 1929, 17, 385—387).—Mathematical. J. W. SMITH.

Experiments in the critical region. III. Energy determinations by means of the Joule effect. K. BENNEWITZ and N. ANDREEVA (Z. physikal. Chem., 1929, 142, 37—66; cf. A., 1926, 1210; 1927, 315).—Two methods of measuring the Joule effect were used, one for medium, the other for low temperatures. The critical isothermals for the gases argon, nitrogen, oxygen, carbon dioxide, and methane were obtained and energy-density diagrams constructed. The use of the Joule effect leads to single values. The application of the Joule-Thomson effect cannot be made, because the values of the specific heat at constant pressure required by it are not definite at the critical point. The critical isotherm for carbon dioxide is higher than that furnished by the pv diagram of Amagat. The reduced Joule curves for the critical temperature for argon, oxygen, nitrogen, and methane as a function of the reduced density coincide. The theorem of corresponding states holds. Conclusions are reached respecting the rotation energy, which appears to be practically unchanged for expansion. This point is of importance for a theory of liquids. The Joule curve for carbon dioxide deviates from the normal curve. On the basis of the theorem of corresponding states this indicates a certain association of the carbon dioxide.

A. J. MEE.

Revision of the density of carbon monoxide. L. R. PIRE and E. MOLES (Anal. Fis. Quím., 1929, 27, 267—272).—The density of carbon monoxide has been redetermined, the mean value being 1.25011 ± 0.00005 g. per litre. Taking for the deviation from Avogadro's law $1 + \lambda = 1.00050$, the most probable value of the at. wt. of carbon is 12.006, in accordance with Aston's value of 12.004 derived from the mass spectrograph.

H. F. GILLBE.

Densities of the alkaline-earth carbonates. T. BATUECAS, A. RANCAÑO, and J. IBARZ (Anal. Fis. Quím., 1929, 27, 290—304).—The following densities have been determined by the pycnometer: calcium carbonate, precipitated, 2.690; calcium carbonate, obtained by thermal decomposition of the oxalate, 2.705; calcite, 2.713; aragonite, 2.929; strontium carbonate, precipitated, 3.586; strontianite, 3.712; barium carbonate, precipitated, 4.290; witherite, 4.284. The molecular contraction on formation of the alkaline-earth carbonates increases with increase of the at. wt.

H. F. GILLBE.

Density, compressibility, and at. wt. of argon. II. G. P. BAXTER and H. W. STARKWEATHER (Proc. Nat. Acad. Sci., 1929, 15, 441—444).—A continuation of recent work (cf. A., 1928, 343) leads to a corrected value of 1.78394 for the normal density of argon, the previous error being due to a trace of hydrogen. The limiting density is not appreciably affected, and the at. wt. is 39.944. The value found for $(PV)_0/(PV)_1$ is 1.00107. Final purification was accomplished by repeated fractionations from chabazite used as an adsorbent and cooled with liquid air. N. M. BLIGH.

Density and cold working. M. MASIMA and G. SACHS (Z. Physik, 1929, 54, 666—673).—Measurements have been made of the decrease in density of brass crystals on stretching and of the change of density on annealing such deformed crystals. The interdependence of internal tension, relaxation, and recrystallisation are discussed. J. W. SMITH.

Heat equilibrium and temperature. E. WERTHEIMER (Z. Physik, 1929, 55, 395—408; cf. *ibid.*, 1925, 32, 596; A., 1926, 1088; 1927, 1132).—Theoretical. Further evidence is put forward to support the statement made in a previous paper that the temperature of a gas is not kinetic, but can be defined only electromagnetically. In the first place there is thermodynamic equilibrium between a mercury thermometer and the atmosphere only if the air is in radiative equilibrium with a black body. Secondly, the second law of thermodynamics requires radiative equilibrium of the gas with a black body.

A. J. MEE.

Measurement of the relative viscosities of gases and vapours. A. WEISSWEILER (Physikal. Z., 1929, 30, 364—367).—A quartz fibre is suspended vertically in a tube and the lower end is turned into a spiral and immersed in oil. A stream of gas or vapour passes through a horizontal tube joined to the vertical tube. The deflexion of the thread is measured on the scale of an ocular micrometer. The magnitude of the deflexion depends on the elastic properties of the fibre and on the streaming velocity, density, and viscosity of the gas. Relative values for the viscosity can readily be calculated; e.g., using air as standard, the viscosity of carbon dioxide at 23° is 0.0001494, in good agreement with results of other observers.

R. A. MORTON.

Vapour pressure of mixtures. G. BREDIG and R. BAYER (Z. physikal. Chem., 1929, 142, 92; cf. A., 1927, 1140, 1142).—The empirical equation used in the former work is only a special case of the more general equation put forward much earlier by van Laar.

A. J. MEE.

Electrical conductivity, thermal expansion, and hardness of magnesium-zinc alloys. G. GRUBE and A. BURKHARDT (Z. Elektrochem., 1929, 35, 315—332).—The conductivity of alloys of magnesium and zinc has been measured at 100°, 150°, 200°, 250°, and 300°. On plotting the values against the composition sharp breaks occur at points corresponding with the formation of the compounds $MgZn_2$ and $MgZn_5$, thus confirming the thermal observations of Chadwick (B., 1928, 268). Dilatometric and Brinell hardness curves also show breaks corresponding with these compounds. The con-

ductivity and dilatometric measurements also afford evidence of physical changes in the eutectic mixtures at lower temperatures; these changes have been confirmed by X-ray observations.

H. T. S. BRITTON.

Distribution of austenite in quenched carbon steels. K. HONDA and A. OSAWA (Sci. Rep. Tohoku Imp. Univ., 1929, 18, 47—58).—X-Ray examination of quenched steels shows that the proportion of austenite retained in the outer layers of the specimens is greater than that in the inner by an amount which increases with rise of quenching temperature and with increasing carbon content. These results have been confirmed by hardness tests and micrographical examination.

A. R. POWELL.

Relation between the lattice constant and the density of solid solutions. S. SEKITO (Sci. Rep. Tohoku Imp. Univ., 1929, 18, 59—68).—The lattice constants for solid solution alloys of copper with aluminium, tin, zinc, and manganese have been determined. From the results obtained the density of the alloys has been calculated using the expression $\rho = \rho_0(100M')/(1 + \alpha p)^3[(100 - p)M' + pM]$, where M is the at. wt. of copper, M' that of the added element, p the percentage of the latter present, α the rate of change of lattice constant for 1% of added element, and ρ_0 the density of pure copper. The values of ρ for the alloys agree closely with the observed d .

A. R. POWELL.

Influence of a third metal on the constitution of brasses. I. Lead. O. BAUER and M. HANSEN (Z. Metallk., 1929, 21, 145—151, 190—196).—The effect of adding up to 2.5% Pb on the equilibria in the copper-zinc system has been investigated with alloys containing more than 52% Cu. The solidification of the ternary alloys takes place in a manner analogous to that occurring in the binary lead-copper system. Molten alloys containing more than 67% Cu separate into two phases at 954—850° according to the scheme: Liquid_{Cu+Pb} → α + liquid_{Pb}. With alloys in which β is the primary crystal phase to form, separation of the lead occurs a few degrees below the beginning of the solidification and takes place over a very narrow temperature range according to the scheme: Liquid_{Cu+Pb} → β + liquid_{Pb}. In the region of the peritectic reaction α + liquid \rightleftharpoons β the two three-phase equilibria α + liquid \rightleftharpoons β (at 905° in the copper-zinc system) and liquid_{Cu+Pb} → α + liquid_{Pb} (at 954° in the copper-lead system) unite to form a four-phase equilibrium α + liquid_{Cu+Pb} \rightleftharpoons β + liquid_{Pb} at 886°. In all cases the end of the solidification is at 326°. The solid solubility of lead in both α - and β -brass is less than 0.1%. The ratio Cu:Zn at the boundaries of the various fields in the copper-zinc diagram is unaffected by the addition of lead.

A. R. POWELL.

Solubility of ammonium hydrogen carbonate in water. E. JANECKE (Z. Elektrochem., 1929, 35, 332—334).—The following solubilities, expressed in weight percentages, are recorded: 13.8°, 15.2; 24.3°, 19.65; 42.25°, 27.6; 48.4°, 30.8; 54.5°, 33.9; 63.6°, 43.2; 74.8°, 53.2; 81.2°, 56.7; 89.8°, 63.1; 105—111°, 90.0; 108—111°, 95.0; 108°, 100. These numbers are considerably larger than those given by

Terres and Behrens (this vol., 141) for temperatures above 20°.

H. T. S. BRITTON.

Solubility of gold in mercury. A. A. SUNIER and B. E. GRAMKEE (J. Amer. Chem. Soc., 1929, 51, 1703—1708).—The solubilities were determined between 80° and 200° (cf. A., 1928, 470); the results are lower than those previously recorded (cf. Britton and McBain, A., 1926, 474), and, up to 160°, are given by $\log N = -1167.4/T + 0.966$, where N = atomic-% of gold. An accurate method of analysing gold amalgams is described.

S. K. TWEEDY.

Salting-out of ethyl acetate. N. SCHLESINGER and W. KUBASOWA (Z. physikal. Chem., 1929, 142, 25—36).—The solubility of ethyl acetate in water, and in 0.1*N*- and *N*-sodium chloride, -potassium bromide, and -potassium iodide solutions was determined at various temperatures. The solubility curves show minima in the neighbourhood of 50—60°. The data obtained were used to test Tammann's theory of salting out. The molecular lowering of solubility, $\lambda = (\log l_0 - \log l)/n$, was calculated, and proves to be dependent on temperature, this being in contradiction with Tammann's theory. The dependence on temperature shows that the heat of dissolution of ethyl acetate in water is altered by the addition of salts. The ratio $\Delta l/\Delta c$, where l is the solubility, and c the concentration of water molecules, was also calculated and found to depend both on temperature and concentration. The mean value of $(\lambda n/\Delta \kappa) \times 10^4$, where $\Delta \kappa$ is the internal pressure increase, and n is the number of g.-mol. of salt in 1000 g. of water, was evaluated for the three salts, and the values were found to be different. This result is not in agreement with Tammann's theory. The complicated phenomena associated with the lowering of the solubility of non-electrolytes by the addition of salts cannot be explained in the simple way suggested by Tammann. The basic assumptions of his theory appear to be questionable. If two salts are added to the non-electrolyte the effect on the solubility is additive.

A. J. MEE.

Sorption of gas by porous matter. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1929, 4, 125—128).—A discussion of the mechanism of the sorption of gases by charcoal, silica gel, and chabazite. The author considers that the gas molecules enter into the molecular cavities left by the driving off of water or, in the case of charcoal, by the decomposition of organic matter, forming a homogeneous solid solution.

C. W. GIBBY.

Adsorption of electrolytes by crystalline surfaces. II. (MLLE.) L. DE BROUCKERE (J. Chim. phys., 1929, 26, 250—275).—See this vol., 757.

Catalysis by the action of subdivided metals. IV. Adsorption isotherms of hydrogen, ethylene, and ethane. B. FORESTI (Gazzetta, 1929, 59, 243—258; cf. A., 1925, ii, 692).—The isotherms for the adsorption by catalytic nickel of hydrogen, ethylene, and ethane have been determined at 21° and at low pressures. Contrary to the results obtained by Schmidt (A., 1926, 134), the relation $L = K\sqrt{p}$ (L —c.c. of gas adsorbed, p —pressure) does not hold, except in the case of ethylene, for nickel which has been evacuated at 21°; with a temperature of evacuation

of 255° the agreement is only approximate and restricted to narrower limits. For such pressures as are commonly employed in determining adsorption isotherms it is possible to obtain curves which conform to the above relation, but it is not necessary to assume that the adsorbed gas is in the atomic state. In fact, consideration of Langmuir's theory shows that the relation may be satisfied quite independently of the dissociation of the adsorbed gas, and the results for ethylene show that it holds in the case of molecular adsorption. The shape of the adsorption isotherm obtained with hydrogen indicates that the active surface of the nickel is heterogeneous and consists of at least two types of adsorbing centres, the more active ones being less numerous than the weaker ones.

O. J. WALKER.

Adsorption of Schaffer's sodium naphthol-sulphonate and the azo-dye orange-ENL by technically important decolorising charcoals. H. I. WATERMAN, J. GROOT, and M. J. VAN TUSSEN-BROEK (*Kolloid-Z.*, 1929, 48, 146—154).—Measurements of the adsorption of orange-ENL by four different kinds of charcoal showed that the adsorptive power decreases in the following order: carboraffin, blood charcoal, purit A, norit T. Similar measurements on the adsorption of Schaffer's β -salt gave the same order.

E. S. HEDGES.

Adsorption as a consequence of polarisation. Adsorption isotherms. J. H. DE BOER and C. ZWIKKER (*Z. physikal. Chem.*, 1929, B, 3, 407—418).—Theoretical. Adsorption of neutral atoms at the surface of an inorganic heteropolar crystal is considered to be due to polarisation of the atoms by the electrostatic field of the lattice ions. The first layer of polarised atoms can then induce similar polarisation in adjacent atoms and thus a multimolecular adsorption film can be formed. The relation between the number of adsorbed layers (n) and the partial pressure of vapour can be expressed by the formula $\log_e p/K_2 p_0 = K_2 K_1^n$, where p_0 denotes the saturation pressure, and all three constants have a physical meaning. The formula agrees well with the values obtained by Hüttig and Juza (this vol., 387) for the adsorption of argon by stannic acid.

F. L. USHER.

Electrical condition of hot surfaces during the adsorption of gases. III. Platinum surface at temperatures up to 850°. G. I. FINCH and J. C. STIMSON (*Proc. Roy. Soc.*, 1929, A, 124, 356—365; cf. A., 1927, 1135; 1928, 1087).—Measurements have been made of the surface charge acquired by a platinum sheet when heated to 850° in a vacuum ($p < 10^{-5}$ mm.), or in contact with oxygen, hydrogen, argon, nitrogen, carbon dioxide, carbon monoxide, and mixtures of various non-reacting gases. The results show that the surface of a freshly-rolled sheet is in an unstable or "un-normalised" condition until it has been heated alternately in contact with hydrogen and oxygen. A similar effect has been observed with nickel, but not with gold or silver (*loc. cit.*). After "normalisation" at 500° the platinum surface exhibits a positive charge of 0.19 volt either in contact with hydrogen or in a vacuum at the ordinary temperature; "normalisation" at 660° leaves the surface uncharged at the ordinary temperature in a vacuum

but still exhibiting a positive charge in contact with hydrogen, but after a similar process at 850° the surface no longer gives a charge at the ordinary temperature. The charge on the "normalised" platinum sheet due to a gas is characteristic of the latter and dependent on the temperature, but is independent of the gas pressure between 1 and 760 mm. It is readily removed by evacuation at 850°. Evidence is cited in support of the view that the vacuum charge is probably a result of structural changes of a permanent nature in the arrangement of the surface atoms of the metal sheet. The experimental results obtained with non-reacting gaseous mixtures enable the gases examined to be placed as follows in order of increasing activity in charging up a hot metal surface: vacuum, argon or nitrogen, carbon monoxide, hydrogen, oxygen. It is suggested that the "normalising" process involves a rearrangement of the surface atoms by a process similar to sintering. The type of adsorption shown by platinum is discussed.

L. L. BIRCUMSHAW.

Stability of unimolecular films. I. Conditions of equilibrium. II. Mechanism of film expansion. III. Dissolution in alkaline solutions. C. G. LYONS and E. K. RIDEAL (*Proc. Roy. Soc.*, 1929, A, 124, 322—333, 333—343, 344—355).—I. A study has been made of the force/area curves of unimolecular films of palmitic acid on the surface of solutions of varying p_H . The results of Gorter and Grendel (A., 1927, 306) could not be reproduced, but Adam's data (A., 1921, ii, 488) are confirmed. The high-pressure region of the curves is practically independent of the nature of the underlying solution, but it increases very slightly in steepness as the solution becomes more alkaline, although the area at zero compression remains unchanged. The more easily compressible form of the film is obtained only at low pressures and on solutions of which the surface layers are definitely acid. The equilibrium spreading pressures of palmitic acid have also been measured on a number of buffer solutions. On acid solutions spreading proceeds slowly, but the rate increases rapidly with increase of alkalinity, and on very alkaline solutions equilibrium is reached practically instantaneously. It is suggested that the attraction of the molecule for surfaces of an acidic nature is very low. This view is confirmed by a study of the latent heat of spreading from a crystal to a unimolecular film on surfaces of varying p_H ; the decrease in free energy on spreading over an alkaline surface is greater than for an acid surface. The conversion of a condensed to an expanded film by alteration of the p_H alone has been achieved in the case of penta-decoic acid.

II. Since contraction and expansion of a film coincide respectively with an increase and a decrease in the adhesional forces holding the polar heads to the surface of the solution, it is inferred that expansion is effected by a gradual tilting of the molecules from the close-packed formation existing in the solid condensed state. The solid condensed film is pictured as composed of molecules possessing asymmetrically attached head-groups, which are all tilted to such an angle that the zigzag chains interlock. The two

limiting areas of 20.6 and 26.1 Å. observed for long-chain compounds in this state (cf. Adam, A., 1922, ii, 687) are determined by the interlocking of the chains after relative displacements between adjacent molecules of two and four carbon atoms, respectively. The view is advanced that in liquid condensed films the molecules are all freely tilted, but are in general oriented parallel to one another. Such a structure is the two-dimensional analogue of the smectic state of liquid crystals (e.g., ammonium oleate). An approximate measure of the asymmetry of various head-groups is made from the limiting areas observed. The expanded state is regarded as a two-dimensional liquid, and the gradual transition from the solid condensed film through the liquid condensed and expanded films to the vapour film is considered to be due to the gradual increase in the angle of tilt of the film molecules as their mutual interactions become weakened compared with the attractive forces between the chain and the surface. These views are supported by the results of measurements of the force-area curves of heptadecylamine.

III. Measurements have been made of the rates of dissolution of unimolecular films of palmitic acid on buffer solutions of varying alkalinity. The film area is slowly reduced at constant pressure, and curves are drawn showing the rate of decrease in area per unit area of film. The rate of decrease is appreciably enhanced by increasing the alkalinity and raising the temperature, and slightly increased by raising the pressure. If the film pressure is kept constant on solutions of p_H 8.5—13.0, complete dissolution does not occur, but some form of relatively insoluble film is left. It is also found that on a fresh buffer solution the dissolution process is initially autocatalytic in nature, but on repetition of the experiments the curves become constant and reproducible. The new form of film is regarded as a bimolecular leaflet, analogous to the elementary leaflet in a soap bubble, and containing both palmitic acid and sodium palmitate. The lower layer of the bimolecular film is less closely packed than the upper on weakly alkaline solutions, but the closeness of packing increases with increasing alkalinity. Dissolution of a unimolecular film begins at nuclei formed by the adsorption of soap molecules beneath the surface, so that when there is initially no soap in the bulk of the solution the process is autocatalytic; with increasing quantities of soap in solution the process loses its autocatalytic nature, until finally the rate of dissolution is proportional to the area of unimolecular film left on the surface. L. L. BIRCUMSHAW.

Wetting power. E. L. GREEN (J. Physical Chem., 1929, 33, 921—935).—A discussion of the subject mainly with reference to spraying with insecticides. L. S. THEOBALD.

Surface "varnishes" and surface solutions of myristic acid. F. EMIR (Compt. rend., 1929, 188, 1667—1670).—Artificial films (varnishes) of myristic acid produced when a drop of a solution in benzene was placed on a water surface (Devaux) were compressed and the surface tension was shown to fall to a final value (14 dynes/cm.) independent of the initial temperature (between 15° and 20°) and tension

(30—50 dynes/cm.), at a rate which increased with rise in temperature. This tension corresponds with the saturation point of the acid and equals that of a film of acid ("surface solution") produced spontaneously, without the use of a solvent, above 15°. After a time there is a further slower and independent fall in the surface tension due to the solubility of the acid, which is greater in water than in 0.05*N*-hydrochloric acid and occurs above 19° and 21°, for the respective liquids. Each mol. occupies 26 Å.² and since the thickness of the film under saturation conditions (16 Å.) is half that of the elementary bimolecular layer of the solid acid determined by X-ray methods, Marcelin's hypothesis (A., 1925, ii, 772) is confirmed. J. GRANT.

Precipitation and surface tension. J. WULFF (Naturwiss., 1929, 17, 389).—An iodine precipitate prepared by molecular rays (Dunoyer, Compt. rend., 1911, 152, 592) is homogeneous only when the collecting plates are free from adsorbed gases and other matter which would cause surface-tension irregularities. When the plate is superficially etched it forms nuclei for the growth of crystals. By weighing the precipitate at various curved glass and silver surfaces a relationship has been established between radius of curvature and thickness of precipitate. This is closely connected with adsorption and diffusion phenomena, and it has been shown that if the radius of curvature is less than 0.4 mm. a multimolecular adsorbed layer is formed. J. W. SMITH.

Form of the electrocapillary curves of soap solutions. D. TALMUD (Kolloid-Z., 1929, 48, 164—165).—The interfacial tension between mercury and solutions of potassium oleate at various concentrations has been measured by Gouy's capillary electrometer method and it is shown that the maxima of the electrocapillary curves do not correspond for different concentrations, but undergo a regular drift. The experiments are considered to explain the observation of Frumkin and Donde (A., 1926, 1092) that air-boundaries of similar solutions have a negative charge when the solution is dilute, but a positive charge when concentrated. E. S. HEDGES.

Mesophases. (Intermediate states of aggregation.) II. Relative orientation of volume elements of a mesophase. III. Aqueous mesophase of salvarsan. H. ZOCHER and V. BIRSTEIN (Z. physikal. Chem., 1929, 142, 113—125, 126—138; cf. this vol., 870).—II. In the nematic and smectic state, differences in surface tension are responsible for the orientation of the volume elements parallel, or perpendicular, as the case may be, to the bounding surface. In some instances slight changes in the surface alter the orientation; e.g., if a glass surface is treated with acid, *p*-azoxyanisole usually sets itself perpendicular to the surface, whereas treatment with alkali induces the parallel orientation. Under certain conditions, mesophases may be subjected to much greater elastic deformation than ordinary crystals. The lines representing the direction of the axes from point to point in the distorted condition are convergent or divergent curves in the nematic state, and convergent or divergent

straight lines in the smectic state; true points of discontinuity are present in both states.

III. The aqueous mesophase of salvarsan is nematic, the smallest suspended drops being constituted of optically negative volume elements. Addition of sucrose or dextrose gives rise to the same twisted structure and consequent optical activity as has been observed with various other nematic phases. Even when such optically active substances are not added, the twisted structure may often be observed, the direction of twist being in either direction indifferently.

R. CUTHILL.

Membrane equilibria and selective absorption.

N. C. WRIGHT (Biochem. J., 1929, 23, 352—357).—The results obtained in experiments with unequal distribution of salts on either side of an artificial membrane in systems containing caseinogen and sodium and calcium chlorides could be quantitatively explained if the degree of dissociation of the protein salts and the Donnan equilibrium were taken into account. The presence of one ion influences the distribution ratio of other ions.

S. S. ZILVA.

Osmotic vapour pressure. II. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 392—400).—Mathematical. A substance passes congruently through a membrane when it diffuses from a greater to a smaller osmotic pressure and incongruently when it diffuses in the reverse direction. (See this vol., 759.)

H. F. GILLBE.

Asymmetric induction. I. Asymmetric synthesis and induction. II. Influence of solvent on the optical activity of the menthyl and bornyl esters of α -keto-acids. A. McKENZIE and A. G. MITCHELL (Biochem. Z., 1929, 208, 456—470, 471—481).—I. The optical activity of *l*-menthyl phenylglyoxylate is investigated in 15 media in light of three different wave-lengths. Mutarotation was observed in solutions in ethyl, *n*-propyl, *n*-butyl, isobutyl, and *l*-amyl alcohols. Both the mutarotation and the asymmetric synthesis of *l*-atrolic acid from the ester are explained in terms of asymmetric racemisation and induction.

II. With *l*-bornyl and *d*-bornyl phenylglyoxylate no mutarotation was observed in acetone, benzene, or chloroform and the mutarotation when observed was much less than with the corresponding *l*-menthyl compound. In methyl alcohol mutarotation was shown by the *l*-compound, but not by the *d*-compound. By the action of magnesium ethyl iodide on *d*-bornyl phenylglyoxylate, asymmetric synthesis of *d*-phenyl-ethylglycolic acid occurs. With *l*-menthyl pyruvate mutarotation was not observed in methyl alcohol, but occurred in ethyl and isopropyl alcohols. With *l*- and *d*-bornyl pyruvate mutarotation was not observed in benzene or methyl alcohol, but occurred in ethyl alcohol, although the rates for the two isomerides were different.

P. W. CLUTTERBUCK.

Dispersity and particle size. R. FÜRTH (Kolloidchem. Beih., 1929, 28, 293—295).—Existing methods of determining the size of particles in sols are discussed.

E. S. HEDGES.

Suspensions of kaolin in various media. R. DUBRISAY, J. TRILLAT, and ASTIER (Compt. rend., 1929,

189, 41—43).—Suspensions of 10 g. of kaolin in 80 c.c. of lithium, sodium, or potassium hydroxide solution settle at a rate which decreases with increase in the concentration of alkali, passes through a minimum, and then increases (cf. this vol., 26). In concentrated solutions the rate is much greater for potassium than for sodium hydroxide. Calcium and barium hydroxides show analogous results, but the supernatant liquid is turbid for solutions more dilute than 0.01*N*. Sulphuric, phosphoric, nitric, and hydrochloric acids show little variation with concentration, except for slight anomalies due to dissolution, and no minimum. X-Ray examination of the particles deposited from water and the alkalis showed the microcrystalline ring structure of dry kaolin, although for weaker alkalis the rings were smaller in size.

J. GRANT.

Validity of Stokes' law for non-spherical particles. A. H. M. ANDREASEN (Kolloid-Z., 1929, 48, 175—179).—Particles of calcined flint were separated into fractions and the velocity of fall was in each case in accordance with Stokes' law.

E. S. HEDGES.

Colloidal sulphur. M. LORA and TAMAYO (Anal. Fis. Quím. [Tecn.], 1929, 27, 110—112).—A hydrosol of sulphur of sufficient stability for use as an injection is prepared by adding drop by drop and with stirring 100 c.c. of a hot alcoholic solution of sulphur to an equal volume of a 1% aqueous gelatin solution and heating the mixture under reduced pressure until about one half of the alcohol has evaporated. The resulting sol shows no precipitation within 7 days and the sediment which forms after this period, at least up to 3 months, may be redispersed by agitation.

H. F. GILLBE.

Gold hydrosols of graded particle sizes without addition of nuclei. P. A. THIESSEN (Kolloidchem. Beih., 1929, 29, 122—146).—Experiments have been carried out on the formation of gold nuclei in solutions of chloroauric acid in the presence of potassium oxalate, hydrogen peroxide, carbon monoxide, sodium citrate, potassium thiocyanate, and under the influence of ultra-violet light. The results show that the spontaneous formation of nuclei in the production of gold hydrosols proceeds with a measurable velocity, and that the number of nuclei formed is proportional to the time and depends on the nature of the reducing substance employed. The velocity of the spontaneous formation of nuclei also depends on the temperature and the previous treatment of the reduction mixture. All processes which bring about the hydrolysis of chloroauric acid reduce the velocity of the spontaneous formation of nuclei. The results have been applied to the provision of a method of preparing gold sols with uniform and graded particle sizes. The method is to add a reducing agent which produces very few nuclei to a solution of chloroauric acid, on which a small amount of reducing agent readily producing nuclei is allowed to act for various graded time intervals.

E. S. HEDGES.

Tartaric acid method for the synthesis of electronegative sols. VIII. Adsorption of *d*- and *i*-sodium tartrate by aluminium hydroxide. A. DUMANSKI and A. JAKOVLEV (Kolloid-Z., 1929,

48, 155—156; cf. this vol., 760).—A definite volume of a suspension of aluminium hydroxide was mixed with a definite volume of an aqueous solution of *d*- or *i*-sodium tartrate (concentrations 0.8—0.1*N*) and after a time the liquid was filtered off and analysed. The *d*-sodium tartrate was more strongly adsorbed than the *i*-sodium tartrate. The possibility of steric hindrance in adsorption is pointed out and it is suggested that an adsorption method for the separation of stereoisomerides of hydroxy-acids may be practicable.

E. S. HEDGES.

Dispersity of dissolved cellulose. K. HESS (Kolloid-Z., 1929, 48, 191—193).—A reply to Zeise (this vol., 505).

E. S. HEDGES.

Change of physico-chemical properties in the region between colloid and molecular disperse systems. II. W. OSTWALD and A. QUAST (Kolloid-Z., 1929, 48, 156—164; cf. this vol., 760).—Measurements have been made of the b. p., viscosity, surface tension, and tendency to froth of aqueous-alcoholic solutions of night-blue and crystal-violet. Measurements of the rise in b. p. of solutions of both dyes indicate a maximum in the particle size of the disperse phase in mixtures containing between 40 and 60% of alcohol, in agreement with the results of former diffusion measurements. With the exception of solutions rich in water, the composition of the dispersion medium has little effect on the surface tension of solutions of the dyes, but the viscosity exhibits a minimum and the tendency to froth a maximum for medium concentrations of alcohol. In general, the employment of solvent mixtures of varying composition is a simple means of obtaining sols with systematically graded degrees of dispersion.

E. S. HEDGES.

Chemistry of crystalline forms of aggregation. **Basic copper compounds.** T. LABANUKROM (Kolloidchem. Beih., 1929, 29, 80—121).—An attempt is made to study the crystallisation forms of substances produced under various conditions with the aim of providing a method of characterisation of both the substances and the conditions of formation. A number of basic copper salts were prepared under different conditions and details are given of their macroscopic and microscopic appearance and of their crystallographic and optical properties. Many photomicrographs are included. A large number of compounds usually obtained only in microcrystalline form have been obtained in morphologically well-defined forms, particularly by the slow hydrolysis of normal salts. The mode of formation of single crystals and their mode of union to form aggregates is quite different in different compounds, even when these are similar crystallographically and in chemical constitution. The topochemical reactions of the crystals were also examined and descriptions are given of the various effects.

E. S. HEDGES.

Stability of coarse particles in solutions. IV. **Formation and removal of liquid sheaths in suspensions of *Bolus alba*. Reversible sol-gel transformation; thixotropism.** H. WERNER (Ber., 1929, 62, [B], 1525—1534; cf. A., 1928, 584).—Thixotropic properties are exhibited by the flocks and sediment formed by dispersed coarse particles of

Bolus alba suspended in water containing electrolytes. The suspended *Bolus* particles are not in immediate contact with one another, but each is completely surrounded by a sheath of liquid. The volume of the liquid in the flocks is very great in comparison with the total volume of *Bolus* particles, the ratio varying according to conditions from 2.6 : 1 to 26.6 : 1. Provided that the dispersing medium does not contain strongly adsorbable substances, the liquid in the *Bolus* flocks is essentially unaltered solution. The individual *Bolus* particles and the liquid surrounding them are fixed in the flocks. The mean thickness of the liquid sheath around the individual *Bolus* particles changes, under otherwise similar conditions, with the type and concentration of the electrolyte; the values found vary between 1.0 and 3.4 μ . Based on Stokes' law, a method is elaborated for determining the mean volume of the sinking flocks and the mean mass of *Bolus* in them. Two processes are operative in the production of *Bolus* flocks: (1) the formation of liquid sheaths round the individual *Bolus* particles, and (2) the union of the particles, more or less completely surrounded by liquid, to flocks. The two processes occur to a great extent independently of one another and according to different laws. H. WREN.

Stability of suspensions. III. **The velocities of sedimentation and of cataphoresis of suspensions in a viscous fluid.** W. O. KERMACK, A. G. MCKENDRICK, and E. PONDER (Proc. Roy. Soc. Edinburgh, 1929, 49, 170—197).—An expression has been obtained for the rate of fall of a spherical particle through a viscous fluid containing a large number of similar spherical particles sedimenting in the same way. A similar expression has been obtained for the velocity of cataphoresis of a single particle in an electrical field when this particle forms one of a large number of similar particles. The result for sedimenting spheres has been extended to sedimenting discs and confirmed by experiments on the sedimentation of suspensions of red blood-corpuscles of various concentrations. Various consequences of these results are discussed, and in particular a simple explanation is obtained of the observation that during cataphoresis in a U-tube, the boundary of the suspension retreating from the electrode tends to become more sharply defined, whilst the other boundary becomes more diffuse.

W. O. KERMACK.

Electrical characteristic of solutions, dyes, and biocolloids. R. FURTH (Kolloidchem. Beih., 1929, 28, 285—292).—The author discusses the electrical properties of particles of one substance immersed in a medium of another substance, when the particles are of molecular, colloidal, or macroscopic dimensions. A method for the investigation of cataphoresis is described, in which electrodes of poorly conducting material are used in place of metallic electrodes.

E. S. HEDGES.

A case of the reversal of adsorption. H. FREUNDLICH and L. L. BURGESS (Z. Elektrochem., 1929, 35, 362—366).—In order to ascertain the effect of the gradual growth of colloidal particles of lead sulphide, and of the consequent diminution in the specific surface, on the amounts of dye which are adsorbed, suitable quantities of a dye were added to

0.1M-lead acetate solution which was then treated with 0.1M-sodium sulphide in equimolecular proportion. The dyes used were fast-acid-violet 10B and rhodulin-violet. As the particles grow increasing amounts of adsorbed dye are released and pass into the liquid phase, the rate for the acid dye being greater than that for the basic dye.

H. T. S. BRITTON.

Coagulation of von Weimarn's Au₇ sols. I. E. IWASE (Bull. Chem. Soc. Japan, 1929, 4, 120—125).—The coagulation by sodium chloride and barium chloride of gold sols prepared by the reduction of gold chloride with formaldehyde in vessels of different materials has been investigated. The coagulation numbers varied only slightly.

C. W. GIBBY.

Study of the values at which flocculation is produced in sols of arsenious sulphide and of ferric hydroxide. M. BOUTARIC and (MLLE.) G. PERREAU (Bull. Acad. roy. Belg., 1928, [v], 14, 666—670; cf. A., 1925, ii, 778).—Sols of arsenic trisulphide were mixed with solutions of different acids of varying concentration, and the times of flocculation were determined spectrophotometrically. The p_H of the intermicellar liquid after flocculation was measured with a quinhydrone electrode, as well as the corresponding acid concentration, and curves were drawn from which by extrapolation the p_H and concentration corresponding with infinitely slow coagulation could be found. The limiting value of p_H for a number of acids differing both in strength and basicity was approximately constant, the mean value being 1.22 for a sol containing 1.55 g. of As₂S₃ per litre. With varying concentration of the colloid, the limiting p_H showed a minimum value for intermediate concentrations, less acid being required for very concentrated and for very dilute sols. Similar experiments with a ferric oxide sol (2.18 g. of Fe₂O₃ per litre), using different bases, gave 5.11 as a mean value of the limiting p_H .

F. L. USHER.

Cataphoretic measurements and the theory of the critical potential. H. R. KRUYT and D. R. BRIGGS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 384—391).—Observations with arsenious sulphide, selenium, and gold sols show that those univalent cations which are strongly adsorbed and cause flocculation at low concentrations, e.g., strychnine and new-fuchsin, reduce the cataphoretic migration velocity at the complete precipitation concentration to approximately the value which is characteristic of multivalent ions at the corresponding concentration. Powis' rule is therefore valid for such cations.

H. F. GILLBE.

Formation of secondary systems of Liesegang rings. II. M. S. DUNIN and F. M. SCHEMJAKIN (Kolloid-Z., 1929, 48, 167—170).—Further experiments (cf. this vol., 645) indicate that the formation of Liesegang rings is more complex than has been supposed, for not only is the space between the ordinary rings occupied by microscopic rings, but the large rings themselves, provided a sufficient number are obtained, can be grouped into periods forming a large-scale ring structure. The experiments were conducted by carrying out the diffusion in tubes 150 cm. in length and leaving them in the dark for 14

years, and the complex periodicity was observed with rings of silver chromate, silver phosphate, and lead iodide. It is suggested that the precipitation is controlled by three critical concentrations, each of which gives rise to its own periodicity. An analogy is suggested between the existence of "dead zones" exhibited in Liesegang ring formations and the similar dead zones which have been observed in the reception of radio waves and the sound of gunfire.

E. S. HEDGES.

Isoelectric point of coproporphyrin and its physiological significance. H. FINK (Naturwiss., 1929, 17, 388—389).—The isoelectric point of the coproporphyrin occurring in yeast is about p_H 4. This coincides with the minimum solubility, and maximum flocculability and adsorbability. An isoelectric solution examined in short-wave light shows a minimum of light emission, and the fluorescence spectrum takes a mean position between the spectra observed with acid and alkaline solutions. The absorption spectrum shows a similar effect. These observations are applied to the explanation of other phenomena observed with coproporphyrin.

J. W. SMITH.

Action of proteins on ferric hydroxide sol. H. FREUNDLICH and G. LINDAU (Biochem. Z., 1929, 208, 91—111).—Different proteins have very different effects on a ferric hydroxide sol with sodium chloride as coagulator. Gelatin and trypsin cause coagulation in the absence of salt; egg-albumin first lowers the coagulation value (sensitising action) and then increases it as the amount of protein is increased, haemoglobin at a given concentration increases the value (protective action). These differences are ascribed to complex formation between the sol and the protein, the complex having a characteristic coagulation value. This is confirmed by the fact that when ferric chloride solution replaces the sol, similar behaviour is observed. These coagulates can be redissolved by dilution with water.

Mixtures of ferric hydroxide sol and protein show a change in coagulation value in course of time; the protective action increases with time at low concentrations and shows an initial decrease followed by an increase at high concentrations of protein. The influence of p_H is small. An explanation of the deposition and dissolution of proteins in plants is suggested.

J. H. BIRKINSHAW.

Calcium acetate gels. I. P. C. L. THORNE and C. G. SMITH (Kolloid-Z., 1929, 48, 113—125).—The properties of calcium acetate gels have been examined with the aim of obtaining a gelatinous substance of definite chemical composition. The gels were prepared by pouring a saturated aqueous solution of calcium acetate into alcohol, the properties of the product varying with the water content of the alcohol. With larger amounts of calcium acetate, sols of the salt in water-alcohol mixtures are formed. The viscosity of these sols is greater than that of the aqueous solution and is at a maximum when the dispersion medium contains 50% of alcohol. Most of the gels are not stable for more than 24 hrs.: they are opalescent at first and gradually soften with time, small nodules of calcium acetate eventually settling

out. In gels which contain a relatively large amount of water, needle-like crystals form radially from numerous crystallisation nuclei, and it is suggested that gelation is an intermediate stage between true solution and crystal formation. The stability of the gels is increased, in some cases to 6 months, by the addition of acetone or various oleates, and in these gels a thread-like structure is visible to the unaided eye. Gels containing sodium oleate exhibit syneresis. Addition of acids or bases produces a decrease in the rate of gelation and the salts of bivalent cations cause a greater retardation than those of univalent cations. The temperature of preparation has little or no influence on the stability of the gels. When dried, the gels become turbid and alcohol is lost, the calcium acetate dissolving in the remaining water; by the addition of alcohol the gel can be formed again. Viscosity measurements indicate that the change from sol to gel takes place between sharp limits.

E. S. HEDGES.

Absorption of water by gelatin. III. The sulphate system. (Miss) W. B. PLEASS (Biochem. J., 1929, 23, 358—372).—Maximum swelling of gelatin occurs in a solution of sulphuric acid at p_H 3.0. Sodium sulphate in concentrations up to 0.5*M* in the presence of sulphuric acid suppresses the osmotic swelling of the gelatin due to the acid. At greater concentrations of this salt there is coagulation of the gelatin. Raising the temperature of solutions in the acid zone causes an increased water absorption by the gelatin. The temperature coefficient of swelling is greater the higher is the temperature, but is decreased by an increase in the concentration of sodium sulphate. The osmotic swelling of gelatin in alkaline solutions is suppressed to a greater degree by solutions of sodium sulphate than by equal molar concentrations of sodium chloride or nitrate. At concentrations of sodium sulphate of 0.7*M* or greater coagulation is induced. At the isoelectric point of gelatin the water absorption in solutions of sodium sulphate is proportional to the logarithm of the salt concentration up to 0.1*M*. At greater concentrations lyotropic swelling is reduced and coagulation occurs in solutions of greater than 0.7*M* concentration. In solutions of sodium sulphate of 0.1—1.0*M* concentration the magnitude of the water absorption of the gelatin is determined chiefly by the sulphate concentration almost independently of the p_H value of the solution. Gelatin in the coagulated condition tends to resist the solvent action of alkaline solutions. Rise in temperature generally causes greater water absorption, the temperature coefficient becoming larger as the temperature rises.

S. S. ŽILVA.

Swelling of gelatin. W. VON MORACZEWSKI and E. HAMERSKI (Biochem. Z., 1929, 208, 299—327).—The swelling of gelatin increases directly with the concentration of salts and increases with rise of temperature, the more rapidly the higher is the temperature. Dilute hydrochloric and sulphuric acids (below 0.001*N*) have a smaller swelling power than distilled water, but from this concentration upwards the swelling power increases rapidly, becoming much greater than with salts until maximal swelling is reached at p_H 1.7—1.8 (0.167*N*), when further increase

of concentration causes a decreased swelling power. These two acids at the same normality have approximately the same swelling power. The effect of acetic acid is more similar to that of salts but stronger, the swelling curve following a uniform course. Alcohol and citrate under some conditions have a smaller swelling power than water. Of the anions investigated, thiocyanate has the greatest swelling power and citrate and tartrate least, whilst of the cations, calcium ions have the greatest power. Salt mixtures show additive swelling power. Addition of acid to salt solutions increases, but of salts to acids decreases the swelling power. Non-electrolytes have a considerably smaller swelling power than electrolytes with the exception of carbamide and thiocarbamide, which equal thiocyanate and calcium ions in their swelling power.

P. W. CLUTTERBUCK.

Alteration of surface tension of gelatin with change of p_H and with small electrolyte concentrations. N. JERMOLENKO (Kolloid-Z., 1929, 48, 141—146).—Measurements of the surface tension of a 0.1% sol of gelatin by the method of capillary rise have shown that a minimum occurs at the isoelectric point at p_H 4.7 and that two maxima occur at p_H 2.85 and 8.3, respectively. These results are in agreement with the observations of Shukov (J. Russ. Phys. Chem. Soc., 1927, 1061), but not with those of Johnston and Peard (A., 1925, ii, 659).

E. S. HEDGES.

Solid phase relations in swelling. W. OSTWALD and P. P. KESTENBAUM (Kolloidchem. Beih., 1929, 29, 1—79).—Attention is directed to the fact that in most researches on swelling the effect of the "solid phase rule" has been neglected. In general, the specific swelling increases with the ratio of the amount of swelling liquid to the solid phase. In the present paper this relation is extensively studied, both experimentally and theoretically. The effect was observed with agar and with hide powder, and detailed quantitative experiments were conducted with gelatin, using both gravimetric and volumetric methods, the agreement between the two methods being good. Experiments conducted with a constant amount of solid phase or, alternatively, a constant amount of swelling liquid gave results in accordance with the above rule. The effect was further studied not only in pure water, but also in solutions of electrolytes. A close similarity is pointed out between the curve relating the degree of swelling to the amount of solid phase and Kroecker's curves relating the degree of adsorption to the amount of adsorbent. The influence of the solid phase effect is greater at higher temperatures. A theory of the solid phase relations has been developed from experiments on the electrical conductivity and nitrogen determination of the part of the gelatin going into solution on swelling, experiments on swelling in electrolytes, the swelling of electrolyte-free gelatin, and the osmosis of gelatin sols. These experiments lead to the view that, in general, solid phase relations are due to soluble substances in the gel, which dissolve in the swelling water to give a solution the concentration of which is proportional to the amount of solid phase; the solution thus produced affects

the course of the swelling. In the case of gelatin in particular, the swelling in pure water depends on the content of calcium sulphate and of degradation products of gelatin. Calcium sulphate hinders swelling and therefore swelling is greatest for large amounts of the swelling liquid, in which the calcium sulphate forms a dilute solution. The theory is well supported by experiments in which substances known to affect the swelling (sodium, calcium, magnesium, and ammonium sulphates, hydrochloric, picric, and sulphosalicylic acids, and tannin) were added: in these experiments the curve representing the solid phase effect was strongly influenced. The most important change was observed in dilute solutions of sulphosalicylic acid (0.16—0.25*N*) and hydrochloric acid (0.0005 and 0.0003*N*), where the ordinary solid phase rule was reversed, the greatest amount of solid phase giving the greatest degree of swelling. Curves obtained with some other addition agents (e.g., picric acid) showed a maximum or a minimum. An analogous effect is shown in the taking up of water by a gelatin sol in a collodion bag, where the amount taken up increases every time the outer water is changed in spite of the fact that electrolytes are being removed. It is noteworthy that sols of electro-osmotic gelatin in the osmometer become more viscous in spite of their increasing dilution, indicating that in a sol of gelatin it is insufficient to consider only the osmotic equilibrium, but that solvation and dispersion must be considered also. E. S. HEDGES.

Flotation and p_H . I. Hydrophobic powders. D. TALMUD (Kolloid-Z., 1929, 48, 165—166).—The powders studied were electrode-carbon and sulphur. These were mixed with a buffer solution of known p_H and one drop of purified petroleum or benzene and shaken; the froth was then separated and analysed. The curves connecting the percentage of flotation with the hydrogen-ion concentration pass through maxima which are close to the region of neutrality.

E. S. HEDGES.

Plastometric studies on the structure of surface layers. A. DE WAELE and G. L. LEWIS (Kolloid-Z., 1929, 48, 126—131).—Data are adduced to show that in colloid and plastic systems the disperse particles are enveloped in a pseudo-solid layer. A method for determining the ratio of the pseudo-solid phase to the volume of the total disperse phase is described. The thickness of the pseudo-solid layer depends on the radius of the particles and is constant over a wide range of concentration for a given solid-liquid system. Experiments are described which throw light on the properties of the layer. Some abnormalities of plastic streaming are described, which are caused by the adsorption of a solid peptising agent at the surface of the particles.

E. S. HEDGES.

Cystine in gelatin-protected noble metal systems. A. STEIGMANN (Kolloid-Z., 1929, 48, 194—195).—The addition of cystine inhibits the reduction of silver salts in the presence of gelatin and lowers the degree of dispersion of colloidal silver. In absence of gelatin, however, cystine accelerates the reduction and protects rather than coagulates colloidal silver. Similar experiments have been conducted on the preparation of sols of other metals by reduction:

in some cases cystine has an inhibiting effect and in others the reverse is true. The influence of cystine on the Ostwald ripening of silver bromide was also investigated and it was found to prevent this process.

E. S. HEDGES.

Special case of syneresis. F. C. JACOBY (Kolloid-Z., 1929, 48, 171—175).—In technical processes, many dye baths are known to exhibit a type of syneresis, the dye being precipitated as an elastic substance when the temperature is raised and subsequently lowered. This phenomenon has been investigated for the case of benzopurpurin 4B extra. The substance separating does not consist of a homogeneous gel, but is a mass of particles each of which has a gelatinous envelope and contains a sol of the dye. The liquid contained in the envelope is poorer in the dye than the original solution. The favourable effect of the addition of certain agents to the bath has been investigated and it is considered that these determine the velocity of formation and size of particles of the product of syneresis.

E. S. HEDGES.

Expansion and contraction of india-rubber laminae, the critical "slipping" temperature (Gleittemperatur) and its displacement by additions. M. KROGER and W. N. YAO (Z. Elektrochem., 1929, 35, 358—362).—The deformation of rubber membranes by blowing has been investigated under varying pressures and at different temperatures. Optical properties, such as double refraction, suggest that the deformation is caused by the slipping of molecules over one another. Data are recorded which show the influence of the time allowed for vulcanisation, and of varying quantities of non-vulcanising agents added to the mix, e.g., magnesium hydroxide, aluminium fluoride, and carbon-black. The pressure to be applied to bring about a particular expansion increases with rising temperature, until a certain temperature (the critical slipping temperature) is attained, above which the pressures necessary to cause the change become less and less. The incorporation of carbon in the rubber tends to raise this critical temperature.

H. T. S. BRITTON.

Kleeman's derivation of the law of mass action. R. F. GOLDSTEIN (Phil. Mag., 1929, [vii], 7, 1193—1197).—A proof is given that the van 't Hoff derivation of the law of mass action is not invalidated by the concept of sepro-unstable molecules, and attention is directed to certain fallacies in Kleeman's derivation (A., 1928, 239).

F. G. TRYHORN.

Functional form of the constant of mass action and atomic activation. R. D. KLEEMAN (Science, 1928, 68, 462).—Previous work (A., 1928, 955) shows that in a gaseous reaction the law of mass action, as generally formulated, breaks down when the volume is sufficiently increased. The mass action constant is not only a function of temperature, but also of the volume and masses of the constituents. The fate of molecules in a gas depends not only on the chances of encounter, but also on previous encounters with other molecules, when activation may occur. The changes in spectra of a substance with temperature show that they are associated with molecular collisions

and their violence. Further, if the pressure in a gaseous system changes continuously, the average activation of any molecule at a given instant probably differs in nature and magnitude from that which obtains at equilibrium.

L. S. THEOBALD.

[Thermodynamic principles.] C. RAVEAU (Compt. rend., 1929, 188, 1662—1665).—A criticism of the fundamental principles of thermodynamic theory with special reference to the conception of entropy, Le Chatelier's principle (*ibid.*, 1543) and the relation between the Clausius and Clapeyron equations (Verschaffelt, this vol., 387, 648).

J. GRANT.

More general formulation of the phase rule. P. KUBELKA (Z. Elektrochem., 1929, 35, 335—337).—A modified form of the phase rule in which attention is paid to forms of energy other than those which are usually considered.

H. T. S. BRITTON.

Partition of sodium between sodium hydroxide and sodium ethoxide or sodium methoxide in ethyl- or methyl-alcoholic sodium hydroxide solutions. J. M. F. CAUDRI (Rec. trav. chim., 1929, 48, 589—592).—From a study of the rates of hydrolysis of phthalide and ethyl acetate in aqueous-alcoholic sodium hydroxide solutions, and the rates of other formation in aqueous-alcoholic solutions, it is concluded that sodium ethoxide is largely converted into sodium hydroxide on the addition of water to an alcoholic solution. In aqueous methyl alcohol the conversion takes place to a much smaller extent.

C. W. GIBBY.

Sodium [hydrogen] maleate : a buffer for the region p_H 5.2—6.8. J. W. TEMPLE (J. Amer. Chem. Soc., 1929, 51, 1754—1755).—Sodium hydrogen maleate, the preparation of which is described, in presence of sodium hydroxide has a buffer range of p_H 5.2—6.8, giving maximum buffering power in the region where phthalate and phosphate buffers have the least. The compositions of buffers for p_H intervals of 0.2 are recorded.

S. K. TWEEDY.

Neutralisation of several mineral polyacids. I. and II. L. MALAPRADE (Ann. Chim., 1929, [x], 9, 104—157).—The theoretical and practical aspects of the study of neutralisation curves of complex acids by measurements of hydrogen-ion concentration or of oxidation potentials are discussed. A platinum or gilt platinum wire (equilibrium being attained much more rapidly with the latter) in a solution of an oxidising acid such as chromic or iodic acid acts as an oxygen electrode, the oxygen pressure (P_{O_2}) and hence the potential depending on the nature of the acid. Since the value of P_{O_2} is independent of p_H it is possible to construct neutralisation curves with oxidising acids by measurement of the oxidation potential during neutralisation. Since the platinum electrode retains its potential for a long period after removal from the acid solution and immersion in another acid of lower oxidation potential, and even after washing with distilled water, accurate and reproducible results are obtained only if the measurements are made with increasing oxidation potentials, since in this case equilibrium is rapidly established. The method was checked by a determination of the neutralisation curve of chromic acid, the results agreeing with those

of Margaillan (A., 1914, ii, 57) and Britton (A., 1924, ii, 704), and was then employed to study the curves of iodic and complex molybdic acids (see below). The neutralisation curve of hydrofluosilicic acid has two points of inflexion, the first corresponding with the formation of the salt Na_2SiF_6 , which is stable only below p_H 3, and the second with the known decomposition of the anion. Hydroferrocyanic acid gives only one point of inflexion corresponding with the normal salt, and the acid can be titrated using phenolphthalein but not methyl-orange as an indicator. In agreement with the values of the ionisation constants (Abbott and Bray, A., 1909, ii, 660) pyrophosphoric acid shows only two points of inflexion, corresponding with $Na_2H_2P_2O_7$ and $Na_4P_2O_7$, respectively. No evidence for the existence of $NaH_2P_2O_7$ or $Na_3HP_2O_7$ was obtained. The curve for orthophosphoric acid differs appreciably from that of pyrophosphoric acid, and thus by a determination of p_H values it is possible to differentiate between two salts for which the ratio P_2O_5/Na_2O is the same. The conversion of a solution of pyro- (p_H 1.42) into ortho- (p_H 1.64) phosphoric acid by boiling can be similarly followed. Arsenic acid gives a curve similar to that of orthophosphoric acid, but the second point of inflexion is less definite. Iodic acid, in agreement with cryoscopic measurements, shows only one point of inflexion, corresponding with $NaIO_3$, but periodic acid gives two points, corresponding, respectively, with NaH_4IO_6 (p_H 4) and $Na_5H_3IO_6$ (p_H 9.6), the latter suffering slight hydrolysis in solution. There is no indication of the formation of $Na_3H_2IO_6$, although this may be due to its great degree of hydrolysis. Iodates and periodates may be determined in the presence of each other by first titrating the total iodine liberated on addition of acidified potassium iodide solution ($IO_3^- \rightarrow 6I$, $IO_4^- \rightarrow 8I$), and then repeating the titration with the previous addition of mannitol to reduce the periodate to iodate.

J. W. BAKER.

Neutralisation of several mineral polyacids. III. Neutralisation curves of acid complexes of tungstic and molybdic oxides. L. MALAPRADE (Ann. Chim., 1929, [x], 9, 159—222; cf. preceding abstract).—A study of the formation of complex acids by the interaction of molybdic and tungstic oxides with phosphoric and silicic acids by measurements of the oxidation potential and by plotting the neutralisation curves by electrometric titration using a hydrogen or quinhydrone electrode, a part of which has been published previously (Malaprade and Travers, A., 1926, 925, 1114). A point of inflexion on the neutralisation curve may correspond with the transition from one acid to another, or the decomposition of the anion. The cases studied in this paper are examples of the latter, the following being a brief summary of the main conclusions. In some cases isolation of the salt corresponding with the point of inflexion was effected. With phosphomolybdic acid, $P_2O_5 \cdot 24MoO_3 \cdot 3H_2O$, the first point of inflexion does not correspond with the formation of the normal salt (which is not indicated by an inflexion), but with the salt $P_2O_5 \cdot 22MoO_3 \cdot 7M_2O$ (barium salt isolated); the second point corresponds with decomposition into the phosphate and molybdate, which is not complete

until the end of the neutralisation. The curve for phosphotungstic acid is similar, but the decomposition of the normal salt begins prior to the occurrence of the inflexion. With silicomolybdic acid, $\text{SiO}_2, 12\text{MoO}_3, 2\text{H}_2\text{O}$, the first point of inflexion corresponds with normal salt formation and the second with the beginning of the decomposition (at a higher p_{H} than that for the phosphomolybdates). A similar curve is obtained with silicotungstic acid, but the second point of inflexion indicates the end of the decomposition of the anion, which is less readily decomposed than the phosphotungstate. Oxidation potential measurements show that in dilute solution periodic acid reacts quantitatively with molybdic acid to yield hexamolybdoperiodic acid, $\text{I}_2\text{O}_7, 12\text{MoO}_3, 5\text{H}_2\text{O}$, the first point of inflexion in the neutralisation curve of this acid corresponding with the formation of the normal salt, the second with its decomposition into molybdate and periodate. Monomolybdoperiodates are similarly decomposed, the *potassium* salt, $\text{MoO}_3, 1.5\text{I}_2\text{O}_7, 1.6\text{K}_2\text{O}, 5\text{H}_2\text{O}$, being obtained by crystallisation from a solution of 6 g. of periodic acid and 50 g. of potassium molybdate which has been just neutralised (phenolphthalein) with potassium hydroxide. Since in dilute solution metatungstic acid, $(\text{WO}_3)_4, \text{H}_2\text{O}$, does not react with phosphoric or silicic acid either in the cold or at 100° , and only partly in concentrated solutions, it is inferred that phospho- and silico-tungstic acids are formed by interaction of phosphoric and silicic acids with the nascent anhydride WO_3 , since metatungstic acid reacts readily under conditions in which it is decomposed into the latter. By analogy this conclusion is extended to the formation of the corresponding complex molybdic acids. The relative stability of phospho- and silico-molybdic acids at various p_{H} values is discussed, the tendency of the former complex to decomposition being the greater, and a theoretical interpretation of the course of the neutralisation curves is given. Various applications of the results (1) to the detection of complex formation of molybdic acid with mineral and organic acids, polyhydric alcohols, and phenols, (2) to the detection of silica (as silicomolybdic acid) even in the presence of phosphoric acid by addition of a solution of an alkali molybdate to the solution and then acidification (with tartaric acid if phosphates are present, the order of addition being important), and (3) the determination of iodates and periodates in the presence of each other, are described, for details of which the original must be consulted.

J. W. BAKER.

Hydrolysis in solutions of beryllium salts. M. PRYTZ (Z. anorg. Chem., 1929, 180, 355—369).—The hydrolysis of a series of solutions of beryllium sulphate and chloride at various concentrations has been studied by electrometric titration with *N*-sodium hydroxide. Curves obtained by plotting p_{H} against equivalents of sodium hydroxide added show three definite divisions: first a continuous rise of p_{H} with addition of alkali until 1 equivalent of sodium hydroxide has been added; secondly, a flat portion where addition of alkali causes no appreciable change in p_{H} ; and finally a point of inflexion occurring when exactly 2 equivalents of sodium hydroxide have been added in the case of the chloride, or slightly less in the case

of the sulphate. Assuming that either $\text{Be}^{++} + \text{H}_2\text{O} = \text{BeOH}^+ + \text{H}^+$ or $2\text{Be}^{++} + \text{H}_2\text{O} = \text{Be}_2\text{O}^{++} + 2\text{H}^+$ represents the course of the hydrolysis, the respective hydrolytic constants $K = A_{\text{H}} \cdot C_{\text{BeOH}^+} / C_{\text{Be}^{++}}$ and $K_0 = A_{\text{H}}^2 \cdot \dots / C_{\text{Be}_2\text{O}^{++}}$ (where A_{H} denotes the hydrogen-ion activity) have been obtained from the first part of the curve. When worked out for the addition of 0.5 equivalent of sodium hydroxide, K shows a continuous decrease with dilution of the beryllium salt, whilst K_0 remains sensibly constant. K_0 is therefore accepted as the real constant and the second of the above equations as representing the mechanism. The mean values of K_0 are: for beryllium chloride 1.7×10^{-7} , for the sulphate 1.4×10^{-7} . The formula of the precipitated beryllium hydroxide is considered to be $\text{Be}_2\text{O}_3\text{H}_2$ (cf. A., 1913, ii, 708) and its solubility product (L) to be $[C_{\text{Be}_2\text{O}^{++}}] \times [C_{\text{OH}}]$. The mean value of L , calculated for the addition of 1.5 equivalents of sodium hydroxide and using the second part of the titration curve, is 2.9×10^{-19} from measurements in solutions of the chloride, and 1.1×10^{-19} from the sulphate.

F. L. USHER.

Hydration of ions. J. BABOROVSKY (Coll. Czech. Chem. Comm., 1929, 1, 315—318).—Kohlrausch's law of independent ionic migration is not exact for fairly concentrated (*N*) solutions. Transport, at this concentration, is purely electrolytic and not electro-osmotic, but in more dilute solutions the latter effect increases with increase in dilution. H. BURTON.

Calculation of heat of dilution by Debye and Hückel's theory. G. B. BONINO and V. VAGLIO (Nuovo Cim., 1928, 5, 115—126; Chem. Zentr., 1929, i, 204).—A more exact interpretation of Debye and Hückel's theory shows that the heat of dilution is the sum of two terms: $U = A\epsilon + B/\sqrt{c}$; B is always positive, whilst A may be positive or negative.

A. A. ELDRIDGE.

Internal pressure of strong electrolytes. H. M. EVJEN and F. ZWICKY (Physical Rev., 1929, [ii], 33, 860—868; cf. A., 1926, 668).—The difference between the thermal properties of dilute solutions and the pure solvent is due to a superposition of a physical effect of the ion on the solvent, or an internal pressure, and a chemical action of the ion on the solvent. The first effect can be calculated by taking account of the ionic atmosphere; the second effect increases linearly with the molar concentration. Satisfactory agreement with experimental results for the thermal expansion and for the compressibility of dilute solutions is obtained. N. M. BLIGH.

Adiabatics of a mixture of liquid and vapour. G. BRUHAT (J. Phys. Radium, 1929, [vi], 10, 107—114).—Mathematical. F. L. USHER.

Tautomerism of α -diketones. Heat of transformation of tautomersides. H. MOUREU (Compt. rend., 1929, 188, 1557—1558; cf. this vol., 929).—Calculation of the heats of transformation of the "B" forms of methylbenzyl- and phenylbenzyl-glyoxal into the "A" forms from the heats of combustion and from the relation $Q = \log K_2/K_1 \times 1.985T_1T_2/(T_1 - T_2)$ gives concordant figures of the order of 2.5 kg.-cal./mol. R. K. CALLOW.

Aluminium-copper-nickel system with aluminium as the chief constituent. H. NISHII.

MURA (Suiyokaishi, 1928, 5, 616—626).—The reactions $\text{liq.} \rightarrow \alpha + \text{CuAl}_2 + T$, $\text{liq.} \rightarrow \text{NiAl}_3 + T$, $\text{liq.} + \text{NiAl}_3 \rightarrow \text{NiAl}_3 + T$, are said to occur where α is a solid solution containing aluminium as the chief constituent, and T is a ternary compound, considered by Haughton and Bingham (A., 1921, ii, 335) to be Cu_2NiAl_5 , but more probably $3\text{CuAl}_2\text{NiAl}_3$. The equilibrium diagram is constructed. CHEMICAL ABSTRACTS.

Equilibrium diagram of the iron-molybdenum system. T. TAKEI and T. MURAKAMI (Sci. Rep. Tohoku Imp. Univ., 1929, 18, 135—153).—The equilibria in the iron-molybdenum system have been reinvestigated by microscopical examination, by the electrical resistance and dilatometric methods, and by magnetic analysis. The γ -field extends to 3% Mo at 1150° and is bounded by a smooth curve joining this point with the A3 and A4 points on the temperature axis. The α -field of solid solution extends to 38% Mo at the eutectic temperature, 1440°, but only to 6% Mo at 20°. The ϵ -phase consists of the compound Fe_3Mo_2 formed at 1450—1500° by the peritectic reaction, $\eta + \text{melt} \rightleftharpoons \epsilon$; it forms a eutectic with 38% Mo with the α -phase. The η -phase is the compound FeMo formed by the peritectic reaction, $\text{melt} + \delta' \rightleftharpoons \eta$, at 1540°; it is decomposed at 1500° according to the eutectoid reaction, $\delta' \rightleftharpoons \delta$. With increasing molybdenum content up to 50% the intensity of magnetisation decreases; the ϵ and η phases are both non-magnetic. Quenching from a high temperature increases the intensity of magnetisation of alloys containing the α and ϵ phases at the ordinary temperature; annealing at 700° causes a reversion to the normal magnetic properties. A. R. POWELL.

Use of internal pressure in metallic systems. System lead-antimony-copper. R. A. MORGEN (Science, 1928, 68, 490—491).—The use of internal pressure, m. p. and b. p. data in the prediction of the nature and extent of miscibility gaps in a ternary system and also the effect of compound formation are discussed in relation to the system lead-antimony-copper. L. S. THEOBALD.

System cupric oxide-sulphur trioxide-water. E. POSNJAK and G. TUNELL (Amer. J. Sci., 1929, [v], 18, 1—34).—The equilibrium in the above system at 50°, 100°, and 200° has been investigated by phase-rule methods. The only solid phases encountered were cupric oxide, anhydrous cupric sulphate, and its penta-, tri-, and mono-hydrates, and the basic salts $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$, $4\text{CuO} \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$, and $3\text{CuO} \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$; no solid solutions were observed. Crystallographic data for these compounds are recorded. R. CUTHILL.

Ternary system $\text{CaO}-\text{CO}_2-\text{SiO}_2$ relative to the setting of mortar. G. F. HUTIG and E. ROSENKRANZ (Z. Elektrochem., 1929, 35, 308—314).—The thermodynamics of the reaction $\text{CaSiO}_3 + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 + \text{SiO}_2$ at 500—800° are discussed. Experiments show that silica, even when in a specially active form, begins to react with calcium carbonate only when subjected to a temperature of 620°. No reaction occurs at the ordinary temperature between freshly precipitated calcium carbonate and hydrated silica during a period

of 6 months, nor when kept for 5 days at either 50°, 100°, or 200°. Analyses of mortars varying in age from 970 to 430 years suggest that they contain chiefly calcium carbonate and silica, and this was confirmed by X-ray observations, which indicate the presence of calcite and quartz but not of wollastonite.

H. T. S. BRITTON.

Equilibrium diagrams of the aluminium-antimony-silicon and the aluminium-antimony-copper systems with aluminium as their chief constituent. T. MATSUKAWA (Suiyokaishi, 1928, 5, 596—603).—Only one compound, AlSb , is recognised. The ternary eutectic of aluminium, antimony, and silicon almost coincides with the binary eutectic of aluminium and silicon. The univariant reaction occurring on the liquidus surface is $\text{liq.} \rightarrow \text{AlSb} + \text{Si}$. In the aluminium-copper-antimony (2%, 4%, 6%) system the univariant reactions on the liquidus surfaces are: $\text{liq.} \rightarrow \text{CuAl}_2 + \text{AlSb}$, $\text{liq.} \rightarrow \text{CuAl} + \text{AlSb}$, and $\text{liq.} + \text{CuAl} \rightarrow \text{CuAl}_2$. At 585° a new reaction of a non-variant system, $\text{liq.} + \text{CuAl} \rightarrow \text{CuAl}_2 + \text{AlSb}$ was found at Sb 2.5, Cu 47, Al 50.5%. The ternary eutectic point almost coincides with the binary eutectic point of the aluminium-copper system. CHEMICAL ABSTRACTS.

Equilibrium between the carbonates and hydrogen carbonates of sodium and potassium in aqueous solution at 25°. A. E. HUNT and S. B. SMITH (J. Amer. Chem. Soc., 1929, 51, 1626—1636).—By combining previous data with new observations on the system sodium hydrogen carbonate-potassium hydrogen carbonate-water, the 25° isotherm for the above quaternary system has been determined. A new salt, $\text{K}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, has been found in the system, but there are no stable salt pairs. S. K. TWEEDY.

The sulphide-sulphate reaction. M. TRAUTZ and S. PAKSCHWER (J. pr. Chem., 1929, [ii], 122, 147—181).—The pressure-temperature curves for the univariant system $\text{ZnS} + 3\text{ZnSO}_4 = 4\text{ZnO} + 4\text{SO}_2$ have been measured by a static-manometric method. The partial pressure of the sulphur dioxide is 1 atm. at 488°. The roasting of zinc sulphide is discussed from the point of view of the phase rule in the light of the results obtained. The reaction of zinc sulphide with calcium, strontium, or barium sulphates begins at 800—850°. For a pressure of 760 mm. equilibrium is reached at 1130—1137°, 1178°, and 1205°, respectively. It is shown that the reaction may take place in two stages: $4\text{ZnS} + 3\text{MSO}_4 = 4\text{ZnO} + 3\text{MS} + 4\text{SO}_2$ and $3(\text{MS} + 3\text{MSO}_4) = 3(4\text{MO} + 4\text{SO}_2)$. The heat of the reaction $\text{CaSO}_3 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O}_2 \text{ aq.} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O} + 81.3 \text{ kg.-cal.}$ has been determined calorimetrically. From this is calculated the heat of formation $\text{Ca} + \text{S}_{\text{rh}} + 1.5\text{O}_2 + 2\text{H}_2\text{O} = \text{CaSO}_3 \cdot 2\text{H}_2\text{O} + 284.3 \text{ kg.-cal.}$ It is shown that the reaction of sulphide with sulphate to yield oxide and sulphur dioxide can proceed through the intermediate stage of sulphite. Moreover, the assumption of equilibria in the fused state is unnecessary. The reaction can take place in solid phases, as may be deduced from the above heat of formation. R. K. CALLOW.

Chemical equilibria involving reactions between two condensed phases. M. MANNHEIMER

(Amer. J. Sci., 1929, [v], 17, 534—542).—Theoretical. A general method is derived for judging the reliability of experimental results relating to equilibria between fused salts and metals. The criterion is based on the fact that the points of the equilibrium are located on stoichiometrically computable curves independent of the special law of mass action, and independent of the true molecular coefficients. The general equations of transformation of the co-ordinate system for change of molecular coefficients are derived.

F. G. TRYHORN.

Transport number of aqueous acetic acid. J. W. McBAIN and C. E. HARVEY (Amer. Electrochem. Soc., May, 1929. Advance copy. 12 pp.).—Direct measurements by the Hittorf method have been made of the transport numbers of the ions of aqueous solutions of acetic acid at concentrations from 0.1*N* to *N* and at temperatures from 14.5° to 26.8°. The transport number of the acetate ion is found to have the mean value of 0.108, which seems to be independent of concentration and temperature. The average value calculated from the transport numbers of strong electrolytes is about 3% lower, but the uncertainty of these data is of this order. Determinations of the *f*, *p*, and migration ratio of solutions containing acetic acid and sodium acetate give no indication of association of the acetate ion with the undissociated acetic acid molecule to form a complex anion.

H. J. T. ELLINGHAM.

Galvanic electricity and cohesion pressure; "space-energy." R. VON DALLWITZ-WEGNER (Z. Elektrochem., 1929, 35, 344—349).—The theory previously developed (A., 1928, 483) is amplified to include the *E.M.F.* of galvanic cells, for which purpose the concept of "space-energy," E_r , is introduced, being equal to $R/\delta - 10KM/\gamma$ kg. per kg.-mol. (R —gas constant, δ —coefficient of cubical expansion, K —cohesion pressure, γ —density, and M —mol. wt.). By considering the change in space-energy consequent on an adiabatic change, an expression has been derived from which the space-energies of the electrodes of a cell can be found. The theory is tested by considering the Daniell cell and the Bunsen and Grove cells. Explanations are advanced to account for the differences between the calculated and actual values.

H. T. S. BRITTON.

Effect of air on the potential of the mercury-mercurous sulphate electrode. M. RANDALL and H. A. STONE (J. Amer. Chem. Soc., 1929, 51, 1752—1754).—Mercury is soluble in dilute sulphuric acid in the presence of oxygen. The potential of the above electrode in moderately concentrated acid (0.2*M*) is negligibly affected by the presence of air.

S. K. TWEEDY.

Polarographic studies with the dropping mercury cathode. II. Influence of temperature V. NEJEDLY (Coll. Czech. Chem. Comm., 1929, 1, 319—333).—The temperature coefficients of the deposition potentials for dilute solutions (0.0001—0.01*N*) of lead, thallous, indium, cadmium, zinc, and manganese chlorides, ferrous and manganous sulphates, have been determined at 17—98°, and that of hydrochloric acid at -1.5° to 92°. With the exception of thallous chloride the values are negative and the

maximum (3×10^{-3}) is shown by hydrogen. The diffusion currents generally increase with rise of temperature, but if heating at 100° is prolonged, a gradual decrease is observed. This diminution is most marked in about 0.0001*N*-solutions. Maxima on the current-voltage curves are observed: these appear at the lower temperatures with 0.001—0.01*N*-solutions, and at about 100° with more dilute solutions. It is presumed that increased adsorption of the salt on the glass surface occurs when a dilute solution of a salt is heated, whereby the solutions become more dilute.

H. BURTON.

Thermodynamic study of lead monoxide. F. ISHIKAWA and E. SHIBATA (Sci. Rep. Tohoku Imp. Univ., 1929, 18, 109—119).—The *E.M.F.* of the cell Pb amalgam|PbO, NaOH|H₂ has been measured at various temperatures and by combining the results with existing data the following thermodynamical quantities have been calculated: PbO(solid) + H₂ (1 atm.) = Pb(solid) + H₂O(liq.) - 17,017 g.-cal., the change in free energy at 25° being -11,639 g.-cal.; Pb(solid) + 0.5O₂ (1 atm.) = PbO(solid) - 51,253 g.-cal., the change in free energy being -44,921 g.-cal.; Pb⁺⁺ + 2OH⁻ = PbO (solid) + H₂O(liq.) with a change of free energy of -20,941 g.-cal. The entropy of lead monoxide at 25° is 18.89 units and its dissociation pressure 1.52×10^{-66} atm.; the product (Pb⁺⁺)(OH⁻) at 25° is 4.55×10^{-16} .

A. R. POWELL.

Cells of molten electrolyte. Cell: copper oxide-molten sodium hydroxide-zinc. G. I. COSTEANU (Compt. rend., 1929, 189, 35—37).—Such cells are produced by placing a stick of zinc, and a moulded electrode of copper oxide paste dried at 1000° under oxidising conditions, in molten sodium hydroxide previously heated at 400° for 4 hrs. in a closed nickel crucible to expel water. Their action depends on oxidation of zinc by the alkali, and reduction of the copper oxide by the hydrogen liberated. There is a fall in potential during the first 30 min. owing to the porosity of the copper oxide electrode, followed by a gradual rise to a final constant value of 1.322 volts. In an atmosphere of nitrogen the *E.M.F.* was 1.200 volts, rising to 1.322 after depolarisation by the addition of sodium peroxide.

J. GRANT.

Variations of *E.M.F.* developed [by metals] in contact with aqueous solutions of electrolytes of varying p_H values and salinities. F. VLES and A. UGO (Compt. rend., 1929, 188, 1550—1552).—In general, the potential-time curve of a metal or an alloy in contact with aqueous solutions of potassium chloride of various concentrations, and adjusted by acid or alkali to various values, shows maxima or minima according to the previous treatment of the electrode, and attains a final value which is determined by certain critical values of p_H and p_x (isopotential points). From the nature of the observed changes in p_H of the solution in certain cases it is considered that the isopotential point is analogous to the isoelectric point of an ampholyte.

J. GRANT.

Conceptions of electrical *P.D.* between two phases and the individual activities of ions. E. A. GUGGENHEIM (J. Physical Chem., 1929, 33, 842—849; cf. Taylor, A., 1927, 1144).—The view is

put forward that "the electric *P.D.* between two points in different media cannot be measured and has not yet been defined in terms of physical realities" and hence has no physical significance. The electrochemical potential, defined as $\bar{\mu}_i = \mu_i - \psi$ where ψ is the electrostatic potential of an ion of type i and charge ϵ_i , and μ_i is the chemical potential, has a real physical significance. The phenomena of diffusion, partition between two media, membrane equilibria, cells with and without liquid junctions, and rates of reaction are completely described in these terms or in such linear combinations of μ_i as can be expressed or defined in terms of $\bar{\mu}_i$; in no case can μ_i or ψ occur separately. Only such combinations of $\bar{\mu}_i$ have physical significance. L. S. THEOBALD.

Current density-potential curves in the region of residual currents. E. LIEBREICH and W. WIEDERHOLT (Z. Elektrochem., 1929, **35**, 367—368).—Attention is directed to the fact that the form of the residual current-potential curve depends on the way in which the current is actually measured—whether the ammeter is placed in the chief circuit, as was the case in the previous work of the authors (A., 1928, 483), or whether it is placed in a circuit including the experimental cell (cf. Müller and Konopicky, this vol., 269). Curves are given showing the differences obtained with a silver cathode in 0.02*N*-sulphuric acid against platinum. Oxidising agents have an effect on the residual current similar to that observed by Müller and Konopicky with oxygen. H. T. S. BRITTON.

Electrolytic polarisation due to retarded crystal growth. H. BRANDES (Z. physikal. Chem., 1929, **142**, 97—112).—When a solution of a metallic salt is electrolysed with a bright platinum electrode the ions liberated are not adsorbed, but pass into the Helmholtz double layer, and the electrode behaves as a condenser, the *P.D.* being directly proportional to the quantity of electricity brought up. If, on the other hand, the ions are deposited on a crystalline electrode of the same metal, depolarisation occurs owing to the ions gradually becoming embodied in the lattice. The depolarisation is proportional to the polarising *P.D.*, but the quotient of the two quantities varies considerably with the temperature, corresponding with the heat of activation required for ionic conduction over the electrode surface.

R. CUTHILL.

Theory of passivity. V. Influence of coating layer on the potential of a metal. W. J. MÜLLER (Monatsh., 1929, **52**, 53—58).—The magnitude of the local current in the closed system metal-electrolyte-coating layer is $i = e/(w_1 + w_2)$, where $e = E.M.F.$ of the system, w_1 = resistance in the pores of the layer, and w_2 = resistance in the layer. The apparent potential, iw_1 , must be deducted from the metal potential in order to give the electrometrically determined potential. This is designated as the correction coefficient and its magnitude is determined by the expression $A = F\kappa^1 / \{F\kappa^1 + (F_0 - F)\kappa\}$, where F is the coated surface, $F_0 - F$ the surface of pores, κ^1 the specific conductivity of covering layer, and κ the specific conductivity of the electrolyte in the pores. The calculated values of this coefficient for various

thicknesses and conductivities of layer and electrolyte show that increased coating increases the value in all cases; for equal values of coating and electrolyte conductivity the coefficient increases with the conductivity of the layer, whilst for equal values of coating and layer conductivity it increases with decreased conductivity of electrolyte. A comparison of the results with the previously found values for the potential of coated aluminium electrodes (Müller and Konopicky, this vol., 269) gives plausible values for the degree of coating. H. BURTON.

Electrolytic oxidation of various organic substances. C. MARIE and G. LEJEUNE (J. Chim. phys., 1929, **26**, 237—249; cf. A., 1928, 1102).—The effect of adding varying quantities of primary aliphatic alcohols (methyl, ethyl, propyl, butyl, and amyl) on the current-potential curves for the electrolysis of sulphuric acid and sodium hydroxide solutions has been studied using anodes of platinum, gold, and nickel. With a solution of sodium hydroxide containing the primary alcohol electrolysis commences at about 0.6 volt (*P.D.* between electrodes). As the potential is increased the current rises rapidly, drops again to a very low value, and finally increases rapidly at 1.6 volts. In the absence of a depolarising substance electrolysis commences only at 1.8 volts. The preliminary unstable region in the current-*P.D.* curve, when a primary alcohol is present, is ascribed to reduction at the anode of the unstable oxide PtO_3 to the stable form PtO_2 and formation of the aldehyde. Addition of the primary alcohols to a solution of sulphuric acid also produces an unstable region in the current-*P.D.* curve, but the final rapid increase of the current commences at 1.1 volts instead of at 1.6 volts. The formation of aldehyde occurs only if the anode is in the state which corresponds with the unstable region on the curve. With a gold anode in acid and in alkaline solution, and with a nickel anode in alkaline solution, there is no unstable region in the current-*P.D.* curve, when alcohols are added to the solution, and the curves are practically normal. The effect of other organic substances, e.g., isopropyl alcohol, aromatic alcohols, and amines, is also described. The nature of the anode is important in oxidations which take place when the electrode is in the unstable state, but since this condition cannot ordinarily be maintained, the only influence of the nature of the anode metal is to determine the value of the anodic overvoltage. O. J. WALKER.

Reaction velocity, concentration, and activity. A. SKRABAL (Z. physikal. Chem., 1929, **B**, **3**, 247—270).—Theoretical. The theory put forward by the author (Monatsh., 1929, **51**, 93) is compared with that of Bronsted. The author's theory assumes that in general there are two types of intermediate products: (a) "Arrhenius intermediate products," which are in equilibrium with the initial reactants, and (b) "van 't Hoff intermediate products," which are in equilibrium with the end-products of the reaction. The latter class of substances is more unstable than the former, and their concentration will be smaller. The "van 't Hoff" intermediate products correspond with Bronsted's "unstable critical complexes," whilst the Arrhenius products correspond with Bronsted's

"intermediate stable complexes." In the first place the velocity of the fundamental reaction $A \rightleftharpoons B$ is considered. Then the velocity of the reaction $A \rightleftharpoons Z \rightleftharpoons B$, in which Z is an intermediate product, is calculated, equations being obtained for the cases where Z is stable or unstable. By comparing the final result with Bronsted's equation it is found to be in agreement, showing that the reaction velocity is directly proportional to the activities of the reacting substances and inversely proportional to the activity coefficients of the unstable intermediate products. There is, however, a difference in so far as according to Bronsted the velocity coefficient of the forward reaction is equal to that of the reverse reaction. The author states that they are different. The analysis of velocity coefficients is then attempted. The general equations which are derived for any media and activity coefficients when the medium is made constant, and when the activity coefficients are constant, become identical with the equations of classical chemical kinetics, and the equations for the intermediate reactions then become identical with those of Bronsted.

A. J. MEE.

Kinetics of the reaction $2NO + O_2 = 2NO_2$ at low pressures and under the influence of a strong magnetic field. G. KORNFELD and E. KLINGLER (*Z. physikal. Chem.*, 1929, B, 4, 37—66).—A special membrane manometer was used for the pressure measurements. The experiments show that at low pressures (down to below 1 mm. total pressure) the reaction $2NO + O_2 = 2NO_2$ is termolecular. There was good agreement between the results, the mean value of the constant for twenty sets lying between 2.8×10^4 and 3.3×10^4 . This is in good agreement with the value obtained by Bodenstein for higher pressures. The reaction is termolecular over very wide changes of the concentrations of nitric oxide and oxygen. The effect of a magnetic field was also studied. There are no changes in the course of the reaction.

A. J. MEE.

Ignition pressures of phosphine mixtures. M. TRAUTZ and W. GABLER (*Z. anorg. Chem.*, 1929, 180, 321—354).—A summary of previous work on the ignition of gas mixtures by expansion is given. New experiments have been carried out to ascertain the influence of the wall material, composition of the mixture, and temperature on the ignition pressure of mixtures of phosphine with oxygen. In general, such mixtures show a definite range of pressure over which spontaneous ignition occurs, the range becoming narrower as the partial pressure of water vapour and the proportion of oxygen increase. Ignition occurs on lowering the pressure slowly to a critical value, but it is often possible by rapid diminution of the pressure to overstep the ignition range, and in such cases ignition can be produced by a slow increase of pressure. The ignition pressures of mixtures of different composition were not noticeably affected by varying the nature of the walls of the containing vessel or by introducing nickel, copper, or iron foil. When the gases were separately dried by cooling at -80° spontaneous ignition occurred on mixing at the ordinary pressure. With mixtures in which the partial pressure of water vapour exceeded 6 mm.

ignition could not be produced by expansion when the proportion of oxygen was greater than 0.5 vol., and with increasing moisture content a still higher proportion of phosphine was required before the mixture could be caused to ignite. Within the range over which ignition could be produced the ignition pressure was found to rise with decreasing moisture content and with decreasing ratio of oxygen to phosphine. Admixture of nitrogen, nitrous oxide, hydrogen, carbon monoxide, carbon dioxide, or ammonia lowered the ignition pressure slightly. All the above experiments were carried out at the ordinary temperature. The ignition pressure increased with rise of temperature. In all cases ignition was preceded by the formation of a phosphorescent mist which was electrically conducting. Mixtures of oxygen and methylphosphine could not be ignited by expansion at the ordinary temperature, and addition of the last-named substance to the phosphine mixtures greatly lowered the ignition pressure.

F. L. USHER.

Decomposition of alkali carbonates in boiling aqueous solution. II. B. L. VANZETTI and A. OLIVERIO (*Gazzetta*, 1929, 59, 288—300; cf. this vol., 661).—From a study of the various electrolytic and hydrolytic equilibria which can occur in dilute aqueous solutions of alkali carbonates it is to be expected that almost complete transformation into the alkali hydroxide will take place by continued boiling of the solution for several days, if the carbon dioxide is removed from the gaseous phase by a current of an inert gas or of the vapour of the solvent. By boiling 0.2*N*- and 0.4*N*-solutions of sodium carbonate, up to 74% of the carbonate was changed into hydroxide in about 6 days; with a 0.2*N*-solution of potassium carbonate 65% decomposition was obtained in 5—7 days. Decomposition occurred both by passing an inert gas (hydrogen or air) through the boiling solution, as well as by reflux distillation with exposure to the atmosphere and by steam distillation. By distilling in a vacuum the decomposition is no longer noticeable owing to the decreased hydrolysis at the lower temperature. The nature of the vessel does not have much effect, as similar results were obtained with glass and with silver vessels. The amount of carbonate transformed into hydroxide is proportional to the square root of the time.

O. J. WALKER.

Decomposition of lithium carbonate in boiling aqueous solution. III. B. L. VANZETTI and A. OLIVERIO (*Gazzetta*, 1929, 59, 300—304; cf. preceding abstract).—With a 0.27*N*-solution of lithium carbonate 71% decomposition to hydroxide was obtained in about 10 days; the velocity of decomposition is in this case somewhat slower than in the case of sodium and potassium carbonates. The percentage decomposition is again proportional to the square root of the time.

O. J. WALKER.

Decomposition of mercurous chloride in concentrated solutions of other chlorides. T. W. RICHARDS and M. FRANÇON (*J. Physical Chem.*, 1929, 33, 936—950).—The decomposition of mercurous chloride in concentrated solutions of lithium, potassium, and caesium chlorides at 25° has been investigated. The order of increasing effect is lithium <

potassium < caesium chloride. The whole question of the effect of solutions of various chlorides on mercurous chloride is discussed, together with the irregularities of the calomel cell. L. S. THEOBALD.

Velocity of autocatalytic decomposition of α -bromopropionic acid in aqueous solutions. J. ZAWIDZKI and J. G. ZAWIDZKI (Rocz. Chem., 1929, 9, 211—245).—See this vol., 34.

Thermal reaction between potassium oxalate and mercuric chloride. W. E. ROSEVEARE and A. R. OLSON (J. Amer. Chem. Soc., 1929, 51, 1716—1724).—The kinetics of the thermal reaction $2\text{HgCl}_2 + \text{C}_2\text{O}_4^{2-} = \text{Hg}_2\text{Cl}_2 + 2\text{Cl}^- + 2\text{CO}_2$ was investigated at 100° and 120° in neutral aqueous solution in the dark. The reaction is of the first order with respect to the mercuric chloride concentration under all conditions, the lowering of the rate on addition of chloride ions being due merely to the effect of the ions on the concentration of this salt. The rate is of the second order with respect to the oxalate concentration, but this velocity is lowered by the presence of oxygen. The rate is nearly inversely proportional to the oxygen concentration when the latter is low, but at higher concentrations the effect of the oxygen is very much diminished. Practically no oxygen is used up in the reaction. The effect of oxygen depends on the amount of iron salts present; traces of the latter can alter the order of the reaction. Since ferric oxalate at 100° loses carbon dioxide and forms ferrous oxalate at a moderate rate, repeated oxidation of the latter by the oxygen present will set up a continuous cycle, the repetition of which would account for the observed catalytic effect of the iron.

S. K. TWEEDY.

Action of hydrogen chloride on alcohol. Influence of electrolytes on the reaction velocity. S. KILPI (Z. physikal. Chem., 1929, 141, 424—450; cf. A., 1914, ii, 189).—The velocity coefficients in the equations previously given have been determined for the action of hydrogen chloride on alcohol in mixtures containing 25 and 50 mol.-% of alcohol at temperatures near to 96.5° and 110°. Mixtures containing sodium chloride and potassium chloride have also been studied. The value of the equilibrium constant C_2/C_1 (where C_1 is the velocity coefficient of the direct and C_2 that of the reverse change) was found to increase with the concentration of electrolyte between the limits 0.05*N* and 0.8*N*, but more slowly as the concentration was increased. Since C_2 has been shown to be independent of the electrolyte concentration, it follows that as the latter becomes greater the velocity of formation of ethyl chloride decreases, and in this respect the behaviour of the alkali chlorides showed no noticeable difference from that of hydrogen chloride within the range of concentration studied. An attempt is made to explain the relation between electrolyte concentration and reaction velocity in terms of the theories of Bronsted and of Debye and Hückel, for which purpose values of the coefficients A' and α' in the expression $A'\sqrt{c}/(1+\alpha'\sqrt{c})$ in the formula of Debye and Hückel were calculated from the experimental data and compared with the theoretical values. The agreement is as good as can be expected in view of the approx-

imate nature of the comparison. The velocity of the direct action of hydrogen chloride on alcohol is proportional to the product of the concentration of hydrogen ion and chlorine ion as determined potentiometrically. The mechanism of the reaction is discussed and the conclusion reached is that it is not possible to distinguish between a direct action of undissociated hydrogen chloride on the alcohol and a reaction $\text{Cl}^- + \text{EtOH} \rightarrow \text{EtCl} + \text{OH}^-$ catalysed by hydrogen ions. F. L. USHER.

Velocity of esterification of fatty acids with ethylene glycol and hydrochloric acid. A. KAILAN and A. SCHACHNER (Monatsh., 1929, 52, 23—52).—The velocities of esterification of *n*- and *iso*-butyric, *n*- and *iso*-valeric, hexoic, and heptonic acids in anhydrous and moist ethylene glycol with hydrogen chloride as a catalyst have been determined at 25°. The unimolecular velocity coefficients (*k*) for *n*-butyric, *n*-valeric, hexoic, and heptonic acids are the same and can all be expressed by the same formula, which is a function of the concentrations of water (*w*) and the catalyst (*c*) (cf. Kailan and Melkus, A., 1927, 749). The values of *k* for *isovaleric* and *isobutyric* acids are 22.4 and 70%, respectively, of those for *n*-butyric acid. In all the cases examined in anhydrous glycol *k* is proportional to *c*, but in moist glycol this relation holds only up to $c = N/6$. With increased *c* the values of *k* increase more rapidly in the moist glycol. The retarding action of water is of the same order as for glycerol and much less than for ethyl alcohol (cf. *loc. cit.*). When $w = 0.03$ — 0.06 mol. per litre, the values of *k* are 30—40% greater in ethyl alcohol than in glycol, and 2.5 times as great in glycol as in glycerol. For $w = 0.7$ and $c = N/6$ the values of *k* are only half as great in alcohol as in glycol and only a little greater than in glycerol. The values of *k* for *n*-butyric acid are about 12% higher than those originally found (*loc. cit.*). Under the conditions used esterification is practically complete. H. BURTON.

Rate of decomposition of solids. V. Rate of decomposition of mercurous carbonate and some metal salt hydrates. B. BRUZZ (Z. physikal. Chem., 1929, B, 3, 427—439; cf. A., 1926, 692).—Further experiments with the apparatus previously described have been made on the rate of decomposition of mercurous carbonate containing 90% of the theoretical amount of carbon dioxide. In every case the velocity rises to a maximum and then decreases, and is largely dependent on the external pressure. The results of a large number of experiments in which the temperature was varied between 125° and 150° and the external pressure between 500 and 1000 mm., plotted with velocities expressed as percentages of the maximum velocity and times as percentages of the time (*z*) required for the attainment of the maximum velocity, give a single curve with a well-defined maximum. Hence it is concluded that the mechanism of the reaction is unaffected by changes in temperature or pressure over the range studied. Since log *z* is shown to be proportional to the reciprocal of the absolute temperature, and 1/*z* has the dimensions of a first-order reaction constant, an expression analogous to the Arrhenius temperature function can be written, viz., $d \log_e z / d(1/T) = E/R$, where *E* is the critical

increment. The value of the latter is found to be 35,000 g.-cal., which is confirmed by two other methods. Experiments on the rate of dehydration of crystals of the hydrated sulphates of manganese, zinc, and sodium showed that although the reaction is apparently confined to the surface, fine grinding of the crystals, while increase the surface area as much as 10^5 times, increased the velocity only 10 times. A theoretical explanation is offered. F. L. USHER.

Oxidation of tungsten. Evidence for the complexity of tungstic oxide, WO_3 . J. S. DUNN (J.C.S., 1929, 1149—1150).—The temperature coefficient of the oxidation of tungsten in air has been determined over the range 700 — 1000° . It is found to be abnormal between 850° and 950° , although over this range the ordinary parabolic oxidation law is obeyed. The abnormal temperature coefficient is therefore not due to a sintering of the oxide film. The results are explained qualitatively if it is assumed that tungstic oxide exists in two forms which are in equilibrium. F. J. WILKINS.

Corrosion of iron. J. F. G. HICKS—See B., 1929, 521.

Acid and salt effects in catalysed reactions.
XX. **Ionisation of acids in salt solutions.** H. M. DAWSON and W. LOWSON (J.C.S., 1929, 1217—1229).—An account is given of a method for the determination of hydrogen-ion concentration from reaction velocity data and its application to the study of the influence of the concentration of a sodium chloride solution on the ionisation constants of acids. The rate of hydrolysis of ethyl acetate in sodium chloride solutions (0 — $4M$) has been measured in the presence of acetic, glycolic, chloroacetic, and dichloroacetic acids as catalysts. Experiments with hydrochloric acid afford a measure of the catalytic activity of the hydrogen ion in the sodium chloride solutions and the observations are not measurably influenced by the interaction of hydrogen and chlorine ions. Hence it is possible to calculate the ionisation constants of other acids from reaction velocity measurements.

The influence of sodium chloride on the ionisation constants of the acids is given fairly accurately by the equation $\log (K_x/K_0) = a\sqrt{x} - bx$, where K_x and K_0 are the ionisation constants of the acid in an xM -solution of sodium chloride and pure water, respectively, a and b are constants approximately independent of the nature of the acid. Divergences from this equation occur with large ($4M$) concentrations of salt, indicating that in these solutions new specific effects, which vary with the nature of the acid, come into play. It is shown that the above logarithmic formula, whilst of the form predicted by the Debye-Hückel theory, has constants which render it quantitatively incompatible with this theory. The theoretically predicted value of the Debye-Hückel coefficient α is much too large. Also, the experimental value is not independent of the nature of the ionic environment.

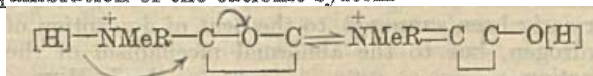
Further, the Bronsted equation (A., 1928, 1336) expressing the relationship between the catalytic coefficient k_m and the ionisation constant K accurately fits data obtained from the acetone-iodine reaction.

F. J. WILKINS.

Autoreduction of sodium silver sulphite. A. STEIGMANN (Kolloid-Z., 1929, 48, 193—194).—Solutions of sodium silver sulphite, with or without a slight excess of sodium sulphite, when kept for several hours deposit a precipitate, which consists partly of silver sulphite and partly of metallic silver. The longer the solution is kept, the higher is the ratio of silver in the precipitate. This autoreduction is strongly catalysed by very small amounts of copper salts. E. S. HEDGES.

Ultra-violet light, insulin, and amino-acid catalysis. J. M. ORT (J. Physical Chem., 1929, 33, 825—841; cf. A., 1928, 487).—The study of the initial stages of the oxidation of dextrose and laevulose and of the effects of amino-acids, insulin, and ultra-violet light by the oxidation potential method has been continued. Amino-acids of the glycine type catalyse the decomposition of hydrogen peroxide and promote its reaction with the active sugar, the view being developed from this and previous work that the reduction intensity in dextrose and laevulose solution at p_H 10 is due to the presence of a small amount of an active form which is in equilibrium with a comparatively inactive and abundant form. Ultra-violet light has a similar but greater effect. Acids of the type represented by glutamic acid are lacking in this catalytic effect, but appear to develop further reducing intensities when the stronger oxidising conditions no longer obtain. Insulin appears to catalyse negatively the decomposition of hydrogen peroxide. The applicability of the law of mass action to the oxidation of these sugars by air or hydrogen peroxide is discussed. Excess of hydrogen peroxide and irradiation destroyed 80% of the sugar in a short time as compared with 20% under all other conditions investigated. Solutions of dextrose without insulin when irradiated for several hours after the removal of air developed reduction potentials exceeding that of a hydrogen electrode in similar solutions. L. S. THEOBALD.

Mechanism of tautomeric interchange and the effect of structure on mobility and equilibrium.
IV. **Mechanism of acid catalysis in the mutarotation of nitrogen derivatives of tetra-acetylglucose.** J. W. BAKER (J.C.S., 1929, 1205—1210; cf. A., 1928, 967).—A number of derivatives of tetra-acetylglucose of the type $(\text{C}_{14}\text{H}_{19}\text{O}_9)\text{NMeR}$ have been prepared and the possibility of mutarotation in the presence of hydrochloric acid consequent on the equilibration of the cationic system



has been investigated. A mutarotation following a unimolecular law is observed, but is found to be due not to an isomeric change but to a decomposition into the parent sugar and the hydrochloride of the base.

The following *p*-substituted benzylmethylamine derivatives were isolated: *p*-methyl-, b. p. $84^\circ/6$ mm. (hydrobromide, m. p. 166°); *p*-chloro-, b. p. $101^\circ/5$ mm. (hydrobromide, m. p. 196°); *p*-cyano-, b. p. $143^\circ/6$ mm. (hydrobromide, m. p. 209 — 210°). Of the substituted methylamines, the di-(*p*-methylbenzyl)-, b. p. $180^\circ/6$ mm. (approx.), di-(*p*-chlorobenzyl)-, b. p. $200^\circ/6$ mm.

(approx.), and di-(*p*-cyanobenzyl)-, m. p. 65° [*hydrochloride*, m. p. 250° (decomp.)], were isolated.

The tetra-acetylglucosidyl derivatives of the bases were prepared from tetra-acetylglucosidyl bromide and the substituted benzylmethylamine: *benzylmethylamide*, m. p. 125° (*hydrochloride*, m. p. 80°); *p*-methylbenzylmethylamide, m. p. 104—105° [*hydrochloride*, m. p. 175° (decomp.)]; *p*-chlorobenzylmethylamide, m. p. 104—105° [*hydrochloride*, m. p. 137° (decomp.)]; *p*-cyanobenzylmethylamide, m. p. 85—86° [*hydrochloride*, m. p. 146° (decomp.)]. Piperidine gives two different products depending on the experimental conditions: *piperidide A*, m. p. 123° (*hydrochloride*, m. p. 126°); *piperidide B*, m. p. 136° (decomp.); [*hydrochloride*, m. p. 130—131° (decomp.)]. The *hydrochlorides* of the diethyl and dimethylamide derivatives of tetra-acetylglucose have m. p. 152—153° and 159—160° (decomp.), respectively.

F. J. WILKINS.

Theory of heterogeneous catalysed reactions. Multiplet hypothesis. Model of dehydrogenation catalysis. A. A. BALANDIN (*Z. physikal. Chem.*, 1929, **B**, **3**, 482).—Corrections to a paper recently published (this vol., 519). F. L. USHER.

Catalytic decomposition of ammonia. II. G. M. SCHWAB and H. SCHMIDT (*Z. physikal. Chem.*, 1929, **B**, **3**, 337—359; cf. Schwab, A., 1927, 946).—The catalytic decomposition of ammonia at the surface of platinum was investigated over a range of 0.25—4 mm. and 10—300 mm. of ammonia, between temperatures of 1100° and 1485° Abs. A new process of obtaining a constant temperature is described. In the first range the decomposition can be expressed by the equation $-dx/dt = k_1[\text{NH}_3]/[\text{H}_2]$. The inhibitive action of nitrogen which has been observed at lower pressures vanishes in this range. The heat of activation is found to be 44,000 g.-cal. per mol. In the second range the decomposition cannot be represented by so simple an equation as the first. In this case the velocity may be represented approximately by $-dx/dt = k_2[\text{NH}_3]^{1.4}/[\text{H}_2]^{2.3}$. The heat of activation in this range is 140,000 g.-cal. per mol. In the lower pressure range the adsorbed ammonia decomposes in part on the active surface. A comparison with previous work on other metals with regard to the heat of activation shows that the decomposition is normal and comparable with other metals only in the lower pressure range. In the higher range the heat of activation is much greater than would be expected. This is not due, as has formerly been supposed, to the heat of desorption of hydrogen, but to the abnormal mechanism of the reaction.

A. J. MEE.

Catalysis of the combustion of sulphur in organic substances. L. BERMEO and A. RANCANO (*Anal. Fis. Quim. [Tecn.]*, 1929, **27**, 113—128).—Unsuccessful efforts have been made to find a substitute for the platinum catalyst employed in Pregl's method for the combustion of sulphur in organic substances, and to derive some relationship between the composition of the catalyst and the structure of the organic compound.

H. F. GILLBE.

Nickel catalyst. I. Catalyst prepared from nickel chloride. T. KUSAMA and Y. UNO (*Bull.*

Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 461—466).—Small quantities of chlorine in nickel catalyst prepared from nickel chloride are not fatal to its activity, since the chlorine remaining in the adsorbed state is in the form of nickel chloride and/or sodium chloride, of which the former is reduced to the metal on heating in hydrogen, whilst the latter does not fuse at the temperature used. Basic carbonate was prepared from nickel chloride and sodium carbonate, washed thoroughly, and changed by heating at 480° into an oxide containing 0.023% Cl. The catalyst prepared by reducing this oxide with hydrogen at 350° was as active as a specimen prepared from the nitrate by reducing in naphthalene, benzene, phenol, and aniline.

J. W. SMITH.

Effect of high-frequency discharges on the dissociation of gases. M. J. MARSHALL and E. H. NUNN (*Amer. Electrochem. Soc.*, May, 1929. *Advance copy*. 11 pp.).—When a high-frequency discharge is passed through a gas there is generally a very rapid increase of pressure during the first few seconds, followed by a much slower increase towards a maximum value. The initial sharp rise of the pressure-time curve is attributed to dissociation of the gas, and from the magnitude of this rise the degree of dissociation can be calculated. The subsequent more gradual rise is ascribed to the heating effect of the current. Unpublished work by F. Potter on helium and oxygen shows that the former does not give the initial rapid rise of pressure, and thus supports this view. The present work on hydrogen and air and an unpublished investigation by G. B. Carpenter on chlorine indicate that a considerable proportion of the molecules of a diatomic gas can be dissociated by means of a high-frequency discharge of suitable type. The degree of dissociation attained increases with increase in the initial pressure of the gas, but it is greatly dependent on the shape and dimensions of the discharge chamber: in particular, the smaller are the electrodes the greater is the dissociation. The bearing of these results on the influence of electrical discharges on chemical reactions is discussed.

H. J. T. ELLINGHAM.

Gaseous combustion in electric discharges. III. Cathodic combustion of dry carbon monoxide detonating gas. G. I. FINCH and D. L. HODGE (*Proc. Roy. Soc.*, 1929, **A**, **124**, 303—317).—Previous investigations with electrolytic gas (Finch and Cowen, A., 1926, 690; 1927, 1146) have been extended to a case of gaseous combustion in which the water contents of the reacting gases could be rigidly controlled, and the cathodic combustion of dry "detonating gas" (a mixture of carbon monoxide and oxygen in equivalent proportions) has been examined under various conditions. The results show that over a considerable range of gas pressure, gap width, and current, combustion is purely cathodic, although under suitable conditions it also occurs in the inter-electrode zone, such combustion being proportional to the current and superposed on the cathodic combustion. The rate *c* of cathodic combustion is directly proportional to the current, depends slightly on the gas pressure, and is considerably influenced by the nature of the cathode material.

Thus the c/i ratio found with a platinum cathode is more than three times that obtained with a copper cathode, and experiments with silver, gold, platinum, palladium, tungsten, tantalum, copper, aluminium, and magnesium cathodes show that combustion is more vigorous at cathodes consisting of freely sputtering metals than at poorly or non-sputtering metals. The cathodic potential falls at the different metals examined vary from 320 to 375 volts. The view is developed that the combustion of dry "detonating gas" in a direct-current discharge is primarily determined by the ionisation of the gases in the cathode zone, both positive and negative ions, but mainly the former, being produced. The electrostatic repulsion between similarly-charged ions greatly reduces the frequency of effective collisions, with the result that the rate of combustion is slow; where combustion occurs at a freely sputtering cathode, the cathode zone contains an abundance of negatively-charged metal atoms, which, by forming electrically neutral metal-gas complexes with positive ions, overcome the electrostatic repulsion and promote combustion. The above conclusions are strongly supported by the fact that three independent methods of calculating the c/i ratio all give results of the same order as those obtained experimentally.

L. L. BIRCHSHAW.

Synthesis of ammonia in the glow discharge. A. K. BREWER and J. W. WESTHAVER (J. Physical Chem., 1929, 33, 883—895).—The synthesis of ammonia in the glow discharge from a mixture of hydrogen and nitrogen (3:1 vols.) at 4—0.1 mm. and under various conditions with different sizes and types of discharge tube has been investigated. Aluminium electrodes were used in discharge tubes of two main types, one U-shaped partly immersed in liquid air and the other bulb-shaped and completely immersed. Electrostatic and magnetic fields were also applied to the discharge. For a given discharge tube and magnetic field, the rate of formation of ammonia is directly proportional to the current passing through the discharge and is constant at a fixed current value. The rate is independent of the pressure and the potential gradient in the discharge. The curves obtained by plotting pressure against time are linear for all the various tubes investigated. The application of a magnetic field of the order of 10^3 gauss affects the character of the discharge, causing sheeting or banding, and with the field at right angles to the electron path, varies the potential necessary to maintain the discharge. A field at right angles to the electric field increases the rate of synthesis of ammonia, whilst a parallel field has no effect. An electrostatic field has little, if any, effect both with alternating and direct current. The current efficiency increases with the length of the discharge column immersed in liquid air, and the power efficiency increases with an increase in diameter of the tube. The data indicate that the reaction is initiated by the positive ions formed in the discharge, and that the rate of synthesis of ammonia is proportional to the rate of formation of positive ions, which, in turn, is proportional to the current. This is suggested as a new electrochemical equivalence law for chemical reactions in discharge tubes.

L. S. THEOBALD.

Anode reactions of fluorine. N. C. JONES (J. Physical Chem., 1929, 33, 801—824; cf. Fichter and co-workers, A., 1926, 1927, and 1928).—From a consideration of the work of previous investigators, together with some new experiments, the author concludes that the chemical action of fluorine on aqueous solutions is the same as the electrolytic anodic reactions plus any further reactions due to the hydrofluoric acid formed. Further, fluorine instead of reacting with the water of the solution forms persulphate from acid sulphate solutions, and perphosphate, percarbonate, and perborate from phosphates, carbonates, and borates, respectively, hydrogen peroxide from alkali, and ethane from potassium acetate solution. It oxidises also cobaltous, chromic, manganous, and plumbous salts. When passed into pure sulphuric acid fluorine yields fluosulphonic acid because the hydrofluoric acid formed combines with the sulphur trioxide of the compound $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ which results when pure sulphuric acid is electrolysed. The primary action which occurs when fluorine acts on cold, concentrated solutions of alkali is the discharge of hydroxyl ions which form hydrogen peroxide; ozonate and ozone arise from secondary reactions. Manganous salts when in excess are oxidised to manganese dioxide, but in the presence of hydrofluoric acid manganic fluoride is formed: permanganate results in both cases only after all the manganous ions have been oxidised. The apparent reduction of dichromate to chromic salt is due to a catalytic reduction by small amounts of hydrofluoric or sulphuric acid present in the solution of perchromic acid which is first formed. In strongly acid solution, oxidation of chromic salts to chromate proceeds as in electrolytic oxidation. Lead dioxide is obtained from plumbous salts and fluorine only in alkaline solution or suspension; in acid solution, the lead tetrafluoride formed is stable. The preparation of fluorine by the electrolysis of fused potassium hydrogen fluoride in a modification of Mathers' magnesium cell (A., 1924, ii, 847) is described. The mechanisms of the above reactions are discussed on the view that the reaction which involves the least expenditure of energy is the one which takes place, and the views of Fichter and co-workers are, in many cases, adversely criticised.

L. S. THEOBALD.

Direct electrolytic preparation of ammonium permanganate. G. RAPIN (Compt. rend., 1929, 188, 1547—1548).—The intense but unstable purple colour obtained at the silico-manganese anode (66% Mn, 23% Si) during the electrolysis at 20° of ammonia solution (d 1.18) with an isolated platinum cathode at 60 volts and 0.2 amp. is considered to be due to the formation of ammonium permanganate. The conductivity of the solution, but not the intensity of colour, is increased by addition of ammonium chloride.

J. GRANT.

Preparation of potassium permanganate by electrolysis. J. ROUDNICK (Bull. Soc. chim. Belg., 1929, 38, 147—159; cf. A., 1923, ii, 118, 319).—The influence of the nature of the electrolyte and electrodes, temperature, and potential, on the yield of permanganate formed electrolytically has been investigated. The best results are obtained by using as

electrolyte solutions of potassium carbonate of medium concentration (e.g., 6*N*) at a low temperature (3–5°). The cathode should have a smaller surface than the anode, which is best made of ferromanganese containing 80% Mn. The optimum potential is 2.45 volts.

B. W. ANDERSON.

Precipitation of manganese dioxide by electrolysis with alternating current. A. P. ROLLET (Compt. rend., 1929, 189, 34–35).—Manganese in concentrations of 10^{-3} to 10^{-2} is completely precipitated as a brown deposit of $\text{MnO}_2 \cdot \text{H}_2\text{O}$ from solutions of nickel salts in the presence of 0.5–0.005*N*-acid by alternating-current electrolysis (50 periods per sec.) with platinum or nickel electrodes. The presence of nickel is essential, and halogen salts give best results. The current density depends on the temperature, which must not exceed 30°, and is 0.2 and 0.7 amp./cm.² at 0° and 20°, respectively. Higher concentrations of manganese require several hours for complete deposition.

J. GRANT.

Electroplating of cadmium from cyanide baths. L. R. WESTBROOK.—See B., 1929, 560.

Anodic formation of the triacetates of nickel and cobalt and Kolbe's reaction. C. SCHALL and C. THIEME-WIEDTMARCKTER (Z. Elektrochem., 1929, 35, 337–344).—The equivalent conductivities of solutions of the anhydrous diacetates of nickel, cobalt, and lead in perfectly dry glacial acetic acid were measured. They were independent of dilution, but not of temperature (cf. Schall and Markgraf, A., 1924, ii, 342; Schall and Melzer, A., 1923, i, 87). Addition of small amounts of water had appreciable effects. Anodic oxidation of nickelous and cobaltous acetates in water-free acetic acid was carried out in an apparatus similar to that used by Schall and Markgraf, with the exception of a device to keep the anode cool. Under certain experimental conditions cobaltic and nickelic acetates could be formed in the anolytes. Chemical and cryoscopic evidence is advanced to support the view that these acetates are complex and are the normal salts of $[\text{X}_3(\text{OAc})_6](\text{OH})_3$, X being either Ni^{III} or Co^{III} .

These salts were also formed by passing ozone, which had been carefully dried over phosphorus pentoxide, through saturated glacial acetic acid solutions of the respective bivalent metallic salts, but as occurred with their anodic formation, there was found to have been formed in the solutions glycollic, glyoxylic, succinic, and oxalic acids. Ethane could be detected in the gases liberated at the anode, and consequently the reactions occurring at the anode in conjunction with the oxidation of the metal ions are considered in connexion with Kolbe's electrosynthesis of hydrocarbons.

H. T. S. BRITTON.

Designation of quantity of light in photochemistry. M. BODENSTEIN and C. WAGNER (Z. physikal. Chem., 1929, B, 3, 456–458).—It is proposed to denote 6.06×10^{23} light-quanta by the name "1 einstein" and the symbol *E*. It is further suggested that intensity of absorbed light (I_{abs}) should be given in einsteins per sec., that *L* should be used to denote number of einsteins, and $[I_{\text{abs}}]$ the number of einsteins absorbed per litre per second.

F. L. USHER.

Light standard for sensitometry, and the Davis-Gibson light filter with copper-cobalt solutions. J. M. EDER (Z. wiss. Phot., 1929, 26, 373–374).—The statement has been made that it is difficult to make the Davis-Gibson light filter owing to the difficulty in obtaining pure cobalt ammonium sulphate. It is pointed out that pure cobalt and ammonium sulphates can be used in equivalent amounts to give the required solution. A. J. MEE.

Photochemical temperature coefficients. W. D. BANCROFT and R. P. ALLEN (Proc. Nat. Acad. Sci., 1929, 15, 445–448).—The view that temperature coefficients of photochemical reactions are relatively small is regarded as incorrect. The Grotthuss theory of chemical depolarisers is applicable to thermal depolarisation, and since exothermic substances can be made unstable by heating, they can be made photosensitive by heating to a suitable temperature. A simple high-temperature ozoniser having porcelain tubes was devised, and used to investigate the decomposition of acetaldehyde. Reaction velocity-temperature curves consist of a rapidly ascending part at low temperatures, followed by a nearly horizontal part, and finally a rapidly ascending part near the region of thermal instability. Conditions at low temperatures are discussed with special reference to the work of Amato (Gazzetta, 1885, 14, 57) on hydrogen and chlorine at –12°. N. M. BLIGH.

Equations for sensitised photolysis. E. BAUR (Helv. Chim. Acta, 1929, 12, 793–806).—Equations for the kinetics of such reactions are derived on the basis of the theory previously advanced (A., 1918, ii, 284) and are examined in the light of the experimental data of various workers.

L. S. THEOBALD.

Behaviour of atomic hydrogen. I. Behaviour towards ethylene. A. KLEMENC and F. PATAT (Z. physikal. Chem., 1929, B, 3, 289–298).—The atomic hydrogen was produced by the resonance method. With ethylene mixed with hydrogen, no smooth hydrogenation would take place when the total radiation from a mercury-vapour lamp was used, but polymerisation products were formed. The formation and properties of the polymerisation products are discussed. Under the action of ultra-violet light the ethylene is decomposed to give acetylene and hydrogen. The acetylene appears to be formed only as an intermediate product. The polymerised substance cannot be further hydrogenated by atomic hydrogen, contains more hydrogen than is to be expected, and it has the peculiar property of absorbing large quantities of oxygen. The possibility of the occurrence of quinquivalent carbon is mentioned. From ethylene, oxygen, and hydrogen, alcohol is formed on illumination. The experiments show that excited mercury atoms can cause a reaction without the intermediate action of hydrogen.

A. J. MEE.

Influence of the intensity of illumination on the velocity of photochemical union of bromine and hydrogen. M. BODENSTEIN, W. JOST, and G. JUNG (J.C.S., 1929, 1153–1158).—It is suggested that the catalyst for the photochemical union of bromine and hydrogen is the bromine atom. This catalyst may be destroyed by a three-body collision (Born and

Franck, A., 1925, ii, 266) in the gas phase, a reaction proportional to the square of the concentration of bromine atoms, or by recombination at the walls of the reaction vessel, a reaction of the first order. An explanation is therefore obtained of the equation Briers and Chapman (A., 1928, 970) used to express the rate of decomposition of their hypothetical catalyst. Further, the mean life of the catalyst calculated on the basis of this theory is 0.14–0.22 sec., a result in satisfactory agreement with that of Briers and Chapman. The hypothesis also demonstrates that the discrepancies apparent between the work of Lütke Meyer and Bodenstein (A., 1925, ii, 218) and Briers and Chapman are illusory. F. J. WILKINS.

Oxidation of hydrogen iodide in the dark and in the light. III. Constitution of iodine solution. IV. Discussion of the light-sensitiveness. C. WINTHER (Z. physikal. Chem., 1929, B, 3, 299–314, 315–336).—III. The equilibria between different components present in a dilute solution of iodine in potassium iodide and in hydrochloric acid were investigated by studying the distribution of iodine between carbon tetrachloride and water, potassium iodide solution, hydrochloric acid, and a mixed solution of potassium iodide and hydrochloric acid. The equilibrium constants were found. In the course of the work the solubilities of iodine in water and in hydrochloric acid were determined. The true distribution coefficient of iodine between carbon tetrachloride and water is 110, both at 20° and 30°. The extinction coefficients of the components were found for a wave-length of 436 μ . There is evidence for the formation of an I_5^- ion in most iodine solutions.

IV. The oxidation of hydrogen iodide in the dark is considered and a corresponding formula for the light reaction is deduced. Previous determinations have shown that the amount of iodine formed in the dark $\Delta_i = kt + k_1 t C_i$, where t is the time and C_i is the iodine concentration. The oxidation in the dark thus consists of two reactions, one of which is proportional to the iodine concentration, the other being independent of it. The second part of this reaction is investigated and the expression found for the total dark reaction is $\Delta_i = kt + (a_1 \sqrt{km_i^2}) / (b_1 + m_i \sqrt{\quad})$ where a_1 , b_1 , and k are constants and m_i and m_t are the masses of iodine ions and total iodine present. The values of the constants are given for 20° and 30°. A similar equation is obtained for the light reaction. It is possible to calculate by certain simple suppositions the velocity of the light reaction from that of the dark reaction by making use of quantitative absorption measurements. The conclusion reached can be supported by many other experiments.

A. J. MEE.

Monatomic iodine and molecular hydrogen. W. D. BANCROFT and D. S. MORTON (Proc. Nat. Acad. Sci., 1929, 15, 438–441).—The conditions under which the halogens, excluding fluorine, react photochemically with hydrogen are discussed generally, and investigated in the case of hydrogen and iodine, different results being obtained with glass and quartz containers. The conclusions reached are that hydrogen is activated by ultra-violet light, but not appreciably by visible light, and that photochemically or catalytic-

ally activated hydrogen and halogens are atomic and react at ordinary temperatures under ultra-violet light; visible light causes hydrogen to react with chlorine at the ordinary temperature, with bromine at 196°, but not with iodine at 350°; molecular hydrogen reacts with monatomic chlorine at ordinary temperatures, with bromine at 196°, but with iodine not appreciably at 350°. These considerations apply to equilibrium rather than to overvoltage concentration conditions. N. M. BLIGH.

Photochemical equilibrium in nitrogen peroxide. II. Dependence of quantum efficiency on wave-length. R. G. W. NORRISH (J.C.S., 1929, 1158–1169; cf. A., 1927, 528).—The quantum efficiency (γ) of the photochemical reaction

$2NO_2 \xrightarrow{\text{light}} 2NO + O_2$ has been measured for six wave-lengths, with the following results: for 5760, 5460, 4360 Å., $\gamma = 0.000$; for 4050 Å., $\gamma = 0.74$; for 3650 Å., $\gamma = 2.10$; and for 3160–2650 Å., $\gamma = 2.07$. The photochemical threshold in the middle of a region over which nitrogen peroxide absorbs strongly, observed by Dickinson and Baxter (A., 1928, 491), has been found to be much sharper than was originally supposed, for, contrary to their result, no photochemical activity was obtained at the wave-length 4360 Å.

F. J. WILKINS.

Kinetics and temperature coefficients of some photochemical reactions in radiations of different wave-lengths. B. K. MUKERJI and N. R. DHAR (J. Physical Chem., 1929, 33, 850–863; cf. this vol., 516).—The temperature coefficients in the light and in the dark have been determined for the following reactions: bleaching of dicyanine, oxidation of iodoform, and reactions between sodium citrate and iodine, sodium malate and iodine, sodium formate and mercuric chloride, potassium oxalate and iodine, sodium potassium tartrate and bromine, quinine sulphate and chromic acid in the presence of sulphuric acid, potassium permanganate and oxalic acid, and chromic and oxalic acids both in the presence of manganese sulphate and sulphuric acid, sodium formate and iodine and sodium nitrite and iodine both in the presence of sodium acetate, ferrous sulphate and iodine, and mercuric chloride and ammonium oxalate in the presence of eosin. The temperature coefficients of the photochemical changes are less than those of the corresponding thermal reactions and depend on the wave-length of the incident radiation, and, in general, the greater is the observed acceleration of the reaction by light, the smaller is the value of the temperature coefficient. All the reactions are accelerated by light of wave-lengths 4725, 5650, and 7304 Å., and in several cases absorption and acceleration are at a maximum at λ 5650 Å. The reactions between sodium malate and iodine and sodium citrate and iodine are both termolecular in the dark. The conception of a photochemical threshold below which radiations of smaller frequencies do not promote a reaction is put forward and values are calculated from the temperature coefficients of the dark reactions. L. S. THEOBALD.

Photography. I. Nature of sensitivity and latent image. F. E. E. GERMANN and D. SHEN

(*J. Physical Chem.*, 1929, 33, 864—872).—Photographic sensitisers are discussed and a bibliography of the sensitising effect of silver iodide in silver bromide emulsions is given. A formula for the preparation of silver iodide emulsions of a large range of grain size is also detailed. Contact of spent developer with dilute acids was found to be accompanied by luminescence and hence washing with water is preferable to the use of a fixing bath. A study of the grain sensitivity of iodide emulsions showed that in those which are unsensitised only 17% of the grains ever develop. Centrifuging and coating of different fractions on various plates of an emulsion of a wide range of grain size failed to show any difference in development between the fractions and the original emulsion. Large and small grains thus appear equally sensitive and, further, insensitivity is not due to lack of sensitising material, but is attributed to rapid reversal.

L. S. THEOBALD.

Photochemistry of silver halides. V. Silver value and fixing process. H. H. SCHMIDT and F. PRETSCHNER (*Z. wiss. Phot.*, 1929, 26, 375—380; cf. A., 1928, 1340; B, 1928, 625).—Various emulsions were used, and it was found that the amount of silver present after fixing was not equal to the amount in the control plate. With the normal plate the amount is smaller after fixing, and therefore some must be lost in the fixing bath. Whether there is a change to silver sulphide is uncertain. There is approximately the same amount of silver after fixing in all the plates. The decomposition of the silver complex solution with the formation of silver sulphide is a diffusion process which proceeds with a slower velocity than the diffusion of the solution from the gelatin. In the gelatin itself there is a silver complex solution, and a silver compound soluble in nitric acid, which can be identified as silver sulphide. The amount of silver remaining in the gelatin is directly proportional to the thickness of the layer and therefore for nodules of emulsion is very high. The diffusion of the complex solution from the thick layers is naturally slower than from thin, and therefore the formation of silver sulphide can proceed further. The method of washing also plays a part. The effect of different fixing baths on the amount of silver remaining in the gelatin is small.

A. J. MEE.

Primary process in the formation of the latent photographic image. S. E. SHEPPARD (*Nature*, 1929, 123, 979—980).—The results of Toy and Harrison (this vol., 660) support the view that the inner photo-electric effects (photo-voltaic and photo-conductance), as also the photographic and photochemical effects, are all derived from the same primary separation of the electron from the bromide ion. The formation of a latent image involves both the segregation of bromine and the aggregation of the silver atoms produced.

A. A. ELDRIDGE.

Photodichroism and photoanisotropy. III. Quantitative measurement of induced photodichroism. F. WEIGERT (*Z. physikal. Chem.*, 1929, B, 4, 83—112; cf. this vol., 871).—The phenomenon of induced photodichroism in developed photographic layers is further discussed. It is a phenomenon of the same general nature as primary

photodichroism and can be produced in almost all light-sensitive colouring matters in layers. The degree of reproducibility of determinations of induced photodichroism is discussed. The phenomenon is influenced, e.g., by changes in the composition and preparation of the emulsion, and the method and time of fixing and development. The effects are different if a dry or a moist layer is excited, and also if the duration and colour of the excitation are altered. The effects of these alterations are studied in detail. The importance of micelle deformation in this connexion is pointed out, it being assumed that this is the primary action in each case.

A. J. MEE.

Mechanism of photochemical changes occurring in a fluorescing electrolyte. J. C. GHOSH (*Z. physikal. Chem.*, 1929, B, 3, 419—426).—Theoretical. The *E.M.F.* generated in a cell containing a solution of a fluorescent material, e.g., alkali fluorescein, in which are two platinum electrodes, one of which is illuminated, is attributed to the formation of an unstable intermediate product, the concentration of which at a time t after exposure to light is $C_n = (\sqrt{k_4 I / \sqrt{k_3}}) \tanh t \sqrt{k_4 I}$, where I is the intensity of the incident light. The *E.M.F.* calculated from Nernst's formula, using values of C_n obtained from the above expression, agrees well with the experimental results of Rule (*Proc. Nat. Acad. Sci.*, 1928, 14, 272).

F. L. USHER.

Photochemical formation of carbonyl chloride. IV. Change at low pressures and an improved interpretation of the mechanism of the reaction. M. BODENSTEIN, S. LENHER, and C. WAGNER (*Z. physikal. Chem.*, 1929, B, 3, 459—478; cf. A., 1928, 254).—The reaction between chlorine and carbon monoxide has been further studied at the ordinary temperature and at low pressures (below 40 mm.) with improved experimental arrangements and with minute precautions against the entry of impurities. The expression for the velocity coefficient obtained previously does not fit the observations at lower pressures and it has been found necessary to make different assumptions regarding the mechanism. It is suggested that, in addition to the changes in the gas phase which result in the removal of chlorine atoms, there is at lower pressures diffusion of COCl and Cl to the walls of the vessel, where they remain adsorbed until recombination occurs. The explanation of the mechanism of the reaction given in an earlier paper (cf. A., 1927, 1154) is regarded as unsatisfactory and it is now considered that the specific influence of carbon monoxide on the recombination of chlorine atoms can be expressed by the equation $\text{COCl} + \text{Cl} = \text{CO} + \text{Cl}_2$, and that direct recombination in the gas phase is negligible. This assumption leads to a simple explanation of the photochemical formation of carbonyl chloride at the ordinary temperature, the individual reactions being (1) $\text{Cl}_2 + E \rightarrow 2\text{Cl}$; (2) $\text{CO} + \text{Cl} \rightarrow \text{COCl}$; (3) $\text{COCl} \rightarrow \text{CO} + \text{Cl}$; (4) $\text{CO} + \text{Cl}_2 + \text{Cl} \rightarrow \text{COCl}_2 + \text{Cl}$; (5) $\text{COCl} + \text{Cl} \rightarrow \text{CO} + \text{Cl}_2$. The inhibitory action of oxygen and the mechanism of the reaction at higher temperatures are also discussed.

F. L. USHER.

Influence of active carbon and of zinc on the formation of complex aldehydes and of

sugars from solutions of potassium hydrogen carbonate under the action of ultra-violet rays. G. MEZZADROLI and T. BABES (*Gazzetta*, 1929, 59, 305—308; cf. this vol., 155).—The reducing power of a 5% solution of potassium hydrogen carbonate exposed to the action of ultra-violet rays increases to a constant value in presence of active carbon (norit), instead of rising to a maximum and then decreasing, as previously found in the absence of carbon. When zinc is present with the carbon the reducing power of the solution is still further increased and reaches a higher constant value. The adsorption of carbon dioxide and hydrogen by the carbon brings about a more intimate contact and facilitates reaction between these two gases. O. J. WALKER.

Photochemical reaction between ethylene glycol and dichromate. E. H. RIESENFELD and O. HECHT (*Z. wiss. Phot.*, 1929, 26, 369—372).—The action of light on a solution of sodium dichromate in ethylene glycol is considered. The presence of water affects the amount of dichromate reduced. For equal amounts of light the ratio of reduction occurring in 1 hr. with water present and water-free preparations was 59:79. Within the range of concentrations 0.2—0.6% of sodium dichromate in ethylene glycol, the amount of decomposition was proportional to the time. A layer of the 0.2% solution 1 cm. thick was sufficient to absorb completely the active radiation. For the light used, 50 milli-equivalents of dichromate, on the average, were reduced per hr., independently of time, concentration, and thickness of layer, with the condition previously mentioned in the case of the latter. A. J. MEE.

Photochemical transformation of *o*-nitrobenzaldehyde. R. WEGSCHEIDER (*Monatsh.*, 1929, 52, 68—72).—The results of Weigert and Brodmann (*A.*, 1925, ii, 1075) on the photochemical transformation of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid in acetone solution are not consistent with the assumption that two quanta are used for 1 mol. of end product. The observations amenable to calculation are explicable on the assumption that a partial inactivation of the light-activated molecules occurs (cf. *A.*, 1923, ii, 49), and agree with the kinetic requirements that the quantum number depends on the region of change. This assumption also explains the different behaviour of solid *o*-nitrobenzaldehyde. H. BURTON.

Photobromination of coumarin. D. M. WILLIAMS (*J.C.S.*, 1929, 1383—1384).—The photobromination of coumarin in carbon tetrachloride or chloroform leads to an equilibrium. Whereas in the thermal reaction the velocity of bromination is greater in chloroform solution (*A.*, 1928, 412), the reverse is true of the photobromination. F. J. WILKINS.

Photographic effect produced by sterols after exposure to ultra-violet rays. J. CLUZET and KOFMAN (*Compt. rend.*, 1929, 189, 45—47).—Sterols exposed to ultra-violet light, X-rays, or radium blacken a photographic plate. Since this property is destroyed by heat (80°) or by infra-red radiation, there is evidence that it is due to gaseous substances produced by irradiation rather than to radiations emitted by the activated sterols (cf. following abstract). J. GRANT.

Photochemical activity of various sterols and the nature of their action. L. HUGOUNENQ and E. COUTURE (*Compt. rend.*, 1929, 189, 47—49; cf. preceding abstract).—Indole, skatole, and the sterols of cod-liver oil, *Bombyx*, and beer yeast darken a photographic plate in direct contact after exposure to ordinary diffused daylight, whilst cholesteryl acetate (*Bombyx*) and sterols of the oils of egg, fresh or red herring, ergot of rye, snail, cow's blood and brain, and biliary calculus are inactive. In some cases the activity is lost after a period in darkness, and in others it is manifested even if the substance and plate are not in direct contact. It is intensified by heat (40°) and oxidising agents (manganese borate), but is absorbed by quartz. These and chemical tests indicating the presence of an aldehyde and active oxygen imply the formation of ozonides at the double linkings of the sterol molecules. J. GRANT.

New photo-reaction with ergosterol. A. STEIGMANN (*Z. wiss. Phot.*, 1929, 26, 363—368).—Alcoholic anthraquinone dissolved in pyridine bleaches alcoholic methylene-blue (1 in 10⁴) reversibly on exposure to light. Shaking with oxygen brings back the colour. Quinone acts in a similar way, but not quinol. To explain this reaction it is stated that the methylene-blue, in itself very photoactive, has no chemical contact with the alcohol, but the anthraquinone has. On exposure, the methylene-blue and anthraquinone take up light energy. This is transferred to the alcohol from the anthraquinone. The activated hydrogen of the $-\text{CH}_2\text{OH}$ group does not act as an acceptor itself, but passes it on to the better methylene-blue hydrogen acceptor, the methylene-blue thereby becoming bleached. When ergosterol (a secondary alcohol) was used instead of ethyl alcohol in this reaction, being dissolved in a non-alcoholic solvent (pyridine), the methylene-blue was rapidly and reversibly bleached at first, but later an irreversible change set in. Control solutions, one containing cholesterol and the other being free from sterol, were used; both were slower than the ergosterol, and the change was irreversible. To explain this reaction experiments were made with ergosterol and methylene-blue alone, and with pyridine and anthraquinone alone, in atmospheres of oxygen. The anthraquinone does not react with the pyridine, but only with the ergosterol, of which it makes the hydrogen atom reactive, so that it bleaches methylene-blue. The explanation is, therefore, similar to that of the reaction with ethyl alcohol. A. J. MEE.

Displacement of iodine from an iodide by a solution in oil of cholesterol or ergosterol irradiated by solar light. E. ROUSSEAU (*Compt. rend.*, 1929, 189, 37—39).—Solutions (0.5%) of ergosterol in olive oil have a greater power of oxidation when irradiated by solar light in a limited supply (17 c.c.) of air than those of cholesterol. The photochemical effect of the total solar radiations measured in terms of the active oxygen equivalent of the iodine liberated from a 20% solution of an iodide is approximately 10 times as great as that of the mercury arc rays 3650, 3341, and 3132 Å., or of the monochromatic radiation 3650 Å. isolated from the same source. J. GRANT.

Modifications of collagenic substances by radiation from radioactive bodies. J. LOISELEUR (Compt. rend., 1929, 188, 1570—1572, and Bull. Soc. Chim. biol., 1929, 11, 635—636).—The action of β -rays from radium or radon on solutions of gelatin or collagen causes a rise in the gold number in the former case and flocculation in both cases. Lead and gold salts have a sensitising action. The effect produced is independent of the temperature between 0° and 37° and is proportional to the intensity of the radiation.

R. K. CALLOW.

General principles underlying oxidation-reduction reactions and chemical combination. I. B. JIRGENSONS (Z. Elektrochem., 1929, 35, 352—358).—A theoretical discussion based on the electronic theory.

H. T. S. BRITTON.

Potassium hexathionate. J. R. PARTINGTON and A. F. TIPLER (J.C.S., 1929, 1382—1383).—Confirmatory evidence has been obtained of the work of Weitz and Achterberg (A., 1928, 381) on the preparation of potassium hexathionate.

F. J. WILKINS.

Complex salts. II. Preparation, properties, and stability of some bisdicarboxylato-copper salts. H. L. RILEY (J.C.S., 1929, 1307—1314).—Copper forms with certain dicarboxylic acids complex salts of the type $\text{Na}_2[\text{CuX}_2(\text{H}_2\text{O})_2]$, displaying a co-ordination number of six. The *dioxalato*-, *dimalonato*-, and *diphthalato*-complex salts of this type have been isolated. It is shown that the stabilities of these complexes decrease in the order: oxalato-, malonato-, phthalato-, carbonato-, and succinato-compound.

F. J. WILKINS.

Tetrathionates. II. Strontium tetrathionate. R. PORTILLO (Anal. Fis. Quim., 1929, 27, 351—357).—Strontium tetrathionate hexahydrate (from a mixture of alcohol and ether) is stable in the air but in a vacuum over sulphuric acid readily loses $4\text{H}_2\text{O}$, especially at 40—50°; dehydration of the resulting dihydrate sets in at about 70°, but is accompanied by decomposition. The densities (d_4^{20}) of the hexa- and di-hydrates are 2.148 and 2.480, respectively, the mol. vol. of the water of crystallisation being 13.8, in agreement with that found by Moles for the water in hydrated crystals. The solubility of strontium tetrathionate in water is less than that of the barium salt at temperatures below 27°, and greater at higher temperatures, the solubility at 0°, 18°, and 30° being 20, 26.3, and 39% by weight, respectively. The molecular heat of dissolution at 17° in 1000 mols. of water is —11.6 kg.-cal.

H. F. GILLBE.

Decomposition of barium sulphate. (MLLE.) G. MARCHAL (Bull. Soc. chim., 1929, [iv], 45, 339—343).—Decomposition of barium sulphate by heat alone is very slight at 1300° and is attributed to the presence of impurities. In presence of silica, alumina, or kaolin, decomposition is accelerated, being initially rapid, but the loss in weight of the sulphate does not exceed 20—25% in 5 hrs. at 1300° (cf. A., 1926, 359, 487; B., 1926, 51).

R. BRIGHTMAN.

Purification of mercury. D. ROLLER (J. Opt. Soc. Amer., 1929, 18, 357—359).—The procedure appropriate to the purification of mercury preparatory to use in photo-electric cells, and a simple centrifugal

mixing device for the preliminary purification by washing with potash, dilute nitric acid, etc., are described.

R. W. LUNT.

Action of gaseous ammonia on mercuric bromide and on mercuric chloride. M. FRANÇOIS (Compt. rend., 1929, 188, 1500—1501).—Dry powdered mercuric chloride or bromide slowly adsorbs ammonia in the cold with the formation of the additive compound $\text{HgCl}_2 \cdot 2\text{NH}_3$ or $\text{HgBr}_2 \cdot 2\text{NH}_3$. The rate of adsorption depends on the nature of the solid surface.

J. GRANT.

Behaviour of amorphous carbon and sulphur compared with that of diamond and graphite; the carbon sulphide of Ciusa. J. P. WIBAUT and E. J. VAN DER KAM (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 501—511).—Only the amorphous forms of carbon are able to fix sulphur when the two elements are heated in a closed tube at 500—600°. Part at least of the sulphur appears to be held to the carbon by valency forces, and the difference between the behaviour of the amorphous and crystalline forms of carbon is ascribed to the relatively high degree of unsaturation of the surface atoms of the amorphous material. There is considerable variation of the force with which the individual sulphur atoms are held, as evidenced by the gradual loss when the material is heated at rising temperatures in a vacuum or in a current of hydrogen; this observation is in accord with the views of Garner and McKie on the differing energy contents of the surface atoms of an amorphous material.

H. F. GILLBE.

Action of air-carbon tetrachloride vapour mixtures on several natural sulphides, thioarsenites, and thioantimonites. K. BRADDOCK-ROGERS (Chem. News, 1929, 138, 385—387).—Galena is decomposed readily at 300—325°, and chalcocite, after first being heated at 300—325° for 15 min., at 500—525°. Covellite is heated first at 275—300°, on account of the rapidity of the initial stages of the reaction, then at 500—525°. Arsenopyrite decomposes very smoothly at 450—460°, but enargite is heated first at 200—225°, then at 300—325°. Cobaltite requires an initial heating at 325—340°, and further heating at 540—560°. Tetrahedrite and jamesonite do not require to be heated during the initial stage of the decomposition, but after 30 min. should be heated at 250—300°; bournonite requires to be heated at 225—250° throughout the decomposition.

H. F. GILLBE.

Action of cyanogen bromide and hydrogen cyanide on titanium tetrabromide. F. OBERHAUSER and J. SCHORMULLER (Ber., 1929, 62, [B], 1436—1441; cf. A., 1927, 756).—The action of cyanogen bromide on titanium tetrabromide in carbon disulphide affords the compound $\text{TiBr}_4 \cdot 2\text{CNBr}$, m. p. 151—152° (corr.) in a sealed capillary, immediately decomposed by moisture. The substance $\text{TiCl}_4 \cdot 2\text{CNBr}$ is obtained similarly. The bromide is transformed by gaseous ammonia into the ammonate, $\text{TiBr}_4 \cdot 2\text{CNBr} \cdot \text{NH}_3$. With ether, titanium tetrabromide yields the compound $\text{TiBr}_4 \cdot 2\text{Et}_2\text{O}$. With anhydrous hydrogen cyanide, titanium tetrabromide affords the substance $\text{TiBr}_4 \cdot 2\text{HCN}$, m. p. 132—133° (corr. decomp.) after darkening at 100°; tensimetric

degradation yields the *adducts* $2\text{TiBr}_4 \cdot 3\text{HCN}$ (172 mm., 70°) and $\text{TiBr}_4 \cdot \text{HCN}$ (72 mm., 70°).

Cyanogen bromide is determined by treatment with about 100 c.c. of dilute ammonia at the ordinary temperature in a closed flask for 10–20 min. The mixture is warmed on the water-bath, diluted with 300 c.c. of water, boiled to expel the bulk of the ammonia, acidified with nitric acid, and titrated with 0.1*N*-silver nitrate solution. Decomposition may be effected with potassium or sodium hydroxide.

H. WREN.

Existence of higher oxides of nitrogen. H. J. SCHUMACHER and G. SPRENGER (*Z. angew. Chem.*, 1929, 42, 697–700).—A discussion of the evidence for the existence of the compound NO_3 .

C. W. GIBBY.

Preparation of ammonium dichromate. Y. T. GERASIMOV (*Trans. Inst. Pure Chem. Reagents*, Moscow, 1927, No. 6, 22–26).—Chromium trioxide is neutralised in unsaturated solution with ammonia, and the mixture evaporated at 50° . Double decomposition of sodium dichromate and ammonium chloride does not give a pure product. Ammonium dichromate is slightly decomposed on boiling in aqueous solution.

CHEMICAL ABSTRACTS.

Monobromoamine. W. MOLDENHAUER [with M. BURGER] (*Ber.*, 1929, 62, [B], 1615–1618).—Bromine reacts with ammonia in anhydrous ether according to the equation $2\text{NH}_3 + \text{Br}_2 = \text{NH}_2\text{Br} + \text{NH}_4\text{Br}$. The bromoamine is too unstable to permit its isolation. It liberates iodine from hydriodic acid and oxidises aqueous sulphite to sulphate. In dilute aqueous solution, bromine and ammonia evolve nitrogen violently, but with increasing concentration of ammonia the initial nitrogen evolution becomes less complete and monobromoamine can be removed from the solution by ether. Decomposition of the bromoamine in aqueous solution is a unimolecular change, probably proceeding according to the scheme: $\text{NH}_2\text{Br} + \text{H}_2\text{O} = \text{NH}_4\text{BrO}$ and $3\text{BrO}^- + 2\text{NH}_3 = 3\text{Br}^- + \text{N}_2 + 3\text{H}_2\text{O}$; the first change only is measured. Sodium hypobromite and ammonia appear to yield nitrogen almost exclusively, small amounts of bromoamine being formed in the presence of concentrated ammonia. Unlike chloroamine, bromoamine is not transformed by an excess of warm ammonia into hydrazine.

H. WREN.

Phosphorous oxide. II. Reciprocal action between phosphorus trichloride and phosphorous acid. L. WOLF, E. KALAEHNE, and H. SCHNAGER (*Ber.*, 1929, 62, [B], 1441–1449; cf. this vol., 662).—The action of phosphorus trichloride on phosphorous acid under widely varied conditions invariably yields yellow to orange, syrupy products from which a trace of phosphorous oxide cannot be isolated by distillation or extraction. A similar product is derived from hydrogen chloride and phosphorous oxide at the atmospheric temperature; if reaction is effected at $-30^\circ/760$ mm., the colourless product consists of phosphorus trichloride and phosphorous acid. The yellow compound is formed by the action of phosphorous oxide on phosphorous acid. The preparation of the oxide from phosphorus trichloride and phosphorous acid is therefore impossible. When heated

above 110° , the yellow product is gradually transformed into red phosphorus. The formation of phosphorous oxide from the trichloride and acetic anhydride or glacial acetic acid could not be confirmed.

H. WREN.

Thermal formation of hydrogen chloride. J. A. CHRISTIANSEN (*Z. physikal. Chem.*, 1929, B, 3, 481).—A correction (cf. this vol., 654).

F. L. USHER.

Hydrogen-chlorine flame. E. B. LUDLAM, H. G. REID, and G. S. SOUTAR (*Proc. Roy. Soc. Edin.*, 1929, 49, 156–159).—The flame of chlorine burning at a jet in hydrogen consists of a livid white portion surrounded by a pale blue cone. When hydrogen burns in chlorine, however, this pale blue cone almost disappears owing to the extensive absorption of chlorine in the violet. The maximum intensity of the continuous spectrum from the white inner portion occurs in the green. It is suggested that the reaction between hydrogen and chlorine proceeds through two stages, (a) $\text{H}_2 + \text{Cl} \rightarrow \text{HCl} + \text{H}$; (b) $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$. The existence of the white flame is ascribed to the combination of free chlorine atoms. In support of this hypothesis it is shown that the white flame is considerably diminished in size when an excess of hydrogen is present.

F. J. WILKINS.

Nitridation of manganese. L. DUPARC, P. WENGER, and C. CIMERMAN (*Helv. Chim. Acta*, 1929, 12, 806–817).—The influence of the following factors on the nitridation of manganese has been investigated: chemical composition of the manganese, duration of the reaction, temperature, pressure, and catalysis by lithium nitride. Pyrophoric manganese oxidises immediately in air and can be converted into the nitride only by removing the mercury from amalgam in a current of nitrogen. In agreement with previous workers, the temperature at which nitrogen commences to be absorbed by commercial manganese varies with the specimen used (500° and 740°). The temperature of maximum fixation of nitrogen also varies with the sample, and both variations are attributed to difference in the silicon and aluminium contents of the manganese. The curves showing the amounts of nitrogen absorbed at various temperatures rise to a maximum and then fall with dissociation of the nitride. At the temperature of maximum absorption the duration of heating has little, if any, effect on the quantity of nitrogen fixed; at low temperatures, equilibrium is reached in 2 hrs. Fixation increases with an increase in pressure over the range studied, viz., up to 60 atm.; the addition of lithium nitride lowers the temperature at which absorption of nitrogen commences, increases the amount absorbed, and accelerates the subsequent dissociation at higher temperatures.

L. S. THEOBALD.

Processes of oxidation. Behaviour of cyanogen bromide and hydrogen cyanide towards iron salts. F. OBERHAUSER and J. SCHORMULLER (*Ber.*, 1929, 62, [B], 1482–1488).—Antimony pentachloride, cuprous or cupric bromide, phosphorus tribromide, and phosphorus trichloride do not appear to give additive compounds with cyanogen bromide. Ferrous bromide is converted by cyanogen bromide at 60° into

the compound $2\text{FeBr}_2\cdot\text{CNBr}$, which decomposes at 160° with partial formation of ferric iron and free cyanogen. With an excess of cyanogen bromide at 100° , ferrous bromide gives the substance, $\text{Fe}_3\text{Br}_8\cdot 3\text{CNBr}\cdot\text{C}_2\text{N}_2$, tensimetric degradation of which gives the compound Fe_3Br_8 , described in the literature as ferric bromide. This compound reacts readily with cyanogen bromide at the ordinary temperature or when gently heated, giving the substance, $\text{Fe}_3\text{Br}_8\cdot 4\text{CNBr}$, m. p. $143\text{--}145^\circ$ (corr., decomp.), which loses its cyanogen bromide completely under the action of ammonia. Treatment of the additive compound with the requisite quantity of bromine at $80\text{--}90^\circ$ gives the substance, $3\text{FeBr}_3\cdot 4\text{CNBr}$, m. p. $96\text{--}98^\circ$ (corr., decomp.) in a closed capillary, which readily loses bromine. The very hygroscopic compound, $\text{Fe}_3\text{Br}_8\cdot 4\text{HCN}$, m. p. $163\text{--}165^\circ$ after softening at 125° , is obtained from its components; it immediately evolves hydrogen cyanide when exposed to air.

H. WREN.

Alkoxonium hexacyanocobaltates. F. HOLZL, T. MEIER-MOHAR, and F. VIDITZ (Monatsh., 1929, 52, 73—82).—When hexacyanocobaltic acid is dissolved in alcohol and then evaporated to dryness in absence of moisture a crystalline ethoxonium derivative is obtained. Treatment of this, dissolved in alcohol and sulphuric acid, with hydrogen chloride affords the compound (I) $[\text{Co}(\text{CN})_6](\text{H}\cdot\text{EtOH})_3$. When I is treated with hydrogen chloride in presence of methyl and propyl alcohols the substances $[\text{Co}(\text{CN})_6](\text{H}\cdot\text{MeOH})_2$ and $[\text{Co}(\text{CN})_6](\text{H}\cdot\text{PrOH})_3$ are produced. These alkoxonium salts are crystalline, not very hygroscopic, easily soluble in water, and titrate as free acids. Treatment of I with pyridine yields tripyridine hexacyanocobaltate, $[\text{Co}(\text{CN})_6]\text{H}_3(\text{C}_5\text{H}_5\text{N})_3$. The formation of these alkoxonium salts is presumably due to reaction between hexacyanocobaltate ions and alkoxonium ions (produced during the treatment of the alcohol with hydrogen chloride, viz., $\text{R}\cdot\text{OH} + \text{H}^+ \rightarrow \text{R}\cdot\text{OH}\cdot\text{H}^+$).

H. BURTON.

New polynuclear co-ordination compounds of cobalt. E. G. V. PERCIVAL and W. WARDLAW (J.C.S., 1929, 1317—1322).—The reaction products obtained when dry air is drawn through an alcoholic solution of cobaltous chloride in the presence of various amines have been investigated. The earlier work of Bucknall and Wardlaw (A., 1928, 1345) has been confirmed and extended to the propylamine derivative. From benzylamine a complex salt of the probable composition $[3\text{R}\cdot\text{Co}(\text{OH})\cdot\text{Co}\cdot 3\text{R}]\text{Cl}_3$ ($\text{R}=\text{CH}_2\text{Ph}\cdot\text{NH}_2$) has been isolated. No definite results have been obtained when the oxidation is carried out in the presence of ethylamine, ethylenediamine, diethylamine, piperidine, or methylamine. All the reactive amines contain the group $\text{CH}_2\cdot\text{NH}_2$.

F. J. WILKINS.

Nitrites. II. Ammines of nickel nitrite. L. LE BOUCHER (Anal. Fis. Quím., 1929, 27, 358—367).—Nickel nitrite tetra-ammoniate has been prepared by passing ammonia over the tetra- or hexapyridinate until all the pyridine has been substituted by ammonia; on keeping in a vacuum desiccator over sulphuric acid the free pyridine, together with part of the ammonia, is removed, leaving the tetra-

ammoniate, which has $d_4^{25} 1.826$. Treatment of the tetra-ammoniate with ammonia leads to the formation of the violet hexa-ammoniate. The equilibrium pressure of ammonia above this compound has been determined from 15° to 115° , and the correspondence of the curve obtained with that found by Ephraim for the supposed penta-ammoniate shows the latter to be merely a mixture of the hexa- and tetra-ammoniates. The tetra-ammoniate possesses an appreciable vapour pressure at temperatures above 100° (19 mm. at 105°), and by heating in a current of dry air at $115\text{--}120^\circ$ the deep green diammoniate is produced. It is of importance that 120° be not exceeded during the process, as decomposition of the nitrite then sets in; it is thus impossible to obtain anhydrous nickel nitrite by complete deamination.

H. F. GILLBE.

Pneumatic apparatus for volumetric micro-analysis. E. SCHILOV (Mikrochem., 1929, 7, 163—184).—Micro-titrations can be carried out with considerable accuracy provided that apparatus is calibrated using mercury and that the pneumatic methods for the manipulation of burettes previously described by the author are used.

J. S. CARTER.

Micro-crystalloscopy in gels. A. MARTINI (Mikrochem., 1929, 7, 236—241).—When carrying out micro-reactions it is often advantageous to use a gel, preferably a collodion gel, as medium. Reactions, especially those involving crystal formation, are often more sensitive than in aqueous media.

J. S. CARTER.

Rapid qualitative analysis. I. Specific and special reactions of the commoner cations and anions. G. GUTZERT (Helv. Chim. Acta, 1929, 12, 713—740).—Specific and special reactions, generally colour reactions with an organic reagent, are enumerated for the following ions: silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, iron, chromium, manganese, nickel, cobalt, zinc, aluminium, barium, strontium, calcium, magnesium, potassium, sodium, ammonium, fluoride, chloride, bromide, iodide, sulphide, thiosulphate, sulphite, sulphate, nitrite, nitrate, phosphate, borate, silicate, carbonate, cyanide, ferro- and ferri-cyanide, thiocyanate, and oxalate. The reactions are suitable for the spot method of analysis. Special conditions are detailed when necessary, and colour reactions common to more than one cation are tabulated.

L. S. THEOBALD.

Perchloric acid as an agent for the clean destruction of organic matter. R. J. C. FABRY (Chemist-Analyst, 1929, 18, No. 2, 8—9).—For the removal of tartaric acid used to prevent precipitation of iron or titanium, the solution (600 c.c.) is kept overnight mixed with nitric acid (15 c.c.) and 20% perchloric acid (10 c.c.).

CHEMICAL ABSTRACTS.

Destruction of organic matter in the determination of ash constituents. E. CHERBULIEZ (Helv. Chim. Acta, 1929, 12, 818—819).—The addition of fuming nitric acid (1 c.c.), or nitrous acid as sodium nitrite, to concentrated sulphuric acid (20 c.c.) and 20% perchloric acid (10 c.c.) gives a rapid means for the destruction of organic matter without leaving foreign, non-volatile substances in solution. The

mixture is warmed for 15 min. and then heated until white fumes appear. If necessary, further quantities of perchloric and fuming nitric acids are added and the treatment is repeated until a colourless sulphuric acid solution is obtained. Chlorine is evolved during the initial warming, but the formation of chlorine dioxide in dangerous concentration is unlikely, since this substance is unstable at the temperature at which the reaction begins. L. S. THEOBALD.

Apparatus for electrometric titrations. A. UHL (Z. anal. Chem., 1929, 77, 280—283).—The apparatus comprises a wide glass tube stoppered at the upper end and having a narrow portion at the lower end which is plugged with a wad of filter paper soaked in potassium chloride solution. The narrow portion is filled with a hot solution of 3 g. of agar and 40 g. of potassium chloride in 100 c.c. of water, which sets to a jelly on cooling. Above this the tube is filled with a comparison solution consisting of a titrated solution of the same type as that under investigation, in which dips a platinised rod electrode terminating in a wire which is joined to one terminal of the galvanometer. The other terminal is connected to a clamping device carrying a pressure contact fixed to the upper part of the tube. One terminal of the contact is connected by means of a platinum or gold strip with a piece of platinum or gold foil fixed round the outside of the lower part of the tube just above the plug, to make contact with the solution being titrated. By means of the clamp the apparatus can readily be attached to the rim of the titrating vessel. A. R. POWELL.

Determination of hydrogen-ion concentration with the antimony electrode. I. I. SHUKOV and G. P. AVSEJEVITSOH (Z. Elektrochem., 1929, 35, 349—352).—The different experience of previous investigators with the antimony electrode is attributed to the variable nature of the electrodes used. A method of preparation is described for an antimony electrode the voltage of which, compared with that of a normal calomel electrode, varies in accordance with the equation: $E = 0.009 + 0.053p_H$ at 14°. This linear relationship was shown to be satisfactory when the electrode was tested in buffer solutions of p_H 2.78—9.19.

The method of preparing the electrode is: first, a thin layer of mercury is deposited electrolytically (thereby forming an amalgam) on a platinum wire, about 1 cm. long, and fused into a glass tube, from a 2% mercuric chloride or mercurous nitrate solution with a current of 0.4—1.0 milliamp. for about 2 min. Too thick a layer leads to the formation of mercury drops and is thus a disadvantage. Secondly, antimony is deposited on the amalgamated platinum, which has been thoroughly dried, from a 25% solution of antimony trichloride in perfectly dry acetone, using an antimony anode and a current of 0.6—2.2 milliamp. for about 30 min. The antimony deposit should be about 2 mm. in thickness. In this way, the antimony amalgam which is first formed becomes covered with a fine crystalline layer of antimony. Thirdly, the electrode is treated with a hot solution of sodium hydroxide.

H. T. S. BRITTON.

Salt error of indicators due to standard alkaline buffers themselves. II. J. W. MCBAIN, M. E. LAING, and O. E. CLARK (J. Gen. Physiol., 1929, 12, 695—710; cf. A., 1926, 590).—A dilute solution of pure sodium hydroxide and a buffer solution which show identical colours when equal quantities of the same indicator are added to each do not necessarily have the same p_H values when the latter are determined electrometrically by means of the hydrogen electrode. The neutralising action of the indicator may be partly responsible for this discrepancy, but the magnitude of this effect is usually small in comparison with the total error, which in certain cases, e.g., with phenol-red and a borate mixture at p_H 7.3, may exceed 2.0 p_H units. No appreciable error occurs with alizarin-yellow G, tropaeolin O, and thymol-violet, but the anomaly may be very considerable with phenolphthalein, o-cresolphthalein, thymol-blue, and phenol-red.

W. O. KERMACK.

Microchemical colour reaction for sulphur. E. GRUNSTEIDL (Z. anal. Chem., 1929, 77, 283—284).—For the detection of free sulphur or of an inorganic or organic sulphide the substance is evaporated with a few drops of sodium hydroxide solution just to dryness, a few drops of a 0.1% solution of sodium cyanide are added, and evaporation is repeated, the residue is moistened with dilute sulphuric acid, and dilute ferric chloride solution added; the formation of the characteristic ferric thiocyanate colour proves the presence of sulphur. A. R. POWELL.

Determination of sulphur in galena and lead. H. LEYSANT.—See B., 1929, 521.

Iodometric determination of thiocyanate. A. SCHWICKER (Z. anal. Chem., 1929, 77, 278—280).—The thiocyanate solution is measured into an excess of 0.1N-iodine solution and 5—10 c.c. of N-ammonium borate solution, or of sodium borate solution and ammonium chloride, are added. After a few minutes 10 c.c. of 2N-sulphuric acid are added and the excess of iodine is titrated with thiosulphate (cf. Thiel, A., 1902, ii, 706). A. R. POWELL.

Determination of nitrogen by Dumas' method. F. HALLA (Mikrochem., 1929, 7, 202—207).—A theoretical consideration of the various equilibria involved suggests that Pregl's method of packing the tube does not of necessity eliminate errors due to the formation of carbon monoxide.

J. S. CARTER.

Colorimetric determination of phosphoric acid. A. Y. LEVITZKI (Nauch. Agron. Zhur., 1927, 4, 783—793).—The solution (80—90 c.c.) containing P_2O_5 (0.02—0.2 g.) is treated with 2.5 c.c. of a solution composed of equal volumes of 10% aqueous ammonium molybdate and concentrated sulphuric acid. After shaking, 0.25 c.c. of a solution obtained by dissolving (heat) 0.25 g. of lead in 5 c.c. of concentrated hydrochloric acid and adding 2—5 c.c. of 10% copper sulphate solution is added, the solution is diluted to 100 c.c., mixed, and compared colorimetrically with standards after 15 min. The method is applied to soils, plants, and fertilisers.

CHEMICAL ABSTRACTS.

Detection of phosphoric acid with ammonium molybdate and benzidine. F. FEIGL (Z. anal. Chem., 1929, 77, 299—300).—To prevent the interference of silica, arsenic acid, and boric acid in the test previously described as specific for phosphoric acid (A., 1928, 1107) the molybdate solution must be treated with 15 g. of tartaric acid per 100 c.c. prior to use; 1 drop of the solution to be tested is mixed with 1 drop of the molybdate solution, warmed over a small flame, treated with 1 drop of the benzidine solution, and exposed to the vapour from an ammonia bottle. A blue colour develops in the presence of more than 1.5 μ g. of phosphorus pentoxide.

A. R. POWELL.

Determination of phosphoric acid in mineral phosphates and fertilisers. G. JORGENSEN.—See B., 1929, 515.

Determination of silicon. T. HECZKO (Z. anal. Chem., 1929, 77, 327—328).—The usual separation of an ignited silica precipitate from oxides of tervalent metals by addition of sulphuric and hydrofluoric acids and volatilisation is greatly accelerated if after addition of the acids an ashless filter paper is added to the crucible; if the filter paper is then ignited in the usual manner, rapid volatilisation is assured.

H. F. GILLBE.

Gravimetric and colorimetric method for the direct determination of sodium. E. R. CALEY [with C. W. FOULK] (J. Amer. Chem. Soc., 1929, 51, 1664—1674).—A method of determining sodium as magnesium sodium uranyl acetate, $\text{NaOAc} \cdot \text{Mg}(\text{OAc})_2 \cdot 3\text{UO}_2(\text{OAc})_2 \cdot 6.5\text{H}_2\text{O}$, is detailed (cf. Barber and Kolthoff, A., 1928, 859). Neglect of certain precautions, such as maintaining the temperature of precipitation at 20°, stirring vigorously during precipitation, etc., as well as an incorrect knowledge concerning the number of molecules of water of crystallisation in the precipitate, serve to explain the non-quantitative nature of the results previously obtained by this method. A modified procedure adapted for the colorimetric determination of sodium is described.

S. K. TWEEDY.

Direct volumetric determination of potassium and sodium, applicable to other alkali and alkaline-earth metals. F. DIAZ DE RADA (Anal. Fis. Quím., 1929, 27, 390—399).—Sodium may be determined volumetrically in neutral or acetic acid solution containing 80—82% of alcohol by precipitation as sodium ferrocyanide with a solution of lithium ferrocyanide; the end-point is recognised either conductometrically or by the production of a bluish-green coloration when a drop of the solution is applied to cobalt nitrate paper. Ammonium, potassium, rubidium, and caesium may also be completely precipitated, at suitable alcoholic concentration, in the same way, although in these cases double salts of the type $\text{Li}_2\text{M}_2\text{Fe}(\text{CN})_6$ are produced; magnesium, barium, strontium, and calcium yield simple ferrocyanides. Potassium may be determined in a solution containing 50% of alcohol by addition of a calcium salt and titration with lithium ferrocyanide solution, whereby calcium potassium ferrocyanide is precipitated; the presence of four to five times the quantity of sodium does not interfere.

Since total sodium and potassium may be determined by the method first described, a complete analysis of a solution containing both sodium and potassium may be effected by direct titration.

H. F. GILLBE.

Determination of purity of potassium and sodium ferrocyanides by titration with zinc sulphate solution. FARBSALZ-G.M.B.H.—See B., 1929, 555.

Micro-chemical mineral analysis. III. A. MARTINI (Mikrochem., 1929, 7, 231—234).—The formation in acid media of a complex caesium zinc gold chloride having a well-defined micro-crystalline structure is a sensitive test for caesium and zinc. A light brown isomorphous complex is formed when zinc is replaced by copper. Molybdenum may be detected by the formation of an orange pyrogallol-acetic acid-piperazine complex. The micro-crystalline structure is triclinic. Vanadium is detectable by the formation of a black, micro-triclinic pyrogallol-o-toluidine complex. Silver may be detected in presence of lead and mercury by the formation of silver methylamine acetate. Photomicrographs of all the compounds are given.

J. S. CARTER.

Systematic spot-analysis. I. K. HELLER and P. KRUMHOLZ (Mikrochem., 1929, 7, 213—222).—Spot tests to be carried out on a porcelain plate are given for the identification of silver, copper, bismuth, mercury, cadmium, nickel, cobalt, iron, chromium, zinc, aluminium, and manganese. The majority of the reactions involved have been described by previous workers. The *p*-dimethylaminobenzylidene-rhodanine test for silver (Feigl, A., 1928, 1108) is also given by mercury, but is specific for silver when carried out in presence of potassium cyanide. The detection of cadmium in presence of copper is based on the fact that cadmium only is precipitated as hydroxide by formaldehyde from solutions of the complex cyanides and that the hydroxide so precipitated is coloured blue in presence of dinitrodiphenylcarbazide.

J. S. CARTER.

Rapid determination of cadmium. G. SEACU and G. SUCIU (Z. anal. Chem., 1929, 77, 340—343).—The neutral solution (100—300 c.c.) is treated with an excess of potassium iodide solution, and heated to boiling; a hot concentrated solution of diethylenediamine copper nitrate is added, and on cooling a coarsely crystalline precipitate of $(\text{CdI}_4)(\text{Cuen})_2$, containing the whole of the cadmium, separates. After washing with the reagent, 96—100% alcohol, and ether, and drying for 5—10 min. in a vacuum desiccator, the precipitate, containing 13.99% Cd, is weighed. Excess of ammonia, ammonium salts, or of free ethylenediamine leads to low results.

H. F. GILLBE.

Colour reaction of copper. S. G. CLARKE and B. JONES (Analyst, 1929, 54, 333—334).—Traces of copper sulphate may be detected and determined by neutralising the solution (which must be free from chloride), rendering slightly acid with sulphuric acid, diluting to 100 c.c., adding ammonium persulphate (1 g.), 1 c.c. of saturated alcoholic dimethylglyoxime, 0.5 c.c. of silver nitrate solution (0.5%), and 2 c.c. of 10% aqueous pyridine, and stirring. The colour is

immediately compared with a standard. A slight opalescence due to traces of chlorides may be discharged by a slight excess of pyridine. As little as 0.01 mg. of copper yields a distinct reddish-violet colour, and not more than 0.1 mg. can suitably be determined.

D. G. HEWER.

Sensitive reaction of cuprous ion. O. FUNAKOSHI (Mem. Coll. Sci. Kyoto, 1929, 12, 155—157).—*p*-Dimethylaminobenzylidenerrhodanine in alcoholic solution forms a sensitive reagent for cuprous ion. In neutral solution a reddish-violet precipitate is formed, and one part of copper in 4×10^6 c.c. can be detected. A large excess of the reagent must be avoided.

C. W. GIBBY.

Rapid determination of mercury. G. SPACU and G. SUCIU (Z. anal. Chem., 1929, 77, 334—340).—The neutral or slightly ammoniacal solution is treated with an excess of potassium iodide solution and heated nearly to boiling; a hot concentrated solution of diethylenediamine copper nitrate is added, and the solution allowed to cool, whereupon there separates a dark violet, coarsely crystalline precipitate, $(\text{HgI}_4)(\text{Cu en}_2)$, which is washed first with a little of the dilute reagent, then with 95% alcohol, and finally with ether. After drying for 5—10 min. in a vacuum desiccator the precipitate, containing 22.49% Hg, may be weighed. Separation of mercury and copper may be effected by addition of ethylenediamine to the neutral solution prior to the precipitation. The method is rapid, not more than 1 hr. being required for complete determination. Since a definite precipitate is produced in 1 c.c. of solution containing 0.000007 g. of mercury, the method may be employed for micro-determinations.

H. F. GILLBE.

Rare earths. XXXI. Ionic migration and magnetism in the separation of the rare earths. P. W. SELWOOD and B. S. HOPKINS (Amer. Electrochem. Soc., May, 1929. Advance copy. 14 pp.).—Kendall's ionic migration method for the separation of the rare earths (A., 1925, ii, 977; 1926, 1117) is investigated. A partial separation of samarium and gadolinium and of erbium and yttrium was effected, but no separation of neodymium and samarium or of praseodymium and neodymium could be obtained. Where partial separation is possible the method cannot compete with established methods of separating the rare earths. The passage of an alcoholic solution of the chlorides of samarium and erbium through a non-homogeneous magnetic field led to no detectable separation, although the magnetic susceptibilities of the salts are in the ratio of about 1:40. It is believed that a very much more powerful magnetic field would be necessary to effect any separation by this method. H. J. T. ELLINGHAM.

Rare earths. XXXII. Fractional hydrolysis of rare earths by electrolysis. H. C. KREMER and L. L. QUILL (Amer. Electrochem. Soc., May, 1929. Advance copy. 6 pp.).—Electrolysis of a solution of rare-earth nitrates with a platinum anode, surrounded by a porous cup, and a molybdenum cathode yields a granular precipitate of hydroxides at the cathode with a current efficiency of 25—50%. This method leads to a partial separation of the constituent rare earths owing to differences in their

basicity. Varying the current density from 0.01 to 0.5 amp./cm.² caused no apparent variation in the efficiency of fractionation. The separation of yttrium from erbium and holmium is conveniently effected by the method.

H. J. T. ELLINGHAM.

Utilisation of the spectrophotometer in the determination of minute amounts of aluminium. E. W. SCHWARTZ and R. M. HANN (Science, 1929, 69, 167—170).—The reaction between aurintricarboxylic acid and aluminium is used as the basis for a spectrophotometric method for the determination of quantities of aluminium of the order 0.0025 mg./100 c.c. and less. The results are preferable to those obtained with a colorimeter.

L. S. THEOBALD.

Potassium cyanate as a reagent for detection of cobalt. B. J. F. DOBBINGTON and A. M. WARD (Analyst, 1929, 54, 327—332).—The addition of varying volumes of *M*-cobalt nitrate solution to 2 c.c. of saturated alcoholic potassium cyanate solution gave for 0.3 c.c. of cobalt solution a deep royal blue with reddish tinge, with 0.1 c.c. a deep royal blue, diminishing to a pale blue for 0.01 c.c. A pale but definite colour was obtained with 0.01 c.c. of a 0.01 *M*-cobalt nitrate solution, but the test is less delicate when carried out in aqueous solution. As little as 0.3 mg. of cobalt may be detected in presence of nickel and with precautions, using a blank test, 1 part in presence of 1000 parts of nickel. In the ordinary analytical scheme, ammonia is added to the solution after dissolving the mixed cobalt and nickel sulphides until slightly alkaline, and then one drop of the solution to 2 c.c. of alcoholic potassium cyanate solution. Ferric iron gives a brown colour which masks the colour of the cobalt complex, but after keeping the ferric salt is precipitated and the blue colour due to cobalt can be seen in the solution; with precautions 1 part of cobalt in presence of 1600 parts of iron may be demonstrated. Copper salts also give blue precipitates, but although the precipitate settles and the colour due to cobalt may be seen in the liquid, it is better to remove the copper by hydrogen sulphide. Uranium, titanous chloride, gold, and vanadium also give coloured solutions or precipitates.

D. G. HEWER.

Rapid determination of various elements after precipitation by the classical methods. I. J. DICK (Z. anal. Chem., 1929, 77, 352—363).—Accurate and rapid analyses may be carried out by thoroughly washing the precipitate in the usual manner, finally washing it with alcohol and ether, and drying it for 5—10 min. in a vacuum at the ordinary temperature. The following precipitates may be so treated: nickel dimethylglyoxime, mercuric sulphide, silver chloride, bromide, iodide, and thiocyanate, lead sulphate, barium sulphate, and calcium oxalate.

H. F. GILLBE.

Potentiometric determinations with ferri-cyanide in alkaline solution. I. Vanadium and hyposulphite. C. DEL FRESNO and L. VALDÉS (Anal. Fis. Quím., 1929, 27, 368—389).—Vanadium may be determined by reduction in acid solution to the quadrivalent state, addition of sodium hydroxide solution, and potentiometric titration with potassium ferri-cyanide solution in an atmosphere

of nitrogen; sodium hyposulphite may be directly titrated by the same method. The reactions involved are $\text{VO}^{2+} + \text{Fe}(\text{CN})_6^{3-} + 4\text{OH}^- \rightarrow \text{VO}_3^{3-} + \text{Fe}(\text{CN})_6^{4-} + 2\text{H}_2\text{O}$, and $\text{H}_2\text{S}_2\text{O}_4 + 2\text{OH}^- + 2\text{Fe}(\text{CN})_6^{3-} \rightarrow 2\text{H}_2\text{SO}_3 + 2\text{Fe}(\text{CN})_6^{4-}$. With increase of hydroxyl-ion concentration the potential curve, prior to the break, is displaced towards the negative side, and the potential change at the end-point is correspondingly increased.

H. F. GILLBE.

Analytical chemistry of tantalum, niobium, and their mineral associates. XIV. Separation of small quantities of tantalum and niobium from titanium. W. R. SCHOELLER and C. JAHN (Analyst, 1929, 54, 320—326).—The solution containing the oxalates of titanium and niobium and the oxalo-earth acids is treated with excess of sodium salicylate and the characteristic orange colour of the salicylic-titanium complex produced. The oxalate ion is then removed from solution by addition of calcium chloride, when the bulky oxalate precipitate carries down the earth acids, leaving the titanium compound unaffected. As the precipitation of the earth acids is not quantitative the titanium is recovered from the filtrate and the treatment repeated. The oxalate precipitates are dissolved in hydrochloric acid, the oxalic acid is destroyed with permanganate, and the earth acids are precipitated as tannin complexes. The ignited precipitates are then submitted to tartaric hydrolysis, being fused with potassium hydrogen sulphate in silica, the product dissolved in a concentrated solution of 0.25 g. of tartaric acid, and the liquid treated while boiling with 5 c.c. of nitric acid. After boiling for 5—15 min. the solution is left for a few hours, the precipitate mixed with a little filter pulp, washed with dilute ammonium nitrate solution, ignited wet, and weighed as $(\text{Ta}, \text{Nb})_2\text{O}_5$. The consistently negative errors of the method are ascribed to incomplete earth acid flocculation at the calcium oxalate precipitation stage, and a correction of 0.0015 g. for quantities of oxides found less than 0.006 g. up to 0.0035 for 0.0260 g. enables serviceable results to be obtained.

D. G. HEWER.

Direct-current amplifier for measuring small currents. J. M. EGLIN (J. Opt. Soc. Amer., 1929, 18, 393—402).—Wynn-Williams' method (Phil. Mag., 1928, [vii], 6, 324) has been improved.

N. M. BLYTH.

Use of the thermionic valve in measurements of ionisation currents. J. A. C. TEEGAN (Nature, 1929, 124, 91—92).

Thermoelements for high temperatures in a reducing atmosphere. J. A. M. VAN LIEMPT (Rec. trav. chim., 1929, 48, 585—588).—The *E.M.F.* developed by tungsten-molybdenum, tungsten-platinum rhodium, and molybdenum-platinum rhodium thermocouples have been measured between 0° and 1500°. The two last-named are particularly suitable for continuous use in a reducing atmosphere. The *E.M.F.* developed by a tungsten-molybdenum couple is very small, attaining a maximum value of 0.81 millivolt at about 600° and decreasing above that temperature.

C. W. GIBBY.

Micro-determination of m. p. using a thermo-element. A. NIETHAMMER (Mikrochem., 1929, 7,

223—226).—The essential feature of the arrangement, which is described in detail, is that a small portion of material at the junction of the thermo-element is observed through a microscope. J. S. CARTER.

Field γ -electroscope and its application to the investigation of radioactive minerals. G. O. ERTSCHIKOVSKI (Trav. Acad. Sci. U.R.S.S., 1928, 3, 127—160).—A description is given of an instrument devised for the purpose of determining the γ -rays at any point of the earth's surface and thus of ascertaining if radioactive substances are present. In the conditions prevailing at Tiouja-Mujun, it was found to be of little value in this respect. T. H. POPE.

Magnesium light as a normal light source for photographic sensitometry and its connexion with the international sunlight standard. J. M. EDER (Z. wiss. Phot., 1929, 26, 353—362).—The light from burning magnesium filtered through a copper-cobalt solution is recommended as a light source for photographic sensitometry. It has the spectral energy distribution of mid-day sunlight of the colour-temperature 5000° Abs. In the visible spectrum the transmission is 0.5; the transmission in the ultra-violet is somewhat greater, but can be compensated. The magnesium light is very similar to the light from the electric arc. A table is given by means of which the transition from one light source to another of a different colour temperature, which is important in the determination of exposure times for panchromatic plates, and for three-colour photography, can be made. The table is prepared for the blue, green, and red spectral ranges and for different light sources. Various sensitive papers are examined. Silver chlorido-gelatin paper sensitised by pinacflavol and sodium nitrite is particularly sensitive to green and yellow; such paper used in a direct copying process has a dominating sensitiveness over this part of the visible spectrum, the sensitiveness here exceeding that for the violet and ultra-violet, and being greater than with any other sensitiser. It is very useful for spectrometric work in the visible spectrum.

A. J. MEE.

Integrating microphotometer for X-ray crystal analysis. W. T. ASTBURY (Trans. Faraday Soc., 1929, 25, 397—401).—See this vol., 745.

Two-circle X-ray spectrometer. W. A. WOOSTER (Trans. Faraday Soc., 1929, 25, 401—402).—The instrument consists, in addition to the usual slits and crystal holder, of a small combined ionisation chamber and electrometer (Schonland) mounted on a vertical circle which is carried on the horizontal circle. It is specially suited to a measurement of reflected beams which fall into "layer" lines, and bears the same relation to the Bragg ionisation spectrometer (the analogue of the one-circle goniometer) as does the two-circle to the one-circle goniometer.

L. L. BIRCHUMSHAW.

Photo-electric method of measuring the light of the night sky. Course of variation through the night. (LORD) RAYLEIGH (Proc. Roy. Soc., 1929, A, 124, 395—408).—The method involves the use of a photo-electric cell and an electrometer with leakage resistance. The intensity of a patch of sky is matched with that of a white screen illuminated by

an incandescence lamp, the brightness being controlled by a resistance in the lamp circuit. The voltage across the lamp is a measure of the intensity of the sky illumination. For the blue region near the green auroral line a rubidium cell is used, and the results indicate a regular diurnal variation with a maximum at midnight. Apart from irregular variations, the value at 6 p.m. in winter is 0.7 or 0.8 of the value at midnight. L. L. BIRCUMSHAW.

Modified Pirani gauge. T. DE VRIES (J. Opt. Soc. Amer., 1929, 18, 333—335).—In each arm of a Wheatstone bridge a carbon- or metal-filament lamp is connected, and provision is made so that the pressure in two of the bulbs in opposite arms is that under measurement. Balance of the bridge is attained by inserting a resistance box in series with one of the two other bulbs, and this balancing resistance may be used as a measure of the gas pressure. The device may be used in the range 0.001—1 mm. Carbon filaments are more satisfactory than metal filaments, and the voltage on the bridge for maximum sensitivity varies with the gas pressure.

R. W. LUNT.

Vacuum recording gauges. K. C. D. HICKMAN (J. Opt. Soc. Amer., 1929, 18, 305—331).—The development, construction, and operation of differential mercury manometers adapted as recording gauges in the range 0.01—5 mm. are described. In principle the device consists of a U-tube containing mercury supported by a pivot; one limb is closed and evacuated, and the other is connected by a flexible connexion to the vessel containing the gas the pressure of which is to be measured. If the pressure in the limb attached to the flexible connexion changes, the mercury will move in the U-tube, which will in consequence move about its pivot to a new position of equilibrium. By attaching an arm to the pivoted U-tube continuous records of pressure may be obtained. It is shown that by appropriate construction a deflexion approximately proportional to the pressure may be obtained.

R. W. LUNT.

All-glass circulating pump for gases. R. LIVINGSTON (J. Physical Chem., 1929, 33, 955).—A vertical modification of the pump designed by Funnell and Hoover (A., 1927, 850), which has less frictional resistance and a decreased sensitivity to the presence of saturated vapours, is described.

L. S. THEOBALD.

Centrifugal filtration device for purification of small amounts of material by recrystallisation. E. L. SKAU (J. Physical Chem., 1929, 33, 951—954).—A simple device is described whereby filtrations can be effected at low temperatures as easily as at the ordinary temperature, and without contamination by dust. The weights of the crystals and mother-liquor can also be determined. The device is particularly suitable for fractional crystallisations of small amounts of material. The meso-form of α -dichlorohexane has been isolated by this means. L. S. THEOBALD.

Leakage of helium through pyrex glass [at 0°]. G. P. BAXTER, H. W. STARKWEATHER, and R. B. ELLESTAD (Science, 1928, 68, 516—517).—Leakage of helium through pyrex glass at 0° at a rate of 0.04 mm.³ per day per cm.² has been observed at 1 atm.

pressure. Mechanical leakage was excluded by comparative experiments at 770 and 627 mm. pressure, when the rate of leakage was approximately the same. The apparatus had previously shown no such effect with argon and had held a high vacuum for a long period before being filled with helium. The helium density determinations by Baxter and Starkweather (A., 1926, 233) are not invalidated.

L. S. THEOBALD.

Cadmium lamp. H. NAGAOKA and Y. SUGIURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 263—270).—A lamp for precision measurements is described.

J. S. CARTER.

Potentiometer. F. J. WATSON (Chem. Eng. Min. Rev., 1929, 21, 312—315).—A potentiometer of sufficient accuracy for carrying out potentiometric titrations or rough determinations of p_H is described. Parts of wireless receiving sets are largely used in the construction.

J. S. CARTER.

Apparatus for fractional distillation under vacuum. A. A. ASHWORTH (J. Inst. Petroleum Tech., 1929, 15, 211—213).—An apparatus for collecting and withdrawing any number of fractions during a distillation under reduced pressure without interrupting the continuity of distillation is described. Distillate from the condenser outlet passes into an upper receiver which is furnished at the lower end with a wide (not less than 3 mm. bore) stop-cock, *A*, leading by a short length of wide tube to a graduated receiver. The latter is also provided at the lower end with a wide stop-cock, *B*, to which are connected a length of heavy rubber tubing and a mercury reservoir. Above the graduated receiver a side-arm and wide stop-cock, *C*, are provided. Stop-cocks *B* and *C* being closed and *A* open, a required fraction of distillate is collected in the graduated receiver; the mercury reservoir is then raised, *A* is closed, and *B* and *C* are opened, and the fraction is thus transferred to any convenient receiver, the mercury being allowed to rise to the level of *C*. *C* is then closed and the mercury reservoir lowered, whereby the graduated receiver is evacuated. *B* is then closed and *C* opened; the portion of distillate that has meanwhile collected in the upper receiver passes into the graduated receiver, and the distillation is continued.

W. S. NORRIS.

Determination of width of pore of earthenware filters by means of the systems air-liquid and liquid-liquid. H. BECHOLD and R. SCHNURMANN (Z. physikal. Chem., 1929, 142, 1—24).—The pore width of various earthenware filters was determined by finding the pressure necessary to filter certain substances. The liquids used were water, methyl alcohol, ethyl ether, ethyl alcohol, *n*-propyl alcohol, isobutyl alcohol, acetone, carbon disulphide, benzene, nitrobenzene, and toluene. The pore widths found by the use of different liquids agreed fairly well if the pores were not larger than 4 μ . For pores larger than this the systems water-air and carbon disulphide-air gave values greater than those obtained with the other systems. For certain of the filters the determinations were repeated by finding the pressure required to filter a liquid mixed with another immiscible liquid (water and isobutyl alcohol). Values

were obtained by this method from 0.5 to 0.1 of those arrived at from the air-liquid systems. This difference may be due to the moistening of the porous walls by the second liquid. It is also thought that the union of invisible drops to form visible drops, which would be conditioned by the differing viscosities of the liquids, may play a part. A. J. MEE.

Weight burette. I. ITABASHI (J. Paints, 1928, 2, 107).—The glass apparatus is suitable for weighing viscous liquids. CHEMICAL ABSTRACTS.

Pipette for exact gas analysis. E. MOLES and L. R. PIRE (Anal. Fis. Quim. [Tecn.], 1929, 27, 107—109).—A modification of Travers' gas pipette is described. H. F. GILLBE.

Graphical method of teaching the thermochemistry of high temperatures. A. STANS-

FIELD (Amer. Electrochem. Soc., May, 1929. Advance copy. 7 pp.).—The method represents diagrammatically the influence of temperature on heats of reaction and the heat evolved or absorbed when the temperature of the reactants or the products is altered. H. J. T. ELLINGHAM.

Nomenclature of inorganic compounds. E. FRITZMANN (J. Russ. Phys. Chem. Soc., 1929, 61, No. 3, Suppl., 3—44). A. C. BORK (*Ibid.*, 45—52).

Russian chemical nomenclature. A. P. SEMENOV (J. Russ. Phys. Chem. Soc., 1929, 61, No. 3, Suppl., 53—55). E. V. ALEXEEVSKI (*Ibid.*, 56).

Early history of the synthesis of closed carbon chains. W. H. PERKIN (J.C.S., 1929, 1347—1363).—A lecture.

Geochemistry.

Relation between the ozone contents of air at the earth's surface and air in the high atmosphere. A. LEPAPE and G. COLANGE (Compt. rend., 1929, 189, 53—54; cf. Dobson, this vol., 419).—The ozone contents of both air at the earth's surface (Paris, 1877—1904) and in the high atmosphere (Arosa, 1927, *loc. cit.*) are at a maximum in June, the former being approximately one half the latter in January and two thirds in June. If the layers of air in the high atmosphere mix only slowly with the troposphere, ozone should exist in appreciable proportions in the lower layers of the stratosphere (cf. Cabannes and Dufay, A., 1927, 1164).

J. GRANT.

Helium content of some Japanese minerals. II. J. SASAKI (Bull. Chem. Soc. Japan, 1929, 4, 111—112; cf. A., 1927, 225).—The helium contents of a number of Japanese minerals have been determined. C. W. GIBBY.

Trinidad well waters. J. S. PARKER and C. A. P. SOUTHWELL (J. Inst. Petroleum Tech., 1929, 15, 138—173).—The Trinidad well salt waters, which are to be regarded as intermediate waters, since they are overlain and underlain by strata containing oil-saturated sands, are essentially hydrogen carbonate waters of low sulphate content, whereas the water of the Gulf of Paria is a chloride water of high sulphate content. Although this might tend to suggest a meteoric origin, it is thought more probable that the well salt waters were originally chloride waters of connate origin which have acquired a high hydrogen carbonate content by interaction with organic matter. The well salt waters on an average closely approximate in total solids content to the sea-water surrounding the island. The latter does not contain any iodine, whereas a variable iodine content is found in the well salt water.

W. S. NORRIS.

Replaceable bases in shales and clays overlying petroliferous strata. E. McK. TAYLOR (J. Inst. Petroleum Tech., 1929, 15, 207—210).—Five clays and shales overlying the petroliferous strata of Trinidad, 12 from Mexico, and 6 from Alsace are shown to have undergone base exchange in salt water

followed by hydrolysis in fresh water, this being in accord with the results found with Rumanian and Venezuelan shales and with the theory previously advanced suggesting a possible relation between base exchange and the genesis of petroleum (this vol., 168). Thus the shales from Trinidad, Mexico, and Alsace have p_H values 8.8—9.4, 8.6—10.5, and 9.0—9.4, respectively, and contain 0.7—5.1, 1.8—6.5, and 1.2—2.1 mg.-equiv. of replaceable calcium per 100 g. of shale, and 24.5—31.4, 33.5—63.5, and 16.2—29.2 mg.-equiv. of replaceable sodium per 100 g. of shale, respectively, (cf. Taylor, *loc. cit.*; Hissink, Internat. Mitt. Bodenkunde, 1922, 12, 81).

W. S. NORRIS.

Morphology and geochemistry of Tiuja-Mujun. A. FERSMAN (Trav. Acad. Sci. U.R.S.S., 1928, 3, 1—92).—The general and morphological characters and the mineralogy and geochemistry of the ore deposits at Tiuja-Mujun are described, and a theory is advanced to explain their origin.

T. H. POPE.

Barytes of the radiferous mine at Tiuja-Mujun. L. L. SOLODOVNIKOVA (Trav. Acad. Sci. U.R.S.S., 1928, 3, 93—104).—The minerals of the successive veins in this mine are described.

T. H. POPE.

Migration of uranium and radium in the principal veins of the Tiuja-Mujun deposits. V. G. CHLOPIN and M. A. PASVIK (Trav. Acad. Sci. U.R.S.S., 1928, 3, 105—110).—In spite of the occurrence of the phenomena of the migration of uranium and radium in these veins, for the ore-mass as a whole the relation between radium and uranium corresponds exactly with the condition of radioactive equilibrium. Two forms of secondary accumulation of the radium are observed; in one the radium is crystallised with barium as copper-yellow radioactive barytes, and in the other, conditioned probably by adsorption, it occurs in masses of ore of colloidal character. T. H. POPE.

Hydrothermal alteration of serpentine. F. G. WELLS (Amer. J. Sci., 1929, [v], 18, 35—52).—When olivine was treated with aqueous solutions of various

inorganic compounds at 100–600° and under pressures of 1–310 atm. a certain amount of dissolution occurred, but in no case was serpentine formed.

R. CUTHILL.

"Terra rossa" as residue from dissolution of marine limestones. WILH. GRAF ZU LEININGEN (Chem. Erde, 1929, 4, 178–187).—A series of comparative analyses of "terra rossa" from a number of localities and of material left after the dissolution of various limestones is adduced as additional evidence in support of the author's view that the first-named substance is to be regarded as a solution-residue of certain marine limestones.

H. F. HARWOOD.

Origin of the strontium in the strata of the lower Muschelkalk and Rot formations near Jena. K. DINGER (Chem. Erde, 1929, 4, 167–177).—The celestine occurring in certain strata of the lower Muschelkalk and Rot formations is not primary, but is due to secondary enrichment. The strontium has been transported in solution, probably as hydrogen carbonate, and precipitated as sulphate by interaction with gypsum, since the deposits of celestine occur only where this mineral is, or has been, present. Spectroscopic and chemical examination of the various strata of the above two formations showed the presence of traces of strontium in practically all cases, derived initially from sea-water through the agency of certain radiolaria which abstract it to form their shells.

H. F. HARWOOD.

Red marls of the Trias formation. H. E. KRAUSS (Chem. Erde, 1929, 4, 188–207).—A number of marls from the red trias formation have been subjected to chemical and rational analysis, and their mineral composition has been calculated. After subtraction of clastic minerals (quartz, felspar, and carbonates) and recalculation of the results to 100% it is found that the ratio of $\text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$ in the residual material is practically the same as that in specimens of "terra rossa." It is therefore concluded that both these substances represent similar products of weathering.

H. F. HARWOOD.

Isomorphous series in the tourmaline group and the genetic relationships between tourmaline and the micas. W. KUNITZ (Chem. Erde, 1929, 4, 208–251).—Theoretical.

H. F. HARWOOD.

Microscopic and spectroscopic investigation of the platinum-bearing rocks of the Bushveld igneous complex (Transvaal). H. SCHNEIDERHOHN (Chem. Erde, 1929, 4, 252–286).—A description is given of the rocks and associated ore minerals from the Rustenburg, Potgietersrust, and Lydenburg districts,

together with an account of the genesis of the deposits. In the pegmatites and contact-metamorphic zone sperrylite and stibiopalladinite occur, whereas in the unaltered intrusive rocks the platinum metals are entirely present in the form of platiniferous sulphides of other metals; free platinum, palladium, and gold are encountered only as secondary occurrences in the weathered rocks. Investigation of the minerals by means of the quartz spectrograph showed that the platinum metals occurred solely in the pyrrhotite, pentlandite, and nickeliferous pyrite, the greatest quantity being present in the oldest minerals. Platinum and palladium are present in practically equal amounts, iridium, rhodium, and ruthenium occur to the extent of 1–10% of the platinum present, whilst osmium is present in traces only.

H. F. HARWOOD.

Chemical and petrological investigation of bituminous rocks of various ages from N. Germany. F. HIEBENTHAL (Chem. Erde, 1929, 4, 343–368).—Bituminous material from four different formations (alluvial, diluvial, tertiary, and cretaceous) has been examined chemically and petrologically. The bitumens from these marine sediments show increasing carbon content with age, but unlike those of terrestrial origin there is no corresponding decrease in the hydrogen content. Elementary sulphur was found in the specimen from the alluvium, and a stable "metabitumen" was detected in the tertiary rock.

H. F. HARWOOD.

Relations of electrode potentials of some elements to the formation of hypogene mineral deposits. B. S. BUTLER and W. S. BURBANK (Amer. Inst. Min. Met. Eng. Tech. Pub., 1929, No. 166, 3–15).—When arranged in order of their electrode potentials, groups of elements exhibit a periodicity and a relation to their occurrence in primary ore minerals.

CHEMICAL ABSTRACTS.

Natrolite of Viagrande (Etna). S. DI FRANCO (Atti R. Accad. Lincei, 1929, [vi], 8, 657–663).—Natrolite occurs as colourless transparent crystals, d 2.19–2.21, more than 1 cm. long and 0.1 cm. diameter in cavities of a very old reddish lava on Etna, in the forms (110), (111), (100), and (010). The more frequent combination is of the prism (110) and the pyramid (111). The crystallographic and optical constants have been determined. Analysis gave H_2O 9.58, SiO_2 46.93, Al_2O_3 27.02, Na_2O 16.43; total 99.96%, agreeing with the formula $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$. On dehydration less than 1% of water is lost at 275°, but nearly the whole of the water is lost between 290° and 315°. This loss is reversible.

F. G. TRYHORN.

Organic Chemistry.

Non-explosive oxidation of propane and the butanes. R. N. PEASE (J. Amer. Chem. Soc., 1929, 51, 1839–1856).—Mixtures of propane and oxygen were passed through pyrex glass tubes heated in a constant-temperature bath at 300–625°, without attempting to render the reaction isothermal. The amounts of propane, oxygen, unsaturated hydro-

carbons, methane, hydrogen, carbon monoxide and dioxide in the products and the proportions of hydrocarbon reacting according to schemes I, II, and III (p. 906) are tabulated. The liquid products have not been examined. In general, unsaturated hydrocarbons and carbon monoxide are the chief products, the amount of methane formed increasing as the

furnace temperature is raised. The results are explained by the occurrence of three types of reaction: (I) dissociation into an unsaturated hydrocarbon and hydrogen or methane; (II) oxidation to an unsaturated hydrocarbon and liquid products, *e.g.*, water, alcohol, or formaldehyde, and (III) the "aldehyde oxidation," *e.g.*, $C_3H_8 + O_2 \longrightarrow C_2H_5 \cdot CHO + H_2O$; $C_6H_5 \cdot CHO + O_2 \longrightarrow CH_3 \cdot CHO + CO + H_2O$ (*cf.* Pope, Dykstra, and Edgar, following). Types I and II are homogeneous gas reactions of the first order with respect to propane. Since they always appear simultaneously, they have probably a common initial stage. When reaction III is prevented they do not occur below 550–600°, but they are subject to excitation by III at lower temperatures. Type III is a faintly luminous chain reaction, promoted by the presence of excess of hydrocarbon, but hindered by dilution with oxygen, methane, nitrogen, carbon dioxide, and hydrogen, which are given in order of increasing effectiveness. The inhibiting action is greater at higher temperatures, so that, under these conditions, the reaction may have a negative temperature coefficient, although it eventually becomes explosive (*cf.* Bone and others, *J.C.S.*, 1904, 85, 693, 1637). A packing of coarsely powdered glass suppresses the reaction and has also a positively catalytic effect, which is destroyed by coating it with potassium chloride. The reaction is also suppressed by using a tube of small bore or by lowering the pressure to 5–10 mm. The oxidation of *n*- and *iso*-butanes proceeds, under these conditions, similarly to, but more readily than, that of propane. *n*-Butane is the more reactive. The optimum conditions for oxidising a paraffin to (a) aldehydes and (b) unsaturated hydrocarbons are discussed.

H. E. F. NOTTON.

Vapour-phase oxidation of isomeric octanes.

I. *n*-Octane. J. C. POPE, F. J. DYKSTRA, and G. EDGAR (*J. Amer. Chem. Soc.*, 1929, 51, 1875–1889).—The oxidation of *n*-octane, vaporised in nitrogen and preheated to the reaction temperature, by sufficient oxygen for complete combustion has been examined by the flow method (a) at constant temperature and (b) with the temperature rising during about 2 hrs. from 200° to 650°. Reaction begins at 200° and, up to 270°, the principal products are aldehyde, acid, traces of peroxide, carbon dioxide, and water. Sharply at 270° a pulsatory reaction begins, accompanied by flashes of white light and by the formation of carbon monoxide. At 300–320° the pulsations disappear and the reaction becomes localised near the entrance of the furnace. Up to 650° the oxygen consumption and formation of carbon monoxide increase, but above this temperature complete combustion occurs with strong pulsations and a bright blue luminescence. The changes observed below 650° are explained by the following reactions: (I) $C_7H_{15} \cdot CH_3 + O_2 \longrightarrow C_7H_{15} \cdot CHO$; (II) $C_nH_{2n+1} \cdot CH_2 \cdot CHO + O_2 \longrightarrow C_nH_{2n+1} \cdot CHO + CO$; (III) $C_nH_{2n+1} \cdot CH_2 \cdot CHO + 1.5O_2 \longrightarrow C_nH_{2n+1} \cdot CHO + CO_2$. The initial reaction, I, is followed at 200–270° by III, which is apparently a homogeneous gas reaction and continues at a slightly increasing rate up to 650°. The chain reaction, II, predominates at 270–650°, the average mol. wt. of the resulting aldehydes

decreasing as the temperature rises. When, at 400°, molecules of the size of butaldehyde or smaller have been produced, further oxidation proceeds much more slowly until the temperature reaches 650°. This explanation is supported by analyses of the gaseous products and by parallel experiments with *n*-butaldehyde and *n*-heptaldehyde. Thus, it is shown that, in the oxidation of 1 mol. of octane to aldehydes and oxides of carbon, the formation of a given quantity of the latter requires 1 mol. of oxygen more than that required to produce the same quantity by oxidising either aldehyde. The oxygen consumed in all experiments with the three substances agrees with that calculated by means of the above equations from the amounts of oxides of carbon formed. The oxidation of heptaldehyde begins at about 150°. Carbon monoxide and dioxide are formed in almost equal amounts up to 235°, when the production of the former suddenly increases and the reaction becomes pulsatory. With butaldehyde the reaction begins at 200° and feeble pulsations are observed at 335°.

H. E. F. NOTTON.

Carotinoids. II. Determination of the degree of unsaturation of polyenes by iodine chloride and perbenzoic acid. R. PUMMERER, L. REBMANN, and W. REINDEL (*Ber.*, 1929, 62, [B], 1411–1418; *cf.* A., 1928, 765).—After prolonged contact with iodine chloride the presence of eleven double linkings in carotin is established, this agreeing with the number found by hydrogenation. The detection of the thirteen double linkings in lycopin by means of iodine chloride depends on the extreme prolongation of the action and the use of an unusually large excess of the reagent; liberation of iodine chloride or iodine from the additive product during titration is not observed. Xanthophyll behaves similarly to carotin. With isoprene, saturation of two double linkings by iodine chloride can be effected only if a large excess of reagent is used. At 0°, the hydrocarbon adds only 1 atom of oxygen from perbenzoic acid and the double linking remaining in the product can be determined by iodine chloride. Bixin adds five mols. of bromine, and not more than six double linkings react with iodine chloride under the most favourable conditions, whereas hydrogenation indicates the presence of nine double linkings; it absorbs only six atoms of oxygen from perbenzoic acid, whereas thiocyanogen at 0° indicates only three double linkings. In $\omega\omega'$ -diphenyloctatetraene four double linkings are detected by bromine, rather less than four by iodine chloride, and 3.2–3.3 by perbenzoic acid. With *r*- and *d*-limonene, iodine chloride indicates 2.2–2.3 double linkings, whereas about 1.6 atoms of oxygen are absorbed by perbenzoic acid at 0°.

Determination of the acid liberated during the titration of the carotin-iodine chloride adduct indicates 6 mols. per mol. of hydrocarbon instead of 3 recorded previously (*loc. cit.*). Considering 2 mols. of halogen acid to correspond with a double linking, the presence of three such "peculiar" linkings is indicated; this agrees with the results of the action of hydrogen and perbenzoic acid.

The absorption curves of xanthophyll, lycopin, and carotin are closely similar.

H. WREN.

Preparation of amylene with a theoretical hydrogen value. H. I. WATERMAN, P. VAN 'T SPIJKER, and H. A. VAN WESTEN (Rec. trav. chim., 1929, 48, 612—615).—An amylene preparation, b. p. below 36° , n_D^{20} 1.3811 (bromine value 208.4), by treatment with the theoretical quantity of bromine (calculated on the bromine value) in carbon tetrachloride at -10° to -15° gave a 50% yield of a mixture of bromides, b. p. $58-62.5/17$ mm., which, when treated with water and a zinc-copper couple at 60° , afforded a very pure amylene, b. p. $36.8-38.4/760$ mm., n_D^{20} 1.3856 [bromine value (McIlhiney) 229.0; thiocyanogen bromine value 228.5]. The hydrogen value determined by the method of Waterman, Perquin, and van Westen (B., 1928, 512) was found to be 100.8% of the theoretical value; the hydrogenation product had b. p. $28.0-28.5^{\circ}$, n_D^{20} 1.3545, in agreement with constants recorded for β -methylbutane (*lit.*). The original amylene preparation therefore consisted largely of the isomeride $\text{CHMe}:\text{CMe}_2$. C. W. SHOPPEE.

Additive products of diacetylenic hydrocarbons. V. GRIGNARD and TCHÉOUFAKI (Compt. rend., 1929, 188, 1531—1534; cf. this vol., 448).— Δ^8 -Tetradecadi-ene yields with bromine in carbon disulphide at the ordinary temperature β -tetra-bromo- Δ^8 -tetradecadiene; at the b. p. only resinous products are formed; at -5° an unstable, oily ζ (?)-dibromide is formed, which yields α -bromo- Δ^8 -heptinene when distilled.

Hydrogenation of diphenyldiacetylene (Straus, A., 1906, i, 77) in presence of platinum oxide-platinum-black yields *cis-cis*-diphenylbutadiene (20%), m. p. $69-70^{\circ}$, dibenzylacetylene (20%), m. p. 80° , and $\alpha\delta$ -diphenylbutatriene, b. p. $185-187/13$ mm., which yields an isomeride, m. p. 95° , when exposed to light. The constitution of this last substance is proved by its ozonolysis to benzaldehyde, unaccompanied by oxalic or glyoxylic acids. Diphenyldiacetylene is converted by boiling with hydrobromic acid into α -bromo- $\alpha\delta$ -diphenylbutadiene, m. p. 92° , which may be reduced by zinc dust in acetone to $\alpha\delta$ -diphenylbutatriene.

R. K. CALLOW.

Action of the zinc-copper couple on methylene iodide. G. EMSCHWILLER (Compt. rend., 1929, 188, 1555—1557).—The action of the zinc-copper couple on methylene iodide in boiling ether yields initially zinc iodomethyl iodide, $\text{CH}_2\text{I} \cdot \text{ZnI}$, which is subsequently decomposed with the production of zinc iodide and ethylene and a small quantity of zinc methylene iodide, $\text{CH}_2(\text{ZnI})_2$. The solution of zinc iodomethyl iodide reacts with iodine to yield methylene iodide, and slowly with water to yield methyl iodide. With water containing oxygen an oxidation product is first formed, hydrolysed with the formation of formaldehyde and zinc iodide. Zinc methylene iodide, like the analogous magnesium compounds (A., 1926, 1224), is decomposed by water to give methane.

R. K. CALLOW.

Formation and fission of glucosides as a method for chemical and biochemical separation of racemic alcohols into their optically active forms. C. NEUBERG, K. P. JACOBSEN, and J. WAGNER (Fermentforsch., 1929, 10, 491—531).—A new method for the resolution of optically active

alcohols is based on glucoside formation with α - or β -acetobromoglucose in the presence of silver carbonate or quinoline. The *dl*-, the *d*-, or the *l*-alcohol *d*-glucoside may be formed, the last two being separated by fractional crystallisation or the *dl*-compound being submitted to asymmetric enzymolysis. In some cases if an excess of alcohol is used the unattacked portion is found to be optically active. Thus by inter-action of 8 mols. of *dl*-borneol with 1 mol. of acetobromoglucose and silver carbonate and removal of the excess of borneol by steam distillation, a tetra-acetylglucoside is obtained which, after complete hydrolysis, yields a specimen of borneol having $[\alpha]_D +1.60^{\circ}$ and containing, therefore, 4.3% excess of the *d*-compound. When only 2 mols. of *dl*-borneol are used, steam distillation yields a laevorotatory borneol, $[\alpha]_D -1.05^{\circ}$, whilst complete hydrolysis of the glucoside yields a dextrorotatory borneol, $[\alpha]_D +1.5^{\circ}$. Similar treatment of *dl*-menthol and steam distillation of the excess alcohol yields a product which is sometimes laevo- and sometimes dextro-rotatory. When a large excess of *dl*-menthol is heated with β -acetobromoglucose and quinoline at 100° it yields a mixture of α - and β -tetra-acetylglucosides, which when heated with 2*N*-alcoholic potassium hydroxide at 60° and then diluted with water yields *l*-menthol- α -*d*-glucoside, which is hydrolysed by *N*-sulphuric acid to yield *l*-menthol, $[\alpha]_D -48.3^{\circ}$ (96.6% pure). If, instead, the partly deacetylated mixed α - and β -glucosides are reacetylated with pyridine and acetic anhydride and the product is crystallised from dilute alcohol, *d*-menthol- β -*d*-tetra-acetylglucoside is obtained, which hydrolyses to *d*-menthol, $[\alpha]_D +10^{\circ}$ to $+40^{\circ}$, whilst oily *l*-menthol- α -*d*-tetra-acetylglucoside is obtained from the mother-liquor and hydrolyses to *l*-menthol, $[\alpha]_D -24^{\circ}$ to -44° . Thus *l*-menthol combines with α -glucose and *d*-menthol with the β -form, a conclusion which is confirmed by the fact that the *l*-mentholglucoside suffers 100% enzymolysis with maltase (α) and is unattacked by emulsin, whilst the *d*-mentholglucoside is hydrolysed to the extent of 93% by emulsin (β), but is unaffected by maltase. By the silver carbonate method methylpropylcarbinol yields, after deacetylation, *dl*-methylpropylcarbinol- β -*d*-glucoside, no resolution taking place. Fractional crystallisation of this glucoside from ethyl acetate yields a glucoside which on hydrolysis gives almost pure *d*-methylpropylcarbinol, $[\alpha]_D +12.8^{\circ}$. By enzymolysis of a 0.5% solution of *dl*-menthol- β -*d*-glucoside with emulsin at 37° and ether extraction when 46% hydrolysis has occurred (by determination of the sugar), *d*-menthol (50—70% purity) is obtained, whilst after removal of the ether continued hydrolysis of the residue yields *l*-menthol (57—79% purity). By similar enzymolysis *dl*-borneol- β -*d*-glucoside yields first *l*-borneol (50—54% purity) and then *d*-borneol (36—51% purity). Resolution of *dl*-methylpropylcarbinol- β -*d*-glucoside (obtained by hydrolysis of the tetra-acetylglucoside with methyl-alcoholic ammonia) by hydrolysis with emulsin is much less complete, the first fraction containing 6% of the *l*-alcohol and the second 13% of the *d*-compound. J. W. BAKER.

β -Methyl- Δ^8 -hepten- ζ -ol and natural *d*-citronellol. J. DÆVRE (Bull. Soc. chim., 1929, [iv], 45, 351—364).—Geraniol, b. p. $117-118^{\circ}/16$ mm.,

d_4^{20} 0.875, 1.4722 , $[\alpha]_D^{25} +1.13^\circ$, bromine value, 167%, obtained from Java citronella oil and containing some *d*-citronellol, when ozonised by the quantitative method (this vol., 542), gave 16% of formaldehyde, 35% of formic acid, and 90% of acetone, indicating that the β -form is the principal constituent. Determination of the α -(limonic) form is not possible on account of the coloration given by the glycolaldehyde formed with the Grosse-Bohle reagent. The large amount of formic acid produced is attributed to formation of the aldehyde peroxide, $\text{OH}\cdot\text{CH}_2\cdot\text{CHO}_2$, yielding, by addition of water, formic acid and formaldehyde. Alcoholic potassium hydroxide converts this geraniol into β -methyl- Δ^8 -hepten- ζ -ol, b. p. $78-79^\circ/14$ mm., $177-178^\circ/760$ mm., d_4^{25} 0.855, n_D^{25} 1.5411 (allophanate, m. p. $99-100^\circ$), together with *d*-citronellol and a viscous residue. The β -methyl- Δ^8 -hepten- ζ -ol when ozonised affords 1% of formaldehyde, 9% of formic acid, and 90% of acetone, indicating that the alcohol is a mixture of 10% of the α - and 90% of the β -form, the proportions being thus unchanged by the action of potassium hydroxide. In accordance with Tiemann (A., 1899, i, 184) agitation with 25% sulphuric acid yields β -methylheptane- $\beta\zeta$ -diol, b. p. $124-126^\circ/14$ mm., d_4^{25} 0.946, n_D^{25} 1.4569, converted into β -methylheptene oxide, b. p. $127-128^\circ/750$ mm., d_4^{25} 0.855, n_D^{25} 1.4288. The conversion of geraniol into methylheptenol is attributed to addition of 1 mol. of water at the double linking nearest to the hydroxyl group and scission of the glycol:

$\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} \longrightarrow$
 $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{OH} + \text{CH}_3\cdot\text{CH}_2\cdot\text{OH}$, evidence of the reducing action of potassium ethoxide being afforded (a) by the formation of methylheptenol in the action of alcoholic potassium hydroxide on natural methylheptenone, b. p. $70-71^\circ/18$ mm., and (b) by the isolation from the viscous fraction of b. p. above $125^\circ/15$ mm., in the action of potassium hydroxide on geraniol, of a liquid condensation product, b. p. $174-180^\circ/16$ mm., formed from 2 mols. of methylheptenone by elimination of water (Léser, A., 1898, i, 512). ζ -Chloro- β -methyl- Δ^8 -heptene, b. p. $59-61^\circ/15$ mm., forms no Grignard reagent, but ζ -bromo- β -methyl- Δ^8 -heptene, b. p. $71-72^\circ/14$ mm., d_4^{25} 1.146, n_D^{25} 1.4720 (obtained in 60% yield using phosphorus tribromide in carbon tetrachloride), reacts readily with magnesium in ether in presence of iodine. When ozonised it affords 6% of formaldehyde, 16% of formic acid, and 76% of acetone, the proportion of α -form having been thus increased to 22%, probably by the hydrogen bromide produced in the reaction. The action of boiling hydriodic acid on methylheptenol yields, in addition to methylheptene oxide, a liquid, b. p. $95-105^\circ/6$ mm., containing mono- and di-iodo-derivatives which reacts readily with magnesium in ether. Repeated treatment of the fraction of b. p. $115-125^\circ/14$ mm. with alcoholic potassium hydroxide to destroy the geraniol afforded a *d*-citronellol, b. p. $119-120^\circ/20$ mm., d_4^{25} 0.866, n_D^{25} 1.4617, $[\alpha]_D^{25} +2.23^\circ$, bromine value 109% (cf. A., 1928, 654; this vol., 542), giving when ozonised 6% of formaldehyde, 18% of formic acid, and 80% of acetone, a result which indicates that natural *d*-citronellol is a mixture of approximately 20% of the α - and 80% of the β -form. Purification of *d*-citronellol through the benzoate, b. p. $190-200^\circ$,

gave a citronellol, b. p. $118-119^\circ/18$ mm., d_4^{25} 0.860, n_D^{25} 1.4572, $[\alpha]_D^{25} +2.3^\circ$, bromine value 96%, affording when ozonised 15% of formaldehyde, 24% of formic acid, and 59% of acetone (cf. A., 1928, 1113). The isomerisation is attributed to the action of hydrogen chloride formed from the benzoyl chloride, since the original *d*-citronellol when heated at $100-150^\circ$ for 2 hrs. in presence of hydrogen chloride gives a product, b. p. $118-119^\circ/17$ mm., d_4^{25} 0.863, n_D^{25} 1.4577, yielding when ozonised 14% of formaldehyde, 28% of formic acid, and 54% of acetone. The transformation is regarded as an exception to the Seytzev-Markovnikov rule, addition of hydrogen chloride at the double linking giving a chloro-derivative from which the α - and β -forms are regenerated in proportions differing from those originally existing by elimination of hydrogen chloride in both the directions possible.

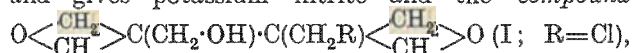
R. BRIGHTMAN.

Mechanism of organic reactions. II. "Non-existence" of a migratory methyl group in the conversion of glyceryl dichlorohydrin into monomethyl glyceryl ether. H. HIBBERT and M. S. WHELEN (J. Amer. Chem. Soc., 1929, 51, 1943-1947).—Contrary to the results of Gilchrist and Purves (A., 1926, 153), methylation of pure glyceryl $\alpha\gamma$ -dichlorohydrin, prepared from epichlorohydrin, with silver oxide and methyl iodide proceeds normally to the β -methyl ether, b. p. $157-159^\circ$, n_D^{25} 1.4550, identified by hydrolysis through the acetate to β -methyl glyceryl ether. Commercial glyceryl $\alpha\gamma$ -dichlorohydrin always gives a mixture of products. Glyceryl $\alpha\beta$ -dichlorohydrin γ -methyl ether, b. p. $153-157^\circ$ (slight decomp.), n_D^{25} 1.4489, is also converted normally through the diacetate into pure α -methyl glyceryl ether. The results emphasise the value of α - and β -methyl glyceryl ethers for identification purposes.

H. E. F. NOTTON.

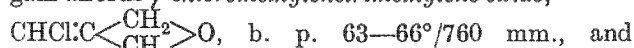
Elimination of the nitro-group from tertiary nitro-compounds. I. Derivatives of "nitroisobutylglycerol." II. Action of sodium amalgam on derivatives of "nitroisobutylglycerol." H. KLEINFELLER (Ber., 1929, 62, [B], 1582-1590, 1590-1597).—I. Nitroisobutylglycerol (nitrotri-hydroxymethylmethane) (cf. Schmidt and Wilkendorf, A., 1919, i, 249) is converted by phosphorus pentachloride mainly into $\alpha\gamma$ -dichloro- β -nitro- β -chloromethylpropane, m. p. 104° , in which the halogen atoms are retained with remarkable firmness. γ -Chloro- β -nitro- β -chloromethylpropan- α -ol, m. p. 127° , γ -nitro- γ -chloromethyl-trimethylene oxide, b. p. $45-46^\circ/9$ mm., $\alpha\gamma$ -dichloro- β -chloromethyl- Δ^8 -propene, b. p. $62-64^\circ/9$ mm., and $\alpha\alpha\gamma$ -trichloro- β -chloromethylpropane, b. p. $77-80^\circ/9$ mm., are obtained in minor amount together with the phosphate of $\alpha\gamma$ -dichloro- β -nitro- β -hydroxymethylpropane. With red phosphorus and bromine, nitrotri-hydroxymethylmethane yields the phosphate described above, $\alpha\gamma$ -dibromo- β -nitro- β -bromomethylpropane, m. p. 85° , $\alpha\gamma$ -dibromo- β -bromomethyl- Δ^8 -propene, b. p. $105-107^\circ/9$ mm., and $\alpha\alpha\gamma$ -tribromo- β -bromomethylpropane, b. p. $133-136^\circ/9$ mm. Reduction of trichloronitroisobutane with aluminium amalgam and alcohol affords $\alpha\gamma$ -dichloro- β -hydroxylamino- β -chloromethylpropane, m. p. 81° , whereas with stannous chloride and alcoholic hydrogen chloride $\alpha\gamma$ -dichloro-

β -amino- β -chloromethylpropane [hydrochloride, m. p. 245—246° (decomp.); picrate, m. p. 180°] is produced. β -Nitro- $\alpha\gamma$ -dibenzoyloxy- β -hydroxymethylpropane, m. p. 122—124°, is obtained as by-product of the preparation of the tribenzoyl compound. The action of alcoholic potassium hydroxide on $\alpha\gamma$ -dichloro- β -nitro- β -chloromethylpropane consumes 3.5 mols. of alkali and gives potassium nitrite and the compound



b. p. 80°/12 mm. Similarly, nitrotrihydroxymethylmethane, its tri- and di-benzoyl derivatives react with 1, 4, and 3 mols. of potassium hydroxide, respectively, with production of potassium nitrite; the substance, $\text{C}_8\text{H}_{14}\text{O}_4$ (cf. I; $\text{R}=\text{OH}$), b. p. 108—112°/9 mm., is prepared from the dibenzoyl compound. The phosphoric ester described above passes when heated into the compound $(\text{CH}_2\text{Cl})_2\text{C}\left<\begin{array}{c} \text{O}\cdot\text{CH}_2 \\ \text{CH}\cdot\text{O} \end{array}\right>C(\text{CH}_2\text{Cl})_2$, b. p. 60—61°/9 mm. The action of thionyl chloride on nitrotrihydroxymethylmethane affords the corresponding sulphite, $\text{C}_4\text{H}_7\text{O}_6\text{NS}$, m. p. 104°, and a second form, m. p. 180°, of nitrotrihydroxymethylmethane; the last-named compound is also obtained by means of phosphorus pentachloride or sulphuryl chloride; it slowly passes into the modification of lower m. p., and may possibly be present in the original material which does not melt sharply. The benzoyl derivative of either form has m. p. 111°.

II. $\alpha\gamma$ -Dichloro- β -nitro- β -chloromethylpropane and the corresponding tribromo-compound are indifferent towards silver, copper, or zinc at varied temperatures and yield amorphous products with sodium, potassium, or their alloy in presence of the customary solvents. When cautiously heated with 4.5% sodium amalgam in the absence of solvent, the trichloro-compound affords $\alpha\gamma$ -dichloro- β -chloromethyl- Δ^a -propene (see above) and γ -chloro- β -chloromethyl- Δ^a -propene, b. p. 30—31°/9 mm., converted by bromine into $\alpha\gamma$ -dichloro- $\alpha\beta$ -dibromo- β -chloromethylpropane, b. p. 140°/10 mm., and γ -chloro- $\alpha\beta$ -dibromo- β -chloromethylpropane, b. p. 115°/10 mm., respectively, and by chlorine into $\alpha\beta\gamma$ -tetrachloro- β -chloromethylpropane, b. p. 99—101°/12 mm., and $\alpha\beta\gamma$ -trichloro- β -chloromethylpropane, b. p. 87°/9 mm., respectively; either compound is hydrogenated in the presence of spongy platinum to γ -chloro- β -chloromethylpropane, b. p. 45°/10 mm. γ -Chloro- β -nitro- β -chloromethylpropan- α -ol with sodium amalgam affords γ -chloromethylenetrimethylene oxide,



γ -methylenetrimethylene oxide, b. p. 35—40°/760 mm., obtained also from γ -nitro- γ -chloromethyltrimethylene oxide. $\alpha\gamma$ -Dibromo- β -nitro- β -bromomethylmethane affords $\beta\epsilon$ -dibromomethyl- Δ^a -hexadiene, b. p. 140—143°/9 mm. (slight decomp.), in addition to $\alpha\gamma$ -dibromo- β -bromomethyl- Δ^a -propene (see above) and γ -bromo- β -bromomethyl- Δ^a -propene, b. p. 70—72°/9 mm. These compounds are converted by bromine in chloroform into $\alpha\beta\epsilon\zeta$ -tetrabromo- $\beta\epsilon$ -dibromomethylhexane, m. p. 115°, $\alpha\alpha\beta\gamma$ -tetrabromo- β -bromomethylpropane, b. p. 185—190°/9 mm. (slight decomp.), and $\alpha\beta\gamma$ -tribromo- β -bromomethylpropane, b. p. 143—145°/9 mm. β -Nitro- $\alpha\beta\gamma$ -tribenzoyloxymethylmethane and sodium amalgam give $\beta\epsilon$ -dibenzoyloxymethyl- Δ^a -hexadiene, b. p. 220°/9

mm., and γ -benzoyloxy- β -methyl- Δ^a -propene, b. p. 120°/50 mm.; $\alpha\beta\epsilon\zeta$ -tetrabromo- $\beta\epsilon$ -dibenzoyloxymethylhexane is described. Nitrobenzene reacts violently with sodium amalgam, giving azobenzene in good yield. With the aliphatic compounds, the alkali metal appears to remove an atom of oxygen from the nitro-group, leaving a nitroso-compound which decomposes into nitric oxide and a radical from which the ultimate products are derived by re-distribution of valencies. H. WREN.

Syntheses of bromomethanedisulphonic acid.

H. J. BACKER (Rec. trav. chim., 1929, 48, 616—621). —Potassium formylbromomethanedisulphonate (this vol., 792) when treated with cold concentrated potassium hydroxide furnishes an 86% yield of potassium bromomethanedisulphonate (cf. Rathke, A., 1872, 388; Kohler, *ibid.*, 1899, i, 488), which can be purified by precipitating the aqueous solution with alcohol; crystallisation from water affords the dihydrate. Barium hydroxide may be used in the above preparation, which is the best method. Bromomethanedisulphonic acid may also be obtained by the following methods: (1) direct bromination of methanedisulphonic acid at 250° for 5 hrs.; (2) addition of the monohydrate of potassium diazomethanedisulphonate (cf. Pechmann and Manck, A., 1896, i, 14) to concentrated hydrobromic acid at 0°; (3) double decomposition of potassium dibromomethanesulphonate (cf. A., 1927, 39) with aqueous potassium sulphite at 130° (yield 20%). The following salts are described and their solubilities tabulated: *strychnine* (trihydrate losing $3\text{H}_2\text{O}$ at 105°, or by boiling with alcohol); *sodium* (dihydrate, crystallographic data); *thallous* (crystallographic data); *barium* (hydrate + 4 or $4\frac{1}{2}\text{H}_2\text{O}$, lost at 100° in a vacuum). The free acid may be obtained by decomposing the barium salt with dilute sulphuric acid or by treating the strychnine salt with barium hydroxide; the use of the latter salt for purification is recommended. The acid (dihydrate, m. p. 125—126°) and its salts are considerably more soluble in water than methanesulphonic acid and its derivatives. C. W. SHOPPEE.

Action of acetic anhydride on carboxylic acids.

A. W. VAN DER HAAR (Rec. trav. chim., 1929, 48, 607—611). —Consequent on the results of Caudri (this vol., 655), the author withdraws his former views on the constitution of the anhydrides (I) and (II) of sugar-beet sapogenin (A., 1928, 68) and ursolic acid (*ibid.*, 644). The compounds are the mixed anhydrides derived from the above acids and acetic acid; I melts at 215°, with conversion into sugar-beet sapogenin anhydride, m. p. 315°, which is largely converted by 0.1N-alcoholic potassium ethoxide into potassium diacetylsulphate, and ethyl acetate; II melts at 200—201°, with conversion into diacetylsulphate anhydride, m. p. 320—322°, and its mol. wt., determined cryoscopically in benzene, agrees with the revised structure. Caudri's results on the titration of acetylopianic acid with alcoholic sodium ethoxide, leading to the production of ethyl acetate in almost theoretical yield (*loc. cit.*), are confirmed.

The action of acetic anhydride on aldehydo- and keto-acids is considered; the formation with phenylhydrazine of a compound, m. p. 173° (containing 10.07,

10-10%N), from opianic acid, but not from acetyl-opianic acid, in acetic acid solution is reported and discussed.

C. W. SHOPPEE.

Anodic formation of the triacetates of nickel and cobalt and Kolbe's reaction. C. SCHALL and C. THIEME-WIEDTMARCKTER.—See this vol., 892.

Velocity of esterification of fatty acids with ethylene glycol and hydrochloric acid. A. KAILAN and A. SCHACHNER.—See this vol., 888.

Esters of α -dimethylbutyric acid. B. B. CORSON, J. S. THOMAS, and D. D. WAUGH (J. Amer. Chem. Soc., 1929, **51**, 1950—1951).— α -Dimethylbutyric acid, formed together with *tert*-amyl alcohol and a *by-product*, b. p. 164—167.5°, n_D^{20} 1.4335, from magnesium *tert*-amyl chloride and carbon dioxide, gives the following esters [b. p. °/746 mm. (corr.), d_4^{25} , and n_D^{25} being given for each]: *methyl*, 125—125.5°, 0.8943, 1.3991; *ethyl*, 141.8—142.2°, 0.8601, 1.3989 (cf. Bouveault, A., 1904, i, 642); *n-propyl*, 164—164.4°, 0.8575, 1.4040; *n-butyl*, 184—184.7°, 0.8566, 1.4098; *n-amyl*, 202.5—203.5°, 0.8544, 1.4140; and *isoamyl*, 192.5—196.5°, 0.8533, 1.4128.

H. E. F. NOTTON.

Action of per-acids on certain unsaturated organic substances and of benzoyl peroxide on a mixture of paraffins. J. BOESEKEN, W. C. SMIT, and GASTER [with M. SLOOFF] (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 377—383).—By the action of perbenzoic or peracetic acid on methyl linoleate the ester of a dioxidostearic acid, m. p. 31°, is produced; hydrolysis at a low temperature yields the free acid, m. p. 79°. Hydrolysis of the triatomic ethylene oxide ring in this substance with dilute sulphuric acid at 80° or with 80% sulphuric acid at 0° yields two isomeric tetrahydroxystearic acids, m. p. 95° and 148°, respectively. Two other dioxidostearic acids, of m. p. 89° and 75°, have been prepared, in which, owing to steric hindrance, the ethylene oxide rings are not hydrolysable by acid. Treatment of ricinelaidic acid with perbenzoic acid yields two oxido-elaidic acids, m. p. 64° and 59°, $[\alpha]_D^{25}$ —17.2° and 3.4°, respectively; on hydrolysis, two trihydroxystearic acids, m. p. 137° and 112°, are formed. The velocity coefficients of the oxidation by peracetic acid of oleic, elaidic, ricinoleic, and ricinelaidic acids, at 18°, are 0.036, 0.023, 0.026, and 0.016, respectively. Determination of this velocity thus serves to differentiate between the oleic and elaidic types. Acids containing a triple linking, e.g., stearolic, are oxidised very slowly by peracetic acid: the primary product is probably a diketonic acid which then undergoes rupture at the ketonic carbon atoms. The group $\text{CMe}\cdot\text{C}\cdot$ is attacked with about the same velocity as is stearolic acid, but the $\text{CH}\cdot\text{C}\cdot$ group is scarcely affected. Tertiary alcohols may be synthesised directly from certain paraffins by treatment with benzoyl peroxide and hydrolysis of the benzoyl ester which is formed together with a large quantity of secondary products.

H. F. GILLBE.

Preparation of *d*-gluconic and galactonic acids. M. HONIG and W. RYZICKA (Ber., 1929, **62**, [B], 1434—1436; cf. Kiliani, this vol., 541).—Dextrose or galactose in 1% aqueous solution is mixed with sufficient 0.1N-bleaching powder solution

to supply one equivalent of oxygen and rather more than sufficient milk of lime to maintain alkalinity. The liquid is kept well stirred and exposed to the light of a quartz lamp until a test portion does not colour starch iodide paper. The heated mixture is then saturated with carbon dioxide, filtered, and the filtrate concentrated in a vacuum to a syrup, which is poured into alcohol. The precipitated calcium gluconate or galactonate is purified by repeated treatment with water and alcohol. Starch syrup may also be used in the preparation of gluconic acid. An alternative process using barium hypobromite and hydroxide is also described, the acids being isolated as the calcium salts.

H. WREN.

Preparation of *d*-glycuronic acid from gum arabic. F. WEINMANN (Ber., 1929, **62**, [B], 1637—1639).—Kordofan gum arabic is heated with 2% hydrochloric acid at 100° until the specific rotation of the solution does not further change and the filtered solution is treated with alcohol, thereby precipitating the gum acids, which are boiled with *N*-sulphuric acid until the optical activity of the solution becomes constant. The solution is neutralised with barium hydroxide and finally barium carbonate, and filtered; the filtrate is boiled with a further small amount of barium carbonate, after which it is concentrated and the barium *d*-glycuronate is precipitated with alcohol. About 50 g. of acid are obtained from 1 kg. of gum.

H. WREN.

Alginic acid from *Macrocystis pyrifera*. W. L. NELSON and L. H. CRETCHER (J. Amer. Chem. Soc., 1929, **51**, 1914—1922).—Mannitol (4—5%) and alginic acid (15%) (sodium salt, $[\alpha]_D^{25}$ —133°) were isolated from the alga. The latter has an equivalent of 179 towards alkali and, when boiled with hydrochloric acid, evolves carbon dioxide (1 mol./equiv.). It is a polyuronic acid, $(\text{C}_5\text{H}_7\text{O}_4\cdot\text{CO}_2\text{H})_n$, with no free aldehyde groups. It is partly decarboxylated by boiling with water or dilute sulphuric acid or by heating at 100° and is hydrolysed by cold 80% sulphuric acid to a new *polyuronic acid* and a syrupy *aldehydo-acid* (barium and cinchonine, m. p. 152° with effervescence, $[\alpha]_D^{25}$ +113.6°, salts), isomeric with glycuronic acid. This is oxidised by bromine water to a gummy product from which *d*-mannosaccharidamide and diphenylhydrazide were prepared. The presence of *d*-mannuronic acid residues in alginic acid is inferred (cf. Hoagland and Lieb, A., 1916, i, 195; Atsuki and Tomoda, A., 1926, 1280; Schmidt and Vocke, A., 1926, 939).

H. E. F. NOTTON.

Polyoxymethylenes, a model of cellulose. H. STAUDINGER (Oesterr. Chem.-Ztg., 1929, **32**, 98—99).—A lecture.

H. WREN.

Hexahydrofarnesal and norhexahydrofarnesal. J. VON BRAUN and E. ANTON (Ber., 1929, **62**, [B], 1489—1491; cf. this vol., 296).—Hexahydrofarnesyl bromide slowly combines with trimethylamine in benzene at 100°, giving the very hygroscopic quaternary *bromide*, which is decomposed by successive treatment with silver oxide and distillation with potassium hydroxide into *hexahydrofarnesyl*dimethylamine, b. p. 155—157°/10 mm., and γ - λ -trimethyl- Δ^8 -dodecene, b. p. 117—120°/12 mm., d_4^{25} 0.7797, n_D^{25} 1.4398, converted by ozonolysis into α -trimethylundecaldehyde, b. p. 133—

135°/9 mm., d_4^{20} 0.8452, n_D^{20} 1.4440, the density of which increases on preservation (*semicarbazone*, m. p. 235—237°). *Hexahydrofarnesal*, b. p. 145—147°/11 mm. (*semicarbazone*, m. p. 248—250°), is prepared by oxidation of hexahydrofarnesol. The pleasant odour of the new aldehydes confirms the conclusion (*loc. cit.*) that the structure $\text{CHMe}_2\cdot\text{R}\cdot\text{CHMe}\cdot\text{CHO}$ is particularly favourable to the strength and quality of odour.

H. WREN.

Influence of active carbon and of zinc on the formation of complex aldehydes and of sugars from solutions of potassium hydrogen carbonate under the action of ultra-violet rays. G. MAZZADROLI and T. BABES.—See this vol., 894.

Associating lactolides. Transformations of aldols. M. BERGMANN, A. MIEKELEY, and E. VON LIPPMANN (Ber., 1929, 62, [B], 1467—1474; cf. A., 1924, i, 1042).— β -Hydroxypropaldehyde is transformed by acetic anhydride and pyridine at the ordinary temperature into the corresponding *lactol*

acetate $\text{CH}_2\text{CH}(\text{OAc})\text{CH}_2\text{OAc}$ or

$\text{O}(\text{CH}_2\text{CH}(\text{OAc})\text{CH}_2)_n\text{O}$, b. p. 122—

d_4^{20} 1.1795, n_D^{20} 1.4490, monomeric at 180° but dimeric in freezing glacial acetic acid. It is converted by hydrogen in presence of spongy palladium and glacial acetic acid into 2- β -acetoxyethyl-1 : 3-dioxan,

$\text{OAc}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OCH}_2)_2\text{CH}_2$, b. p. 115—118°/

12 mm., d_4^{20} 1.0998, n_D^{20} 1.4415, dimeric as vapour at 180°, unimolecular in glacial acetic acid. When hydrolysed by *N*-sodium hydroxide, the acetoxy-compound affords 2- β -hydroxyethyl-1 : 3-dioxan, b. p. 102—103°/10 mm., d_4^{20} 1.1057, n_D^{20} 1.4566, which does not react with phenylhydrazine or reduce Fehling's solution, whereas acids convert it into trimethylene glycol and acraldehyde. Treatment of 2- β -hydroxyethyl-1 : 3-dioxan with silver oxide and methyl iodide gives 2- β -methoxyethyl-1 : 3-dioxan, b. p. 70—72°/9 mm., n_D^{20} 1.4334, hydrolysed to methyl alcohol, trimethylene glycol, and acraldehyde under conditions which do not effect the hydrolysis of *trimethylene glycol monomethyl ether*, b. p. 153°/768 mm., n_D^{20} 1.4126. 2- β -Hydroxyethyl-1 : 3-dioxan is prepared synthetically by the action of sodium hydroxide on 2- β -chloroethyl-1 : 3-dioxan, b. p. 74—75°/9 mm., n_D^{20} 1.4542, obtained by the action of hydrogen chloride on acraldehyde and trimethylene glycol.

Acetylcycloaldol (*loc. cit.*) is converted similarly by hydrogen into 4-methyl-2- β -acetoxy-*n*-propyl-1 : 3-dioxan, $\text{OAc}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OCH}_2)_2\text{C}_3\text{H}_5\text{Me}$, b. p. 114—

116°/15 mm., n_D^{20} 1.4347, dimeric as vapour, also obtained when the monomeric acetylcycloaldol is passed with hydrogen at 200°/22 mm. over palladised asbestos. It is hydrolysed by alkali hydroxide to 4-methyl-2- β -hydroxypropyl-1 : 3-dioxan, b. p. 100°/15 mm., and by acids to crotonaldehyde and butane- γ -diol, b. p. 108—109°/12 mm., n_D^{20} 1.4418.

H. WREN.

Stereoisomerism of oximes. T. P. RAIKOWA (Ber., 1929, 62, [B], 1626—1637).—The observation that those unsymmetrical oximes which form an

exception to the Hantzsch-Werner theory are capable of adding hydrogen cyanide directly, whereas those which harmonise with the theory do not possess this ability, shows that addition does not occur, as previously assumed, at the double linking between the C and N atoms, but at some other portion of the oxime molecule. A second double linking can be produced in suitable cases by desmotropic change; $\text{R}\cdot\text{C}(\text{CH}_3)\cdot\text{N}\cdot\text{OH} \rightarrow \text{R}\cdot\text{C}(\text{CH}_2)\cdot\text{NH}\cdot\text{OH}$, thus yielding ψ -oximes which may be produced directly by the oximation of the enolic forms of aldehydes and ketones. The essential condition for the formation of a ψ -oxime is the presence in one at least of the hydrocarbon residues of a mobile hydrogen atom which can wander to the nitrogen atom. This condition is fulfilled by all the oximes of aldehydes and ketones in which one valency of the oximino-group is attached directly to a methyl or methylene residue; a methene group appears incapable of allowing desmotropic change. The transformation of the oximino- to the hydroxylamino-group causes free movement in the nitrogen atom, and the oxime consequently loses its ability to exist in stereoisomeric modifications according to Hantzsch and Werner.

The ψ -oximes, $\text{C}(\text{C})\cdot\text{NH}\cdot\text{OH}$, are closely related to the hydroxamic acids $\text{C}(\text{O})\cdot\text{NH}\cdot\text{OH}$, with which they share the ability to give intense red colorations with ferric chloride. Examination of a large series of oximes shows that only those members which are constitutionally capable of desmotropic change give a colour with the reagent, whereas those in which such change is impossible do not react. The behaviour of an oxime towards ferric chloride is therefore a ready criterion of its behaviour towards hydrogen cyanide and the Hantzsch-Werner theory. The oximes are tested in alcoholic solution or, if not preformed, it is usually sufficient to boil the carbonyl compound in alcoholic solution with hydroxylamine hydrochloride and to test the cold solution. *cyclopentanone*, *cyclohexanone*, *menthone*, *carvone*, *pulegone*, and *camphor* in which the methylene group is present in the ring pass into desmotropic ψ -oximes like the purely aliphatic compounds. Caution is required in applying the test to certain aldoximes on account of their ready oxidisability to hydroximic or hydroxamic acids. The group $\text{C}(\text{NH})\cdot\text{N}\cdot\text{OH}$ does not appear capable of desmotropic change to $\text{C}(\text{N})\cdot\text{NH}\cdot\text{OH}$, whereas the transition $\text{R}\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OH} \rightleftharpoons \text{R}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{OH}$ is possible.

H. WREN.

Dioximes. LII. G. B. SEMERIA and B. SOMIGLIANO (Gazzetta, 1929, 59, 258—265).—The rate of formation of methylglyoxime from oximinoacetone and hydroxylamine at different acidities has been studied (cf. Olander, A., 1927, 1036). Hydroxylamine is determined by adding iodine and determining the excess, making a correction for the reaction between iodine and oximinoacetone, and the results are plotted in the form of curves for 13 different p_H values, from 1.2 to 12. The velocity of reaction increases rapidly as the p_H increases.

E. W. WIGNALL.

Hydrolysis of acetylated sugars and similar substances. G. ZEMPLÉN and E. PACSU (Ber. 1929, 62, [B], 1613—1614).—Acetyl compounds of sugars which do not possess reducing groups after

hydrolysis can be hydrolysed in methyl-alcoholic solution on the water-bath with minimal amounts of sodium methoxide. The instances described include mannitol from the hexa-acetate, β -glucosan from the triacetate, sucrose from the octa-acetate, thioisotrehalose from the octa-acetate, salicin from its penta-acetate, and α -methylmannoside from the tetra-acetate. The acetates of reducing sugars are similarly hydrolysed, but the solutions become yellowish-brown, so that it is preferable to use the cold chloroform process. H. WREN.

Ultra-violet light, insulin, and amino-acid catalysis [in the oxidation of sugars]. J. M. ORT.—See this vol., 889.

Decomposition of sugars and glucosamines in a dilute alkali solution. R. MASUI (Osaka J. Med., 1928, 27, 1437—1446).—The quantity of methylglucose produced by distillation of a slightly alkaline solution decreases in the order: *laevulose*, *dextrose*, glucosamine, the residue being lactic acid. A phosphate buffer retards the decomposition of *dextrose*.

CHEMICAL ABSTRACTS.

Behaviour of *dextrose* when heated in alkaline solution. F. FISCHLER, K. TÄUFEL, and S. W. SOUCl (Biochem. Z., 1929, 208, 191—211).—The effect of temperature, time of heating, and concentration on the acids produced by the action of alkali hydroxide on *dextrose* was studied. Rise of temperature up to 140—150° increases the amount of acid formed; above this the amount decreases. Using dilute alkali (0.7*N*) the yield of acid increases with time of reaction at 98.5° and at 140°; in the latter case it reaches a constant value after 4 hrs. With 10*N*-potassium hydroxide the constant value is reached in $\frac{1}{2}$ hr. With increase in the amount of alkali there is a rapid increase in the amount of acid, followed by a slow decrease. In very concentrated solution there is no caramelisation. The lowest sugar concentrations give the highest percentage of acid.

The acids formed were qualitatively investigated; indications of carbon dioxide, acetic, lactic, and glycollic acids were obtained using both 1.2*N*- and 10*N*-alkali, and at the lower concentrations formic and oxalic acids in addition. Using 1.2*N*-alkali, distillation of the acidified product yielded 7.2%, steam distillation 10.1%, ether extraction 49.7% of the total acid and 29.5%, 35.1%, and 8.9%, respectively, with 10*N*-alkali. J. H. BIRKINSHAW.

Mechanism of tautomeric interchange and the effect of structure on mobility and equilibrium. IV. Mechanism of acid catalysis in the mutarotation of nitrogen derivatives of tetra-acetylglucose. J. W. BAKER.—See this vol., 889.

γ -Acetyl- $\alpha\beta$ -isopropylideneglucose and its rearrangement into ζ -acetyl- $\alpha\beta$ -isopropylideneglucose. K. JOSEPHSON (Svensk Kem. Tidskr., 1929, 41, 99—106).—Prolonged treatment of γ -acetyl- $\alpha\beta$ -isopropylideneglucose (I) with slightly diluted acetic acid and subsequent removal of volatile products at 30—35°/vac. affords γ -acetyl- $\alpha\beta$ -isopropylideneglucose (II), m. p. 125—126° (corr.), $[\alpha]_D^{20}$ yellow—20.1° in water. Treatment of II with acetone and anhydrous copper sulphate at the ordinary temperature regenerates I. The rotation of an aqueous solution of II

shows no change after 16 hrs., but when a drop of dilute ammonia is added, isomerisation into ζ -acetyl- $\alpha\beta$ -isopropylideneglucose, m. p. 144—146° (cf. Fischer and Noth, A., 1918, i, 225), is complete after 5 min. Whilst II is stable in acetic acid solution rearrangement does take place in a slightly acid medium, and the velocity of the change has been measured polarimetrically at p_H 5.81, 6.75, and 7.1. The velocity is approximately proportional to the concentration of hydroxyl ions, and is of the same order as that of mutarotation of a reducing sugar. Rapid isomerisation occurs at about p_H 9. The conversion of Robison's hexosemonophosphate into zymophosphate is considered to involve a similar rearrangement. H. BURTON.

Crystalline tetra-acetyl- α -glucose. H. H. SCHLUBACH and I. WOLF [with P. STADLER] (Ber., 1929, 62, [B], 1507—1509).—The action of silver carbonate on β -acetochloroglucose in moist ether proceeds so slowly that isomerisation of the product to the equilibrium mixture of tetra-acetyl- α - and - β -glucose occurs. Reaction occurs much more rapidly in highly purified acetone to which water has been added in definite amount and leads to the isolation of 2 : 3 : 4 : 6-tetra-acetyl- α -glucose, m. p. 107—108°, $[\alpha]_D^{20}$ +138.9° in chloroform, $[\alpha]_D^{20}$ +139.4° to +83.1° in alcohol within 14 days or immediately on addition of ammonia. H. WREN.

Displacement of the equilibrium between normal and γ -galactose in solution. H. H. SCHLUBACH and V. PROCHOWNICK (Ber., 1929, 62, [B], 1502—1507).—The observation of Riiber and Minsas (A., 1926, 1228) that γ -galactose is formed from the two normal forms of galactose with absorption of heat indicates the probable displacement of the equilibrium in favour of the γ -form as the temperature is raised. This is indicated by observation of the variation of the specific rotation of the equilibrium mixture in pyridine with varying temperature and confirmed by treatment of such mixtures with acetic anhydride and preparation of the β -variety of penta-acetyl- γ -galactose. In boiling pyridine the β -form of γ -galactose appears to be present in 23.4% proportion. H. WREN.

Triphenylmethyl ether of mannose. New tetra-acetylmannose. B. HELFERICH and J. F. LEETE (Ber., 1929, 62, [B], 1549—1554).—*d*-Mannose is converted by triphenylmethyl chloride at the atmospheric temperature into β -*d*-mannose 6-triphenylmethyl ether, m. p. 160—170° after softening at 140°, $[\alpha]_D^{20}$ -2.0° in chloroform, $[\alpha]_D^{20}$ -3.7° to 20.4° in pyridine. Treatment of the crude product with acetic anhydride affords β -tetra-acetyl-*d*-mannose 6-triphenylmethyl ether, m. p. 204—206° (corr.), $[\alpha]_D^{20}$ -2.6° in chloroform, and α -tetra-acetyl-*d*-mannose 6-triphenylmethyl ether, m. p. 130.5—131.5° (corr.), $[\alpha]_D^{20}$ -73.4° in chloroform (possibly accompanied by a second, isomorphous form, m. p. 123—124°), separated from one another by crystallisation from alcohol. Either form is hydrolysed to *d*-mannose 6-triphenylmethyl ether described above. Hydrogen bromide in glacial acetic acid transforms the β -tetra-acetate into 1 : 2 : 3 : 4-tetra-acetyl- β -*d*-mannose, m. p. 135.5—136.5° (corr.), $[\alpha]_D^{20}$ -22.5° in chloroform; in aqueous

solution in ordinary glass tubes mutarotation is observed, ascribed, at least in part, to migration of acyl groups catalysed by alkali. Further acetylation gives β -penta-acetyl-*D*-mannose, m. p. 116° , $[\alpha]_D^{25} -24.1^\circ$ in chloroform. The assignation of the triphenylmethyl group to the position 6 is based on the conversion of the tetra-acetylmannose by phosphoryl chloride in pyridine into tetra-acetyl- β -*D*-mannose-6-chlorohydrin, m. p. $142-143^\circ$, $[\alpha]_D^{25} -7.6^\circ$ in chloroform, the chlorine atom of which reacts very sluggishly, whereas in Freudenberg's diisopropylidenemannose-1-chlorohydrin it is highly reactive. Similarly, with thionyl chloride ditetra-acetyl- β -*D*-mannose 6-sulphite, m. p. $173-175^\circ$ (corr.), $[\alpha]_D^{25} -33.1^\circ$ in chloroform, is obtained.

H. WREN.

Model experiments based on the theory of alcoholic fermentation. I. Degradation of diisopropylidene-fructose sulphate. H. OHLE and J. NEUSCHELLER (Ber., 1929, 62, [B], 1651-1658).—It is assumed that in the initial stage of alcoholic fermentation the sugar or its phosphate must undergo dehydrogenation to yield reactive compounds which suffer fission between the γ - and δ -carbon atoms and that therefore oxidation products of dextrose or laevulose must exist which, under very mild conditions, decompose into three-carbon or simpler products. With diisopropylidene-glucose or α -diisopropylidene-fructose it does not appear possible to limit the action to the oxidation of the *sec*-carbinol group 3 to the keto-group, whereas β -diisopropylidene-fructose gives 2-ketodiisopropylidene-gluconic acid. Potassium β -diisopropylidene-fructose sulphate hemihydrate, incipient decomp. about 210° , $[\alpha]_D^{25} -21.91^\circ$ (also *anhydrous*; corresponding sodium salt, incipient decomp. about 200° , $[\alpha]_D^{25} -22.53^\circ$), is oxidised by potassium permanganate at 100° without marked production of sulphate ions if the oxygen used does not exceed 2 atoms, but much material remains unchanged. With increasing amounts of oxygen reaction occurs with formation of a dextrorotatory intermediate, the production of which is at a maximum with 6 atoms of oxygen. Under these conditions about 15% of the material is oxidised to carbon dioxide and sulphuric acid, 15% remains unchanged, about one third is converted into 4 mols. of carbon dioxide and 1 mol. of the compound, $\text{CO}_2\text{K} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{SO}_3\text{K}$, which darkens at 250° but does not melt below 300° (prepared also from glycollic and chlorosulphonic acids in pyridine), whereas the remainder affords the dextrorotatory tri-

potassium salt $\text{CMe}_2 \begin{array}{l} \text{O} \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{SO}_3\text{K} \\ \text{O} \cdot \text{CH} \cdot \text{CH}(\text{CO}_2\text{K})_2 \end{array}$ Hydrolysis of the last-named salt with *N*-hydrochloric acid at 100° yields acetone, sulphuric acid, methylglyoxal, glycollic acid, and carbon dioxide, the yield of methylglyoxal, isolated as the disemicarbazone, being 75-80%. If hydrolysis is effected at about 35° and interrupted as soon as the solution is optically inactive, the yield is only about 30%. It appears therefore that the salt first loses the isopropylidene group and yields the sulphuric ester of dihydroxyacetone, which subsequently gives methylglyoxal and sulphuric acid.

H. WREN.

Thio-sugars and their derivatives. XIV. α -Glucosulphose [α -thiogluco-]. W. SCHNEIDER

and H. LEONHARDT (Ber., 1929, 62, [B], 1384-1389; cf. A., 1928, 872).—The sodium compound of β -thiogluco- is preserved in aqueous acidic solution until mutarotation is complete and the dried product of the reaction is treated with acetic anhydride and pyridine at 0° , thus yielding a mixture of α - and β -thiogluco- penta-acetates, separated into its components by fractional crystallisation from alcohol. α -Thiogluco- penta-acetate has m. p. $128-129^\circ$, $[\alpha]_D^{25} +132.6^\circ$ in *s*-tetrachloroethane. It is hydrolysed by sodium methoxide to the sodium compound $\text{C}_6\text{H}_{11}\text{O}_5\text{SNa} \cdot 2\text{H}_2\text{O}$, m. p. $129-130^\circ$ (decomp.) after softening at 100° when rapidly heated, $[\alpha]_D^{25} +142.93^\circ$ in water [also *anhydrous*, m. p. 155° (decomp.) after becoming yellow at 130°]. Free α -thiogluco- is strongly dextrorotatory in aqueous solution, but the specific rotation slowly diminishes and attains an equilibrium value about $15-20^\circ$ higher than that observed with the equilibrium mixture from the corresponding β -compound. $\alpha\alpha$ -Diglucosyl disulphide, from the sodium compound and iodine, has $[\alpha]_D^{25} +535.5^\circ$, whereas the value $[\alpha]_D^{25} -149.3^\circ$ is now recorded for the β -derivative.

H. WREN.

Synthesis of sucrose. A. PICTET and H. VOGEL (Ber., 1929, 62, [B], 1418-1422; cf. A., 1928, 510, 741; Zemplen, this vol., 683).—Full details are given of the preparation of tetra-acetyl- γ -fructose, the condensation of the tetra-acetates of glucose and γ -fructose, and the isolation and hydrolysis of sucrose octa-acetate.

H. WREN.

Unusual course of the solubility of calcium hydroxide in dilute solutions of sucrose. P. FUCHS (Ber., 1929, 62, [B], 1535-1538).—The solubility at $17-17.5^\circ$ is determined by successive addition to the sugar solution of known concentration of *N*-sodium hydroxide and a slight excess of about $2N$ -calcium chloride solution. After 5 min. the mixture is filtered and the filtrate is titrated with *N*-hydrochloric acid in presence of methyl-orange. The solubility of calcium hydroxide at first increases uniformly with increasing concentration of sucrose, passes through a maximum and minimum, and then again increases uniformly. The curve closely resembles the pressure-volume graph of a non-ideal gas somewhat below its critical temperature.

H. WREN.

Optical rotation and atomic dimensions. VIII. Halogenohepta-acetyl derivatives of melibiose and maltose. Structures of bioses and of cellulose. D. H. BRAUNS (J. Amer. Chem. Soc., 1929, 51, 1820-1831).—The isolation in a pure state of fluoromelibiose hepta-acetate, m. p. 135° , $[\alpha]_D^{25} +149.7^\circ$ (all rotations measured in chloroform); chloromelibiose hepta-acetate, m. p. 127° , $[\alpha]_D^{25} +192.5^\circ$; bromomelibiose hepta-acetate, m. p. 116° , $[\alpha]_D^{25} +209.9^\circ$; fluoromaltose hepta-acetate, m. p. $174-175^\circ$, $[\alpha]_D^{25} +111.1^\circ$; chloromaltose hepta-acetate, m. p. 125° , $[\alpha]_D^{25} +159.5^\circ$ (cf. Foerg, A., 1902, i, 347), and bromomaltose hepta-acetate, m. p. $112-113^\circ$, $[\alpha]_D^{25} +180.1^\circ$, obtained crystalline with great difficulty (cf. Fischer and Armstrong, A., 1902, i, 746), is described in detail. The specific rotations of these derivatives of α -bioses, unlike those of the β -bioses (cf. A., 1928, 157), show agreement with the regular relationship observed

among the corresponding derivatives of the monose sugars. This difference in behaviour is explained by means of models which show that, under certain conditions, the oxide rings of β -bioses may face one another, bringing the halogen atoms under the influence of secondary valencies proceeding from the opposite ring, whereas with α -bioses this is impossible. The models also give formulæ for cellulose and cellobiose in agreement with their chemical properties and X-ray diffraction spectra. H. E. F. NOTTON.

Constitution of nodakenin, a new glucoside from *Peucedanum decursivum*, Maxim. II. J. ARIMA (Bull. Chem. Soc. Japan, 1929, 4, 113—119).—Nodakenetin (A., 1927, 599; this vol., 430) treated with bromine in chloroform gives a bromo-derivative, m. p. 230—231°, converted by alcoholic potassium hydroxide into *nodakilic acid*, $C_{13}H_{16}O_3 \cdot CO_2H \cdot H_2O$, m. p. 214—215° (methyl ester, m. p. 133—134°); the acid is considered analogous to coumarilic acid. Nodakenetin is oxidised by boiling aqueous chromic acid to 7-hydroxycoumarin-6-carboxylic acid, m. p. 244—246° (decomp.) to 260—261° (decomp.) (according to rate of heating), identified by decarboxylation to umbelliferone, and synthesised by the interaction of 4-resorcylic acid and malic acid in sulphuric acid; methyl 7-methoxycoumarin-6-carboxylate, m. p. 165—166°, is prepared from degradation and synthetical products. E. W. WIGNALL.

Constitution of sinistrin. H. H. SCHLUBACH and W. FLORSHEIM (Ber., 1929, 62, [B], 1491—1493).—Extraction of the fresh bulbs of *Scilla maritima* with cold water followed by treatment of the extracts with lead acetate and fractional precipitation with alcohol permits the isolation of sinistrin B, $(C_6H_{10}O_5)_4$, $[\alpha]_D^{20}$ —30.6° in water, and sinistrin A, $(C_6H_{10}O_5)_2$, $[\alpha]_D^{20}$ —25.3° in water. The last-named substance is converted by methyl sulphate and alkali hydroxide into a compound closely resembling methylulin and converted by oxalic acid into 3:4:6-trimethylfructose (2:5) (cf. Schlubach and Elsner, this vol., 51; Haworth and Learner, A., 1928, 510). Sinistrin B appears to be a tetrafructose anhydride.

H. WREN.

Starch. II. Potato starch. K. HESS and F. A. SMITH (Ber., 1929, 62, [B], 1619—1626; cf. 1928, 1225).—The influence of pre-treatment of starch with pyridine on its acetylation depends on the induced swelling of the starch for which the water content of both materials is responsible. Dry starch does not swell in anhydrous pyridine. The ease of acetylation increases with increased degree of swelling. The isolation by Brigl and Schinle (this vol., 299) by the author's process (*loc. cit.*) of a starch acetate "rapidly" soluble in chloroform to a homogeneous viscous solution has led to a repetition of the work with varied amounts of pyridine and acetic anhydride, whereby readily soluble products are not obtained; under similar conditions amylose affords a freely soluble acetate corresponding with Brigl and Schinle's starch acetate. Treatment of starch with warm water below the swelling temperature causes layer-wise dissolution without altering the microscopic appearance of the granules except in regard to diameter. The aqueous solution yields preparations with the properties of

starch amylose when treated with alcohol. Prolonged treatment of a fraction thus obtained with boiling water causes increased reducing power and diminished optical activity, whilst the solution becomes markedly more acidic. Treatment of natural starch with warm water causes an irregular development of acidity in the solvent which is not apparently related to the amount of carbohydrate yielded to the water in the corresponding period.

In contrast to natural starch, the product regenerated from starch acetate by hydrolysis with methyl-alcoholic ammonia can be dissolved only with difficulty in cold *N*-sodium hydroxide. Comparison of the optical activities of solutions of the product and natural starch (prepared by protracted heating with 0.81*N*-alkali at 60°) appears to confirm the identity of the substances. The specific rotation of natural starch in solutions of differing concentration with respect to carbohydrate and sodium hydroxide is tabulated. H. WREN.

New series of starch depolymerisation products. A. PIOTET and H. VOGEL (Helv. Chim. Acta, 1929, 12, 700—713).—By heating dry starch with 3 parts of dry glycerol at 220° followed by dilution with alcohol etc. isotrihexosan, $(C_6H_{10}O_5)_3$, m. p. 260—262° (decomp., after colouring at 235°), $[\alpha]_D^{20}$ +166.5° in water, was obtained. It gave the starch-iodine test, and did not reduce Fehling's solution or aqueous potassium permanganate; when warmed with hydrochloric acid it was converted into dextrose. It was unattacked by emulsin but malt-diastase gave dextrinose. Boiling acetic anhydride produced a monoacetate, m. p. 156—160°, decomp. 200°, $[\alpha]_D^{20}$ +154.8° in chloroform, not coloured by iodine; hydrolysis by sodium methoxide caused regeneration of isotrihexosan.

isoTrihexosan when treated with concentrated hydrochloric acid under cooling formed isotrihexose, $C_{18}H_{32}O_{16}$, decomp. 155—160°, $[\alpha]_D^{20}$ +102.1° in water (osazone, m. p. 169—170°, decomp. 180°), which reduced Fehling's solution but was not coloured by iodine. Treatment by warm dilute aqueous oxalic acid led to a mixture of dextrose and dextrinose (cf. Syniewski, A., 1900, i, 79), m. p. 67—68°, decomp. 200° (Syniewski gave m. p. 82—85°) [monohydrate, m. p. 94—96°, decomp. 200°; osazone, m. p. 167° (lit. 152—153°); octa-acetate, m. p. 157° (identical with maltose octa-acetate, m. p. 158°)].

isoTrihexosan was further depolymerised by heating with glycerol at 240°, when the dihexosan dextrinose, $(C_6H_{10}O_5)_2$, m. p. 185—186° (decomp.), $[\alpha]_D^{20}$ +151.0° in water (hexa-acetate, m. p. 140—143°, $[\alpha]_D^{20}$ +145.5° in chloroform), was formed. Iodine coloured dextrinose a reddish-brown, whilst concentrated hydrochloric acid at the ordinary temperature converted it into dextrinose (above). An attempt to reverse the last change by heating dextrinose at 175° under 12 mm. pressure led only to a substance, m. p. 130—140°, $[\alpha]_D^{20}$ +149.2° in water, different from the dextrinose obtained by the depolymerisation of starch, e.g., in not colouring with iodine.

An aqueous solution of isotrihexosan, on long keeping at the ordinary temperature, more quickly at 50—60°, deposited the polymeric isopolyhexosan,

sinters at 235°, decomp. 245°, which, on warming with hydrochloric acid, gave dextrose alone. It was depolymerised by hot water, hence $[\alpha]_D +166.7^\circ$ in water and mol. wt. 486 [corresponding with $(C_6H_{10}O_5)_3$] are untrustworthy. Acetylation by acetic anhydride and pyridine gave a *peracetyl* derivative, $[\alpha]_D +177.4^\circ$ in chloroform, the mol. wt. of which suggested the formula $(C_6H_{10}O_5)_{12}$ for isopolyhexosan.

R. J. W. LE FÈVRE.

Nature of inulin. H. H. SCHLUBACH and H. ELSNER (Ber., 1929, 62, [B], 1493—1502).—Examination of the literature discloses the existence of a lengthy series of fructose anhydrides from the simplest member to inulin. With decreasing solubility in water the mol. wt. increases and the specific rotation sinks. There appears to be a polymeric homologous series similar to Staudinger's polyoxymethylenes and for which the nomenclature "polylævans" is proposed. Inulin is to be regarded as a mixture of polymerides of high mol. wt., their nature varying with the botanical origin of the material and the time of harvesting. "Purification" of inulin merely effects the removal of the lower and therefore more freely soluble polymerides. The conflicting evidence does not permit conclusions with regard to the nature of the forces operative within the inulin molecule and the presence of phosphoric and silicic acids is unexplained. Polarimetric observations during the hydrolysis of inulin by acids has led Tanret to regard the product as a mixture of 12 mols. of lævulose with 1 mol. of dextrose, and the last-named sugar has been isolated as such from β -inulin. The production of dextrose by the acidic hydrolysis of inulin is established as follows: (1) triacetylululin is cautiously hydrolysed by acetyl bromide, hydrogen bromide, and glacial acetic acid, the product is debrominated with silver carbonate and acetylated with acetic anhydride and sulphuric acid. Penta-acetyl- α -glucose is thereby obtained crystalline. Intermediately a mixture of acetylated hexoses, probably mainly tetra-acetyl- γ -fructose, is produced. Crystalline penta-acetyl- α -glucose is also obtained by the action of acetic anhydride and sulphuric acid on triacetylululin. Examination of the reducing power of the mixture obtained by the hydrolysis of inulin with 0.05*N*-sulphuric acid according to Willstätter, Schudel, and Bertrand discloses the presence of about 8% of aldoses, thus agreeing closely with Tanret's observations. It is not maintained that dextrose is necessarily a constitutive component of inulin, since the partial isomerisation of γ -fructose to dextrose during hydrolysis is not impossible, although it is not observed during the hydrolysis of sucrose under identical conditions. It is possible that the terminal free hydroxyl group which would be present in inulin if a chain structure is assumed is substituted by the glucose residue in such a manner that its reducing group is united to the reducing group of the fructose chain. Inulin would thus resemble a sucrose in which the γ -fructose residue is replaced by a series of these residues.

H. WREN.

Polysaccharides. XXXIX. Enzymic degradation of chitin and chitosan. I. P. KARRER and A. HOFMANN (Helv. Chim. Acta, 1929, 12, 616—637).

—Natural chitin is attacked very slowly by enzymes; it is therefore prepared by dissolution in hydrochloric acid and reprecipitation by water. Chitinase decomposes this prepared chitin at the optimum p_H (5.2) and 36° with the formation of *N*-acetylglucosamine, $[\alpha]_D +55.6^\circ$, 85% degradation being accomplished in 10 days.

Chitosan at p_H 4.4—4.5 and 36° gives the hydrochloride of a *polyglucosamine* (tri- or tetra-glucosamine compound?), the base of which is liberated by treatment of the salt with diethylamine solution; by hydrolysis with hydrochloric acid it gives glucosamine hydrochloride.

R. J. W. LE FÈVRE.

Effect of aniline on cellulose triacetate. H. LE B. GRAY, T. F. MURRAY, jun., and C. J. STAUD (J. Amer. Chem. Soc., 1929, 51, 1810—1814).—The reaction of cellulose triacetate with aniline at (a) 183°, and (b) 148—151°, has been followed polarimetrically and by acetyl determinations [final content: (a) 2.0%, (b) 10.4% Ac]. The initial and final stages are slow with an intermediate period of rapid change. No appreciable reaction occurs at 20—30°. The changes in composition, solubility, and rotatory power indicate that the triacetate undergoes hydrolysis and not a change analogous to mutarotation (cf. Knoevenagel, B., 1915, 134). The product may be reacylated to cellulose triacetate.

H. E. F. NOTTON.

Lignin and cellulose. X. Aromatic nature of lignin. K. FREUDENBERG, W. BELZ, and C. NIEMANN (Ber., 1929, 62, [B], 1554—1561; cf. A., 1928, 1227).—The investigation is concerned with isolated lignin which may possibly have suffered chemical change during isolation. Bromine in hydrobromic acid causes substitution; there is no evidence of addition. Polymerised coniferyl alcohol behaves similarly in all respects and 5-bromovanillic acid shows close analogy in its behaviour. The similarity is particularly marked in the behaviour of the methyl group during bromination; the aromatic union of the methoxyl group is also indicated by its behaviour towards hydriodic acid. It may therefore be assumed that the 17% of methoxyl present in isolated lignin belongs to a system of the vanillin type; this harmonises with the observation that at least 5—6%, possibly as much as 12%, of the lignin is composed of piperonal components. The vanillin components of lignin are differentiated sharply from polymerised coniferyl alcohol by their insolubility in alkali hydroxide; a part of the methoxyl groups in lignin is transformed by hydriodic acid into phenolic hydroxyl. After deduction of the oxygenated groups, the expression $[CH_{1.4}]_x$ remains for the fundamental hydrocarbon of lignin. For saturated aliphatic or hydroaromatic hydrocarbon residues the terms $[CH_{1.7}]_x$ to $[CH_{2.2}]_x$ must be fulfilled. Since the presence of reactive double linkings is not indicated, the probability of the aromatic nature of lignin is hereby strengthened. The high refractive index (n_D —about 1.61) is also evidence of its aromatic nature.

Methylcellulose is practically unaffected by bromine in hydrobromic acid.

H. WREN.

Lignin. II. R. O. HERZOG and A. HILLMER [with E. PAERSCH and E. HELLRIEGEL] (Ber., 1929, 62, [B], 1600—1602; cf. A., 1927, 342, 861; Freuden-

berg, preceding).—It is assumed that atmospheric oxygen plays an essential part in the union of the lignin components in nature. The action of air or oxygen on *isoeugenol*, followed by dissolution of the product in ether and precipitation with light petroleum, yields a *product* differing from vanillin, dehydrovanillin, *disoeugenol*, and dehydrodisoeugenol. Analyses of the product and its non-crystalline acetate indicate the union of 2 mols. of *isoeugenol* with addition of oxygen. The material is not hydrogenated in presence of platinum-black. Its ultra-violet absorption curve has the form typical of *isoeugenol*, coniferyl alcohol, and lignin. It gives a reddish-violet colour with phloroglucinol and hydrochloric acid.

Cautious treatment of rye straw at the ordinary temperature with 2% methyl-alcoholic sodium hydroxide in the absence of light and air yields, after electro-dialysis, a lignin soluble in alkali and (colloidally) in water. The mol. wt. in resorcinol indicates the presence of about two coniferyl residues. Its absorption spectrum in the ultra-violet is exactly similar to those of other types of lignin. It is not reduced by hydrogen in presence of platinum-black.

H. WREN.

Free halogenated aliphatic amines. M. DE MONTMOLLIN and E. ZOLLIKER (Helv. Chim. Acta, 1929, 12, 610—616).—Treatment of ethyl chlorobutyl ether with alcoholic ammonia gave β -ethoxybutylamine, b. p. 140—145°, accompanied by diethoxydibutylamine, b. p. 225—235°. Displacements of ethoxyl by halogen were accomplished by heating the ethoxy-amines with the appropriate aqueous halogen acid in a sealed tube; β -chlorobutylamine, b. p. 50°/40 mm. [hydrochloride; hydrobromide; picrate, m. p. 124° (lit. 142°); benzoyl derivative, m. p. 69°], and *di*- β -chlorodibutylamine, b. p. 91°/11 mm. (hydrobromide), were thus prepared.

Reduction of β -ethoxypropionitrile by sodium and alcohol gave γ -ethoxybutylamine, b. p. 142—143°, from which γ -bromobutylamine, b. p. 57°/18 mm. (hydrochloride; hydrobromide), was obtained.

Methoxyl and propoxyl groups were not so easily replaced by halogen as ethoxyl. The following compounds were prepared incidentally: γ -methoxybutylamine, b. p. 128—130° (picrate, m. p. 110—112°); phenylthiocarbamide derivative, m. p. 84°, and γ -propoxybutylamine, b. p. 160° (picrate, m. p. 101°); phenylthiocarbamide derivative, m. p. 67°.

R. J. W. LE FÈVRE.

Synthesis of ephedrine and structurally similar compounds. II. Ephedrine homologues; resolution of ephedrine. R. H. F. MANSKE and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 1906—1909).—The new synthesis of ephedrine (this vol., 441) has been extended to other primary aliphatic amines and to β -keto-aldehydes. The simultaneous formation of an isomeride analogous to ϕ -ephedrine is not usually observed. Hydrochlorides of the following m. p. have been prepared: β -ethylamino- α -phenylpropan- α -ol, m. p. 198° (corr.); β -ethylamino- α -phenylbutan- α -ol, m. p. 226°; β -(8-hydroxyethylamino)- α -phenylpropan- α -ol, m. p. 166°; β -benzylamino- α -phenylpropan- α -ol, m. p. 184—185°; β -(β -phenylethylamino)- α -phenylpropan- α -ol, m. p. 207—208°; β -ethylamino- α -p-ethylphenylpropan- α -ol; m. p. 208°;

β -ethylamino- α -2:5-dimethylphenylpropan- α -ol, m. p. 221°, and β -ethylamino- α -p-tolyloethyl alcohol, m. p. 208°. *dl*-Ephedrine is conveniently resolved by means of mandelic acid and *vice versa*, *d*-ephedrine *d*-mandelate and *l*-ephedrine *l*-mandelate having m. p. 170°, sintering from 167°. Synthetic *l*-ephedrine is identical with the natural product.

H. E. F. NOTTON.

Compounds of mono-, di-, and tri-methylamines, ethylenediamine, and choline with flavianic acid. H. SIEVERS and E. MÜLLER (Z. Biol., 1929, 89, 37—40).—The following salts of flavianic acid are described (the figures in parentheses are the number of mols of acid combined with 1 mol. of base): methylamine (1), decomp. 265—268° after darkening at 230°; dimethylamine (1), decomp. 230—235° after darkening at 200°; trimethylamine (1), decomp. 217—223° after darkening at 210°; ethylenediamine (2), decomp. 265—267°; choline (1), chars when heated. The solubilities of these salts in water and alcohol at 18—19° are given.

H. BURTON.

Hydrolysis of polypeptides, their derivatives and amides by N-alkali, erepsin, trypsin, and trypsin-kinase. E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1929, 10, 544—555).—The action of *N*-sodium hydroxide, erepsin, and trypsin-kinase on a large number of polypeptides, their halogenoacyl derivatives and amides has been investigated, comparative experiments with different specimens of enzymes being made. The results are summarised below in groups classified according to the structure of the polypeptides, the order in each class being that of decreasing ease of hydrolysis. Erepsin (at p_H 7.8 and 37°) hydrolyses (a) glycylglycine (I), glycylglycylglycine (II), glycyl-di- (III), -tri- (IV), and -tetra- (V) glycylglycine; (b) *dl*-valylglycylglycine (VI), glycylglycyl-*dl*-valine (VII), m. p. 147—149° [from chloroacetyldiglycyl-*dl*-valine (VIII), m. p. 169—171° (decomp.)], glycyl-*dl*-valine (IX), glycylglycyl-*dl*-valine (X), m. p. 219—221° (decomp.) [from chloroacetylglycyl-*dl*-valine (XI), m. p. 170°], *dl*-leucylglycyl-*dl*-valine (XII), m. p. 244—245° (decomp.) [dl- α -bromoisohexoylglycyl-*dl*-valine (XIII), m. p. 143—145°], trimethyldiglycylglycine (XIV), decomp. 230—235° [from dl- α -bromoisovaleryldiglycylglycine (XV), m. p. 171—173° (decomp.)], *dl*-valylglycine (XVI), *dl*-valylglycyl-*dl*-leucine (XVII), *dl*-valyl-*dl*-alanine (XVIII) and XXX [dl-alanyl-*dl*-valine (XIX) is not attacked]; (c) glycyl-*dl*-leucine (XX), glycylglycyl-*dl*-leucine (XXI), m. p. 240° (decomp.) [from chloroacetylglycyl-*dl*-leucine, (XXII), m. p. 153°], *dl*-leucylglycyl-*dl*-leucine (XXIII), glycylglycyl-*dl*-leucine (XXIV), m. p. 206—208° (decomp.) [from chloroacetyldiglycyl-*dl*-leucine (XXV), m. p. 176—177° (decomp.)]; (d) *dl*-leucylglycyl-*dl*-valine (XXVI), *dl*-valylglycyl-*dl*-leucine (XXVII), m. p. 242—244° (decomp.) [from dl- α -bromoisovalerylglycyl-*dl*-leucine (XXVIII), m. p. 169°], *dl*-leucylglycyl-*dl*-leucine (XXIX), *dl*-valylglycyl-*dl*-valine (XXX), m. p. 233—235° (decomp.) [from dl- α -bromoisovalerylglycyl-*dl*-valine (XXXI), m. p. 179—180°]; (e) *dl*-leucylamide (XXXII), *dl*-leucylglycylamide (XXXIII), glycyl-*dl*-leucylamide (XXXIV) (hydrobromide, m. p. 175—179°) [from bromoacetyl-*dl*-leucylamide (XXXV), m. p. 173—174°] and glycylamide (XXXVI) are only slightly attacked by erepsin, whilst *dl*-leucyl-*dl*-

leucylamide (XXXVII) (hydrobromide) [from *dl*- α -bromoisohexoyl-*dl*-leucylamide (XXXVIII), m. p. 141—143°] is not hydrolysed. With trypsin-kinase, at p_H 8.4 and 37°, (a) I, II, and III are attacked only slightly, whilst IV and V are unaffected; (b) XXX, XIV, VII, X, and VI are slightly hydrolysed, whilst IX and XVI are unattacked; (c) XXIV, XXI, and XX suffer slight hydrolysis; (d) XXVI, XXVII, XXIX, and XXX are hydrolysed, the last only slightly; (e) none of these amides is hydrolysed. The following polypeptides and their amides are hydrolysed by *N*-sodium hydroxide, the order again being that of decreasing degree of hydrolysis: XXIV, VII, XIV, X, XXI, VI, XXXIV, XXXIII, XXXVI, XXXII, XII, XX, XXXVII, XXIII, IX, and XXX, whilst XVI, XVIII, and XIX are unattacked. The specimen of *dl*-valylglycylglycine obtained by Abderhalden, Sah, and Schwab (this vol., 178) was readily hydrolysed by *N*-sodium hydroxide, but another specimen prepared in the same manner and having the same m. p. and mixed m. p. was unattacked, the reason for this difference not being understood. All the halogenoacyl derivatives are hydrolysed by *N*-sodium hydroxide, the order of decreasing ease of hydrolysis being, chloroacetyl-triglycylglycine, -diglycylglycine, XXV, -glycylglycine, VIII, XV, XXII, chloroacetyl-*dl*-leucine, XI, *dl*- α -bromoisovaleryl-glycylglycine, chloroacetyl-*dl*-valine, XXXI, XXVIII, *dl*- α -bromoisovalerylglycine, and *dl*- α -bromopropionyl-*dl*-valine. J. W. BAKER.

Specific action of erepsin and trypsin on certain groups in polypeptides. E. ABDERHALDEN and O. HERRMANN (Fermentforsch., 1929, 10, 586—590).—In the hydrolysis of *d*-alanyl-glycyl-*l*-phenylalanine, m. p. 220°, $[\alpha]_D^{20} +34.02^\circ$ (from *d*- α -bromopropionylglycyl-*l*-phenylalanine, m. p. 150°), in 0.1*M*-solution with erepsin at p_H 7.8 and 37°, the dextro-rotation gradually diminishes as hydrolysis proceeds, whilst with trypsin at p_H 8.4 and 37° it rapidly becomes laevorotatory, pointing to the formation of *l*-phenylalanine, $[\alpha]_D -35.1^\circ$. *l*-Leucylglycyl-*d*-alanine ($[\alpha]_D +12.1^\circ$ and therefore containing a little of the racemic compound) on hydrolysis may yield either *l*-leucylglycine ($[\alpha]_D +86^\circ$) and *d*-alanine, or glycyl-*d*-alanine ($[\alpha]_D -50^\circ$) and *l*-leucine. With erepsin, yeast extract, and kidney and liver extracts this tripeptide rapidly becomes laevorotatory, showing that *l*-leucine is formed. With trypsin (which has very little action) and dog's pancreas juice a slight rise in the dextro-rotatory value is observed. These results agree with earlier conclusions that erepsin attacks those portions of the polypeptide molecule which contain a free amino-group, and trypsin those containing a free carboxyl group. J. W. BAKER.

Comparative study of the hydrolysis of polypeptides and their derivatives at various hydrogen-ion concentrations, with erepsin and trypsin-kinase. Optimal hydrogen-ion concentration for the action of these enzymes. E. ABDERHALDEN and A. SCHMITZ (Fermentforsch., 1929, 10, 591—609).—The velocity of hydrolysis of various polypeptides and their derivatives with different concentrations of sodium hydroxide, and with erepsin and trypsin-kinase at various p_H values, has been studied. At a

given hydrogen-ion concentration tetrapeptides such as glycyl-*dl*-leucylglycyl-*dl*-leucine (I) (phenylurethane, decomp. 144—145°) are more rapidly hydrolysed than tripeptides such as *dl*-leucylglycyl-*dl*-leucine (II), hydrolysis of the former still being possible with 0.2*N*-sodium hydroxide. The phenylurethanes are much more rapidly hydrolysed than the parent polypeptides, suffering considerable hydrolysis even with 0.1*N*-sodium hydroxide. Chloroacetyl-*dl*-leucylglycyl-*dl*-leucine (III) is more rapidly hydrolysed than the free polypeptide, but not so readily as the phenylurethane. Similarly, *dl*- α -bromoisohexoylglycyl-*l*-tyrosine is more rapidly hydrolysed than *dl*-leucylglycyl-*l*-tyrosine (IV) (phenylurethane, decomp. 130°). With *N*-hydrochloric acid, which hydrolyses the free polypeptides only very slowly, chloroacetyl-*dl*-alanine and III are hydrolysed, but much more slowly than with *N*-sodium hydroxide. The optimum p_H values for hydrolysis by erepsin or trypsin-kinase differ with various polypeptides. Thus the velocity of hydrolysis of II with erepsin is greater than that of IV, but in both cases the optimal p_H value is 7.8—8.4. With trypsin-kinase, however, the optimal p_H values for II, IV, and I are, respectively, 8.4, 7.8—9.0 (unchanged velocity over this range), and 9.0. Yet another type of curve is obtained with triglycyl-*dl*-phenylalanine. The various halogenoacyl and other derivatives of these polypeptides behave in still another manner towards trypsin-kinase. Although the various curves differ in form (the results being somewhat complicated by the products of the reaction) all show a maximal velocity of hydrolysis at p_H 7.1, that is, at about the neutral point. In the enzymolysis of the halogenoacyl derivatives no fission of the halogenoacyl group occurs. J. W. BAKER.

Influence of α - and β -amino-acids, hippuric acid, sarcosine, aniline, and dipeptides on the velocity of decomposition of polypeptides with erepsin and trypsin-kinase. E. ABDERHALDEN and O. HERRMANN (Fermentforsch., 1929, 10, 610—616).—The effect of these addenda on the hydrolysis of various polypeptides by erepsin or trypsin-kinase is different with each polypeptide. It was anticipated that substances containing a free amino-group in the α -position would affect erepsin hydrolysis and those with a free carboxyl group would affect hydrolysis by trypsin, but the action is much more complicated. The results do not lend themselves to summarisation. With erepsin, hippuric acid always has a retarding influence the magnitude of which varies with the substrate, but with trypsin-kinase it has an accelerating action except with chloroacetyl-*l*-phenylalanine as substrate. The retarding effect of the addenda varies with the hydrogen-ion concentration, but only with hippuric acid in enzymolysis by erepsin is the maximum effect observed at the optimal p_H hydrolysis value. The addition of various dipeptides, with the exception of *dl*-leucylglycine and glycyl-*dl*-norvaline, which exhibit a strong retarding influence, has no effect on the hydrolysis of *dl*-leucylglycyl-*dl*-leucine with trypsin. J. W. BAKER.

Influence of the free amino-group in polypeptides on their hydrolysis with *N*-alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN,

L. DINERSTEIN, and S. GENES (Fermentforsch., 1929, 10, 532—543).—The following polypeptides, prepared by usual methods, suffer enzymolysis with trypsin-kinase (free from erepsin) at p_H 8.4 and 37°: *dl*- α -bromoisohexoylglycylglycine, *dl*- α -bromoisohexoyl-*dl*-leucylglycylglycine, the phenylurethane, naphthalene-2-sulphonyl, *p*-chlorobenzoyl, m. p. 183°, and *p*-nitrobenzoyl, m. p. 163—165°, derivatives of *dl*-leucylglycylglycine, *p*-chlorobenzoyl, m. p. 246—247° (I), and *p*-nitrobenzoyl (II), m. p. 232° (decomp. corr.), derivatives of *dl*-alanylglycylglycine, but *dl*- α -bromopropionylglycylglycine, *dl*-leucylglycylglycine (III), *dl*-alanylglycylglycine (IV), and its naphthalene-2-sulphonyl derivative are unattacked. With the exception of III and IV none of these is attacked by trypsin-free erepsin at p_H 7.8 and 37°. All are readily hydrolysed by *N*-sodium hydroxide at 37° in 0.1*M*-solution. Of the derivatives of IV, II is the most rapidly and V the most slowly hydrolysed with alkali. J. W. BAKER.

Derivatives of cyanomalonic acid. F. PABST (Arch. Pharm., 1929, 267, 325—352).—Ethyl cyanoacetate reacts with potassium cyanate giving ethyl cyanocarboxylamidooacetate, m. p. 162—163° (decomp.) (corresponding methyl ester, m. p. 128°; $+1\frac{1}{2}H_2O$, m. p. 116°) (cf. Frerichs and Hartwig, A., 1906, i, 74), strongly acidic substances, which form salts with metallic carbonates, weakly basic amines, and alkaloids. They are converted into carbon dioxide and cyanoacetamide when boiled with water, whilst when heated near their m. p. they undergo further condensation, forming the monomethyl and the monoethyl ester amides of dicyanomalonimide [*ferric*, *silver*, and *barium* ($+1$ and $6H_2O$) salts] which are stronger acids than acetic acid. When treated with alcoholic potassium hydroxide and benzyl chloride, the monomethyl ester (m. p. 103°) and the monoethyl ester amides (m. p. 86°) of benzylcyanomalonic acid are obtained, whilst hot benzyl alcohol affords the corresponding monobenzyl ester amide, m. p. 148° (*silver* salt), and dibenzyl cyanomalonate, m. p. 73—74° (*sodium*, m. p. 267°, *potassium*, and *silver* salts). The mono-ester anilides of cyanomalonic acid are obtained when a sodiocyanoacetic ester is treated with phenylcarbamide (cf. Micheal and Cobb, A., 1908, i, 947); ethyl ester anilide, m. p. 145° (*silver* salt); methyl ester anilide, m. p. 146° (*silver* salt). The corresponding methyl (m. p. 103°) and ethyl (m. p. 104.5°) ester anilides of benzylcyanomalonic acid do not form salts. Cyanomalondianilide, m. p. 192°, obtained when the ester amides or ester anilides are heated with aniline (*silver* and *ferric* salts), or when sodiocyanoacetanilide is treated with phenylcarbamide, affords benzylcyanomalondianilide, m. p. 215°. The following are prepared in a similar manner: cyanomalondimethylanilide, m. p. 178°; cyanomalondi-*p*-anisidide, m. p. 215° (*silver* salt); cyanomalondi-*m*-toluidide, m. p. 186°; cyanomalondi-*p*-toluidide, m. p. 221°. S. COFFEY.

Dicyanic acid. T. L. DAVIS and K. C. BLANCHARD (J. Amer. Chem. Soc., 1929, 51, 1806—1810).—The presence of dicyanic acid in aqueous solutions of cyanic acid is inferred on similar evidence to that adduced in the case of nitrobiuret solutions (cf. this vol., 919). Thus, the formation of allophanates from

alcohols and aqueous cyanic acid is due to the direct action of the dicyanic acid (cf. Behal, A., 1919, ii, 301), and not to a secondary reaction between the carbamate and cyanic acid. Ethyl carbamate is partly converted in presence of alcohol at 100° into ethyl allophanate. In aqueous solution cyanic acid and carbamide do not give biuret. A concentrated solution of potassium cyanate acidified with acetic acid gives, after a few mins., the biuret reaction, but contains no biuret. With aniline this solution gives α -phenylbiuret in addition to phenylcarbamide.

H. E. F. NOTTON.

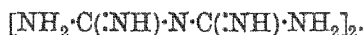
Dearrangement of nitrocarbamide and its application in syntheses. T. L. DAVIS and K. C. BLANCHARD (J. Amer. Chem. Soc., 1929, 51, 1790—1801).—The primary decomposition of nitrocarbamide at 160—170° (cf. Thiele and Lachman, A., 1896, i, 207) into (a) nitroamide and cyanic acid, and (b) ammonia and the compound $NO_2 \cdot N \cdot CO$, is inferred from the formation of water, nitrous oxide, cyanic acid, carbon dioxide, ammonia, ammonium cyanurate, and traces of ammeline, carbamide, and biuret. Solutions of nitrocarbamide in warm water or cold concentrated sulphuric acid contain nitroamide; the latter may be used at 0° to effect nitrations (cf. A., 1927, 863). Nitrocarbamide is formed from nitroamide, silver cyanate, and hydrochloric acid at 0°. Air-dried nitrocarbamide, but not that dried over phosphoric oxide, decomposes in presence of traces of alkali. In aqueous solution it forms a convenient source of cyanic acid, giving with primary amines monosubstituted carbamides, e.g., *p*-carbamidobenzoic acid, m. p. above 275°, and *n*-butylcarbamide, m. p. 96° (cf. Werner, J.C.S., 1919, 115, 1101), and with secondary amines α -dialkylcarbamides, e.g., oily α -*di-n*-butyl- (*picrate*, m. p. 82—83°) and α -*diisooamyl*- (*oxalate*, m. p. 101.5—102°; *picrate*, m. p. 72.8—73.9°) carbamides. Dipropylamine gives α -dipropylcarbamide and α -*di-n*-propylbiuret, m. p. 129—129.4°; *n*-propylaniline gives α -phenyl- α -*n*-propylcarbamide, m. p. 89.4—89.8° [*picrate*, m. p. 118—118.5°; *oxalate*, m. p. 71—72° (decomp.)], and α -phenyl- α -*n*-propylbiuret, m. p. 151°. α -Phenyl- α -*n*-butylcarbamide has m. p. 50.5—51.1°. The monoalkyl derivatives may be isolated by evaporating their aqueous solutions, but the dialkyl and arylalkyl derivatives are partly decomposed into amine and cyanic acid. These last also decompose at the m. p. into alkylanilines and cyanuric acid. Nitrocarbamide reacts but slightly with anhydrous alcohols. In presence of water it gives esters of carbamic and allophanic acids. H. E. F. NOTTON.

Dearrangement of nitrobiuret; application in synthesis. T. L. DAVIS and K. C. BLANCHARD (J. Amer. Chem. Soc., 1929, 51, 1801—1806).—The reactions of nitrobiuret in aqueous solution indicate that it decomposes primarily into nitroamide and dicyanic acid, $NH_2 \cdot CO \cdot N \cdot CO$, and to a smaller extent into carbamide and nitrocyanic acid, $NO_2 \cdot N \cdot CO$. A fresh cold solution does not give the biuret test, but when heated it evolves carbon dioxide and nitrous oxide (cf. Thiele and Uhlfelder, A., 1899, i, 118), forming carbamide and a product which gives the biuret reaction, but leaves only cyanuric acid when evaporated. The reactions of the solution with

alcohols and amines indicate that this product is dicyanamic acid. Thus, nitrobiuret and potassium hydroxide give in absolute alcohol no reaction, in 80% alcohol potassium allophanate (32% of the theoretical), and in 50% alcohol carbamide but no allophanate. Gradual addition of water to nitrobiuret in ethyl, *n*-propyl, or *n*-butyl alcohol gives mixtures of alkyl carbamates and allophanates; *tert*-butyl alcohol gives carbamate only, and *iso*amyl alcohol allophanate only. The carbamates are produced by a secondary reaction between the alcohols and allophanates. Nitrobiuret gives with aqueous ammonia at 100° biuret (60% of the theoretical) and with amines in warm aqueous solution good yields of the following substituted biurets: α -methyl-, m. p. 166.5—167°; α -ethyl-, m. p. 154—154.5°; α -*n*-propyl-, m. p. 147.2—147.6°; α -*n*-butyl-, m. p. 129.1—129.5°; α -benzyl-, m. p. 174.5—175°; α -phenyl-, m. p. 165°; α -*p*-tolyl-, m. p. 199°; α -(α -naphthyl)-, m. p. 217.3—217.6°; $\alpha\alpha$ -dimethyl-, m. p. 141—141.5°; $\alpha\alpha$ -diethyl-, m. p. 139—139.2°; $\alpha\alpha$ -di-*n*-propyl-, m. p. 129—129.4°; $\alpha\alpha$ -di-*n*-butyl-, m. p. 144.8—145°; α -phenyl- α -ethyl-, m. p. 155.2—155.8°; and α -phenyl- α -*n*-propyl-, m. p. 151—151.5°. Nitrobiuret does not give triuret with carbamide in warm water, but with biuret it gives tetrauret, $\text{NH}_2\cdot[\text{CO}\cdot\text{NH}]_3\cdot\text{CO}\cdot\text{NH}_2$. A solution of nitrobiuret in cold concentrated sulphuric acid gives up its nitro-group quantitatively in the nitrometer and may be used at 0° to effect nitrations.

H. E. F. NORTON.

Diguanides. I. Constitution of the complex compounds of diguanide with heavy metals.
II. Depressing action of diguanides on blood-sugar. K. H. SLOTTA and R. TSCHESCHE (Ber., 1929, 62, [B], 1390—1398, 1398—1405).—I. Examination of a series of substituted diguanides shows that the formation of complex metallic compounds occurs only with derivatives in which the hydrogen atoms of the three imino-groups are not replaced. The complex compounds are therefore formulated



Cyanocarbamide is converted by successive treatment with alcoholic methylamine at 100° and sulphuric acid into *methylguanylcyanamide sulphate*, $[\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NHMe}]_2\cdot\text{H}_2\text{SO}_4$, m. p. 228—230° (slight decomp.), which does not yield a copper compound. *Carboethoxymethylcyanamide*, b. p. 100°/3 mm., from the sodium derivative of carboethoxycyanamide and methyl sulphate, is converted by concentrated aqueous ammonia into trimethylmelamine, m. p. 115°. Addition of amines to dicyanamide furnishes the following *hydrogen sulphates*: $\alpha\epsilon$ -di-

methylidiguanide, $\text{NHMe}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NHMe}\cdot\text{H}_2\text{SO}_4$, decomp. 200°; $\alpha\epsilon$ -diallyldiguanide; $\alpha\alpha\epsilon\epsilon$ -tetramethylidiguanide, decomp. 142° after softening at 133—135°. *N*-Methylguanythiocarbamide is transformed by boiling ethyl bromide into *N-methyl-S-ethylguanythiocarbamide hydrobromide*, m. p. 173—175° (incipient decomp.), converted by methylamine and dimethylamine into α : N^{β} -dimethyldiguanide hydrobromide, $\text{NHMe}\cdot\text{C}(\text{NMe})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2\cdot\text{HBr}$, decomp. 240—

245°, and α : N^{β} -trimethyldiguanide hydrobromide, m. p. 185—190°. *s*-Triphenylguanidine and cyanamide in benzene and ether afford α : N^{β} : γ -triphenyldiguanide, decomp. 118—120°. *s*-Trimethylguanidine (*hydrogen sulphate*) and *s*-triphenetidyldiguanidine could not be caused to react similarly with cyanamide. The dicyanomethylamide, m. p. 235—238° after softening at 221°, of Madelung and Kern (A., 1922, i, 438) is a polymerised compound. Diguanide, decomp. 142°, is obtained crystalline by treatment of diguanidesulphate with a solution of sodium in boiling ethyl alcohol. The action of ethyl chloroacetate on diguanide affords

diguanido- ϵ -acetic acid hydrochloride, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}\cdot\text{HCl}$, decomp. 148°, with minor amounts of 2-amino-6-imino-1:4-endomethylene-1:3:5-triazine hydrochloride (cf. I), m. p. 215° (decomp.). Similarly, $\alpha\alpha$ -dimethyldiguanide yields $\alpha\alpha$ -dimethyldiguanido- ϵ -acetic acid hydrochloride, decomp. 178—180°, and 2-dimethylamino-6-imino-1:4-endomethylene-1:3:5-triazine hydrochloride, m. p. 176° (decomp.).

II. The physiological action of diguanides depends on the presence of at least one unsubstituted amino-group. In the series α -methyl-, ethyl-, propyl-, isobutyl-, *iso*amyl- maximum activity is observed with the methyl derivative; this is also the case with the allyl compound in the sequence allyl-, crotyl-, *iso*-amylenyl-, *iso*hexenyl-. Among $\alpha\alpha$ -di-derivatives the methyl compound is most potent. No advantage is gained by the introduction of the phenyl or anisyl group or the acetic acid residue.

The following substituted diguanides are prepared by addition of the requisite amine to cyanoguanidine: α -propyldiguanide sulphate, $[\text{NHPr}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2]_2\cdot\text{H}_2\text{SO}_4$, m. p. 193—196°; α -isomyldiguanide sulphate, m. p. 168—170°; $\alpha\alpha$ -dimethyldiguanide hydrochloride, m. p. 235°; $\alpha\alpha$ -diethyldiguanide sulphate, decomp. 202°; very hygroscopic $\alpha\alpha$ -diallyldiguanide hydrochloride, m. p. 100—110°; α -crotyldiguanide sulphate, m. p. 165—168° [(?) *N*-crotylphthalimide, $\text{C}_{12}\text{H}_{12}\text{ON}_2$, b. p. 178—180°/12 mm., m. p. 76°]; α -isoamylenyldiguanide sulphate, m. p. 153—154°; $\alpha\alpha'$ -methyl- Δ^8 -pentenyldiguanide sulphate, decomp. 226°; α -*p*-anisyldiguanide hydrochloride, m. p. 235°. Treatment of guanyl-*S*-ethylthiocarbamide (*hydrobromide*, decomp. 166°), prepared from guanythiocarbamide carbonate and ethyl bromide (preferably in presence of water), with amines leads to loss of ethyl mercaptan and production of the following diguanides: α - β' -hydroxyethyldiguanide sulphate, decomp. 148°; α - β' -thioethyldiguanide hydrogen sulphate, decomp. 201°; ethylenebisdiguanide sulphate, $[\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2]_2\cdot\text{H}_2\text{SO}_4$, decomp. 300°; hexamethylenebisdiguanide hydrogen sulphate, decomp. 205—210° after softening at 195°; decamethylenebisdiguanide sulphate, m. p. 115°, decomp. 122°.

H. WREN.

Organomagnesium halides. H. GILMAN, E. L. ST. JOHN, and N. B. ST. JOHN (Rec. trav. chim., 1929, 48, 593—596).—The optimum conditions for the preparation of organomagnesium halides previously determined (this vol., 800) for small-scale preparations are found to hold for operations on a larger scale, and

in some cases better yields are obtained. In general, the halide, in 6 equivalents of ether, can be added to the magnesium in 0.5–0.75 hr. The detailed preparation of Grignard reagents from *n*-butyl bromide (yield 91%), benzyl chloride (yield 91%), bromobenzene (yield 98%), and α -bromonaphthalene (yield 96%), and the yields obtained by conversion with carbon dioxide into the corresponding carboxylic acids, are given. When a solution of magnesium α -naphthyl bromide in ether is cooled, the etherate crystallises. C. W. SHOPPEE.

Relative reactivities of organic halides. Relative rate of formation of Grignard reagents. H. GILMAN and R. J. VANDERWAL (Bull. Soc. chim., 1929, [iv], 45, 344–349).—The relative reactivities of a series of organic halogen compounds have been compared by observing the time required for a positive result with the Gilman and Schulze colour test (A., 1925, ii, 1011; cf. this vol., 303). The test measures the reaction (i) $RX + Mg \rightarrow R \cdot Mg \cdot X$, but negative results due to the alternative reaction $2RX + Mg \rightarrow R \cdot R + MgX_2$ preceding (i) (cf. this vol., 179) are not a serious source of error in comparing reactivities of magnesium organohalides of the same class (cf. Gilman, Zocllner, and Dickey, this vol., 800). Among the normal alkyl (propyl to octyl) bromides and iodides the reactivity thus measured decreases as the size of the alkyl group increases. Comparison of the yields of magnesium alkyl bromides indicates an alternating effect in the series ethyl to octyl bromide. The order of reactivity with the butyl bromides is: *n* < *iso* < *sec* < *tert*. Only an approximate result could be obtained with *tert*-butyl bromide and by noting the time at which ebullition commences. With the bromotoluenes the *para* is the most, the *ortho* the least reactive; measurements were made in presence of iodine as activator. 1-Bromonaphthalene is much less reactive than 2-bromonaphthalene, both in presence and absence of iodine as catalyst, an observation agreeing with the less aromatic and more aliphatic properties shown by β -substituted naphthalene derivatives generally and with the observed order of reactivity: *n*-octyl bromide > bromocyclohexane > bromobenzene. Comparing the reactivity of alkyl halides with the same alkyl but different halogens, the fluorides are remarkably inert, the chlorides standing midway between these and the bromides or iodides. Aryl iodides are more reactive than the corresponding bromides, but alkyl bromides are slightly more reactive than the iodides, comparison being less exact, since the reaction $2RX + Mg \rightarrow R \cdot R + MgX_2$ is readier with the iodides than with the bromides. Treatment of alkyl iodides with mercury in purification appears to reduce their reactivity slightly. R. BRIGHTMAN.

Influence of pressure on the formation of Grignard reagents. H. GILMAN, R. J. VANDERWAL, and F. E. BROWN (Bull. Soc. chim., 1929, [iv], 45, 350–351).—The rate of formation of magnesium *n*-butyl bromide, measured by the technique previously described (cf. this vol., 303), is slightly greater under 2–3 atm. than at atmospheric pressure. No acceleration was observed with chlorobenzene, either on heating for 4½ hrs. at 90° in a sealed tube or under 63–96 atm. at ordinary temperatures. R. BRIGHTMAN.

Preparation of magnesium *n*-butyl bromide. P. BORGSTROM, F. C. WAGNER, and H. C. GRIFFIN (J. Amer. Chem. Soc., 1929, 51, 1861–1865).—Preparations using 6–10 mols. of *n*-butyl bromide are described. The highest yields are obtained when the bromide is added to the magnesium at such a rate (1 mol. in 40 min.) that the concentration of unchanged bromide is always very small. It is unnecessary to use more than the theoretical amount of magnesium. The yield of Grignard reagent, 92.5% of the theoretical, or 94.3% allowing for recovered bromide, is in good agreement with that given by Gilman and McCracken (A., 1924, i, 23). H. E. F. NOTTON.

Alkylation of tetra- and tri-cyanocadmie acid. F. HOLZL (Monatsh., 1929, 51, 397–419).—The action of silver nitrate on potassium cadmicyanide, $K_2[Cd(CN)_4]$, yields a mixture of the complex salts $Ag[Cd(CN)_3]$ and $Ag_2[Cd(CN)_4]$, which dissolves in water at 60° with precipitation of silver cyanide, the pure salt $Ag[Cd(CN)_3]$ crystallising from the aqueous solution. When this salt is methylated with methyl iodide a series of complex methylated derivatives of the acid $H[Cd(CN)_3]$ containing only methylcarbylamine groups, are obtained, the unmethylated cyano-groups undergoing partial, stepwise hydrolysis to yield complex salts containing several atoms of trivalent cadmium united by single cyano-bridges. These compounds, however, are unstable and readily react with water to yield derivatives of quadrivalent cadmium. Thus the action of an excess of methyl iodide on the salt $Ag[Cd(CN)_3]$ for 10 days in the dark, extraction of the solid product with chloroform, and crystallisation from dilute methyl alcohol yields the compound $C_6H_{15}O_8N_6Cd_4$ (I), which has a weakly alkaline reaction in aqueous solution and yields carbylamine when heated alone or with alkali. Alternative structures for this compound are suggested, the most probable being $[NC \cdot Cd(OH)(OH_2) \cdot (CN \cdot Cd(OH)(OH_2))_3 \cdot CNMe]$. Similar methylation with a large excess of methyl iodide, extraction of the solid product with chloroform, and crystallisation from absolute methyl alcohol yields the compound $Cd_2C_4H_5O_2N_3$, which qualitatively resembles I: the most probable formula is $[Cd(OH)(CN) \cdot CN \cdot Cd(OH)(CNMe)]$. Alkylation of potassium cadmicyanide with methyl sulphate yields complex salts of quadrivalent cadmium containing 3 or 6 cadmium atoms united by a double cyano-bridge derived similarly by partial hydrolysis of the simple compound $[Cd(CN)_2(CNMe)_2]$. Thus the action of a large excess of methyl sulphate on finely-powdered, dry potassium cadmicyanide in the dark for 8 days, filtering from the solid product (II), removal of the excess of methyl sulphate from the filtrate by distillation in a vacuum, and extraction of the residue with methyl alcohol yields a compound which gives carbylamine with alkali, and barium sulphate on prolonged heating with barium chloride and hydrochloric acid, and is probably $[Cd(CNMe)_{3or4}](Me_2SO_4)_n$. Extraction of the solid product II with methyl alcohol and fractional crystallisation from this solvent to remove potassium methyl sulphate yields the compound $[Cd(OH)(CNMe) \cdot (CN)_2 \cdot Cd \cdot (CN)_2 \cdot Cd(CN)(CNMe)]$. The action of methyl sulphate on a saturated aqueous

solution of potassium cadmicyanide for 2 days, extraction of the solution with ether, and crystallisation of the residue from the ether from methyl alcohol yields the compound $\text{Cd}_6(\text{CN})_{11}(\text{CNMe})(\text{OH})$, for which three possible formulæ are given among which decision cannot be made. In all these complex salts (the mechanism of the formation of which is discussed) a quantitative determination of nitrile and carbylamine groups by Guillemard's method (A., 1908, i, 718) proves that in every case only methylcarbylamine and no nitrile groups are present. The relation of these results to those of Enklaar (A., 1925, i, 1394) is discussed and it is suggested that the liberation of normal (stable) hydrogen cyanide by the action of hydrogen sulphide on potassium cadmicyanide and similar complex cyanides is no evidence of its existence as such in the co-ordination sphere, since the labile (*iso*-)form if liberated would immediately isomerise to the stable form under the influence of hydrogen sulphide (cf. also Slotta and Jacobi, this vol., 304). Alkylation with ethyl iodide was not possible.

J. W. BAKER.

Preparation of pure cyclohexene. H. I. WATERMAN and H. A. VAN WESTEN (Rec. trav. chim., 1929, 48, 637—640).—*cyclo*Hexene, b. p. 83.05—83.15°/758 mm., n_D^{20} 1.44657, containing a trace of *cyclo*hexanol as the sole impurity, can be obtained by fractional distillation of Poulenc's product. Careful fractionation, followed by treatment with sodium under reflux for 7 hrs. and refractionation, afforded pure *cyclo*hexene, b. p. 82.8°/759 mm., n_D^{20} 1.44637. The product of the catalytic reduction was pure *cyclo*hexane, 1.42425. C. W. SHOPPEE.

Ring strain and radical formation. III. G. WITTIG and M. LEO (Ber., 1929, 62, [B], 1405—1410; cf. A., 1928, 642, 1233).—In the series, $-\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_n\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2-$ ($n=1-4$), the position of the very broad absorption band in the spectrum of the first two homologues corresponds with that of the monomeric tridiphenylmethyl, whereas with the third and fourth radical it resembles that of the moderately dissociated hexaphenylethane. The marked differentiation in the optical properties of the di-radicals is in harmony with expectations based on models; intramolecular union of the terminal radical valencies is impossible in the first two cases, but the ring strain allows such union for a di-radical with a longer methylene bridge.

p-Benzoylbenzyl bromide, m. p. 112°, from *p*-methylbenzophenone and bromine at 150°, is converted by ethyl disodiummalonate into *ethyl di-p-benzoylbenzylmalonate*, separating according to conditions of crystallisation in two dimorphous, interconvertible forms, m. p. 103—104° and 108—109°, respectively. Hydrolysis and decarboxylation give only resinous products. The ester is transformed by magnesium phenyl bromide into *ethyl di-p-hydroxydiphenylmethylbenzylmalonate*, $(\text{OH}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2)_2\text{C}(\text{CO}_2\text{Et})_2$, m. p. 173.5—174.5°, converted by hydrogen chloride in ether into *ethyl di-p-chlorodiphenylmethylbenzylmalonate*, readily hydrolysed to the glycol. Dehalogenation of the chloride by copper powder under nitrogen yields a pale brown solution not at all resembling that of the radicals described previously; exposure of the radical

solution to oxygen causes remarkably slow decolorisation to a pale yellow.

α , δ -Diphenylbutane is converted by benzoyl chloride and aluminium chloride into α , δ -*di-p-benzoylphenylbutane*, m. p. 150°, transformed by magnesium phenyl bromide into α , δ -*di-(p-hydroxydiphenylmethylphenyl)butane*, m. p. 140—145°. α , δ -*Di-p-chlorodiphenylmethylphenylbutane*, m. p. 159—161°, is transformed by copper powder into the corresponding *di-radical*, which, like its oxidation product, could not be caused to crystallise. H. WREN.

Reactions of nitrosulphonyl chlorides. I. Reactions of hydrazine hydrate with *o*-nitrosulphonyl chlorides. A. T. DANN and W. DAVIES (J.C.S., 1929, 1050—1055).—The reaction between warm hydrazine hydrate and 2-chloro-5-nitro-*p*-toluenesulphonyl chloride is expressed as follows: $2\text{R}\cdot\text{SO}_2\text{Cl} + 2\text{NH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{O} = 2\text{R}\cdot\text{SO}_2\text{H} + \text{N}_2 + 2\text{H}_2\text{O} + \text{NH}_2\cdot\text{NH}_2\cdot 2\text{HCl}$ and is a general reaction unless the sulphinic acid is too unstable. If carried out in the cold the primary hydrazide can sometimes be isolated. 2-Chloro-5-nitro-*p*-toluenesulphinic acid, m. p. 131.5°, prepared by the interaction of hydrazine hydrate with 2-chloro-5-nitro-*p*-toluenesulphonyl chloride, on methylation gives 2-chloro-5-nitro-*p*-toluenesulphone, m. p. 145—146°. 2-Chloro-5-nitro-*p*-toluenesulphonylhydrazide, m. p. 110—113°, was prepared in the cold; it reacts with cinnamaldehyde in warm anisole solution to give *cinnamaldehyde-2-chloro-5-nitro-p-toluenesulphonylhydrazide*, dark red, m. p. 95°. *o*-Nitrobenzenesulphonylhydrazide, m. p. 110°, can be prepared below 0°; 6-chloro-4-nitro-*o*-toluenesulphonylhydrazide, m. p. 127°, and 2-chloro-6-nitro-*p*-toluenesulphonylhydrazide, m. p. 125°, can be prepared in the usual way. *p*-Nitrobenzoyl chloride reacts with hydrazine hydrate in benzene solution giving *p*-nitrobenzoylhydrazide, m. p. 217°. Benzaldehyde-*p*-nitrobenzoylhydrazide, m. p. 259°, may be used as a delicate test for benzaldehyde. *s*-Di-*p*-nitrobenzoylhydrazine has m. p. 291°. C. W. GIBBY.

Octahydronaphthalene from tertiary decahydronaphthol. S. NAMETKIN and E. GLAGOLEV (Ber., 1929, 62, [B], 1570—1573, and J. Russ. Phys. Chem. Soc., 1929, 61, 535—540; cf. A., 1926, 508).—The octahydronaphthalene, obtained by the action of potassium nitrite on 9-aminodecahydronaphthalene hydrochloride, is converted by perbenzoic acid in chloroform into the corresponding *oxide*, $\text{C}_{10}\text{H}_{16}\text{O}$, b. p. 82—83°/8—9 mm., d_4^{20} 1.003, n_D^{20} 1.4847, transformed by water into the *glycol*, $\text{C}_{10}\text{H}_{16}(\text{OH})_2$, isolated as a mixture of isomerides. Dehydration of the glycol affords *hexahydronaphthalene*, b. p. 75—76°/8 mm., d_4^{20} 0.9726, n_D^{20} 1.5322. The octahydronaphthalene is therefore the Δ^9 -compound. H. WREN.

Behaviour of *cis*- and *trans*-decahydronaphthalene towards bromine and aluminium bromide. Isomerisation of hydrindane. N. D. ZELINSKI and M. B. TUROVA-POLLAK (Ber., 1929, 62, [B], 1658—1663; cf. A., 1925, i, 1053).—Treatment of *cis*-decahydronaphthalene, b. p. 192.7—193°/755 mm., with excess of bromine gives a *hexabromonaphthalene*, m. p. 312°, whereas the corresponding *trans*-compound yields a *hexabromonaphthalene*, m. p. 269°; the compound of m. p. 311—312° is also

obtained by bromination of naphthalene. *cis*-Decahydronaphthalene when treated with aluminium bromide and hydrogen bromide at the ordinary temperature gives mainly an additive product, $C_{10}H_8 \cdot AlBr_3$, from which little of the ketone $C_{10}H_{17} \cdot COMe$ [semicarbazone, m. p. 252° (decomp.)] is obtained by treatment with aluminium chloride; the part of the hydrocarbon which does not unite with the aluminium bromide undergoes partial isomerisation to *trans*-decahydronaphthalene. Under similar conditions, aluminium bromide does not appear to react with decahydronaphthalene. Hydrindane, b. p. 166°/758 mm., n_D^{20} 1.4683, is converted by aluminium bromide at 100° into *trans*-hydrindane mixed with a more fundamentally isomerised hydrocarbon; a product, $(C_9H_{14})_3$, m. p. 192—193°, formed by polymerisation of partly dehydrogenated hydrindane, is also produced.

H. WREN.

Rubrene. Mechanism of formation, an intermediate chloro-compound. C. MOUREU, C. DUFRAISSE, and J. ROBIN (Compt. rend., 1929, 188, 1582—1584).—When an ethereal solution of diphenylphenylacetylenylmethyl chloride is allowed to undergo spontaneous dissociation in the cold (several months), or is heated at 70° for 30 min., an intermediate crystalline compound, $C_{42}H_{28}Cl$, m. p. 217°, is formed, which is slowly transformed into rubrene in cold ethereal solution and more rapidly on warming.

C. C. N. VASS.

Rubrene. New oxide of rubrene. C. MOUREU, C. DUFRAISSE, and L. ENDERLIN (Compt. rend., 1929, 188, 1528—1530).—In addition to the dissociable peroxide RO_2 (A., 1926, 945; 1928, 53), rubrene forms a stable oxide, RO , m. p. 200° ($+C_6H_6$) and 325°, which is obtained by the action of 15% nitric acid, chromic acid, or permanganate on rubrene, or by reduction of the peroxide by zinc and acetic acid. It is reduced to rubrene by iron and acetic acid or by hydriodic acid. Oxidation yields only dibenzoylbenzene. The relation of rubrene to its oxides is parallel to that of haemoglobin to its oxides, and suggests that the characteristic properties of the latter are due to the hydrocarbon part of the molecule.

R. K. CALLOW.

Polynuclear aromatic hydrocarbons and their derivatives. IV. Naphthaphenanthrenes and their quinones. E. CLAR (Ber., 1929, 62, [B], 1574—1582; cf. this vol., 435, 689).—The mixture of ketones, mainly *o*-tolyl 9-phenanthryl ketone (*loc. cit.*), is converted by distillation chiefly into 1 : 2 : 3 : 4-dibenzanthracene, whilst from the more sparingly soluble portions *naphtha-2' : 3'-1 : 2-phenanthrene*, m. p. 293—294° in a sealed capillary, is isolated by repeated crystallisation from xylene. The last-named hydrocarbon is also prepared by distillation of 1 : 2-*phthalylphenanthrene*, m. p. 269—270°, with zinc dust. 1 : 2-*Phthalylphenanthraquinone*, its *o*-diazine, not molten below 375°, and 1 : 2-*benzoanthraquinone-2' : 1' : 3 : 4-phenazine*, subliming at about 300°/vac., are described. α -Naphthoyl chloride and 2-methyl-5 : 6 : 7 : 8-tetrahydronaphthalene are converted by aluminium chloride in benzene into 3- α -naphthoyl-2-methyl-5 : 6 : 7 : 8-tetrahydronaphthalene, b. p. about 265°/13 mm., m. p. 142—143°; 3- β -naphthoyl-2-methyl-

5 : 6 : 7 : 8-tetrahydronaphthalene, m. p. 103—104°, is prepared similarly. Either ketone is transformed by distillation with copper powder into *naphtha-2' : 3'-2 : 3-phenanthrene*, m. p. 263—264°. 2 : 3-*Phthalylphenanthrene*, m. p. 272—273°, and 2 : 3-*phthalylphenanthraquinone*, m. p. 318°, are described. The diquinone is converted by phenylhydrazine into the *quinhydrone*, $C_{22}H_{12}O_4$, m. p. about 375° (decomp.), and by *o*-phenylenediamine into the *phenazine*, $C_{23}H_{14}O_2N_2$, subliming at about 300°/vac.

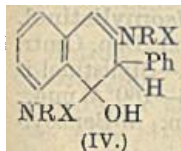
H. WREN.

Phenyl- and *o*-tolyl-thiocarbimides as reagents for primary aromatic amines. T. OTTERBACHER and F. C. WHITMORE (J. Amer. Chem. Soc., 1929, 51, 1909—1911).—These reagents have the advantage that they may be used in presence of water or alcohol and form no by-products. The following derivatives of *s*-diphenylthiocarbamide were prepared in hot or cold alcoholic solution: *p*-methyl-, m. p. 141°; *o*-methyl-, m. p. 136°; *m*-methyl-, m. p. 94°; *p*-bromo-, m. p. 148°; *o*-bromo-, m. p. 146°; *m*-bromo-, m. p. 97°; *p*-chloro-, m. p. 152°; *o*-chloro-, m. p. 156°; *m*-chloro-, m. p. 116°; *p*-iodo-, m. p. 153°; 2-bromo-4-methyl-, m. p. 154.5°; 2 : 4-dimethyl-, m. p. 133.5°; 4-hydroxy-2-methyl-, m. p. 167.5°; *p*-hydroxy-, m. p. 150°; also the following derivatives of *p*'-methyl-*s*-diphenylthiocarbamide: *p*-methyl-, m. p. 132°; *o*-methyl-, m. p. 158°; *m*-methyl-, m. p. 140°; *p*-bromo-, m. p. 143°; *o*-bromo-, m. p. 128°; *m*-bromo-, m. p. 101°; *p*-chloro-, m. p. 134.5°; *o*-chloro-, m. p. 140°; *m*-chloro-, m. p. 124°; *p*-iodo-, m. p. 150°; 2-bromo-4-methyl-, m. p. 132°; 2 : 4-dimethyl-, m. p. 143.5°; 4-hydroxy-2-methyl-, m. p. 182.5°; *p*-hydroxy-, m. p. 158°; *p*-methoxy-, m. p. 138°; and *o*-methoxy-, m. p. 126°. The *diphenylthiourethanes*, m. p. 172° and m. p. 168°, respectively, of phenylhydrazine and hydrazobenzene, and phenyl-, m. p. 154°, and *p*-tolyl-, m. p. 160°, thiocarbimides were obtained similarly.

H. E. F. NOTTON.

Steric hindrance and the Grignard reaction. Colour reactions of organometallic compounds. H. GILMAN and L. L. HECK (Ber., 1929, 62, [B], 1379—1384; cf. Gilman and others, A., 1925, ii, 1011; 1928, 160; this vol., 303).—The observation of von Braun and others (A., 1918, i, 107; 1920, i, 30) that β -methyl-anilinoethyl chloride and bromide do not react with ketones appears at variance with the universality of the authors' colour reaction of compounds containing the group $C \cdot MgX$ and Michler's ketone. It is found that in these cases the colour is only slowly developed, thus supporting the hypothesis that the sluggishness is due to steric hindrance. On the other hand, the Grignard reagents from triphenylmethyl chloride and bromomesitylene give an immediate colour. β -Methyl-anilinoethyl chloride is prepared by the successive addition of magnesium ethyl bromide and β -chloroethyl *p*-toluenesulphonate to methylaniline in ether. Its Grignard derivative is transformed by *n*-butaldehyde into *s*-diphenyldimethyltetramethylenediamine (picrate, m. p. 203°) and the aminocarbinal $NMePh \cdot C_6H_4 \cdot CHPr^a \cdot OH$ (picrate, m. p. 145; chloroplatinate, m. p. 209°, decomp. 211°) (cf. von Braun and co-workers, A., 1918, i, 107). Magnesium mesityl bromide is converted by carbon dioxide into 2 : 4 : 6-trimethylbenzoic acid in 50% yield. H. WREN.

N-Methyl derivatives of 2-phenylnaphthylene-1:3-diamine. W. S. KENTISH (J.C.S., 1929, 1169—1175).—The isomerism of the α - and β -*NN'*-dimethyl-2-phenylnaphthylene-1:3-diamines (cf. Lees and Thorpe, J.C.S., 1907, 91, 1282; Gibson, Kentish, and Simonsen, A., 1928, 1128) has been re-examined. The β -dimethyl base (I) is represented as *NN'*-dimethyl-2-phenylnaphthylene-1:3-diamine, and the α -dimethyl base (II) as 3-methylamino-1-methylimino-2-phenyl-1:2-dihydronaphthalene. By treatment at the ordinary temperature with 1 mol. of nitrous acid, II affords α -3-nitrosomethylamino-1-methylimino-2-phenyl-1:2-dihydronaphthalene (III), dimorphous (unstable α_1 -form, yellow needles, m. p. 154°; stable α -form, orange-red prisms, m. p. 154°), reconverted into II by reduction with tin and hydrochloric and acetic acids at 100° in nearly theoretical yield; III can neither be methylated nor condensed with *p*-toluenesulphonyl chloride, but treatment with excess of nitrous acid slowly converts it into β -1:3-dinitrosomethylamino-2-phenylnaphthalene, m. p. 179°, which by reduction yields I. α -3-Acetylmethylamino-1-methylimino-2-phenyl-1:2-dihydronaphthalene with nitrous acid furnishes β -3-acetylmethylamino-1-nitrosomethylamino-2-phenylnaphthalene, m. p. 198°, reduced by tin and hydrochloric and acetic acids to β -3-acetylmethylamino-1-methylamino-2-phenylnaphthalene, m. p. 147°, which by hydrolysis with concentrated hydrochloric acid yields I. Similarly 3-*p*-toluenesulphonyl- β -*NN'*-dimethyl-2-phenylnaphthylene-1:3-diamine affords 1-nitroso-3-*p*-toluenesulphonyl- β -*NN'*-dimethyl-2-phenylnaphthylene-1:3-diamine, m. p. 183°, giving I by reduction and hydrolysis. These results show that the $\alpha \rightarrow \beta$ transformation is effected by nitrous acid and is unassociated with the nature of the substituent in the 3-position. It is suggested that



nitrous acid adds on at the methylimino-double linking, giving IV (R=Me; X=NO), which then loses water. In support, it is shown that the "acetyl acetate" of 2-phenylnaphthylene-1:3-diamine (V) (Atkinson and Thorpe, J.C.S., 1906, 89, 1906) has the structure IV (R=Ac; X=H), since, by treatment with cold 5% aqueous sodium hydroxide it loses water, giving diacetyl-2-phenylnaphthylene-1:3-diamine, m. p. 272° (cf. lit.). It is concluded that V has a mono-imino-structure.

It is consistent with the suggested structures that β -3-nitrosomethylamino-1-methylamino-2-phenylnaphthalene, m. p. 248°, has a deep red colour and yields highly coloured solutions, whereas the α -mono-nitrosoamine (III) gives but slightly coloured solutions. C. W. SHOPPEE.

Perylene and its derivatives. XXIII. K. FUNKE and H. WOLF (Monatsh., 1929, 52, 1—6).—Reduction of 3:9-dichloro-4:10-dinitroperylene (I) (Zinke, Funke, and Lorber, A., 1927, 350) with phenylhydrazine in boiling xylene takes place through an intermediate compound (constitution not established), and gives 3:9-dichloro-4:10-diaminoperylene (II), needles with copper-red metallic lustre (diacetyl and dibenzoyl derivatives). Nitration of 3:9-dibromoperylene suspended in acetic acid with potassium

nitrate and sulphuric acid affords 3:9-dibromo-4:10-dinitroperylene (III), reduced as above to 3:9-dibromo-4:10-diaminoperylene (IV). During acetylation or benzoylation of III and IV a partial (in some cases a total) elimination of halogen occurs (cf. Jungmans, A., 1913, i, 1070). Whilst I and II are unaffected by boiling with aniline, III and IV yield 4:10-diaminoperylene, steel-blue rods (dibenzoyl and di-*p*-bromobenzoyl derivatives), which differs from the diamino-derivative previously described (this vol., 550). This last compound is postulated as the 3:10-derivative, since oxidation of the original dinitro-compound (A., 1927, 350) with concentrated sulphuric acid gives perylene-3:4:9:10-diquinone.

H. BURTON.

Catalytic reduction of nitro-compounds. M. BUSCH and K. SCHULZ (Ber., 1929, 62, [B], 1458—1466).—Reduction is effected in boiling alcoholic 5% potassium hydroxide solution, the hydrogen being obtained by decomposition of hydrazine hydrate under the influence of palladised calcium carbonate. Reaction proceeds more readily in methyl than in ethyl alcohol: thus, under defined conditions, nitrobenzene in ethyl alcohol yields almost exclusively azoxybenzene, whereas in methyl alcohol it gives azobenzene; with increased amounts of catalyst, hydrazobenzene and, finally, aniline are produced. Nitrophenols which can yield pseudo-acids are more readily reduced. *o*- and *p*-Nitrophenols give the corresponding aminophenols; the *m*-compound is reduced similarly in methyl alcohol. *m*-Nitrobenzenesulphonic acid yields the aminobenzenesulphonic acid. The phenylenediamines are obtained from *o*- and *p*-nitroaniline, whereas *m*-nitroaniline yields the azoxy-compound in ethyl alcohol, but *m*-phenylenediamine in methyl alcohol. Under similar conditions, azoxybenzene is reduced almost quantitatively, azobenzene to the extent of 50%, to hydrazobenzene, whereas the last-named compound is almost indifferent. With the nitrotoluenes the absorption of hydrogen increases in the sequence

In ethyl alcohol azoxy-, azo-, and a mixture of azo- and hydrazotoluenes are obtained in the three cases, whereas in methyl alcohol *o*-nitrotoluene gives *o*-toluidine in excellent yield, *m*-nitrotoluene affords *m*-hydrazotoluene and *m*-toluidine, whereas *p*-nitrotoluene gives a mixture of *p*-azo- and *p*-hydrazo-toluene and *p*-toluidine. With halogenonitrobenzenes the hydrogen first reduces the nitro-group, the activity of which is enhanced by the halogen atom. With the *o*- and *m*-compounds the azoxy-compounds are produced in small yields; only in the case of *p*-bromonitrobenzene is the azoxy-derivative the main product (probably by reason of its sparing solubility in alcohol). In general, halogenoazobenzenes predominate in ethyl alcohol, varying amounts of halogenoanilines and aniline in methyl alcohol. H. WREN.

Action of bromine on mixed ethers. L. C. RAIFORD and D. M. BIROSEL (J. Amer. Chem. Soc., 1929, 51, 1776—1778).—Phenyl allyl ether and excess of bromine in chloroform give 2:4-dibromophenyl β -*y*-dibromopropyl ether, b. p. 220—223°/10 mm., and 2:4:6-tribromophenol, but no 2:4:6-tribromo-

phenyl βγ-dibromopropyl ether, m. p. 42.5–43.5°, prepared from tribromophenyl allyl ether and bromine. Phenyl methyl, ethyl, *n*-propyl, and isobutyl ethers are brominated at the ordinary temperature to 2 : 4 : 6-tribromo-derivatives. 2 : 4 : 6-Tribromophenyl *n*-propyl and isopropyl ethers are not attacked by bromine, but phenyl isopropyl, *sec*.-butyl, and *tert*.-butyl ethers and 2 : 4-dibromophenyl isopropyl ether give tribromophenol, which is also formed to the extent of 10% and 20%, respectively, from anisole and phenetole. The dealkylation is effected by hydrogen bromide formed in the reaction and does not occur (except with the *tert*.-butyl ether) in presence of sodium acetate. 4-Chloro-2-nitrophenyl and 2 : 4 : 6-trinitrophenyl βγ-dibromopropyl ethers, m. p. 55°, and m. p. 102°, were prepared from the corresponding allyl ethers (cf. Fairbourn, A., 1927, 131). 2 : 4-Dibromophenyl and 2 : 4 : 6-tribromophenyl isopropyl ethers have b. p. 156°/18 mm., and b. p. 190°/30 mm., m. p. 40°, respectively. H. E. F. NOTTON.

Purification of picric acid. S. R. BENEDICT (J. Biol. Chem., 1929, 82, 1–3).—Picric acid, for the purpose of the colorimetric determination of creatinine, is best purified by crystallisation from glacial acetic acid, or by dissolution in sodium carbonate, separation of the sodium salt, and decomposition of the latter with dilute hydrochloric acid.

C. R. HARRINGTON.

Organic compounds of sulphur. XIII. Action of aliphatic diazo-compounds on sulphur aryl chlorides and mercaptans. A. SCHÖNBERG, O. SCHÜTZ, and J. PETER (Ber., 1929, 62, [B], 1663–1670; cf. this vol., 447).—Diphenyldiazomethane and sulphur *o*-nitrophenyl chloride react readily in anhydrous ether, giving nitrogen and *o*-nitrophenyl diphenylchloromethyl sulphide, $\text{C}_6\text{H}_4\text{Cl-S-C}_6\text{H}_4\text{-NO}_2$, decomp. about 137° depending greatly on the rate of heating. It is converted by *o*-nitrophenyl mercaptan in boiling benzene into *di*-*o*-nitrophenylthioldiphenylmethane, $\text{C}_6\text{H}_4(\text{S-C}_6\text{H}_4\text{-NO}_2)_2$, m. p. (indef.) about 146° (decomp.), and by phenyl mercaptan into phenylthiol-*o*-nitrophenylthioldiphenylmethane, m. p. (indef.) 134°. 9-Chloro-9-*o*-nitrophenylthiofluorene, decomp. about 120° according to the rate of heating, from *o*-nitrophenyl mercaptan and diphenylenediazomethane in ether, is converted by phenyl mercaptan in boiling benzene into 9-phenylthiol-9-*o*-nitrophenylthiofluorene, m. p. about 127–129°. Diphenyldiazomethane and sulphur phenyl chloride in ether yield phenylthiol-diphenylmethyl chloride, converted by *o*-nitrophenyl mercaptan into phenylthiol-*o*-nitrophenylthioldiphenylmethane. Diphenyldiazomethane and phenyl mercaptan give phenyl diphenylmethyl sulphide, m. p. 78°. α -Naphthyl mercaptan is transformed by diphenyldiazomethane into α -naphthyl diphenylmethyl sulphide, m. p. 77–78°. Benzyl diphenylmethyl sulphide has m. p. 70.5°. 9-Phenylthiofluorene, m. p. about 215° (decomp.), is prepared from diphenylenediazomethane and phenyl mercaptan. Di- β -naphthyl ketone hydrazone, m. p. 148°, is transformed by yellow mercuric oxide into *di*- β -naphthyl diazomethane, which passes in boiling benzene into *di*- β -naphthyl ketazine, m. p. 263–264° in a closed capillary. H. WREN.

Nitration of methane- and ethane-sulphon-*p*-phenetidides. F. REVERDIN (Helv. Chim. Acta, 1929, 12, 786).—The author acknowledges that ethanesulphonyl-*p*-phenetidine and its 2-nitro- and acetyl derivatives described by him (this vol., 310) as new were first prepared by Autenrieth and Bernheim (A., 1905, i, 47). Two other minor mistakes are rectified. R. J. W. LE FEVRE.

Preparation of aminonaphthols. W. F. BROWN, J. C. HERBEN, and J. R. WITHROW (J. Amer. Chem. Soc., 1929, 51, 1766–1769).—1 : 6- and 1 : 7-Aminonaphthols (hydrochlorides) are obtained in about 58% yield, some loss occurring through volatilisation, by fusing the corresponding naphthylaminesulphonic acids in an open vessel with sodium hydroxide at 305° (cf. Cassella, D.R.-P. 69458; Sachs, B., 1906, 369, 1143). Acetylation of 1 : 6-aminonaphthol, m. p. 190.6° (corr.) (picrate, m. p. 170°), by the method of Kehrman and Engelke (A., 1809, i, 150) gives an impure product, m. p. 195–220°. H. E. F. NOTTON.

Carbamides and thiocarbamides from vanillylamine; constitution and taste of pungent principles. N. A. LANGE, H. L. EBERT, and L. K. YOUSE (J. Amer. Chem. Soc., 1929, 51, 1911–1914).—The following have been prepared from vanillylamine and the appropriate carbimide or thiocarbimide: 4-hydroxy-3-methoxybenzylcarbamide, m. p. 178.5° (corr.), and α -phenyl- β -4-hydroxy-3-methoxybenzylcarbamide, m. p. 190.5°; also derivatives of α -*p*-hydroxym-methoxybenzylthiocarbamide, m. p. 167.5°; β -phenyl-(I), m. p. 138–138.5°; β -*p*-tolyl-(II), m. p. 138.5–139°, and β -*o*-tolyl-(III), m. p. 138–138.5°. Compounds I, II, and III have a pungent taste accompanied by slight bitterness; the rest are tasteless. H. E. F. NOTTON.

Constitution of mylistinol and isomylistinol. K. KAFUKU and N. ISHIKAWA (Bull. Ind. Dep. Centr. Res. Lab. Formosa, 1928, 24, 27–34).—Mylistinol is 5-hydroxyeugenol ethyl ether, b. p. 156–160°/5 mm.; the methyl ether has b. p. 134°/6 mm. 5-Benzoylmylistinol has m. p. 55.5–57°.

CHEMICAL ABSTRACTS.

Methone as a reagent for aldehydes. D. VORLÄNDER (Z. anal. Chem., 1929, 77, 241–268).—Methone (5 : 5-dimethyldihydroresorcinol) yields characteristic condensation products of the enolic acid type with aqueous or alcoholic solutions of true aldehydes, 2 mols. of methone condensing with 1 mol. of aldehyde with the elimination of 1 mol. of water; in glacial acetic acid 2 mols. of water are removed yielding characteristic anhydrides. Both acids and anhydrides crystallise well, are almost insoluble in the cold solvents used, and have well-defined m. p.; they are thus suitable for the detection and identification of aldehydes. The following compounds are described: methylenedimethone, $\text{CH}_2(\text{C}_6\text{H}_{11}\text{O}_2)_2$, m. p. 189° (corr.) (anhydride, m. p. 171°); ethylenedimethone, $\text{CH}_2\text{Me}(\text{C}_6\text{H}_{11}\text{O}_2)_2$, m. p. 139° (anhydride, m. p. 173–174°); propylenedimethone, $\text{CH}_2\text{Me-CH}(\text{C}_6\text{H}_{11}\text{O}_2)_2$, m. p. 154–156° [anhydride, m. p. 142–143° (corr.)]; isovalerylenedimethone, $\text{CH}_2\text{Pr}^s\text{-CH}(\text{C}_6\text{H}_{11}\text{O}_2)_2$, m. p. 154–155° [anhydride, m. p. 172–173° (corr.)]; and compounds with the following aldehydes: heptaldehyde,

Me[CH₂]₅·CH(C₈H₁₁O)₂, m. p. 103° (*anhydride*, m. p. 112°); acetaldehyde, CH₃·CH·CH(C₈H₁₁O)₂, m. p. 192° (*anhydride*, m. p. 162—163°); crotonaldehyde, m. p. 183° (cf. Fricke, 1922, i, 300) (*anhydride*, m. p. 167°); glycollaldehyde, $\text{O}-\text{C}_8\text{H}_{11}\text{O}$
 $\text{CH}_2\cdot\text{CH}\cdot\text{C}_8\text{H}_{11}\text{O}_2$, m. p. 237.5° (corr.) [*acetyl compound*, C₂₀H₂₆O₅, yellow, m. p. 205—206° (corr.)], also formed by interaction of chloroacetaldehyde and methone; glyceraldehyde, $\text{O}-\text{C}_8\text{H}_{11}\text{O}$
 $\text{HO}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_8\text{H}_{11}\text{O}_2$, m. p. 197.5° (corr.) (*anhydride*, m. p. 172°); glyoxal, CHO·CH(C₈H₁₁O)₂, m. p. 186° (corr.) (*anhydride*, m. p. 224°); methylglyoxal, COMe·CH(C₈H₁₁O)₂, m. p. 164° (corr.); malonaldehyde, m. p. 235—237°; glyoxylic acid (*anhydride*, m. p. 233—234°); *ethyl ester*, m. p. 122—124°; cinnamaldehyde, two isomeric forms, yellow crystals, m. p. 161° (corr.), from cold solutions and white prisms, m. p. 212—214° (corr.), from hot solutions (*anhydride*, m. p. 174—175°); cuminaldehyde, m. p. 170—171° (*anhydride*, 172—173°); *p*-hydroxybenzaldehyde, m. p. 188—190° (corr.) (*anhydride*, m. p. 246°); *acetyl compound*, m. p. 205—206°; *benzoyl compound*, m. p. 204°; *p*-anisaldehyde, m. p. 144—145° (corr.) (*anhydride*, m. p. 243°); salicylaldehyde, *anhydride*, m. p. 208° (corr.); *o*-chlorobenzaldehyde, m. p. 205° (corr.) (*anhydride*, m. p. 224—226°); vanillin, *anhydride*, m. p. 227—228°; piperonaldehyde, *anhydride*, m. p. 219—220°; dimethylaminobenzaldehyde, m. p. 192—194°; furfuraldehyde, m. p. 160° (decomp.) (*anhydride*, m. p. 162—165°). Isatin and methone in glacial acetic acid give a brown solution from which a yellowish flocculent precipitate is obtained on adding water; this *anhydride*, C₂₄H₂₅O₄N, has m. p. 283—285°; most other ketones do not react with methone under these conditions.

A. R. POWELL.

Action of aluminium chloride and metallic aluminium on hydroxylic compounds. J. POSTOWSKY and B. LUGOWIK (J. pr. Chem., 1929, [ii], 122, 141—146).—When *m*-cresol is boiled with 10% of anhydrous aluminium chloride, 3 : 6-dimethyl-xanthene is formed in 5% yield, accompanied by di-*m*-tolyl ether. When benzhydrol is boiled with aluminium powder, *s*-tetraphenylethane (30%) and diphenylmethane (5%) are formed. *s*-Tetraphenylethane is evidently formed by way of diphenylmethyl, for diphenylmethane yields only 3% of *s*-tetraphenylethane when heated with aluminium. Benzoin, when boiled with aluminium powder, yields 15% of tetraphenylfuran. The dehydrogenating action of aluminium powder is shown by the conversion of benzyl-aniline into benzyldeneaniline. R. K. CALLOW.

Photochemical activity of various sterols and the nature of their action. L. HUGOTENQ and E. COUTURE.—See this vol., 895.

Photographic effect produced by sterols after exposure to ultra-violet rays. J. CLUZET and KOFMAN.—See this vol., 895.

Displacement of iodine from an iodide by a solution in oil of cholesterol or ergosterol irradiated by solar light. E. ROUSSEAU.—See this vol., 895.

New photo-reaction with ergosterol. A. STEIGMANN.—See this vol., 895.

Conversion of naphthenic acids into naphthenes. G. КОМПА (Ber., 1929, 62, [B], 1562—1570).—Fractional distillation of the methyl esters of naphthenic acids derived from Baku petroleum does not lead to the isolation of individuals. Hydrolysis of appropriate fractions followed by distillation of the acids yields only a constant-boiling mixture (b. p. 147—148°/8 mm.) containing about 37% of deca- and 63% of undeca-naphthenic acid, from which suitable crystalline salts or derivatives could not be obtained. The mixed acids are therefore transformed by phosphorus pentachloride into their chlorides, which, when fractionally distilled, afford *undecanaphthenyl chloride*, C₁₁H₉·COCl, b. p. 106.5—108°/8 mm. (non-crystalline *anilide* and *p*-*toluidide*). *Ethyl* and *methyl undecanaphthenates* have b. p. 247—248.5°/762 mm., *d*₄²⁰ 0.92356, *n*_D²⁰ 1.44818, and b. p. 236—237°/763 mm., *d*₄²⁰ 0.93528, *n*_D²⁰ 1.44984, respectively. Hydrolysis of the methyl ester affords *undecanaphthenic acid*, b. p. 271—272°/763.5 mm., *d*₄²⁰ 0.9707, *n*_D²⁰ 1.4637 (*silver salt*). Reduction of the ethyl ester with sodium and alcohol yields *undecanaphthenol*, b. p. 236.5—237.5°, *d*₄²⁰ 0.90245, *n*_D²⁰ 1.46469 (*cinnamate*, b. p. 219—220°/7 mm., *d*₄²⁰ 1.00222, *n*_D²⁰ 1.53728, and its non-crystalline *tribromide*), converted by phosphoryl chloride and phosphorus pentachloride into *undecanaphthenyl chloride*, b. p. 74—78°/7 mm., *d*₄²⁰ 0.89318, and thence by sodium and alcohol into undecanaphthene, C₁₁H₂₀, b. p. 183.5—184.5°/764.5 mm., *d*₄²⁰ 0.81284, *n*_D²⁰ 1.44834. Since the hydrocarbon thus obtained is identical with that isolated by Markovnikov and Oglobin from Baku naphtha, it follows that the undecanaphthenic acid of the naphtha is a carboxylated derivative of the undecanaphthene present in the same type of petroleum. H. WREN.

Molecular compounds of bile acids with fatty acids and alcohols. II. Hyodeoxycholic acid. III. Cholic acid. H. RHEINOLDT (Z. physiol. Chem., 1929, 182, 251—254, 255—258; cf. this vol., 443).—Melting-point curves for binary mixtures of hyodeoxycholic acid and cholic acid with various fatty acids and an alcohol were obtained. There was no evidence of compound formation; the eutectic mixture in each case contained about 1% of the bile acid. The eutectic temperatures determined were: palmitic acid, 59° and 55.5°; stearic acid, 65.5° and 61°; stearolic acid, 45.5° and 44.5°; brassidic acid, 58° and 57.5°; behenolic acid, 54° and 55°; cetyl alcohol, 45.5° and 45°, respectively.

J. H. BIRKINSHAW.

Bufodeoxycholic acid. II. T. OKAMURA (J. Biochem. Japan, 1928, 10, 5—9; cf. A., 1928, 1272).—Bufodeoxycholic acid (*methyl ester*, m. p. 167°; *ethyl ester*, m. p. 171—173°), when oxidised with chromic acid, affords a *diketo-acid* (*α*), m. p. 230°, which is quickly converted into an *acid* (*β*), m. p. 251°, the *ethyl ester* of which is more stable than that of the *α*-acid. On reduction, the *α*-acid affords *bufocholanic acid*, m. p. 236°, —20.3° (*ethyl ester*, C₂₆H₄₄O₂, m. p. 108—111°). CHEMICAL ABSTRACTS.

Electrochemical reduction of benzoic acid. F. FICHTER and I. STEIN (Helv. Chim. Acta, 1929, 12,

821—826).—Cathodic reductions of solutions of benzoic acid in sulphuric acid and ethyl alcohol leads only to benzyl alcohol and not to ethyl $\Delta^{1,2}$ -dihydrobenzoate as stated by Somlo (cf. this vol., 776).

R. J. W. LE FEVRE.

Oxidation of toluene to benzoic acid by potassium dichromate and sulphuric acid. O. Y. MAGIDSON and V. I. MAKSMOV (J. Chem. Ind. Moscow, 1928, 5, 1102).—At first the product is chiefly benzoic acid, but later this is partly oxidised yielding carbon dioxide. The fall in the yield at the end of the reaction is probably due to increased viscosity interfering with efficient stirring. Rise of temperature increases the yield by decreasing the viscosity, and accelerates the process. An excess of sulphuric acid is favourable, probably owing to decrease of viscosity. The yield, calculated from the dichromate used, is for 60% acid, 25%; for 65% acid, 37%; for 70% acid, 50%; more concentrated acid is unfavourable. Only a large excess of toluene increases the yield. Various salts, particularly those of iron or nickel, accelerate the reaction; sodium chloride causes complete decomposition of the toluene.

CHEMICAL ABSTRACTS.

Identification of *o*-, *m*-, and *p*-hydroxybenzoic acids. F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1929, 51, 1947—1949).—Application of the method of Lyman and Reid (A., 1917, i, 334) to the preparation of the *p*-nitrobenzyl esters of these acids causes, in addition, partial etherification. The ether-esters, obtained by refluxing the acids in aqueous acetone with excess of *p*-nitrobenzyl bromide and sodium hydroxide, are more suitable for their identification than are the esters, obtained by using 1 mol. of bromide. The 2-, m. p. 166—168° (*p*-nitrobenzyl ester, m. p. 137—139°); 3-, m. p. 193—196° (*p*-nitrobenzyl ester, m. p. 142—144°), and 4-, m. p. 259—261° (*p*-nitrobenzyl ester, m. p. 196—197° regarded by Lyman and Reid as *p*-nitrobenzyl *p*-hydroxybenzoate, which has actually m. p. 180—182°), *p*-nitrobenzyl-oxybenzoic acids are obtained by hydrolysing the ether-esters with potassium carbonate in 50% aqueous alcohol.

H. E. F. NOTTON.

Reduction of ethyl diphenylglycidate with sodium and alcohol. (MNE.) P. BILLON-BARDON (Compt. rend., 1929, 188, 1412—1413).—Reduction of ethyl diphenylglycidate with sodium (18 atoms) and alcohol yields α -hydroxy- β -diphenylpropionic acid (diphenyl-lactic acid) in 60% yield, together with diphenylethane and a small amount of a substance, b. p. 180—215°/15 mm. Attack is thus limited, as in the case of the Grignard reagent (A., 1926, 950), to the oxido-group, and it is suggested that after this initial attack the presence of the group OMgX or ONa on the α -carbon atom greatly reduces the reactivity of the carbethoxyl group.

J. W. BAKER.

Phenolhalogenophthaleins. F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1929, 51, 1865—1875).—Ethyl 4-aminophthalate is converted through 3:4-dicarbelhoxybenzenediazonium borofluoride, decomp. 125° (cf. Balz, A., 1927, 654), into ethyl 4-fluorophthalate, b. p. 165—170°/25 mm., hydrolysed by sodium hydroxide to 4-fluorophthalic acid, m. p. 147—

148° in a closed tube. 4-Fluoro-, m. p. 76—78°, b. p. 260°/746 mm.; 4-chloro-, m. p. 98°, b. p. 284°/750 mm.; 4-bromo-, m. p. 108—109°, b. p. 290—293°/750 mm.; 4-iodo-, m. p. 125—126°, and 3-iodo-, m. p. 159—161°, -phthalic anhydrides are prepared by heating the corresponding acids alone, or with acetic anhydride. Crystallographic data are given for the 4-substituted anhydrides. 3-Iodophthalic anhydride, phenol, and zinc chloride at 115—130° give only phenol-3-iodophthalein, m. p. 252—254°, which is converted by fusion with potassium hydroxide into *m*-hydroxybenzoic acid and *pp'*-dihydroxybenzophenone (cf. Baeyer, A., 1880, 650). The 4-halogenated anhydrides, however, give the following mixtures of phenol-4- and -5-halogenophthaleins: -4- and -5-fluoro-, m. p. 230—240°; -4- and -5-chloro-, m. p. 214—233°; -4- and -5-bromo-, m. p. 226—236°, and -4- and -5-iodo-, m. p. 240—255°. These give on alkaline fusion *pp'*-dihydroxybenzophenone and both *m*- and *p*-hydroxybenzoic acids.

H. E. F. NOTTON.

Grignard reagents from *p*-dibromobenzene. H. GILMAN, N. J. BEABER, and H. L. JONES (Rec. trav. chim., 1929, 48, 597—602).—The formation of the bis-organomagnesium compound (*p*) $\text{C}_6\text{H}_4(\text{MgBr})_2$, and its conversion by carbon dioxide into terephthalic acid reported by Houben (A., 1906, i, 21: cf. Pink, J.C.S., 1923, 123, 3418; Quelet, A., 1927, 890) has been confirmed. By employing 15-mesh magnesium and extended refluxing in an ether-benzene mixture, an apparent yield of 4.2% of terephthalic acid was obtained, whilst with several equivalents of a 12.75% copper-magnesium alloy (cf. Gilman, Peterson, and Schulze, A., 1928, 253) the apparent yield was increased to 23.5%. The terephthalic acid yielded methyl terephthalate (mixed m. p.) but was contaminated with *p*-bromobenzoic acid and probably other acids of higher mol. wt. On the assumption that this acid constitutes the sole impurity, titration experiments indicate that the true yield of terephthalic acid is about 7.7%, but the method used to remove the greater part of the *p*-bromobenzoic acid from the reaction product (extraction with chloroform) entails some loss of terephthalic acid. Attention is directed to the theoretical complexity of the reaction between magnesium and simple polyhalogen compounds.

C. W. SHOPPEE.

cycloHexyl alkyl phthalates. R. ADAMS and J. F. HYDE, Assrs. to NEWPORT Co.—See B., 1929, 511.

Condensation of aromatic aldehydes with nitromethane. M. G. S. RAO, C. SRIKANTIA, and M. S. IYENGAR (Helv. Chim. Acta, 1929, 12, 581—583).—Condensations of vanillin, 2-hydroxy-4-methoxy-, 2:4-dimethoxy-, 4-methoxy-2-ethoxy-, and 5-nitro-2:4-dimethoxy-benzaldehyde with nitromethane in the presence of ammonium acetate and acetic acid are described. The following compounds were obtained respectively: vanillylidenenitromethane, m. p. 166°; 2-hydroxy-4-methoxy-, m. p. 171—172°; 2:4-dimethoxy-, m. p. 104°; 4-methoxy-2-ethoxy- ω -nitrostyrene, m. p. 102°; and 5- ω -dinitro-2:4-dimethoxystyrene, m. p. 214°. The yields were about 80% of the theoretical. R. J. W. LE FEVRE.

Photochemical transformation of *o*-nitrobenzaldehyde. R. WEGSCHEIDER.—See this vol., 895.

Mobility of symmetrical triad prototropic systems. V. New triad system (methylenes-azomethine). C. K. INGOLD and C. W. SHOPPEE (J.C.S., 1929, 1199—1204).—Condensation of *p*-anisaldehyde with benzylamine in an atmosphere of hydrogen at 100° affords *p*-methoxybenzylidenbenzylamine (I), m. p. 42°, reconverted by hydrolysis with 2*N*-sulphuric acid into its congeners (*benzylamine picrate* has m. p. 198°). A similar condensation yields *benzylidene-p*-methoxybenzylamine (II), b. p. 217°/17 mm., giving by hydrolysis benzaldehyde and *p*-methoxybenzylamine [*picrate*, m. p. 188° (decomp.); *benzoate*, m. p. 135°]. Interconversion of I and II occurs in 1.45*N*-alcoholic sodium ethoxide at 85°; at equilibrium the product contains 78.9% of I and 21.1% of II, giving an equilibrium ratio $k_1/k_2=0.268$. Methylenbenzylamine, m. p. 48° (cf. lit.), and benzylidenemethylamine, b. p. 90—91°/30 mm. (improved method of preparation described), are stable towards aqueous alkali and towards 1.46*N*- and 2.92*N*-alcoholic sodium ethoxide at 100°, but the former is partly converted into the latter in the presence of potassium hydroxide at about 300° or of 1.45*N*-alcoholic sodium ethoxide at 190°. The present position relating to the study of prototropy is summarised, and the isomeric change undergone by substitution products of benzaldoxime *N*-benzyl ether (lit.) is discussed.

C. W. SHOPPEE.

Catalytic influences in three-carbon tautomerism. I. Sodium alkoxides. G. A. R. KON and R. P. LINSTAD (J.C.S., 1929, 1269—1282).—Conditions under which mobilities of neutral tautomeric substances are measured have been standardised, and the behaviour of the tautomerides $C_5H_9 \rightleftharpoons C \cdot CHX$ (I) and $C_5H_9 \rightleftharpoons C \cdot CH_2X$ (II) ($X=COMe$ or CO_2Et) has been studied. In addition to the standard reagent, *N*-sodium ethoxide, the effect of other alkoxides on the ketones I, II has been examined; the order of efficiency is *isopropoxide* > *propoxide* > *ethoxide* > *methoxide* (> *hydroxide*) (cf. Ingold and Shoppee, this vol., 556), which is the sequence anticipated for an ionic mechanism of tautomeric change (Ingold, Shoppee, and Thorpe, A., 1926, 939). All these catalysts produce the same equilibrium mixture; the presence of water has little effect on the mobility of the ketones, but a considerable retarding influence in the case of the esters I, II owing to greatly increased hydrolysis. The mobility is best measured by the velocity of equilibration of the isomeride II, since there appears to be a small but definite equilibrium between the isomeride I, ethyl or methyl alcohol, and an ethoxy- or methoxy-additive compound; the methoxyl or ethoxyl group is provisionally assumed to occupy the β -position.

cyclohexylidenacetone (I; $X=COMe$), b. p. 83—84°/12 mm., $d_4^{25} 0.95188$, $n_D^{25} 1.49224$, and *cyclohexenylacetone* (II; $X=COMe$), b. p. 77°/11 mm., $d_4^{25} 0.93760$, 1.47389, both yield the same equilibrium mixture containing 30% of the former (cf. Dickens, HUGH, and KON, A., 1928, 887); the velocity coefficient $(k_1+k_2) \times 10^4$ is 700 min.⁻¹, with a half-change period of 9.9 min. Combined high fractions from the distillation of products obtained with sodium ethoxide as catalyst furnish by redistillation a constant-boiling fraction of b. p. 99—101°/9 mm., containing 70% of

1-ethoxycyclohexylacetone (*semicarbazone*, m. p. 174°); experiments with sodium methoxide similarly afford 1-methoxycyclohexylacetone (*semicarbazone*, m. p. 181—182°).

Ethyl *cyclohexylidenacetate* (I; $X=CO_2Et$) and ethyl *cyclohexenylacetate* (II; $X=CO_2Et$) yield by treatment with alcoholic sodium ethoxide the same equilibrium mixture, containing 57% of the latter (cf. Birch, KON, and NORRIS, J.C.S., 1923, 123, 1361; Linstead and May, A., 1927, 1167); the coefficient of the velocity of interconversion $(k_1+k_2) \times 10^4$ is 8.1 min.⁻¹, with a half-change period of 14.1 hrs. The combined fractions from the distillation of equilibrated products by redistillation afford a fraction, b. p. 128°/15 mm., which is ethyl 1-ethoxycyclohexylacetate, b. p. 122°/11 mm., 1.45753, $d_4^{25} 0.9865$, hydrolysed by potassium hydroxide to 1-ethoxycyclohexylacetic acid, m. p. 50—51° (*silver salt*, m. p. 216°).

C. W. SHOPPEE.

Isomerism of substituted aromatic phenacylamines. (Stereochemistry of the saturated tervalent nitrogen atom.) E. WEDEKIND and E. BRUCH (Annalen, 1929, 474, 73—112).—The existence of isomerism in various tertiary amines, with and without an asymmetric carbon atom in one of the groups, has been investigated. By the action of ethylene chlorohydrin on benzylethylamine or of ethyl iodide on benzyl- β -hydroxyethylamine the same *benzylethyl- β -hydroxyethylamine*, b. p. 134—136°/10 mm. (*methiodide*, m. p. 104°; *ethiodide*, m. p. 106°), is obtained. Similarly from *cyclohexylamine* by either method the same *cyclohexylethyl- β -hydroxyethylamine* (I), b. p. 119—120°/14 mm., 240—241°/750 mm., results, both specimens giving the same *methiodide*, m. p. 160—161° (Miss, DISS., Kiel, 1922, found one specimen, m. p. 172.5°) (*ethiodide*, m. p. 179—180°; *picrate*, m. p. 78—80°). Epi-iodohydrin reacts with I to yield *cyclohexylethyl- β -hydroxyethylglycidylammonium iodide*, $(C_6H_{11})(C_2H_4 \cdot OH)(CH_2 \cdot CH \cdot CH_2)NEtI$ m. p.

216—217°. Methylamine and *cyclohexylamine* react with epichlorohydrin to yield, respectively, $\alpha\gamma$ -di-(*phenylmethylamino*)- β -hydroxypropane, m. p. 82°, and $\alpha\gamma$ -di-(*cyclohexylamino*)- β -hydroxypropane, m. p. 72—73° (*dinitrosoamine*, m. p. 115—116°). By the action of ω -bromoacetophenone and anhydrous potassium hydroxide on γ -chloro- α -*p*-tolylamino- β -hydroxypropane (from *p*-toluidine and epichlorohydrin; COHN and FRIEDLANDER, A., 1904, i, 866) is obtained *p*-tolyl-phenacylglycidylamine (α -amine), m. p. 145°. The same amine is obtained by the action of epi-iodohydrin on *p*-tolylphenacylamine with anhydrous potassium hydroxide at 120—125°, but is accompanied in this case by the β -amine, m. p. 157°. That this isomerism is not dependent on the presence of an asymmetric carbon atom in one of the radicals attached to the tervalent nitrogen atom is shown by the reaction of ω -bromoacetophenone with *p*-tolylisobutylamine, b. p. 135°/19 mm. (from *p*-toluidine and isobutyl bromide), in the presence of anhydrous potassium hydroxide, which yields *p*-tolylphenacylisobutylamine (α -amine), m. p. 128° (colourless *oxime*, m. p. 97°). The same α -amine is obtained, together with a substance $C_{22}H_{19}O_2N$, m. p. 156°, by the action of *p*-tolylphenacylamine [*oxime*, m. p. 94°; *picrate*, m. p. 108—

109° (decomp.)] on *isobutyl iodide* in the presence of potassium carbonate, but when the latter is replaced by anhydrous potassium hydroxide, a β -amine, m. p. 67° (colourless *oxime*, m. p. 130—131°), is obtained together with *phenacylidene-p-toluidine*, $C_6H_4Me \cdot N : CH \cdot C(=O)Ph$, decomp. 215°. The nature of the isomerism is revealed by heating the α - and β -amines with acetic acid. The α -amine, in agreement with the structure assigned, is converted by loss of 1 mol. of water into 3(?)-phenyl-5-methyl-1-*isobutylindole*, m. p. 52°, whilst the β -amine suffers fission yielding acet-*p*-toluidide and is therefore a secondary amine, *phenyl α -(p-toluidino)isoamyl ketone*, $C_6H_4Me \cdot NH \cdot CHBu^s \cdot C(=O)Ph$, identical with the synthetic product obtained by the action of *p*-toluidine on *phenyl α -bromoisoamyl ketone*, b. p. 151—153°/12 mm. (by the Friedel-Crafts reaction from benzene and α -bromoisoheptyl bromide), together with a substance, m. p. 111—112°. Hence the β -isomeride is formed by alkylation of the *p*-tolylphenacylamine at the methylene group instead of the imino-group. Similarly *p-chlorophenylisobutylamine*, b. p. 135—136°/12 mm. (from *p*-chloroaniline and *isobutyl bromide*), condenses with ω -bromoacetophenone in the presence of concentrated potassium carbonate solution to yield *p-chlorophenylphenacylisobutylamine*, m. p. 109—110°, but by the action of *isobutyl iodide* on *p-chlorophenylphenacylamine* in the presence of potassium hydroxide the products are *phenyl α -p-chloroanilino-isoamyl ketone*, m. p. 80.5°, and a substance, decomp. 235—236°. The former suffers fission by heating with acetic acid, yielding acet-*p*-chloroanilide. When *p-chlorophenylphenacylamine* and *isobutyl iodide* are heated with an excess of potassium carbonate the product is *phenacylidene-p-chloroaniline*, m. p. 196°. By heating β -chloroethyl alcohol with methyl-aniline in a sealed tube, *NN'*-diphenylpiperazine is obtained.

J. W. BAKER.

Structure of metal ketyls. I. The Schmidlin formula. C. B. WOOSTER (J. Amer. Chem. Soc., 1929, 51, 1856—1860).—The formula, $R_2C:O \cdots M$, for the metallic ketyls, proposed by Schmidlin ("Das Triphenylmethyl," 1914, pp. 186—188) to indicate that all the reactions of these substances are preceded by dissociation into ketone and metal, is shown to be incorrect. Addition of ethyl bromide to monosodium-benzophenone in liquid ammonia gives no ethane (cf. A., 1928, 760), whereas sodium liberates the theoretical quantity of ethane from a mixture of ethyl bromide and benzophenone in this solvent, the benzophenone remaining unchanged. As an alternative to Schlenk's mechanism for the reactions of these derivatives (cf. A., 1911, i, 545; 1913, i, 1205), it is suggested that in presence of a substance capable of reacting with the very active disodio-derivative, the reaction, $R_2CNa \cdot ONa + R_2CO \longrightarrow 2R_2CONa$, may be completely reversible.

H. E. F. NOTTON.

Nitration of phenyl *p*-tolyl ketone and phenyl *m*-xyllyl ketone. L. CHARDONNENS (Helv. Chim. Acta, 1929, 12, 649—662).—3-Nitro-4-methyldiphenyl ketone is produced by the action of nitric acid (*d* 1.4) at 75—80° on 4-methyldiphenyl ketone. The same compound is obtained synthetically from 3-nitro-*p*-toluoyl chloride and benzene. Reduction

by iron and glacial acetic acid gives 3-amino-4-methyldiphenyl ketone, m. p. 107.5° (lit. 109°, 108—110°). Nitration of 4-methyldiphenyl ketone by mixed acid at -10° leads to the 3:3'-dinitro-derivative, m. p. 133.5—134° (lit. 135°) (also obtained by nitration of 3'- or 3-nitro-4-methyldiphenyl ketone), from which 3:3'-diamino-4-methyldiphenyl ketone, m. p. 130°, is derived by iron-hydrochloric acid reduction. More prolonged nitration by mixed acids gives 3:5:3'-trinitro-4-methyldiphenyl ketone, m. p. 171° (lit. 173°), also obtained by similar nitration either of 3'-nitro-4-methyldiphenyl ketone or of the condensation product of 3:5-dinitro-*p*-toluoyl chloride with benzene in the presence of aluminium chloride.

3:5-Dinitrobenzoyl chloride, toluene, and aluminium chloride afford 3':5'-dinitro-4-methyldiphenyl ketone, m. p. 135.5—136° (lit. 134°), which gives by long nitration by mixed acids 3:5:3':5'-tetranitro-4-methyldiphenyl ketone, m. p. 196—198°.

Nitration of 2:4-dimethyldiphenyl ketone by nitric acid, *d* 1.4, at 80° gives 5-nitro-2:4-dimethyldiphenyl ketone, m. p. 62—63° (also synthesised from 5-nitro-2:4-dimethylbenzoyl chloride, benzene, and aluminium chloride), accompanied by less 3-nitro-2:4-dimethyldiphenyl ketone, m. p. 79.5—80° (similarly synthesised from the analogous 3-nitrobenzoyl chloride). The corresponding 5- and 3-amino-2:4-dimethyldiphenyl ketones have m. p. 103.5—104° and 84°, respectively.

2:4-Dimethyldiphenyl ketone is nitrated by nitric acid, *d* 1.5, at -20° to give 5:3'-dinitro-2:4-dimethyldiphenyl ketone, m. p. 144.5°, identical with the product of similar nitration of either 3'- or 5-nitro-2:4-dimethyldiphenyl ketone, whilst with mixed acids it yields 3:5:3'-trinitro-2:4-dimethyldiphenyl ketone, m. p. 139—140°, also formed by nitration of 3'-nitro-2:4-dimethyldiphenyl ketone or of 3:5-dinitro-2:4-dimethyldiphenyl ketone, m. p. 111—112° (synthesised from 3:5-dinitro-2:4-dimethylbenzoyl chloride, benzene, and aluminium chloride).

3':5'-Dinitro-2:4-dimethyldiphenyl ketone, m. p. 110° (prepared from 3:5-dinitrobenzoyl chloride, *m*-xylene, and aluminium chloride), is nitrated by mixed acid at the ordinary temperature to 3:5:3':5'-tetranitro-2:4-dimethyldiphenyl ketone, m. p. 187—188°.

R. J. W. LE FEVRE.

Reactivity of positive hydrogen atoms. II. Dibenzyl ketone. W. DILTHEY and B. STALLMANN (Ber., 1929, 62, [B], 1603—1609; cf. A., 1927, 770).—The second methylene group of dibenzyl ketone is capable of reaction with aldehydes in presence of piperidine, but the normal diethylenic compounds are not in general obtained. The course of the change consists in the primary reaction of the aldehyde and piperidine to form the arylidenedipiperidine, $CHR(NC_5H_{10})_2$, which is converted by the ketone into piperidine and the piperidino-compound of the ethylenic compound $CHR(NC_5H_{10}) \cdot CHPh \cdot CO \cdot CH_2Ph$ (existing in two racemic forms by reason of the asymmetric carbon atoms); the adduct is transformed by acids into piperidine and the ethylenic compound. Benzaldehyde and dibenzyl ketone react in the presence of 1.25 mols. of piperidine in alcoholic solution at the ordinary temperature to give the two forms of γ -keto- α -piperidino- $\alpha\beta$ -triphenyl-*n*-butane, m. p. 147—148° and 121—122°, respectively; a

picrate of the mixture, m. p. indef. 132—138°, is described. The variety of m. p. 122° is also obtained from benzylidenedipiperidine and dibenzyl ketone in alcohol. The adducts are transformed by warm acids into benzylidenedibenzyl ketone. Similarly anisaldehyde affords the two γ -keto- α -piperidino- $\beta\delta$ -diphenyl- α -p-methoxyphenyl-*n*-butanes, m. p. 126° and 156°, respectively; a *picrate*, m. p. 147—148°, is described. Attempts to resolve the isomeride of m. p. 126° by bromocamphorsulphonic or tartaric acid were unsuccessful. The adducts are converted by acids into anisylidenedibenzyl ketone, m. p. 101—102°. Piperonal gives a *mixture*, m. p. 135—150°, of the isomeric γ -keto- α -piperidino- $\beta\delta$ -diphenyl- α -3 : 4-methylenedioxyphenyl-*n*-butanes from which piperonylidenedibenzyl ketone, m. p. 122—123°, is derived. The mixture of γ -keto- α -piperidino- $\beta\delta$ -diphenyl- α -4'-dimethylaminophenyl-*n*-butanes, m. p. 143—155°, is converted into *p*-dimethylaminobenzylidenedibenzyl ketone, m. p. 110°. Dibenzyl ketone gives piperidino-adducts with the three nitrobenzaldehydes or their dipiperidino-derivatives, but the yields are smaller, probably by reason of the greater stability of the arylidenepiperidines. Salicylaldehyde, nitro- or bromo-salicylaldehyde, and hydroxynaphthaldehyde do not afford solid piperidino-intermediates, but give chromones by loss of water involving the second methylene group. Cinnamaldehyde gives the two forms of triphenylcyclohexanone. Piperonylidenedipiperidine, m. p. 69—71°, *p*-nitrobenzylidenedipiperidine, m. p. 86—88°, and *m*-nitrobenzylidenedipiperidine, m. p. 93—95°, are described. *o*-Nitrobenzaldehyde gives an unstable compound, m. p. 73—75°.

H. WREN.

Reactivity of positive hydrogen atoms. III. Catalytic reactions. W. DILTHEY (Ber., 1929, 62, [B], 1609—1612; cf. preceding abstract).—Since the reaction between benzaldehyde, dibenzyl ketone, and piperidine proceeds in three distinct stages with isolable intermediate products, the action of the secondary base is not regarded as catalytic. The extent to which other bases can be considered to act catalytically in the Knoevenagel reaction is discussed.

H. WREN.

Steric hindrance in Hoesch reaction. I. ORTIO (Sci. Rep. Tôhoku, 1929, 18, 121—128).—*m*-Chlorobenzonitrile condenses with resorcinol in presence of ethereal hydrogen chloride and zinc chloride yielding 3'-chloro-2 : 4-dihydroxybenzophenone (52% yield), m. p. 197—197.5°, and with phloroglucinol giving 3'-chloro-2 : 4 : 6-trihydroxybenzophenone (39%), m. p. 169.5—170° after shrinking at about 110°. Similarly, *p*-chlorobenzonitrile and resorcinol or phloroglucinol afford 4'-chloro-2 : 4-dihydroxybenzophenone (67%), m. p. 151—152°, or 4'-chloro-2 : 4 : 6-trihydroxybenzophenone (43%), m. p. 169—169.5° (trimethyl ether, m. p. 175°), respectively. Whilst *o*-chlorobenzonitrile and *o*-toluonitrile do not undergo the Hoesch reaction, *o*-chlorophenylacetonitrile condenses with the above phenols yielding 18 and 13% of 2 : 4-dihydroxyphenyl 2-chlorobenzyl ketone, m. p. 142° (oxime, m. p. 225—226°), and 2 : 4 : 6-trihydroxyphenyl 2-chlorobenzyl ketone (+H₂O), m. p. (anhydrous) 172—172.5°, respectively. The steric hindrance effect of an *ortho* substituent is partly sur-

mounted by interposing a methylene group between the benzene nucleus and the cyano-group. The above ketones give the Dimroth reaction (A., 1926, 297) with boroacetic anhydride. H. BURTON.

Application of the Hoesch reaction to nitrobenzonitriles. M. YAMASHITA (Sci. Rep. Tôhoku, 1929, 18, 129—133).—See A., 1928, 1136.

Unusual instance of "pinacolin" transformation. H. KLEINFELLER and F. ECKERT (Ber., 1929, 62, [B], 1598—1600).—Benzil is converted by dimagnesium acetylenyl bromide into $\alpha\zeta$ -diketo- $\alpha\beta\zeta$ -tetraphenylhexinene- $\beta\zeta$ -diol, m. p. 154°, transformed by boiling aqueous sodium hydroxide into benzoic acid and $\alpha\delta$ -diphenyl- Δ^{β} -butinene- $\alpha\delta$ -diol, m. p. 145° (cf. Dupont, A., 1910, i, 379), and by boiling alcoholic hydrogen chloride into $\alpha\beta\zeta$ -tetraphenyl- Δ^{γ} -hexinene- $\alpha\zeta$ -trione, m. p. 213° (trioxime, m. p. 237°).

H. WREN.

Tautomerism of α -diketones. H. MOUREU (Compt. rend., 1929, 188, 1413—1416).—By determination of the refractive indices it is shown that, at various temperatures, the same position of equilibrium between the A and B forms of methyl- and phenyl-benzylglyoxals (this vol., 449) is reached starting with either pure form. An equilibrium mixture of the former diketone at 70° contains approximately 70% of the A form, whilst one of the latter at 100° contains more than 70% of the B form.

J. W. BAKER.

Perylene and its derivatives. XXIV. A. PONGRATZ (Monatsh., 1929, 52, 7—12).—Treatment of perylene-3 : 9-dicarboxylic acid (A., 1927, 1190) with thionyl chloride at 100°, or with phosphorus pentachloride in nitrobenzene at 150°, affords the corresponding *chloride*, dark red, which condenses with benzene in presence of aluminium chloride yielding 3 : 9-dibenzoylperylene, m. p. 291—292°. With toluene a *ditoluoylperylene*, m. p. 309—310°, is obtained: this is not identical with the di-*o*-toluoyl derivative previously described (*loc. cit.*). When 3 : 9-dinaphthoylperylene, m. p. 321—322° (from naphthalene and the acid chloride in presence of carbon disulphide and aluminium chloride), is treated with manganese dioxide in sulphuric acid solution a dibenzisoviolanthrone is probably formed (cf. A., 1928, 177).

H. BURTON.

Characteristic colour reaction of quinones and the atomic grouping CH₂(C:E)₂ (E=multivalent element). W. KESTING (Ber., 1929, 62, [B], 1422—1424; cf. A., 1928, 1015).—If alcoholic solutions of *p*-benzoquinone, α - or β -naphthaquinone are mixed with similar solutions of substances containing the group named above and ammonia or alkali is cautiously added, an intense blue colour is developed. The reaction is shown by malononitrile, ethyl cyanoacetate, malonate, acetoacetate, and benzoylacetate, cyanoacetamide, acetylacetone, and benzoylacetone, but not by fluorene, diphenylmethane, indene, or phloroglucinol, in which the group forms part of a ring. Anthraquinone and its derivatives, phenanthraquinone, and anthradiquinone do not react. The solvent must be able to function as a base or, if indifferent, must be treated with a sufficient amount of basic substance.

H. WREN.

Anthraquinol-1 : 5-dicarboxydilactone. R. SCHOLL and L. WANKA [with H. HAHLE and W. LEONHARDT] (Ber., 1929, 62, [B], 1424—1433; cf. this vol., 567).—Anthraquinol-1 : 5-dicarboxydilactone is most conveniently prepared by the action of sulphuric acid and copper powder at the ordinary temperature on anthraquinone-1 : 5-dicarboxylic acid; short treatment affords the monolactonecarboxylic acid. 1 : 5-Diacetamidoanthraquinone, suspended in acetic acid containing acetic anhydride and sodium acetate, is converted by chlorine at 80° in absence of direct sunlight into 4 : 8-dichloro-1 : 5-diacetamidoanthraquinone, not molten below 300°, hydrolysed by concentrated sulphuric acid to 4 : 8-dichloro-1 : 5-diaminoanthraquinone, m. p. 305° (sulphate). The diamine is converted through the diazonium sulphate and 4 : 8-dichloro-1 : 5-dicyanoanthraquinone, not molten below 300°, into 4 : 8-dichloroanthraquinone-1 : 5-dicarboxylic acid, decomp. about 250° (ethyl ester, m. p. 154°). The acid is transformed by copper powder and sulphuric acid into 4 : 8-dichloroanthraquinol-1 : 5-dicarboxydilactone, which behaves towards alcohol and sodium hydroxide in the same manner as the unsubstituted dilactone. The dichloro-acid is transformed by potassium phenoxide at 140—150° into 4 : 8-diphenoxyanthraquinone-1 : 5-dicarboxylic acid, incipient decomp. about 273° (potassium salt; corresponding chloride; 4 : 8-di-p-nitrophenoxyanthraquinone-1 : 5-dicarboxylic acid, decomp. 325—326° after darkening); it is reduced by zinc dust and ammonia to 4 : 8-diphenoxyanthracene-1 : 5-dicarboxylic acid, m. p. 344—345° (pyridinium salt; sulphonic acid). 4 : 8-Diphenoxyanthraquinol-1 : 5-dicarboxydilactone is described. 4 : 8-Di-p-toloxyanthraquinone-1 : 5-dicarboxylic acid darkens at 280° and blackens at 317°. The 4 : 8-dichloro-acid, thiophenol, and potassium hydroxide in boiling aqueous solution afford 4 : 8-diphenylthiolanthraquinone-1 : 5-dicarboxylic acid, m. p. about 312° (decomp.), from which 4 : 8-diphenylthiolanthraquinol-1 : 5-dicarboxydilactone is derived. 4 : 8-Di-p-tolylthiolanthraquinone-1 : 5-dicarboxylic acid, m. p. 308°, decomp. 310° (potassium salt), and the corresponding dilactone are described. 4 : 8-Dichloroanthraquinone-1 : 5-dicarboxylic acid loses carbon dioxide when heated with aniline, whereas its ethyl ester affords ethyl 4 : 8-dianilinoanthraquinone-1 : 5-dicarboxylate, slowly hydrolysed to 4 : 8-dianilinoanthraquinone-1 : 5-dicarboxylic acid, m. p. 320° (decomp.) [potassium salt], which yields 4 : 8-dianilinoanthraquinol-1 : 5-dicarboxydilactone, m. p. 348° after softening; sodium 4 : 8-dianilinoanthraquinol-1 : 5-dicarboxylate is described. Ethyl 4 : 8-di-p-toluidinoanthraquinone-1 : 5-dicarboxylate, m. p. 248°, the corresponding dicarboxylic acid, m. p. 312—313° (decomp.), and 4 : 8-di-p-toluidinoanthraquinol-1 : 5-dicarboxydilactone have been prepared. H. WREN.

Dyes of the anthraquinone series. K. WEINLAND, Assr. to GRASELLI DYESTUFF CORP.—See B., 1929, 512.

1 : 2-Phenanthraquinone. L. F. FIESER (J. Amer. Chem. Soc., 1929, 51, 1896—1906).—Reduction with sodium sulphite of the azo-dye from *p*-sulphobenzenediazonium chloride and 2-phenanthrol gives 1-amino-2-phenanthrol, darkening from 210° (hydro-

chloride, decomp. 250°), from which 1-acetamido-2-phenanthrol, m. p. 295° (all m. p. uncorr.), its acetate, m. p. 222°, and 1-diacetamido-2-phenanthryl acetate, m. p. 125°, are prepared. The last two are converted by distillation at 3 mm. into 2-methyl-4 : 5-(1 : 2-phenanthro)oxazole, m. p. 120°. The hydroxyamine is oxidised by chromic acid to brilliant red 1 : 2-phenanthraquinone, m. p. 216° (decomp.), softening at 195°. This is reduced by sodium hyposulphite to 1 : 2-dihydroxyphenanthrene, m. p. 178°, the dimethyl ether, m. p. 102°, of which is not identical with 2 : 3-dimethoxyphenanthrene (Pechorr, A., 1900, i, 489). 1 : 2 : 4-Triacetoxypheanthrene, m. p. 186°, obtained in poor yield from the quinone, acetic anhydride, and sulphuric acid, is converted by hydrolysis with sodium hydroxide in an atmosphere of nitrogen and aeration of the cold solution into the red sodium salt of 2-hydroxy-1 : 4-phenanthraquinone, m. p. 188° (methyl ether, m. p. 172.5°). The silver salt of this quinone gives with allyl bromide in benzene 4-allyloxy-1 : 2-phenanthraquinone, m. p. 128°, and 2-hydroxy-3-allyl-1 : 4-phenanthraquinone, m. p. 157°. 2-Hydroxy-1 : 4-phenanthraquinone is converted by boiling aqueous sodium hydroxide into 1-acetyl-2-naphthylglyoxylic acid, m. p. 181° (decomp.) (methyl ester, m. p. 112°), which gives the same oxidation products in acid and alkaline solutions as does 2-acetyl-1-naphthylglyoxylic acid (this vol., 567). 1 : 2-Phenanthraquinone is converted by sodium hydrogen sulphite into 1 : 2-dihydroxyphenanthrene and sodium 1 : 2-dihydroxyphenanthrene-4-sulphonate (corresponding potassium and *p*-toluidine, m. p. 240°, salts), oxidised by chromic and sulphuric acids to sodium 1 : 2-phenanthraquinone-4-sulphonate. With *p*-toluidine hydrochloride in aqueous solution this gives the corresponding *p*-toluidine salt, but with *p*-toluidine itself or sodium hydroxide it undergoes disproportionation, 2 mols. giving 1 : 2-dihydroxyphenanthrene-4-sulphonate (1 mol.) and an unknown oxidation product. The sulphonic radical in the quinone-sulphonate is, thus, attached more firmly than it is in most compounds of this type, since no 4-*p*-toluidinophenanthraquinone is formed.

H. E. F. NOTTON.

Phenanthraquinones related to alizarin and purpurin. L. F. FIESER (J. Amer. Chem. Soc., 1929, 51, 1935—1942).—1 : 2-Phenanthraquinone (preceding abstract), zinc dust, and sodium acetate in boiling acetic anhydride give 1 : 2-diacetoxypheanthrene, m. p. 146—147°, which is oxidised by chromic and acetic acids to 1 : 2-diacetoxy-9 : 10-phenanthraquinone, m. p. 257° (corr.), hydrolysed by alcoholic sodium hydroxide to dark red 1 : 2-dihydroxy-9 : 10-phenanthraquinone (green chromium and aluminium lakes). 1 : 2 : 4-Triacetoxypheanthrene is oxidised by chromic and acetic acids at 40° to 1 : 2 : 4-triacetoxy-9 : 10-phenanthraquinone, m. p. 227—228° (decomp.), which is hydrolysed in an inert atmosphere to the green sodium salt of dark red 1 : 2 : 4-trihydroxy-9 : 10-phenanthraquinone (also + EtOH). Reductive acetylation of 3-hydroxy-1 : 4-phenanthraquinone (this vol., 567) gives 1 : 3 : 4-triacetoxypheanthrene, m. p. 138°, from which dark red 1 : 3 : 4-triacetoxy-9 : 10-phenanthraquinone, decomp. 240°, softening from 220°, and 1 : 3 : 4-tri-

hydroxy-9:10-phenanthraquinone are prepared. The colour reactions and dyeing properties of the new hydroxyphenanthraquinones are compared with those of related anthraquinone and phenanthraquinone derivatives. They do not assume tautomeric forms, since they are reconvertible into the original acetates. 4-Amino-3-phenanthrol and acetic anhydride in pyridine give 4-acetamido-3-phenanthryl acetate, m. p. 211°, which gives when distilled at 3 mm. 2-methyl-4:5-(4:3-phenanthro)oxazole, m. p. 155°, oxidised by chromic acid to the corresponding 9:10-phenanthraquinone derivative, m. p. 282°. 4-Diacetamido-3-phenanthryl acetate (Werner, A., 1902, i, 437) is oxidised to the 9:10-quinone, m. p. 207°, hydrolysed by sodium hydroxide in aqueous alcohol in absence of air to 4-diacetamido-3-hydroxy-9:10-phenanthraquinone, decomp. 255—260°. Further hydrolysis is accompanied by complete decomposition and the desired 4-amino-3-hydroxyphenanthraquinone is not obtained.

H. E. F. NOTTON.

Perylene and its derivatives. XXV. A. ZINKE and W. HIRSCH [with H. KOLMAYR] (Monatsh., 1929, 52, 13—22).—Treatment of 3:4:9:10-tetrachloro-*perylene* (Zinke, Pongratz, and Funke, A., 1925, i, 384) with concentrated sulphuric acid at 150° in a current of carbon dioxide yields perylene-3:4:9:10-diquinone (I) (this vol., 568). Similar treatment of 3:9-dichloro-4:10-diacetyl- or 3:9-dichloro-4:10-dibenzoyl-*perylene* at 120—130° affords perylene-3:9-quinone (II), the acyl group being eliminated as the corresponding acid. Reduction of II with alkaline sodium hyposulphite and subsequent treatment with the appropriate aryl chloride gives the dibenzoate, m. p. 312—314°, and di-*p*-bromobenzoate, m. p. 359—360°, of 3:9-dihydroxyperylene (cf. A., 1926, 71). 3:9-Dichloroperylene is oxidised by sulphuric acid at 140—150° to II, in turn partly oxidised at 180° to I. The oxidation product of hexachloroperylene could not be obtained crystalline. The compound (C₂₀H₁₀O₂)₂·H₂O, previously described (A., 1926, 71), should be deleted from the literature, as it is essentially II.

H. BURTON.

Bixin. I. J. RINKES (Rec. trav. chim., 1929, 48, 603—606).—The degradation product, C₈H₁₀O₃, of methylbixin, considered to be methyl 1-formyl-2- or -3-methyl-1:3-pentadienecarboxylate, by oxidation with silver oxide gives methyl hydrogen β-methylmuconate, m. p. 121°, which depresses the m. p. of methyl hydrogen *cis-cis*-β-methyl muconate (m. p. 129°) of Pauly and Will (A., 1918, i, 525), who give m. p. 125°. Subsequent hydrolysis of the ester, m. p. 121°, with 10% alkali affords *trans*-β-methylmuconic acid, m. p. 229°, also obtained by heating *cis-cis*-methylmuconic acid with concentrated sodium hydroxide (cf. *loc. cit.*).

The following attempt to synthesise methylsuccinaldehyde was unsuccessful: the semilactone of β-methylmuconic acid was converted into β-methylmucondiamide, m. p. 218°, by the method of Pauly and Will (*loc. cit.*); treatment of the latter with sodium hypochlorite furnished *isoprenediurethane*, m. p. 160—161°, which by treatment with 5% sulphuric acid yielded, not the foregoing aldehyde, but methyl 2-methylpyrrole-*N*-carboxylate, b. p. 80°/20 mm.,

converted by hot 10% potassium hydroxide and subsequent acidification into 2-methylpyrrole, b. p. 142—150°.

C. W. SHOPPEE.

Camphorophorone. I. Action of hydroxylamine. G. SANNA (Gazzetta, 1929, 59, 232—243).—Accounts of the action of hydroxylamine on camphorophorone are discordant (cf. Koenigs and Eppens, A., 1892, 626; 1893, i, 361; Kerp and Müller, A., 1898, i, 265; Harries and Maftus, A., 1899, i, 629; Wallach, A., 1904, i, 752). In agreement with Harries, the action of hydroxylamine hydrochloride and sodium hydrogen carbonate in a boiling mixture of ether and alcohol is found to give dihydrocamphorophoronyl-hydroxylamine(I), $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{CHMe}-\text{CO} \end{array} > \text{CH} \cdot \text{CMe}_2 \cdot \text{NH} \cdot \text{OH}$, m. p.

120°, of which an oxalate, m. p. 154°, a semicarbazone, m. p. 190°, and, by the action of concentrated nitric acid, a nitro-derivative, m. p. 50°, are prepared. When the above substances act, however, in boiling aqueous alcohol, a true camphorophoroneoxime (II), m. p. 95°, is obtained. Further, when the ketone is heated in methyl alcohol with free hydroxylamine and sodium methoxide, the products are dihydrocamphorophoronehydroxylamineoxime, (III), m. p. 160°, and a camphorophoroneoxime, m. p. 115° (IV), isomeric with II and with the oxime of m. p. 80—82° (cf. Kerp, *loc. cit.*). The compound III is readily oxidised in alcoholic solution, giving a blue nitroso-compound. It furnishes a benzylidene derivative, m. p. 145°, and a benzoyl derivative, m. p. 160—168° (decomp.); when it is kept in ethereal solution over sulphuric acid, it is converted into yet another camphorophoroneoxime, m. p. 40° (V.) When III is reduced by sodium and alcohol, it gives the diamino-derivative, 2-amino-3-α-aminoisopropyl-2-methylcyclopentane, of which the hydrochloride when distilled loses ammonia to form a substance, probably $\text{CH}_2 < \begin{array}{c} \text{CH} \\ | \\ \text{CHMe}-\text{CH} \cdot \text{NH} \end{array} \text{CMe}_2$. It was

hoped that suitable treatment of III might lead to an isocamphorophorone, but the action of acids gave a mixture of products, including 6-methyl-3-isopropylidene-2-piperidone. The structures of the camphorophoroneoximes are discussed.

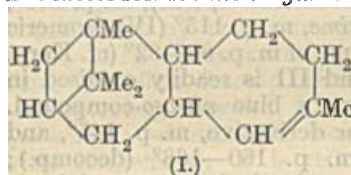
E. W. WIGNALL.

Mono- and sesqui-terpenes. X. Active caryophyllene. E. DEUSSEN and P. HACKER (J. pr. Chem., 1929, [ii], 122, 261—283).—Distillation in steam of the crude ozonide obtained by ozonolysis of γ-caryophyllene in chloroform solution gave (1) in the distillate: formic acid and an oil (semicarbazone, m. p. 207°), separable by fractionation into two constituents of b. p. 85—90°/11 mm. (semicarbazone, m. p. 170°) and 140—145°/11 mm. (semicarbazone, m. p. 210°); and (2) in the non-volatile residue: a yellow oil [semicarbazone, m. p. 120°; thiosemicarbazone, m. p. 165° (decomp.)]. Oxidation of the last compound by 27% nitric acid at 90° afforded succinic acid and caryophyllenic acid, α¹³ + 5·40° (10% in ethyl acetate) (silver and potassium salts), which was converted into isovaleric and acetic acids by alkali fusion and into dibromocaryophyllenic acid, C₉H₁₂O₄Br, by bromination with phosphorus pentachloride and bromine in a sealed tube.

R. J. W. LE FEVRE.

Caryophyllene series. II. Clovene and isoclovene. G. G. HENDERSON, R. O. O. McCONE,

and J. M. ROBERTSON (J.C.S., 1929, 1368—1372; cf. A., 1926, 298).—Dehydration of caryophyllene alcohol with anhydrous oxalic acid yields clovene, b. p. 111—113°/10 mm., d_4^{20} 0.924, n_D^{20} 1.4980, identical with that obtained by the use of phosphoric oxide. The liquid hydrocarbon, b. p. 110—114°/9 mm., d_4^{20} 0.926, 1.5010, obtained as a by-product in the hydration of caryophyllene by Wallach and Walker's method (A., 1893, i, 101), and also the sesquiterpene, b. p. 110—114°/10 mm., d_4^{20} 0.933, n_D^{20} 1.5020, obtained by heating caryophyllene dihydrochloride with quinoline, are probably identical with clovene. Clovene is attacked by potassium permanganate, but no definite oxidation products have been isolated; it gives neither eudalene nor cadalene when heated with sulphur and therefore belongs neither to the eudesmene nor to the cadinene group of sesquiterpenes. By dehydrating caryophyllene alcohol, prepared from caryophyllene and sulphuric acid monohydrate in the presence of dry ether at 0°, by a modification of Wallach and Walker's method (*loc. cit.*), clovene and isoclovene, $C_{15}H_{24}$, b. p. 130—131°/12 mm., d_4^{20} 0.943, 1.5039, $[\alpha]_D^{20}$ -53.6° in alcohol, were obtained. The latter forms a *monohydrochloride*, m. p. 87°, a *monohydrobromide*, m. p. 75° (from which the hydrocarbon may be regenerated), and an unstable *dibromide*, and is more unstable than clovene. *isoclovene* is completely decomposed by heating to its b. p. with phosphoric oxide. When a solution of *isoclovene hydrochloride* in glacial acetic acid is treated with silver acetate, the *acetate of isoclovene alcohol*, m. p. 25—26°, is obtained, which is converted by methylalcoholic potassium hydroxide into *isoclovene alcohol*, m. p. 98°, $[\alpha]_D^{20}$ +227° in alcohol. Formula I is assigned to clovene (cf. Semmler and Mayer, A., 1911, i, 73; Deussen, A., 1926, 1252).



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A. I. VOGEL.

Higher terpene compounds. XXXVIII.

Amyrins and lupeol. L. RŮŽICKA, H. W. HUYSER, M. PREIFFER, and C. F. SEIDEL (Annalen, 1929, 471, 21—39).—The conflicting evidence concerning the saturated or unsaturated character of α - and β -amyrin is discussed. Catalytic reduction of the amyryns fails even with hydrogen at 280°/80 atm. with platinum-black or with a platinum oxide catalyst, the original substance being recovered unchanged. With ozone in carbon tetrachloride solution either α - or β -amyrin takes up 5 mols. of ozone to yield an *ozonide*, decomp. about 100°, which was unchanged in composition after keeping for 4 years. On the other hand, with perbenzoic acid it takes up only 0.5 atom of oxygen, behaving like the saturated tetrahydroabietic acid with which it was compared. The molecular refractivity of α -, b. p. 235°/0.1 mm., d_4^{25} 0.9857, n_D^{25} 1.5420, and β -, b. p. 235°/0.1 mm., d_4^{25} 0.9807, 1.5409, -amyrylene, obtained by the action of phosphorus pentachloride and alkali on the parent alcohols, indicates the presence of three double linkings, thus pointing to the presence of two double linkings in the original amyryns. Moreover, the latter readily give a yellow colour with tetranitromethane, a reaction which

is never known to occur with a saturated compound, although some unsaturated compounds fail to give this test. The isomeric alcohol lupeol also gives the yellow colour with tetranitromethane, but is readily reduced with hydrogen on a platinum oxide catalyst in acetic acid at 60—70° to *dihydrolupeol*, m. p. 201—202°, $[\alpha]_D^{20}$ -17.5°, which fails to give the colour test. Thermal decomposition of the mixed amyryns at 440—460° in a current of carbon dioxide yields a liquid distillate from which a *hydrocarbon*, $C_{15}H_{26}$ (?), b. p. 115—125°/15 mm., d_4^{16} 0.924, n_D^{16} 1.500, is isolated. This by catalytic dehydrogenation with selenium yields the same *trimethylnaphthalene*, b. p. 147—148°/16 mm., d_4^{25} 1.008, n_D^{25} 1.6093 (*picrate*, m. p. 127—128°; *styphnate*, m. p. 153—154°), as is obtained by direct dehydrogenation of amyryl itself, and which is possibly identical with the product obtained by Brunner (this vol., 71). When oxidised with potassium ferricyanide this naphthalene derivative gives a *naphthalenetri-carboxylic acid*, which is not readily purified, but affords (silver salt method) crystalline *methyl*, m. p. 153—154°, and *ethyl*, m. p. 80—81°, esters.

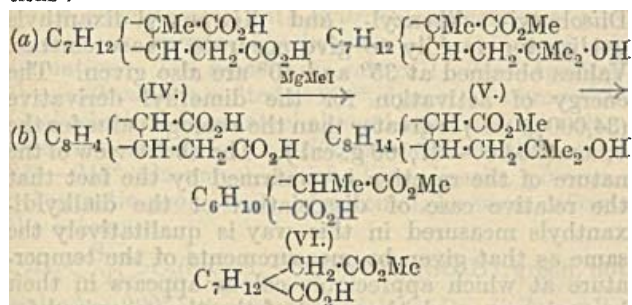
J. W. BAKER.

Higher terpene compounds. XXXIX.

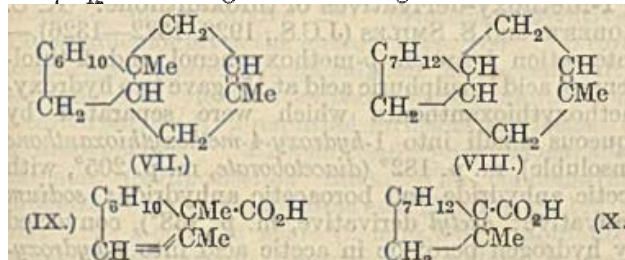
Cedrene. L. RŮŽICKA and J. A. VAN MELSEN (Annalen, 1929, 471, 40—72).—Cedrene (from cedarwood oil) yields a dibromide (I) which is converted by boiling potassium hydroxide partly into the original cedrene and partly into a mixture, b. p. 155—160°/12 mm., of bromocedrene (II) and hydroxyisocedrene (III). The bromocedrene is stable to alkalis, but is reduced to cedrene by sodium and alcohol, the relationships being represented thus: $C_{12}H_{20} \left\{ \begin{array}{l} -CHBr \\ -CMe \end{array} \right.$

(I) $\longrightarrow \left\{ \begin{array}{l} -CHBr \\ -CMe \end{array} \right.$ (II) + $\left\{ \begin{array}{l} -CH.OH \\ -CMe \end{array} \right.$ (III). Oxidation of cedrene with chromic and acetic acids yields cedrone (40%) and cedrenketone-acid (10%), which is further oxidised to cedrenedicarboxylic acid, both acids being identical with those obtained by ozonolysis of cedrene (Semmler and Spornitz, A., 1912, i, 573). Ozonolysis of cedrone or oxidation of the ozonide with chromic and acetic acids yields *norcedrenketone-acid*, b. p. 174—175°/0.4 mm., m. p. 113—114° (*semicarbazone*, m. p. 242—244°), oxidised by sodium hypobromite to *norcedrenedicarboxylic acid* (IVa or b), m. p. 209°. Whereas in cedrenedicarboxylic acid both carboxyl groups are similar and both react in the following series of reactions, in *norcedrenedicarboxylic acid* they are differently bound in the molecule, one being unreactive. Thus esterification of IV with methyl alcohol and sulphuric acid yields only a *methyl hydrogen ester*, m. p. 97°, and only one ester group in the *dimethyl ester*, b. p. 157°/0.4 mm. (prepared from the *silver salt*), is hydrolysed by 0.1N-alcoholic potassium hydroxide. Bromination of IV with phosphorus tribromide and bromine yields only a *monobromo-acid*, m. p. 213—214°, which is converted by 10% sodium hydroxide or dilute hydrochloric acid into an unsaturated acid, $C_{11}H_{18}O_2$ (IX or X), m. p. 90—91°, d_4^{20} 0.9781, n_D^{20} 1.4637 (crystallographic data by NANNENGA) (*ethyl ester*, b. p. 90°/0.5 mm.). Magnesium methyl bromide reacts with only one ester group in methyl *norcedrenedicarboxylate* to yield an *ester carbinol* (Va or b), $C_{16}H_{28}O_3$, b. p. 135°/0.4 mm.,

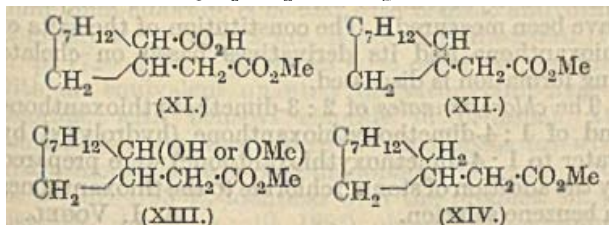
in which the ester group is resistant to hydrolysis; this is converted by oxidation with chromic and acetic acids into a *hydrogen ester* (VIa or b), C_1 (not pure, 11.3% OMe instead of 14.5%), in which the ester group is now readily hydrolysed, and which is converted through its *silver* salt into the *dimethyl ester*, b. p. 165—170°/12 mm., d_4^{25} 1.107, n_D^{25} 1.4750, of an acid, $C_{10}H_{16}O_4$, which could not be obtained crystalline and for which the name cedrocampaic acid is suggested. On the basis of these results the ring containing the double linking in cedrene cannot be higher than six-membered, and these reactions may be represented on the basis of two alternative partial formulæ for norcedrenedicarboxylic acid thus:—



Cedrene must be represented by either VII or VIII, neither Semmler's (A., 1915, i, 427) nor Deussen's (A., 1928, 70) formulæ being admissible, the group C_6H_{10} or C_7H_{12} containing the third ring of cedrene which,



if the second ring is six-membered, can only be a three- or four-membered ring. Ozonolysis of the unsaturated acid IX or X yields a monocarboxylic acid $C_{12}H_{18}O_5$, m. p. 166—167°, a substance, m. p. 187—189°, and liquid products, oxidation of which has led to no definite results. Catalytic reduction of IX or X (the dimethyl ester of which yields a *diphenylcarbinol*, m. p. 82—83°, with magnesium phenyl bromide) in presence of platinum oxide gives a *dihydro-acid*, b. p. 121°/0.5 mm., m. p. 61—62° (the ester of which does not react with magnesium phenyl bromide), the *ethylamide*, b. p. 122—124°/high vacuum, of which is converted by phosphorus pentachloride into a



chlorine-free *nitrile*. Electrolysis of methyl hydrogen norcedrenedicarboxylate (XI) gives a mixture of an

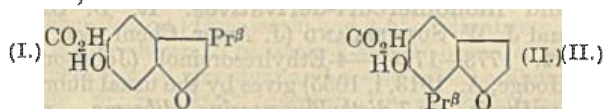
unsaturated ester (XII), $C_{13}H_{20}O_2$, and the corresponding saturated hydroxy- and methoxy-esters (XIII), from which after heating with alcoholic potassium hydroxide, hydrolysis with hydrogen iodide, and ozonolysis of the product to destroy the unsaturated acid, is obtained a saturated acid (XIV) $C_{12}H_{20}O_2$, m. p. 61—62°, which, however, depresses the m. p. of the isomeric dihydro-acid (above). J. W. BAKER.

Photo-bromination of coumarin. D. M. WILLIAMS.—See this vol., 895.

Rotenone, the active principle of Derris root. III. Molecular formula of rotenone. S. TAKEI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 369—371; see A., 1928, 765).—Rotenone and isorotenone are considered to be *cis-trans* ethylenic isomerides.

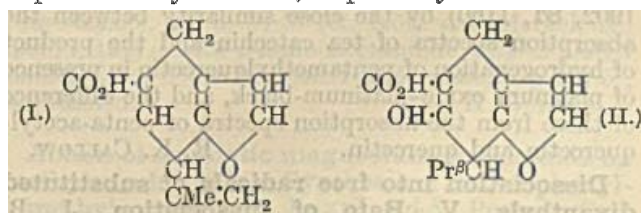
E. W. WIGNALL.

Rotenone, the active constituent of Derris root. IV. Rotenic acid. S. TAKEI and S. MIYAJIMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 510—518; see preceding abstract).—Consideration of the reactions of rotenic acid suggest two possible formulæ (I or II).



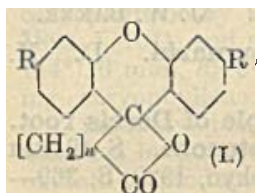
By the action of magnesium isopropyl bromide on 5-methoxycoumaran-2-one, 5-methoxy-2-hydroxyisopropylcoumaran, m. p. 70°, was obtained, and from this 5-methoxy-2-isopropylcoumarone, which formed a resin, m. p. about 150°. This product should be identical with rotenol monomethyl ether (A., 1928, 765) if I were the formula for rotenic acid. As the two substances differ widely, II is more probably the formula. B. W. ANDERSON.

Rotenone, the active constituent of Derris root. V. Tubaic acid. S. TAKEI and M. KOIDA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 519—524; cf. preceding abstract, also A., 1928, 1017).—Tubaic acid and dihydrotubaic acid, unlike rotenic acid, are optically active, having $[\alpha]_D^{25}$ —76.0° and $[\alpha]_D^{25}$ —82.2°, respectively. Both acids are easily converted into their respective phenols, *tubanol* and *dihydrotubanol*. *Tubanol methyl ether* is oxidised by ozone to a sweet-smelling oil which reduces Fehling's solution, gives the iodoform reaction, and forms a *p-nitrophenylhydrazone*, m. p. 156°. The oil therefore contains the group $\cdot CMe$; on further oxidation with iodine and potassium hydroxide it forms a methoxy-carboxylic acid, $C_{10}H_{16}O_4$, m. p. 140°. The ethylene linking in tubaic acid is thus probably in a 2-allyl group, and this acid and dihydrotubaic acid may be represented by I and II, respectively.



Fusion with alkali converts tubaic acid into its more stable isomeride, rotenic acid. B. W. ANDERSON.

Colour on the basis of molecular strain. VII. Effect of polymembered ring formation. A. N. DEY and S. DUTT (J. Indian Chem. Soc., 1929, 6, 289—293).—Condensation of adipic acid with resorcinol in presence of sulphuric acid at 170—180° affords the *fluorescein* (I) ($R=OH$, $n=4$), m. p. above 286°, whilst with *m*-diethylaminophenol at 120—



130°, the *rhodamine* (I) ($R=NEt_2$, $n=4$), sinters at 168°, is obtained. The corresponding *fluoresceins* from pimelic, m. p. 164°, suberic, m. p. 140°, azelaic, m. p. 172°, and sebacic acids, sinters at 166°, and the *rhodamines* from suberic, m. p. 147°, azelaic, m. p. 126°, and sebacic acids, m. p. 142°, are obtained similarly. The intensity of the colour of these dyes in solution is inversely proportional to the stability of the ring systems of the anhydrides of the acids used (cf. Dutt and Thorpe, A., 1925, i, 141; Dutt, A., 1926, 830; 1927, 1006). H. BURTON.

Diethyl- and dihexyl-fluoresceins; dibromo- and monomercuri-derivatives. R. B. SANDIN and J. W. SUTHERLAND (J. Amer. Chem. Soc., 1929, 51, 1773—1775).—4-Ethylresorcinol (Johnson and Hodge, A., 1913, i, 1055) gives by the usual fluorescein synthesis 2:7-diethylfluorescein (dibromo-, m. p. above 300°, and red anhydromercuri-derivatives), and 4-hexylresorcinol (Dohme and others, A., 1926, 838) gives 2:7-dihexylfluorescein (dibromo-, m. p. 180—181°, and anhydromercuri-derivatives). The new fluoresceins are precipitated from cold solutions of their sodium salts by acetic acid in a yellow lactonoid form and from boiling solutions by hydrochloric acid in a dark brown quinonoid form (cf. Orndorff and Hemmer, A., 1927, 671). H. E. F. NOTTON.

Tea catechin from green tea. M. TSUJIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 252—261).—A new catechin has been isolated in a yield of 0.14% from green tea by extraction with ethyl acetate and fractionation of the extract. *Tea catechin* has m. p. 237—238°, $[\alpha]_D^{25} -69^\circ$ in alcohol, and yields a penta-acetyl derivative, m. p. 151—152°, and a tetramethyl derivative, m. p. 153—154°. Colour reactions are described. It differs from *l*-epicatechin (Freudenberg and Purmann, A., 1923, i, 697; 1924, i, 868) only in being anhydrous. Phloroglucinol is obtained by decomposition with 50% potassium hydroxide solution. The formation of phloretic acid, which is obtained from phloretin under these conditions, is not observed. Controlled oxidation of tetramethyl tea catechin by permanganate yields veratric acid. Further support is afforded to the catechin formula of Perkin and Yoshitake (J.C.S., 1902, 81, 1160) by the close similarity between the absorption spectra of tea catechin and the product of hydrogenation of pentamethylquercetin in presence of platinum oxide-platinum-black, and the difference of these from the absorption spectra of penta-acetylquercetin and quercetin. R. K. CALLOW.

Dissociation into free radicals of substituted dixanthyls. V. Rate of dissociation. J. B. CONANT and M. W. EVANS (J. Amer. Chem. Soc., 1929, 51, 1925—1935).—The autoxidation of di-*n*-

butyldixanthyl has been followed in bromobenzene solution. The first 0.6 mol. of oxygen absorbed is apparently used entirely in peroxide formation, but afterwards side reactions occur. In the first stage the reaction is unimolecular, with a high temperature coefficient, and its rate is practically uninfluenced by the substitution of air for oxygen, or by the addition of the usual autoxidative catalysts and antioxidants. This indicates that the rate actually being measured is that of the dissociation of the dixanthyl into free radicals which are then rapidly oxidised. The values of $k \times 10^3$ for some dialkyldixanthyls (cf. A., 1925, i, 955; 1926, 158, 842; 1927, 975) are, at 25°: dimethyl-, 1.79; diethyl-, 1.99; di-*n*-propyl-, 11.9; di-*n*-butyl-, 12.6; diisomyl-, 10.0; di-*n*-amyl-, 6.95. Diisobutyl-, dibenzyl-, and diisopropyl-dixanthyls oxidise too rapidly to give accurate measurements. Values obtained at 35° and 40° are also given. The energy of activation for the dimethyl derivative (34,000 g.-cal.) is greater than the average value for the others (26,000—27,100 g.-cal.). The above view of the nature of the reaction is confirmed by the fact that the relative ease of dissociation of the dialkyldixanthyls measured in this way is qualitatively the same as that given by measurements of the temperature at which appreciable colour appears in their bromobenzene solutions and of the time required for them to produce a visible amount of Prussian-blue in an aqueous solution of potassium ferricyanide and ferric chloride. H. E. F. NOTTON.

1-Methoxy-derivatives of thioxanthone. K. C. ROBERTS and S. SMILES (J.C.S., 1929, 1322—1326).—Interaction between *p*-methoxyphenol and 2-thiobenzoic acid in sulphuric acid at 15° gave two hydroxymethoxythioxanthenes which were separated by aqueous alkali into 1-hydroxy-4-methoxythioxanthone (insoluble), m. p. 182° (diacetoborate, m. p. 205°, with acetic anhydride and boroacetic anhydride; sodium derivative; acetyl derivative, m. p. 138°), converted by hydrogen peroxide in acetic acid into 1-hydroxy-4-methoxythioxanthone dioxide, m. p. 184° (also produced by alkylation of 1:4-dihydroxyxanthone), and 4-hydroxy-1-methoxythioxanthone (soluble), m. p. 270° (decomp.) (dihydrochloride; perchlorate; acetyl derivative only, m. p. 133°, with boroacetic anhydride and acetic anhydride). Aqueous-alkaline methylation of the latter gave 1:4-dimethoxythioxanthone, but no sulphone was obtained with hydrogen peroxide and acetic acid. The relative stabilities of the salts of 1-hydroxy-4-methoxy- and 4-hydroxy-1-methoxythioxanthenes were measured under the conditions previously described (this vol., 824). The absorption spectra of solutions of the thioxanthenes in concentrated hydrochloric acid and in acetic anhydride have been measured. The constitution of the salts of thioxanthone and its derivatives based on chelate ring formation is discussed.

The chlorostannates of 2:3-dimethoxythioxanthone and of 1:4-dimethoxythioxanthone (hydrolysed by water to 1:4-dimethoxythioxanthone) were prepared by the addition of stannic chloride to the thioxanthenes in benzene solution. A. I. VOGEL.

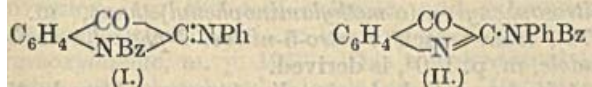
Condensation of di-*o*-thiobenzoic acid with aromatic hydroxy-compounds. R. N. SEN and

S. C. SEN-GUPTA (J. Indian Chem. Soc., 1929, 6, 267—277).—Treatment of di-*o*-thiobenzoic acid with phenols in presence of sulphuric acid at 100° affords, in the majority of cases studied, hydroxythioxanthenes (cf. Smiles, J.C.S., 1910, 97, 1290; 1911, 99, 1533). Thus *o*-, *m*-, and *p*-cresols give 2-hydroxy-3-methylthioxanthone, m. p. 210—212° (benzoyl derivative, m. p. 129—130°), 2-hydroxy-4-methylthioxanthone, m. p. 190° (decomp.) after shrinking at 170°, and 4-hydroxy-1-methylthioxanthone, m. p. 234° (decomp.; sodium salt; benzoyl derivative, m. p. 176—177°), respectively. The ammonium salts of these thioxanthenes dye wool greenish-yellow shades from an acid bath. Reduction of these ketones with zinc dust and sodium hydroxide solution affords colourless solutions of xanthidols which when treated with hydrochloric acid give pink colorations, presumably because of *o*-quinonoid salt formation. The ammonium salt of 1-nitro-4-hydroxythioxanthone, not melted at 280°, dyes wool a brownish-black shade. Pyrocatechol condenses with di-*o*-thiobenzoic acid to give 1:2-dihydroxythioxanthone, m. p. 245—248° (decomp.), which, like alizarin, possesses polygenetic properties. Resorcinol, however, affords the substance,

$C_6H_4 \begin{smallmatrix} S \\ \diagup \diagdown \\ CO \end{smallmatrix} C_6(S \cdot C_6H_4 \cdot CO_2H)(OH)_2(SO_3H)$, green, not melted at 280° [tetrapotassium salt (red); disilver salt], whilst resorcinol dimethyl ether yields *o*-carboxyphenyl 1:2:4-dimethoxythioxanthonyl sulphide, not melted at 280° (potassium salt). Pyrogallol furnishes *o*-carboxyphenyl 1:2:3:4-trihydroxythioxanthonyl sulphide, m. p. above 280° (triacetyl derivative). Phloroglucinol gives the lactone, m. p. 166°, of *o*-carboxyphenyl trihydroxyphenyl sulphide (ammonium salt); salicylic acid yields a sulpho-2-hydroxythioxanthone-3-carboxylic acid; β -naphthol furnishes the lactone of *o*-carboxyphenyl α -2-hydroxy-6:8-disulphonaphthyl sulphide (tetrapotassium salt). The condensation products from di-*o*-thiobenzoic acid (1 mol.) and 1:2:3- and 1:3:5-cresotic acids (2 mols.) dye mordanted wools shades varying from yellow to reddish-brown.

H. BURTON.

Isatin anils. I. Isomerism of isatin-2-anil. R. K. CALLOW and E. HOPE (J.C.S., 1929, 1191—1199).—The existence of two tautomeric forms of isatin-2-anil (Pummerer, A., 1911, i, 231), recently disputed by Rupe and Apotheker (A., 1927, 61), has been confirmed and two benzoyl derivatives, I and II, isolated. When isatin-2-anil, m. p. 126° (decomp.),



best prepared from hydrocyanocarbodiphenylimide and aluminium chloride, is heated with benzoic anhydride (2 mols.) at 100° for 2 hrs. *N*-benzoylisatin-2-anil (I), m. p. 172—173°, is produced (also obtained, together with an equivalent quantity of isatin-2-anil hydrochloride, with benzoyl chloride in benzene). Its constitution was established by hydrolysis (*a*) with hydrochloric acid to *o*-benzamidophenylglyoxylic acid, m. p. 192—193.5°, identical with the product, m. p. 196—197° (decomp.; lit. 188°), obtained by warming *N*-benzoylisatin with dilute sodium hydroxide followed by treatment with hydrochloric acid, (*b*) with

alkali to aniline, and (*c*) with boiling 50% alcohol and a little hydrochloric acid to *o*-benzamidophenylglyoxylanilide, m. p. 183—184°, identical with the compound obtained from *o*-benzamidophenylglyoxylic acid, thionyl chloride, and aniline. The aniline salt, m. p. 120—121° (decomp.), from *o*-benzamidophenylglyoxylic acid and aniline in ether, is converted into the acid by phosphorus pentachloride in benzene: *o*-benzamidobenzaldehyde, m. p. 73—74°, is obtained on boiling *o*-benzamidophenylglyoxylic acid with aniline and a little iodine. *N*-Benzoylisatin, m. p. 213—214°, best prepared by heating isatin with benzoic anhydride for 1 hr. at 150—160°, when heated with 50% alcohol and a little hydrochloric acid yielded *o*-benzamidophenylglyoxylic acid and its ethyl ester, m. p. 80°. Heating of I with aniline and a little iodine at 100° afforded *o*-benzamidophenylglyoxylanilideanil, m. p. 204—205° (decomp.). Isatin-2-anil reacts with benzoyl chloride in dry pyridine to give isatin-2-benzanilide (II), m. p. 131°, the constitution of which follows from the production of isatin and benzanilide on boiling with water. The "isatin- β -phenylhydroxylamine" obtained by Rupe and Apotheker (*loc. cit.*) from isatin and β -phenylhydroxylamine is now shown to be isatin-3-anil-*N'*-oxide, since on reduction with zinc dust and acetic acid 3-anilinoxindole, m. p. 192.5° (decomp., in an evacuated capillary tube), was obtained, identical with the compound obtained by similar reduction of isatin-3-anil.

A. I. VOGEL.

Heterocyclic compounds. IV. Interaction of ethyl cyclohexanone-2-carboxylate with arylamines. I. Synthesis of tetrahydrophenanthridones. H. K. SEN and U. BASU (J. Indian Chem. Soc., 1929, 6, 309—318).—When ethyl cyclohexanone-2-carboxylate is heated with an arylamine at 150—190°, a mixture of diarylcarbamide and cyclohexanone-2-carboxylarylamide results. The following are described: cyclohexanone-2-carboxy-anilide (I), m. p. 104—105°; *p*-toluidide, m. p. 108—109°; *m*-4-xylidide, m. p. 125—126°; β -naphthylamide, m. p. 149°, and *p*-acetamidocanilide, m. p. 182.5°. These compounds give violet colorations with alcoholic ferric chloride, indicating that they react in the enol form. When I is heated at 100° with concentrated sulphuric acid, 5:6:7:8-tetrahydrophenanthridone, m. p. 273°, is produced. The following are prepared similarly: 3-methyl-, m. p. 286—288°; 1:3-dimethyl-, m. p. 270—271°, and 3:4-benzo-5:6:7:8-tetrahydrophenanthridones, m. p. 291—292°.

When ethyl cyclohexanone-2-carboxylate is treated with aniline at the ordinary temperature, reaction occurs between the amino- and keto-groups resulting in the formation of ethyl 2-anilino- Δ^1 -cyclohexene-1-carboxylate, m. p. 57.5° (cf. Kotz and Merkel, A., 1909, i, 157): with *p*-aminoacetanilide, ethyl 2-*p*-acetamidocanilino- Δ^1 -cyclohexene-1-carboxylate, m. p. 191.5°, is obtained.

H. BURTON.

Action of aromatic magnesium compounds on methylsuccinimide. Synthesis of 2:5-diphenyl-1-methylpyrrole. R. LUKES and V. PRELOC (Coll. Czech. Chem. Comm., 1929, 1, 334—345).—See A., 1928, 897.

Mechanism of Fischer's indole synthesis. P. W. MEYER, G. KNOLLER, K. HERBST, and A. TRISSLER (Annalen, 1929, 471, 113—145).—The following mechanism: $C_6H_5 \cdot NR \cdot NH \cdot CR : CH_2 \longrightarrow$

$C_6H_5 \cdot \begin{matrix} CH_2 \cdot CHR \\ | \\ NR \cdot NH \end{matrix} \longrightarrow C_6H_5 \cdot \begin{matrix} CH \\ | \\ NR \end{matrix} \cdot CR$ derives some support from the isolation of oxindole from the reduction of 3-hydroxycinnoline and the formation of 3-phenylindole from 4-phenyltetrahydrocinnoline. Dibenzyl ketone condenses with *as*-phenylmethylhydrazine in acetic acid solution to give 3-phenyl-2-benzyl-1-methylindole, m. p. 129—130°; using the appropriate hydrazines 3-phenyl-2-benzyl-1-ethyl-, and 3-phenyl-1 : 2-dibenzyl-indoles are obtained, m. p. 106° and 138°, respectively. Amyl nitrite and dibenzyl ketone react in presence of sodium ethoxide and ethyl alcohol to form isonitrosodibenzyl ketone, m. p. 116°, which with *as*-phenylmethylhydrazine gives the oxime of 2-benzoyl-3-phenyl-1-methylindole, m. p. 165° (pale yellow needles) and 195° (deep yellow needles) (corresponding 1-ethyl compound, m. p. 150°). *iso*-Nitrosodibenzyl ketone forms with phenylhydrazine a phenylhydrazone, m. p. 185°, but treatment with hydroxylamine hydrochloride produces $\alpha\beta$ -diisonitroso- $\alpha\gamma$ -diphenylpropane, m. p. 213°.

Dibenzyl ketone diphenylhydrazone, m. p. 71—72°, affords 1 : 3-diphenyl-2-benzylindole, m. p. 124°, by boiling with alcoholic hydrogen chloride. *o*-Nitrophenylpyruvic acid underwent the following condensations: (1) by long contact with benzylphenylhydrazine in acetic acid solution 3-*o*-nitrophenyl-1-benzylindole-2-carboxylic acid, m. p. 186°, is obtained; (2) with boiling alcoholic *as*-phenylmethylhydrazine the phenylmethylhydrazone of *o*-nitrophenylpyruvic acid, m. p. 110° with carbon dioxide elimination, is formed; boiling ethyl-alcoholic hydrogen chloride transforms it into 3-*o*-nitrophenyl-1-methylindole-2-carboxylic acid, m. p. 226°; (3) with diphenylhydrazine the diphenylhydrazone of *o*-nitrophenylpyruvic acid, m. p. 125°, is produced, from which 1-phenyl-3-*o*-nitrophenylindole-2-carboxylic acid, m. p. 220°, is prepared. Ethyl *o*-nitrophenylpyruvate similarly yields a diphenylhydrazone, m. p. 107°, and a phenylmethylhydrazone, m. p. 99°, from which ethyl 3-*o*-nitrophenyl-1-methylindole-2-carboxylate, m. p. 107°, is derived.

II (with K. HERBST).—3-Hydroxycinnoline, when boiled with red phosphorus and hydrogen iodide, yields oxindole. 3-Hydroxydihydrocinnoline gives a dibenzoyl derivative, m. p. 167°.

p-Xylylhydrazine condenses with (1) dibenzyl ketone in alcoholic solution with formation of the xylylhydrazone, m. p. 105° (converted by alcoholic hydrogen chloride into 3-phenyl-2-benzyl-4 : 7-dimethylindole, m. p. 139°); (2) with formic acid to produce 2-*p*-xylylformhydrazide, m. p. 135°. This compound treated with methyl sulphate and sodium hydroxide solution gives 2-*p*-xylyl- $\alpha\beta$ -dimethylformhydrazide, b. p. 172—174°/9 mm., from which, by hydrolysis with concentrated hydrochloric acid, 2-*p*-xylyl- $\alpha\beta$ -dimethylhydrazine, b. p. 106—108°/9 mm., is obtained. This hydrazine condenses with dibenzyl ketone in acetic acid solution with formation of dibenzyl ketone 2-*p*-xylyl- $\alpha\beta$ -dimethylhydrazone [two stereoisomerides (?), m. p. 86° and 104°], from which

3-phenyl-2-benzyl-1 : 4 : 7-trimethylindole, m. p. 108°, is formed by heating with hydrochloric acid; (3) with pyruvic acid in ethereal solution, to give the xylylhydrazone, m. p. 172° (decomp.); (4) with *o*-nitrophenylpyruvic acid in alcoholic solution to produce the xylylhydrazone, m. p. 156°.

Diphenylhydrazine reacts with: (1) propiophenone in acetic acid solution yielding the diphenylhydrazone, m. p. 83°, and 1 : 2-diphenyl-3-methylindole, m. p. 116°, successively; (2) phenyl isopropyl ketone, under the previous conditions, giving a diphenylhydrazone, m. p. 72°, from which is formed by the action of alcoholic hydrogen chloride at 0° 1 : 2-diphenyl-3 : 3-dimethylindolinium chloride, m. p. 196° (decomp.) [corresponding perchlorate, m. p. 209° (decomp.)]. The chloride is hydrolysed by boiling with water, 1 : 2-diphenyl-3 : 3-dimethyl-2-indolinol,

$C_6H_5 \cdot \begin{matrix} CMe_2 \\ | \\ NPh \end{matrix} \cdot CPh \cdot OH$, m. p. 156° (decomp.) (*O*-methyl ether, obtained by treatment with potassium methoxide and methyl alcohol, m. p. 118°), being produced. 1 : 2-Diphenyl-3 : 3-dimethylindoline, m. p. 104°, is obtained from the last substance by reduction with acetic acid and zinc dust. By the interaction of phenyl isopropyl ketone and diphenylhydrazine some *o*-anilinophenylisobutyrophenone, m. p. 96—98° [*N*-nitroso-derivative, m. p. 115° (decomp.)], from which the *C*-nitroso-derivative, m. p. 146° (decomp.), is isolated.

III (with A. TRISSLER).—By the action of ethereal hydrogen chloride on ethyl 3-phenylazocrotonate a mixture of 1-(*o*- and *p*-chlorophenyl)-3-methylpyrazolones, m. p. 165° after sintering at 160°, is produced. Ethyl acetoacetate forms an *o*-chlorophenylhydrazone, which with aqueous-alcoholic sodium carbonate gives 1-*o*-chlorophenyl-3-methylpyrazolone, m. p. 201°.

An acetone solution of pyruvic acid phenylmethylhydrazone, when treated with nitric acid fumes, gives pyruvic acid 4-nitrophenylmethylhydrazone, decomp. 150°, from which, by treatment with aqueous-alcoholic hydrogen chloride and zinc dust, *NN'*-dibenzoyl-*N*-methyl-*p*-phenylenediamine, m. p. 165°, is obtained.

Methylation of 4-nitro-2-aminostilbene with methyl sulphate and sodium carbonate solution gives 4-nitro-2-dimethylaminostilbene, m. p. 75°, accompanied by 4-nitro-2-methylaminostilbene, m. p. 172°. Treatment of the *N*-nitroso-derivative, m. p. 175°, of the last compound with bromine in chloroform solution gives the hydrobromide of $\alpha\beta$ -dibromo- β -(4-nitro-3-nitrosophenyl)- α -(*o*-methylaminophenyl)ethane, m. p. 274°, from which 6-nitro-5-nitroso-2-phenyl-1-methylindole, m. p. 170°, is derived.

4-Hydroxytetrahydrocinnoline (prepared by reduction with red phosphorus and hydrogen iodide of 4-hydroxycinnoline) has m. p. 220° (decomp.). 4-Phenylcinnoline, by warming with zinc dust, alcohol, and ammonia, gives 4-phenyldihydrocinnoline, m. p. 115—116° [treatment of which (or of 4-phenylcinnoline) with water, acetic acid, and amalgamated zinc gives 3-phenylindole], which by catalytic reduction in acetic acid solution (platinum as catalyst) yields 4-phenyltetrahydrocinnoline, m. p. 83° (hydrochloride, m. p. 201°; picrate, m. p. 128°).

o-Nitrophenylacetamide, reduced by hot aqueous ferrous sulphate and ammonia, gives *o*-aminophenyl-

acetamide (monohydrate, m. p. 93°; acetyl derivative, m. p. 130°; o-β-naphtholazo-derivative, m. p. 252°).

The following compounds are also described: α-2:5-dichlorophenyl-β-formhydrazide, m. p. 222°; α-2:5-dichlorophenyl-α-methyl-β-formhydrazide, m. p. 112°; α-2:5-dichlorophenyl-α-methylhydrazine, b. p. 142—148°/15 mm. (acetyl derivative, m. p. 134°); αα-diphenyl-β-formhydrazide, m. p. 116.5°; and αα-diphenyl-β-methyl-β-formhydrazide, m. p. 68°; b. p. 160—180°/18 mm.

The authors conclude that neither their own theory nor that of Robinson satisfactorily explains the Fischer indole synthesis. R. J. W. LE FEVRE.

Condensation of o-aminobenzaldehyde with ketodicarboxylic and diketocarboxylic esters. G. KOLLER [with H. RUPPERSBERG and E. STRANG] (Monatsh., 1929, 52, 59—67; cf. A., 1928, 1024).—Ethyl acetonedicarboxylate condenses with o-aminobenzaldehyde in presence of alcohol and a small amount of sodium hydroxide forming ethyl 2-carboethoxymethylquinoline-3-carboxylate, m. p. 64—66° after sintering. Hydrolysis of this with aqueous-alcoholic potassium hydroxide gives the corresponding dicarboxylic acid, decomp. 230°, which on thermal decomposition yields 2-methylquinoline-3-carboxylic acid, m. p. 234°, and when distilled with zinc dust affords 2-methylquinoline. Similar condensation of o-aminobenzaldehyde and ethyl acetone-mono-oxalate yields an ester, C₁₄H₁₃O₃N, m. p. 92—93°. The acid, C₁₂H₉O₃N, m. p. 141° (decomp.), from this eliminates carbon dioxide when heated in a vacuum above its m. p., forming a ketone (I) (probably 3-acetylquinoline), C₁₁H₉ON, b. p. 182°/12 mm., m. p. 100—101° (phenylhydrazone, m. p. 165—166°; oxime, m. p. 206—207°). Oxidation of I with chromic oxide and dilute sulphuric acid gives quinoline-3-carboxylic acid, and condensation with benzaldehyde in presence of dilute alcohol and a small amount of potassium hydroxide yields a benzylidene derivative, m. p. 223—224°. Methyl 2:4-dihydroxyquinoline-3-carboxylate (A., 1927, 674) is converted by heating with alcoholic ammonia into 2:4-dihydroxyquinoline-3-carboxylamide, m. p. 295° (decomp.), which when treated with phosphoryl chloride at 100° affords 2:4-dichloro-3-cyanoquinoline, m. p. 167—168° (cf. Gabriel, A., 1919, i, 38). Reduction of this with hydrogen in presence of alcohol, sodium acetate, and palladised charcoal gives 3-cyanoquinoline (II), m. p. 108°, which after hydrolysis, conversion into the acid chloride, and subsequent treatment with ammonia in benzene yields quinoline-3-carboxylamide, m. p. 195°. This is dehydrated by heating with phosphoryl chloride into II. Unlike the 2- and 4-cyano-derivatives, conversion of II into 3-acetylquinoline by the action of magnesium methyl iodide was unsuccessful.

Ethyl acetonedioxalate and o-aminobenzaldehyde afford an ester, C₁₈H₁₇O₆N, m. p. 129°, together with a small amount of a substance, m. p. 142°.

H. BURTON.

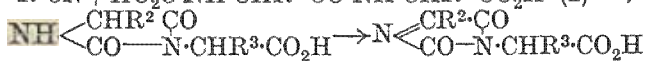
α-Phenylfluorenoquinoline-γ-carboxylic acid. J. LOEVENICH and A. LOESER (J. pr. Chem., 1929, [ii], 122, 285—288).—When an alcoholic solution of 2-aminofluorene, benzaldehyde, and pyruvic acid is boiled, there results 2-phenylfluorenoquinoline-4-carb-

oxylic acid, m. p. >300° (sodium, ammonium, silver salts; ethyl ester, m. p. 174°; methyl ester, m. p. 172°). R. J. W. LE FEVRE.

Hydantoins. XLVIII. Polypeptide hydantoins from hydantoin-1-acetic acid. A. G. RENFREW and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 1784—1789).—The effect of substituents on the reactivity of the 5-methylene group in hydantoin towards aldehydes is discussed (cf. this vol., 330). Ethyl hydantoin-1-acetate and anisaldehyde in glacial acetic acid containing sodium acetate and acetic anhydride give the sodium salt, decomp. above 300°, of 5-p-anisylidenehydantoin-1-acetic acid, m. p. 215—216° (also +EtOH). Condensation is not effected by piperidine. The product is reduced by hydriodic acid at 105° to 5-p-hydroxybenzylhydantoin-1-acetic acid, m. p. 201°, and converted by methyl iodide and potassium hydroxide in methyl alcohol into products which are reduced by hydriodic acid to 5-p-hydroxybenzyl-3-methylhydantoin-1-acetic acid (Hahn and Renfrew, A., 1925, i, 581). Ethyl hydantoin-1-acetate and sodium methoxide in methyl alcohol give ethyl 3-methylhydantoin-1-acetate, m. p. 91—92°, which yields with anisaldehyde the two isomeric 5-p-anisylidene-3-methylhydantoin-1-acetic acids. No evidence of condensation with aldehydes otherwise than at the 5-methylene group has been obtained.

H. E. F. NOTTON.

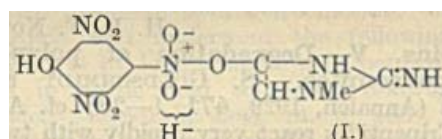
Proteins. V. Degradation of polypeptides by hypobromites. S. GOLDSCHMIDT and K. STRAUSS (Annalen, 1929, 471, 1—20; cf. A., 1927, 983).—Tripeptides react very rapidly with two mols. of alkali hypobromite and then rather more slowly with a third mol. The initial stages of the reaction are the same as those which occur with a dipeptide (loc. cit.), but after elimination of the terminal amino-acid residue as a nitrile, ring formation to a hydantoin derivative occurs, the latter being further oxidised to a dehydrohydantoin (II) by the hypobromite:



The latter can sometimes be isolated in a crystalline form or as its crystalline potassium salt, but all, on hydrolysis, yield the α-keto-acid COR²CO₂H (usually isolated as its phenylhydrazone) and the amino-acid NH₂·CHR³CO₂H. Thus alanyl-valylglycine, m. p. 241° (from bromopropionylvalylglycine, m. p. 204°), alanyl-leucylglycine, alanylalanyl-leucine, m. p. 246° (from bromopropionylalanyl leucine, m. p. 180°), and dialanylglycine, m. p. 208° (from the bromopropionyl compound, m. p. 194°), all yield acetonitrile and, respectively, 5-isopropyl-, m. p. 227°, α-isobutyl-, m. p. 183°, -1: α-dehydrohydantoin-3-acetic acid (II, R³=H), 5-methyl-1:5-dehydrohydantoin-3-isohezoic acid (II, R³=CH₂Pr³), and 5-methyl-1:5-dehydrohydantoin-3-acetic acid (potassium + H₂O salt), whilst valylalanylglycine, m. p. 220° (from α-bromo-isovalerylalanylglycine, m. p. 167°), yields the last-named together with isobutyronitrile. Alanylglycyl-leucine, unlike the above tripeptides, takes up 5 mols. of hypobromite, since the carboxylamino-acid (I)

loses carbon dioxide to yield glycyl-leucine, which is further degraded to leucine and cyanic acid, the latter being converted by more hypobromite into carbamide. Tetrapeptides react similarly with hypobromite. Thus *trialanylglycine*, m. p. 254° (decomp.) (from *bromopropionylaldanylglycine*, m. p. 217°), and *leucylalanylvallylglycine*, m. p. 250—256° (decomp.) (from the α -*bromoisohehexoyl* compound, m. p. 206°), yield, respectively, aceto- and *isovalero*-nitriles and the corresponding *dehydrohydantoins*, which could not be crystallised, but on hydrolysis yield pyruvic acid, glycine, and, respectively, alanine and valine. *Alanyl-glutamic acid* (copper salt) (from α -*bromopropionyl-glutamic acid*, m. p. 123°) with hypobromite yields acetonitrile and glutamic acid. J. W. BAKER.

Constitution of red isomeride of creatinine picrate responsible for Jaffé's colour reaction. W. K. ANSLOW and H. KING (J.C.S., 1929, 1210—1216).—A red isomeric form of creatinine picrate, m. p. 213° after turning yellow at 160—170°, is obtained by instantaneous acidification with hydrochloric acid of the red solutions obtained by the addition of alkali to an aqueous suspension of yellow creatinine picrate, m. p. 220—221°. It forms a red *barium* salt (also produced from the yellow compound) and is converted into yellow creatinine picrate when boiled with water. It is concluded that red creatinine picrate is I and



that this compound is responsible for the red colour in Jaffé's colour reaction for creatinine (cf. Jaffé, A., 1886, ii, 1056; Folin, A., 1904, ii, 375; Greenwald and Gross, A., 1924, ii, 508; Chapman, A., 1909, ii, 948; Greenwald, A., 1925, i, 839; Weise and Trop, A., 1928, 1267). Support for this formula is given by the isolation of a red *sodium* salt from the interaction of acetone and 2:4-dinitrophenol in the presence of sodium ethoxide (cf. Reissert, A., 1904, i, 389). Contrary to the statement of Greenwald and Gross (*loc. cit.*), it is found that the addition of creatinine to alkaline solutions of 2:4-dinitrophenol and of 3-methylpicric acid gives orange-red solutions after keeping for several minutes. When alkaline solutions of 2:4-dinitrophenol, 2:6-dinitrophenol, 3-methylpicric acid, and 2:4-dinitro- α -naphthol-7-sulphonic acid containing creatinine are gradually treated with hydrochloric acid, a transient red colour is obtained at neutrality which disappears with excess of acid; the colour is not obtained from the acid side. Ionisation of the enolic form or ionisation of the reactive methylene compound is therefore an essential preliminary to the formation of the co-ordination complex, and this condition is most readily obtained by salt formation in alkaline solution. A. I. VOGEL.

Catalytic hydrogenation of cyano-compounds. Reduction of ethyl phenylcyanopyruvate, ethyl benzoylcianoacetate, and ethyl benzylidenecyanoacetate. H. RUPE and B. PIEPER (Helv. Chim. Acta, 1929, 12, 637—649).—Ethyl cyanophenylpyruvate in aqueous alcoholic solution absorbed 2

mols. of hydrogen in 24 hrs. at 50—55° with a nickel catalyst with the formation of 2:3-diketo-4-phenylpyrrolidine, m. p. 295° after colouring at 200° [*benzoyl* derivative, m. p. 218°; *monomethyl* derivative, m. p. 197—198°; *quinoxaline* (from *o*-phenylenediamine), m. p. not given; *phenylhydrazine*, m. p. 224—225°].

Ethyl cyanobenzoylacetate (prepared from ethyl benzoylacetate, sodium, and cyanogen chloride in 70% yield) was reduced in aqueous-alcoholic solution at 68—73° with a nickel catalyst to *ethyl α -benzoylpropionate*, b. p. 143—144°/10 mm. The last-named ester formed with semicarbazide hydrochloride, phenylhydrazine, and hydroxylamine hydrochloride, 1-*carbamyl*-3-phenyl-4-methyl-5-pyrazolone, m. p. 193°, 1:3-diphenyl-4-methyl-5-pyrazolone, m. p. 195°, and 3-phenyl-4-methylisooxazole, m. p. 117°, respectively. When the hydrogenation was interrupted, the *aldimine*, $\text{NH}\cdot\text{CH}\cdot\text{CHBz}\cdot\text{CO}_2\text{Et}$, m. p. 81—82°, was isolated; by hydrolysis with hydrochloric acid acetophenone was obtained. Catalytic hydrogenation of ethyl benzylidenecyanoacetate led to the *anil* from the half-aldehyde of ethyl hydrogen benzylmalonate and ethyl β -amino- α -benzylpropionate. This, by boiling with alcoholic hydrogen chloride gave the *semi-aldehyde* of *ethyl hydrogen benzylmalonate* (isolated as *semicarbazone*, m. p. 121°; *phenylhydrazine*, m. p. 143°), which, by acid hydrolysis, afforded β -phenylpropionaldehyde (*semicarbazone*, m. p. 113°; *oxime*, m. p. 93—94°), accompanied by β -amino- α -benzylpropionic acid, m. p. 225° (*sulphate*), from which, by treatment with potassium cyanate, 5-benzylhydro-uracil, m. p. 248°, was prepared.

R. J. W. LE FEVRE.

Naphthoisindigotins. A. WAHL and J. LOBECK (Compt. rend., 1929, 188, 1683—1685).—Naphthisatin (benzisatin) and oxindole condense in alcohol containing a trace of ammonia or piperidine, or when ground together, giving α -benzisatin (I) and β -benzisatin (II). By heating with acetic anhydride containing a few drops of mineral acid I is converted into *benzisindigotin* (also obtained directly from naphthisatin and oxindole by condensation in acetic and hydrochloric acids), which, by reduction with zinc and acetic acid in the presence of acetic anhydride yields a α -*acetyl-leucobenzisindigotin*, m. p. above 300°. *Sodium*, *potassium*, *calcium*, *barium*, and *silver* salts derived from α -benzisindigotindisulphonic acid are obtained from the leuco-base by treatment with excess of sulphuric acid, dilution, neutralisation, and addition of the appropriate metallic salt. By heating with acetic anhydride containing a trace of sulphuric acid, II affords β -benzisindigotin, converted by zinc and acetic acid into a *diacetyl-leuco- β -benzisindigotin*.

The action of hydrogen sulphide in cold methylalcoholic solution on naphthisatin furnishes a *di-naphthodisulphisatide* (III), containing 3 atoms of sulphur, the third of which cannot be removed by extraction; the substance nevertheless behaves normally, decomposing in boiling pyridine to yield α -*naphthoxindole* (*benzylidene* derivative, m. p. 241°) and α -*dinaphthoisindigotin*; the decomposition is also effected by sodium hydroxide or carbonate or by ammonia. Treatment of III with cuprous chloride affords $\alpha\alpha'$ -*dinaphthoisindigotin*, converted by an excess of sulphuric acid into a sulphonic acid.

The α -benzisoindigotindisulphonic acid dyes wool a violet-black, not fast to washing, whilst the α' -dinaphtho-compound gives a fast bluish-black.

C. W. SHOPPEE.

Reaction between sugars and their degradation products and nitrogenous substances. I. Formation of glyoxalines. K. BERNHAUER (Z. physiol. Chem., 1929, 183, 67—73).—The velocity of formation of methylglyoxaline by the action of zinc hydroxide and ammonia on various sugars increases with rise of temperature. Thus, the separation of the zinc salt is complete after 2 hrs. at 100°, but requires 24 hrs. at 40° and 6 weeks at the ordinary temperature. The concentration of the ammoniacal zinc hydroxide is important, best results being obtained with a 20—25% solution of ammonia saturated with zinc hydroxide. The yield of the methylglyoxaline is somewhat greater with dihydroxy-acetone than with dextrose, and is increased by addition of formaldehyde. During the action of ammoniacal zinc hydroxide on methylglyoxal, no separation of the zinc salt of methylglyoxaline occurs unless formaldehyde is present, thus confirming the results of Sjollem and Kam (A., 1916, i, 791); in presence of acetaldehyde dimethylglyoxaline results. The intermediate formation of methylglyoxal during the reaction with dextrose is proved by the isolation of derivatives from the steam distillate of the reaction mixture.

H. BURTON.

Glyoxaline derivatives. IV. Degradation of histidine to γ -hydroxyornithine. W. LANGENBECK and R. HUTSCHENREUTER (Z. physiol. Chem., 1929, 182, 305—310).—Fission of *l*-histidine methyl ester with sodium hydroxide and benzoyl chloride (cf. Kossel and Edlbacher, A., 1915, i, 295) and subsequent treatment of the product with methyl-alcoholic hydrochloric acid (cf. Windaus, Dörries, and Jensen, A., 1922, i, 60) affords methyl α , δ -dibenzamido- γ -keto-*n*-valerate, $[\alpha]_{D}^{25}$ yellow —40.4° in pyridine. Reduction of this with hydrogen in presence of platinum oxide and acetic acid yields the lactone (I), m. p. 222°, of α , δ -dihexahydrobenzamido- γ -hydroxy-valeric acid (II), m. p. 236—240°, together with a small amount of an isomeride, m. p. 248°. Hydrolysis of I with concentrated hydrochloric acid gives hexahydrobenzoic acid, whilst treatment with 1% sodium hydroxide solution at 0° and subsequent acidification with acetic acid furnishes about 20% of II, the remainder being recovered unchanged by acidifying with hydrochloric acid. When II is heated with acetic acid at 100° a substance, m. p. 245—246°, is produced, indicating that isomerisation of I occurs during the treatment with alkali. Reduction of ethyl benzamidoacetate with hydrogen in presence of platinum oxide and acetic acid yields ethyl hexahydrobenzamidoacetate, m. p. 76°.

H. BURTON.

Pyrimidines. CVII. Examination of yeast nucleic acid for 5-methylcytosine. T. B. JOHNSON and H. H. HARKINS (J. Amer. Chem. Soc., 1929, 51, 1779—1784).—The pyrimidine fraction from protein-free yeast nucleic acid, prepared by a modification of Steudel's method (A., 1924, i, 104), is shown by the acetylcarbinol test (this vol., 705) to be free from

thymine and 5-methylcytosine, although a positive reaction may be obtained if the fraction contains nucleosides. 5-Methylcytosine may be completely separated from thymine by two precipitations as the phosphotungstate.

H. E. F. NOTTON.

Copper compounds of diethylbarbituric acid. N. W. ROMANOWA (Arch. Pharm., 1929, 267, 370—372).—When copper sulphate solution is added to a solution of sodium diethylbarbiturate (Medinal), a violet compound is first obtained, containing two sodium atoms, one copper atom, and four veronal residues. With a larger proportion of copper acetate or copper sulphate solution until an alkaline reaction is obtained, cupric acetoveronal, and cupric sulphato-veronal, bright blue compounds, $\text{CET}_2 \cdot \begin{matrix} \text{CO-NH} \\ \diagup \quad \diagdown \\ \text{CO-NR} \end{matrix} \cdot \text{CO}$

(R=—Cu·CO₂Me and —CuSO₄), are obtained. The addition of still more copper salt solution affords bright blue copper-veronal compounds containing 20—26% Cu.

S. COFFEY.

Quinazolines. I. T. BHATTACHARYYA, P. K. BOSE, and J. N. RAY (J. Indian Chem. Soc., 1929, 6, 279—287).—Substituted 4-keto-1:4-dihydroquinazolines are obtained from acetylated arylamines and ethyl aminoformate in presence of phosphoric oxide and toluene. They are occasionally formed from the amine and ethyl acetamidoformate, and in this case the acetylcarbamide, NHAr·CO·NHAc (I), is also produced. Thus, *m*-toluidine and ethyl acetamidoformate yield a mixture of acetyl-*m*-tolylcarbamide (I, Ar=*m*-Me·C₆H₄), m. p. 123°, and 4-keto-2:7-dimethyl-1:4-dihydroquinazoline, m. p. 244°, also obtained from *m*-acet-toluidine and ethyl aminoformate. *m*-Anisidine affords acetyl-*m*-anisylcarbamide, m. p. 200°, and 4-keto-7-methoxy-2-methyl-1:4-dihydroquinazoline, m. p. 257°; aniline gives acetylphenylcarbamide and the amidine, NHPh·CMe₂·N·CO₂Et, whilst *o*-toluidine, *m*-4-xylidine, *o*-phenetidine, and *o*-anisidine afford only the corresponding acetylcarbamides, m. p. 168°, 194°, 203°, and 197°, respectively. The following substituted 4-keto-1:4-dihydroquinazolines are obtained from the requisite acylamine and ethyl aminoformate: 2-methyl- (II), m. p. 231° [the 2:3-dimethyl derivative, m. p. 112—113° (lit. 110—111°), is obtained by the action of methyl iodide and methyl-alcoholic sodium hydroxide on II, and is formulated as 4-keto-2:3-dimethyl-3:4-dihydroquinazoline (cf. Bogert and Gotthelf, A., 1900, i, 608; Bogert and Seil, A., 1907, i, 560)]; 2:6-dimethyl-, m. p. 240° (picrate, m. p. 196—198°); 2:8-dimethyl-, m. p. 240° (picrate, m. p. 164°), methylated to the 2:3:8-trimethyl derivative, m. p. 107°; 2:6:8-trimethyl-, m. p. 266° (lit. 271°; picrate, m. p. 197°), methylated to the 2:3:6:8-tetramethyl derivative, m. p. 146° (2:6:8-trimethyl-3-ethyl derivative, m. p. 190°); 6-methoxy-2-methyl-, m. p. 257°, methylated to the 6-methoxy-2:3-dimethyl derivative, m. p. 131°; 8-methoxy-2-methyl-, m. p. 243° (3-methyl derivative); 6-ethoxy-2-methyl-, m. p. 220° (3-methyl derivative, m. p. 148°); 8-ethoxy-2-methyl-, m. p. 225°; 2-phenyl-, m. p. 223° [3-methyl derivative, m. p. 133° (lit. 131°)]; 2-ethyl-, m. p. 227—228° (lit. 225°); 8-methyl-2-ethyl-, m. p. 215°, and 6-methyl-2-ethyl-, m. p. 227° (3-methyl derivative, m. p. 111°). Acet- α - and - β -

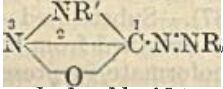
naphthalides react with ethyl aminoformate yielding 4-*keto*-2-methyl-7:8-benzo-, m. p. 322°, and 4-*keto*-2-methyl-5:6-benzo-1:4-dihydroquinazolines, m. p. 293° (3-methyl derivative, m. p. 156°), respectively.

H. BURTON.

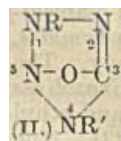
Action of heat on allophanic amides. J. BOUGAULT and J. LEBOUCCQ (Compt. rend., 1929, 188, 1406—1407).—By the action of aniline, *p*-toluidine, and phenylhydrazine on allophanoyl chloride are obtained, respectively, the corresponding anilide, *p*-toluidide, and phenylhydrazide, m. p. 218°. When heated at 200—210°, the first two evolve ammonia, yielding, respectively, *s*-diphenyl- and *s*-di-*p*-tolyl-carbamide (soluble in alcohol) and cyanuric acid. By similar decomposition the phenylhydrazide yields only ammonia and phenylurazole, identical with the product obtained by Pinner (A., 1888, 687).

J. W. BAKER.

New group of hydrazomethylenes. M. BUSCH and W. SCHMIDT [with P. BOHRISCH and O. LUSCH] (Ber., 1929, 62, [B], 1449—1457).—The product of the action of nitrous acid on $\alpha\delta$ -diphenylthiosemicarbazide is shown to be 1:3-endoxy-1-phenylazo-2-

phenylhydrazomethylene,  (I) (R =

R = Ph) (colourless monohydrochloride). It undergoes complicated hydrolysis by acids, yielding nitrogen, a neutral substance, m. p. 83°, and phenylazocarbanilide. Reduction with aluminium yields $\alpha\delta$ -diphenylsemicarbazide, m. p. 176°, and phenylazocarbanilide. With ammonium sulphide $\alpha\delta$ -diphenylsemicarbazide is produced, whereas hydrogen sulphide in alcohol affords $\alpha\delta$ -diphenylthiosemicarbazide; zinc dust and acetic acid give diphenylsemicarbazide. Treatment of endoxyphenylazophenylhydrazomethylene with alcoholic alkali hydroxide gives 3:5-endoxy-1:4-diphenyltetrazole (II; R = R' = Ph), which explodes when strongly heated. The new



ring is stable towards hydrochloric acid below 220°. It is reduced with difficulty to ammonia, aniline, phenylcarbamide, and small amounts of phenylhydrazine. 1:3-endoxy-1-phenylazo-2-vic-m-xylylhydrazomethylene, m. p. 101°, 3:5-endoxy-1-phenyl-4-vic-m-xylyltetrazole, m. p. 174°, 1:3-endoxy-1-vic-m-xylylazo-2-phenylhydrazomethylene, m. p. 91—92°, vic-m-xylylazocarbanilide, m. p. 124.5°, and 3:5-endoxy-4-phenyl-1-vic-m-xylyltetrazole, m. p. 122—123°, are described. Phenylthiosemicarbazide affords the unstable 1:3-endoxy-1-phenylazohydrazomethylene, m. p. 60—62° (decomp.) [hydrochloride, m. p. 189—190°; benzoyl derivative, m. p. 166°; potassium compound, m. p. 185—190° (decomp.) after darkening at 110°]. The following endoxyhydrazomethylenes are described (cf. I): R = *p*-tolyl, R = Ph, m. p. 127°; R = *o*-tolyl, R' = Ph, m. p. 99°; R = R' = *o*-tolyl, m. p. 62°; R = Ph, R' = α -naphthyl, m. p. 125°; R = α -naphthyl, R' = Ph, m. p. 90° (hydrochloride); R = Ph, R' = 3-naphthyl, m. p. 89—90°; R = Ph, R' = Et, m. p. 45° (hydrochloride); R = Ph, R' = allyl, m. p. 43° (hydrochloride); R = *p*-tolyl, R' = allyl, m. p. 59° (hydrochloride); and the following tetrazoles (cf. II): R = *p*-tolyl, R' = Ph, m. p. 158°; R = *o*-tolyl, R' = Ph, m. p. 117°; R = R' = *o*-tolyl, m. p. 128°; R = Ph, R' = α -

naphthyl, m. p. 160°; R = α -naphthyl, R' = Ph, m. p. 177—178°; R = Ph, R' = β -naphthyl, m. p. 213—214°.

H. WREN.

Porphyrin syntheses. XXIII. Syntheses of coproporphyrins. III and IV. H. FISCHER, K. PLATZ, and K. MORGENROTH (Z. physiol. Chem., 1929, 182, 265—288).—Two of the four possible coproporphyrins (tetramethyltetra- β -carboxyethylporphyrins) have been previously synthesised (A., 1928, 1384), and the remaining two are now obtained by similar methods. When bis-(5-carboxy-4-methyl-3- β -carboxyethylpyrryl)methane is eliminated in acetic acid solution, carbon dioxide is eliminated and (5-bromo-4-methyl-3- β -carboxyethylpyrryl)-(5-bromo-4-methyl-3- β -carboxyethylpyrrolenyl)methene hydrobromide, m. p. above 250°, results (cf. A., 1927, 1206). Condensation of bis-(2:4-dimethyl-3- β -carboxyethylpyrryl)methene hydrobromide with bis-(2-bromo-3-methyl-4- β -carboxyethylpyrryl)methene hydrobromide (I) in presence of hydrobromic and acetic acids or by the succinic acid method gives only small amounts of coproporphyrin IV. With an equimolecular mixture of I and bis-(4-methyl-2-bromomethyl-3- β -carboxymethylpyrryl)methene hydrobromide in presence of succinic acid at 175—180°, about 30% of coproporphyrin IV [tetramethyl ester, m. p. 168—169° after sintering at 161° (complex copper salt, m. p. 216—217°; haemin derivative); tetraethyl ester, m. p. 152° (corr.; complex copper salt, m. p. 180—181°)], is obtained. Treatment of haemopyrrolecarboxylic acid (A., 1928, 902) with hydrogen cyanide and chloride in chloroform solution affords after hydrolysis of the isolated iminochloride haemopyrrolecarboxylic acid aldehyde, m. p. 155° [(corr.); semicarbazone, m. p. 190° (corr.) with discoloration at 160°; oxime, m. p. 152° (corr.); methyl ester (II), m. p. 89°]. This condenses with cryptopyrrole in presence of alcoholic hydrobromic acid yielding (4:5-dimethyl-3- β -carboxyethylpyrryl)-(3:5-dimethyl-4-ethylpyrrolenyl)methene hydrobromide, decomp. 217° (corr.) after darkening at 190°, whilst similar condensation of II and cryptopyrrolecarboxylic acid affords (4:5-dimethyl-3- β -carboxomethoxyethylpyrryl)-(3:5-dimethyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide, m. p. 138° (corr.).

Treatment of a mixture of (2-bromo-3-methyl-4- β -carboxyethylpyrryl)-(2-bromo-3-methyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide and (2:3-dimethyl-4- β -carboxomethoxyethylpyrryl)-(2:4-dimethyl-3-ethylpyrrolenyl)methene hydrobromide with succinic acid at 165—170° affords coproporphyrin III (hydrochloride). The tetramethyl ester of this exists in two modifications, m. p. 146—148° (unstable) and 172°, respectively.

[With A. TREIBS.]—The coproporphyrin isolated from the urine and faeces of a case of congenital porphyria (van den Bergh, Regniers, and Muller, Archiv fur Verdauungskrankheiten, 1928, 42, 306) is shown to be identical with coproporphyrin III.

H. BURTON.

Acetates of porphyrin and haemin: constitution of rhodoporphyrin. H. FISCHER, G. HUMMEL, and A. TREIBS (Annalen, 1929, 471, 237—285).—Haemin extracted with acetic anhydride gives acetic anhydride-haemin (chlorohaemin diacetate)

from which hæmin can be regenerated by treatment of a chloroform solution by boiling acetic acid. Chlorohæmin diacetate when treated with hydrobromic and acetic acids in a sealed tube produces hæmatoporphyrin hydrochloride; when heated with methyl alcohol and a trace of either sulphuric acid or hydrogen chloride it yields a *tetramethylhæmatoporphyrin iron salt*, $C_{38}H_{44}O_6N_4FeCl$; whilst with hot collidine it gives *collidine-hæmin*, $C_{34}H_{32}O_4N_4FeCl.C_8H_{11}N$.

The preparation of the following compounds is described: *pyrroporphyrin acetate*, m. p. 183°; *mesoporphyrin acetate*, m. p. 225° (complex copper salt, $C_{38}H_{40}O_6N_4Cu$, m. p. 197°); *mesorhodin acetate*, m. p. 225°; *protoporphyrin acetate*, m. p. 231°; *phylloporphyrin acetate*, m. p. 220°; *rhodoporphyrin diacetate*; *rhodoporphyrin monomethyl ester*, m. p. 330° after sintering at 285° (which by decarboxylation gives pyrroporphyrin) [acetate, $C_{30}H_{32}N_4(CO_2Me)(CO_2Ac)$, m. p. 208°; complex iron salt]; *coproporphyrin I-acetate*, m. p. 182°; *uroporphyrin acetate*; *mesoacetoxylhæmin acetate*, m. p. 235°; *mesochlorohæmin acetate*, m. p. 260°; *mesoacetoxylhæmin dimethyl ester*, m. p. 237°; *protoacetoxylhæmin acetate*, m. p. 204°; *prochlorohæmin acetate*, m. p. 248° (converted into the previous compound by treatment in chloroform solution by 5% sodium hydroxide solution); *protohæmatin acetate*; *dimethylhæmatin*, m. p. 232°; *phylloacetoxylhæmin acetate*, m. p. 327°; *phyllochlorohæmin acetate*, m. p. 329°; *pyrroacetoxylhæmin acetate*; *pyrrochlorohæmin acetate*, m. p. 271°; *coproacetoxylhæmin acetate I*; *ætioacetoxylhæmin*; *rhodoporphyrin anhydride*; *rhodoporphyrin monomethyl ester anhydride*; *phylloporphyrin anhydride*; *pyrroporphyrin anhydride*; *mesoporphyrin anhydride*; *mesochlorohæmin anhydride*; *protoporphyrin anhydride*. R. J. W. LE FEVRE.

Synthesis of chlorin. H. FISCHER and H. HELBERGER (Annalen, 1929, 471, 285—304).—The hæmin resulting from the treatment of porphyrin hydrochloride in acetic acid solution with a solution of ferric acetate and sodium chloride in acetic acid is suspended in isoamyl alcohol and sodium added in an atmosphere of hydrogen. From the mixture of porphyrin iron salts, chlorin iron salts, perhydrochlorin, chlorin, and traces of porphyrin, so produced, chlorin and perhydrochlorin are extracted by 18% hydrochloric acid solution. Final separation, by 8% hydrochloric acid solution, gives *chlorinmonocarboxylic acid*, m. p. 217° (corr.) (decomp.) (sodium, potassium, and ammonium salts; methyl ester, m. p. 152° [corr.]; methyl ester copper complex), transformed by 3% oleum at 100° into *anhydride-a*, m. p. 285° (decomp.), and *anhydride-b*, m. p. 282° (decomp.), by saturated methyl-alcoholic potassium hydroxide in a sealed tube at 180° into porphyrinmonocarboxylic acid (methyl ester, m. p. 217°), and by heating with zinc dust and acetic acid into impure porphyrinmonocarboxylic acid. Complex salts, $C_{33}H_{40}O_2N_4R$, of chlorinmonocarboxylic acid with iron ($R=FeCl$), copper ($R=Cu$), and magnesium are described.

R. J. W. LE FEVRE.

Degradation of chlorophyll by alkali. A. TREIBS and E. WIDEMANN (Annalen, 1929, 471, 146—235).—Phæophytin is a mixture of phæophytin-

a, m. p. 178—180° (sintering at 150°), and phæophytin-*b*, m. p. 190—195° (sintering at 170°). The analytical figures obtained for chlorin-*e* are in agreement with those previously given for rhodin-*g*. By the action of diazomethane in acetone, chlorin-*e* methyl ester, m. p. 215° (corr.), and rhodin-*g* ester, m. p. 251° (corr.), are obtained; these are hydrolysed by short treatment in pyridine solution with methyl-alcoholic potassium hydroxide, whilst treatment of chloroform solutions with copper acetate in methyl-alcoholic solution yields chlorin-*e* ester and *rhodin-g ester* copper salts, both m. p. 225° (corr.).

The actions of the following reagents on chlorin-*e* and rhodin-*g* were examined in detail: (A) 30% methyl-alcoholic potassium hydroxide; (B) A and $\frac{1}{2}$ vol. of pyridine in which the substance is previously dissolved; (C) B with addition of magnesia; (D) vol. of pyridine and 1 vol. of 5% sodium oxide in methyl alcohol; (E) $\frac{1}{2}$ vol. of pyridine and 1 vol. of 25% methyl-alcoholic sodium hydroxide.

Chlorin-*e* treated with reagent E in a silver vessel under pressure at 125°, rhodin-*g* treated with reagent D at 130°, or phæophytin (*a+b*) treated with reagent B at 100° all led to the isolation of *verdoporphyrin*, $C_{32}H_{34}O_4N_4$ [dimethyl ester, m. p. 280° (corr.); copper salt, $C_{32}H_{32}O_4N_4Cu$; magnesium complex (*verdophyllin*)], further degradation of which by E, B, D, and sulphuric acid produced rhodoporphyrin, rhodoporphyrin plus a trace of pyrroporphyrin, some phylloporphyrin, and pyrroporphyrin, respectively. By-products in the decomposition of chlorin-*e* include *chlorin-3* and *chlorin-10* [identical with phytochlorin-*f* (?) [methyl ester, m. p. 203° (corr.); methyl ester copper salt, m. p. 210° (corr.)]. Verdoporphyrin is contained in the cyano- and glauco-porphyrins of Willstätter.

Treatment of chlorin-*e* according to conditions C at 150°, rhodin-*g* according to conditions D at 140°, and phæophytin (*a+b*) according to conditions B gave rhodoporphyrin [magnesium complex (*rhodophyllin*); dihydrochloride; dimethyl ester, m. p. 268° (corr.); dimethyl ester copper complex, $C_{34}H_{36}O_4N_4Cu$, m. p. 243° (corr.); dimethyl ester iron complexes: *rhodohæmin ester*, $C_{34}H_{36}O_4N_4FeCl.MeOH$, m. p. 294° (decomp.), and $C_{34}H_{36}O_4N_4FeCl$]. Oxidation of rhodoporphyrin dimethyl ester in chloroform solution by lead dioxide and acetic acid produced a *xanthoporphinogen*, m. p. 284°.

Rhodoporphyrin under conditions E in a sealed tube gave pyrroporphyrin, whilst erythrophyllin and erythroporphyrin (Willstätter) with reagent B gave pyrroporphyrin; it is concluded that erythroporphyrin is very pure rhodoporphyrin.

From rhodin-*g* and reagent D at 150° (in sealed tube) a mixture of phyllo-, pyrro-, and rhodoporphyrins was obtained. *Phylloporphyrin hydrochloride* and *phylloporphyrin ester copper salt*, m. p. 255° (corr.), are described. Phylloporphyrin when treated with sodium ethoxide in pyridine solution gave *phyllochlorin* [methyl ester, m. p. 164° (decomp.)], which by reduction with zinc dust and acetic acid gave a *leuco-compound*. From the porphyrin mixture obtained above from rhodin-*g* pyrroporphyrin [copper complex; *pyrroporphyrin ester copper complex*, m. p. 231° (corr.)] was obtained; from it *pyrrochlorin* was prepared analogously to phyllochlorin; when warmed

with sulphuric acid it was converted into pyrro-rhodin.

Distribution coefficients of, and spectroscopic measurements for, the derivatives described are tabulated.

R. J. W. LE FÈVRE.

Blood colouring matters. X. Specificity of hæmoglobin and von Krüger's reaction. F. HAUROWITZ (Z. physiol. Chem., 1929, 183, 78—87).—The rate of denaturation of oxyhæmoglobins by sodium hydroxide (von Krüger's reaction) depends on the source; thus, human oxyhæmoglobin is transformed into cathæmoglobin in 40—50 sec., whilst the conversion with ox oxyhæmoglobin is not complete until after 24 hrs. The cathæmoglobin formed is precipitable by ammonium sulphate. Spectroscopic investigation of the change shows it to be unimolecular. The characteristic bands of cathæmoglobin are not visible in alkaline solution but appear when carbon dioxide is passed into the solution.

H. BURTON.

Action of formic acid on oxy- and chlorohæmins. A. HAMSÍK (Z. physiol. Chem., 1929, 183, 103—112).—Treatment of the potassium derivative (I) of oxyhæmin with 95% formic acid in methyl-alcoholic solution affords formylhæmin (cf. A., 1927, 1100). Protoporphyrin is best prepared from oxyhæmin by treatment with 80% formic acid and iron powder. Similar treatment of acetone-chlorohæmin with 85% formic acid also yields protoporphyrin; with more concentrated acid a brown product results. When I is treated with oxalic, 95% formic, or acetic acid in presence of methyl alcohol or acetone, dissolution is greatest with the first and least with the last acid.

H. BURTON.

Ring openings with benz- $\alpha\beta$ -isooxazoles. H. LINDEMANN and H. CISSÉE (J. pr. Chem., 1929, [ii], 122, 232—260).—Methyl 5-nitroindoxazen-2-carboxylate was reduced by stannous chloride and hydrochloric acid to the 5-amino-ester, m. p. 206° (acetyl derivative, m. p. 210°; diacetyl derivative, m. p. 130°), which by hydrolysis with sulphuric acid gave 5-amino-indoxazen-2-carboxylic acid, decomp. 160° (with formation of 4-amino-2-hydroxybenzonitrile, m. p. 182°) (acetyl derivative, decomp. 260—280° with production of acetamidosalicylonitrile, m. p. 288°). The ethyl ester, m. p. 147° (acetyl derivative, m. p. 186—187°), of the last-named when treated with hydrazine hydrate yielded the hydrazide of 5-acetamidindoxazen-2-carboxylic acid, m. p. 218°, which, with nitrous acid, was transformed into the corresponding azide, m. p. 155° (decomp.) [which, by boiling with the appropriate alcohols, afforded the *n*-propyl, *n*-butyl, and isoamyl esters of 5-acetamidindoxazen-2-carboxylic acid, m. p. 205°, 248°, and 215° (decomp.), respectively; the three related amines, obtained from these by hydrochloric acid hydrolysis, had m. p. 138° (decomp.), 104° (decomp.), 145°, respectively]. The above azide was boiled with aqueous acetic acid with the production of 2-amino-5-acetamidindoxazen, m. p. 222° (diacetyl derivative, m. p. 256°: this by warming with 2*N*-sodium hydroxide solution passed into 3-*o*-hydroxy-*p*-acetamidophenyl-5-methyl-1:2:4-oxdiazole, m. p. 210°, also obtained by reducing with stannous chloride and hydrochloric acid the analogous

nitro-oxdiazole), and either from the hydrolysis of this compound with aqueous sulphuric acid or by reduction of 5-nitro-2-aminoindoxazine with stannous chloride 2:5-diaminoindoxazen, m. p. 141°, was obtained.

2-Amino-5-acetamidindoxazen gave 2-hydroxy-5-acetamidindoxazen, m. p. 160—165° (decomp.), by diazotisation. This, by heating with formic acid, produced 2-hydroxy-4-acetamidobenzhydroxamic acid, m. p. 218°. The last two compounds by warming with propionic acid or anhydride respectively afforded 2-hydroxy-4-acetamidobenzpropionylhydroxamic acid, m. p. 194°, dissolution of which in 2*N*-sodium hydroxide solution led to 5-acetamido-1-benzisooxazolone, m. p. 320°.

Methyl 5-aminoindoxazen-2-carboxylate was converted by Sandmeyer's reaction into methyl 5-chloroindoxazen-2-carboxylate, which by long contact with 2*N*-sodium hydroxide solution yielded the acid, decomp. 171° (with remelting above 300°). Either the previous ester or acid when boiled with 2*N*-sodium hydroxide passed into 4-chloro-2-hydroxybenzonitrile, m. p. 155° (at 180—200° the clear mass formed a cyaphenin derivative).

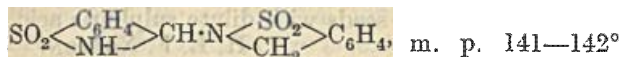
The above 5-chloro-methyl ester when boiled with hydrazine in ethyl-alcoholic solution afforded the hydrazide of 5-chloroindoxazen-2-carboxylic acid, decomp. 192°; this with sodium nitrite produced the corresponding azide, m. p. 142° (decomp.). Warming the last compound with acetic acid gave bis-(5-chloro-2-indoxazeryl)carbamide, m. p. 260°, whilst boiling with acetic anhydride produced 5-chloro-2-acetamidindoxazen, m. p. 186° (corresponding amine, m. p. 135°), from which 3-*o*-hydroxy-*p*-chlorophenyl-5-methyl-1:2:4-oxdiazole, m. p. 79°, was formed by warming with sodium hydroxide solution.

A parallel series of experiments was performed from methyl indoxazen-2-carboxylate, m. p. 69° (obtained from the 5-amino-ester by diazotisation), the following compounds being described: indoxazen-2-carboxylic acid, m. p. 140—141° (with formation of salicylonitrile); the corresponding hydrazide, m. p. 143°, and azide, m. p. 95°; *s*-bis-2-indoxazerylcarbamide, m. p. 244°; 2-aminoindoxazine, m. p. 110° (acetyl derivative, m. p. 155—156°).

R. J. W. LE FÈVRE.

Aromatic sulphonamides. J. KOETSCHET and P. KOETSCHET (Helv. Chim. Acta, 1929, 12, 669—699).—Benzaldehyde-*p*-sulphonamide is prepared in higher yields than by Dakin's method (A., 1917, i, 542) by warming "chloramine-T" with a mixture of water, *p*-toluenesulphonamide, and hydrochloric acid. Its α -naphthyl- and *p*-nitrophenyl-hydrazones have m. p. 254—255° and 256—257°, respectively. By methylation (alkali and methyl sulphate) it yields the dimethylsulphonamide, m. p. 134—137° (phenylhydrazone, m. p. 170—171°), accompanied by the monomethylsulphonamide, m. p. 119—119.5° (phenylhydrazone, m. p. 163—164°). Benzaldehyde-*p*-sulphonamide undergoes Cannizzaro's reaction giving *p*-sulphonamidobenzyl alcohol, m. p. 119—120°, and the corresponding benzoic acid, m. p. above 280°.

An improved method for the preparation of the *N*-sodium salt of *o*-toluenesulphonchloroamide is described. Treatment of "o-chloramine-T" with boiling aqueous acetic acid gives a compound (I),

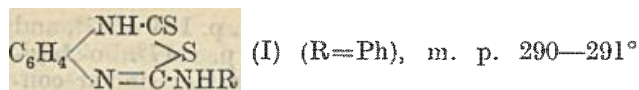


This, with the appropriate hydrazines, forms the *phenylhydrazone*, the *α-naphthylhydrazone*, and the *p-nitrophenylhydrazone* of *ψ-o-sulphonamidobenzaldehyde*, m. p. 198°, 206—208°, and 250°, respectively. In the mother-liquors from these condensations is found 1-S-dioxy-2:3-dihydro-*αβ*-benzothiazole (internal anhydride of *o-sulphonamidobenzyl alcohol*), m. p. 112.5—113°. The compound I is unaffected by boiling aqueous hydrochloric acid, but is resolved into its constituents (*ψ*-aldehyde and anhydro-alcohol) by treatment with sodium hydrogen sulphite and sulphur dioxide; methylation (methyl sulphate and alkali) gives *methyl-ψ-o-sulphonamidobenzaldehyde* (isolated as the *phenylhydrazone*, m. p. 153—154°), 1-S-dioxy-2-methyl-2:3-dihydro-*αβ*-benzothiazole (internal anhydride of *N-methyl-o-sulphonamidobenzyl alcohol*), m. p. 122—123°, and the true *-methyl* derivative of I, m. p. 263°.

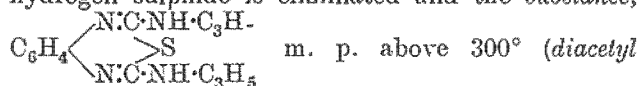
The compound $\text{SO}_2 \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{N} \end{array} \text{C} \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Me}$, m. p. 225°, may be conveniently prepared by chlorinating a solution of *o*-toluenesulphonamide in aqueous sodium hydroxide. R. J. W. LE FEVRE.

4-mp-Dihydroxyphenylthiazoles. T. B. JOHNSON and E. GATEWOOD (J. Amer. Chem. Soc., 1929, 51, 1815—1819).—*Acetamidoacetothioamide*, m. p. 123—124°, from acetamidoacetonitrile and ammonium sulphide in alcohol, gives with 3:4-dihydroxyphenyl chloromethyl ketone (cf. Stolz, A., 1905, i, 106; Hantzsch, A., 1888, 574) in alcohol 4-mp-dihydroxyphenyl-2-acetamidomethylthiazole hydrochloride, m. p. 188—190°, which is hydrolysed by hydrochloric acid to 4-mp-dihydroxyphenyl-2-aminomethylthiazole hydrochloride, m. p. 225—230°. Methylaminoacetonitrile (Heimrod, A., 1914, i, 327) and acetic anhydride in benzene give an acetyl derivative converted by alcoholic ammonium sulphide into *acetmethylamidacetothioamide*, $\text{NMeAc} \cdot \text{CH}_2 \cdot \text{CS} \cdot \text{NH}_2$, m. p. 156—157°. This yields with the chloro-ketone 4-mp-dihydroxyphenyl-2-acetmethylamidomethylthiazole hydrochloride, m. p. 186—188°, hydrolysed to 4-mp-dihydroxyphenyl-2-methylaminomethylthiazole (+EtOH), m. p. 128—130° (hydrochloride, m. p. 220—225°). *α*-Acetamidoisobutyrothioamide, m. p. 185—186° (cf. Hellsing, A., 1904, i, 563) is similarly converted into 4-mp-dihydroxyphenyl-2-*α*-acetamidoisopropylthiazole, m. p. 198—200° (hydrochloride, m. p. 188—189°), and 4-mp-dihydroxyphenyl-2-*α*-aminoisopropylthiazole hydrochloride, m. p. 210—215°. The following 4-mp-dihydroxyphenylthiazoles were also prepared: 2-thiol- (+H₂O), m. p. 250°; 2-phenyl-, m. p. 164—165°; 2-amino-, hydrochloride, m. p. 230—235°, and 2-methylamino-, hydrochloride, m. p. 275—280°. The new thiazoles are all physiologically active. H. E. F. NOTTON.

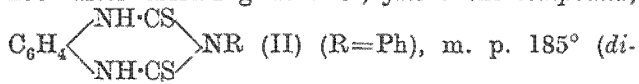
Lengthened *o*-di-derivatives of benzene and their ring closure. Formation of polymembered heterocyclic compounds from substituted phenyl-enecarbamides. T. N. GHOSH and P. C. GUHA (J. Indian Chem. Soc., 1929, 6, 181—195).—When 1:2-di(phenylthiocarbamido)benzene, $\text{C}_6\text{H}_4(\text{NH} \cdot \text{CS} \cdot \text{NHPh})_2$, is heated with hydrochloric acid (*d* 1.19), aniline and the compound,



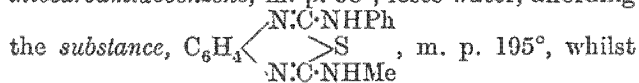
(acetyl derivative, m. p. 160°; corresponding disulphide, m. p. 210°, obtained by oxidation of I with iodine), result; this substance is also formed by the action of 20% potassium hydroxide solution on the thiocarbamide. Similarly, 1:2-di-(*o*-tolylthiocarbamido)benzene, m. p. 161°, yields the compound (I, R=*o*-Me·C₆H₄·), m. p. 300° (acetyl derivative, m. p. 200°), also formed from 1-phenylthiocarbamido-2-*o*-tolylthiocarbamidobenzene, m. p. 136°; 1:2-di-(*p*-tolylthiocarbamido)benzene, m. p. 178°, gives the compound I (R=*p*-Me·C₆H₄·), m. p. 300° (acetyl derivative, m. p. 200°; disulphide, m. p. 190°), obtained also from 1-phenylthiocarbamido-2-*p*-tolylthiocarbamidobenzene, m. p. 165°; 1:2-di-(*m*-4-xylylthiocarbamido)benzene, m. p. 145°, affords the compound I (R=C₆H₃Me₂·), m. p. 295° (acetyl derivative, m. p. 296°; disulphide, m. p. 172°); 1:2-di(methylthiocarbamido)benzene, m. p. 175°, furnishes the compound I (R=Me), m. p. 168° (disulphide, m. p. 194°); 1-phenylthiocarbamido-2-allylthiocarbamidobenzene, m. p. 245°, yields the compound I (R=C₃H₅·), m. p. 293° (disulphide, m. p. above 300°). The substance I (R=Ph, C₆H₄=C₆H₃Me), m. p. 265° (acetyl derivative, m. p. 185°; disulphide, m. p. 137°), is obtained from the di(phenylthiocarbimide) derivative, m. p. 142°, of *o*-tolylene-diamine. When 1:2-di(allylthiocarbamido)benzene is treated with concentrated hydrochloric acid, hydrogen sulphide is eliminated and the substance,



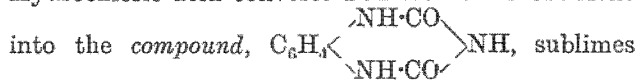
derivative, m. p. 185°, obtained by the action of acetic anhydride on the thiocarbamide), is formed. 1-Phenylcarbamido-2-phenylthiocarbamidobenzene, m. p. 200° after shrinking at 140°, yields the compound,



sulphide, m. p. 128—130°), whilst 1-phenylcarbamido-2-*p*-tolylthiocarbamidobenzene, m. p. 165°, gives the substance II (R=*p*-Me·C₆H₄·), m. p. 175—176° (disulphide, m. p. 164°). 1-Phenylcarbamido-2-methylthiocarbamidobenzene, m. p. 98°, loses water, affording



1-phenylcarbamido-2-allylthiocarbamidobenzene, m. p. 160°, furnishes the compound I (R=Ph, CS=CO). Hydrochloric acid converts 1:2-dicarbamidobenzene



above 300° (acetyl derivative, m. p. 190°), but 1:2-di-(phenylcarbamido)benzene, m. p. 220°, is unaffected.

When *o*-phenylthiocarbamidoaniline (III) (*N*-carboethoxy-derivative, m. p. 288—290°; *o*-nitrobenzylidene derivative, m. p. 215°; *m*-nitrobenzylidene derivative, m. p. 153—154°; *salicylidene* derivative, m. p. 180°) is heated with concentrated hydrochloric acid, *o*-phenylenethiocarbamide, m. p. 301—302° (lit. 290°; acetyl derivative, m. p. 200°; disulphide, m. p. 230°), results: this is also formed from the analogous

o-tolyl-, m. p. 160°, *p*-tolyl- (IV), m. p. 146—147°, and *methyl-thiocarbamidoanilines*, m. p. 117°. *o*-Allyl-thiocarbamidoaniline, m. p. 115°, under similar conditions, yields 2-allylamino-*benzthiazole*, m. p. 180° (acetyl derivative, m. p. 198°). Oxidation of III and IV with ferric chloride solution affords the compounds, $\text{C}_6\text{H}_4\text{--}\begin{array}{c} \text{N}=\text{C--NHR} \\ \text{NH--S} \end{array}$ (R=Ph and *p*-C₆H₄Me, respectively), m. p. 155—156° and 93°, respectively. Similar oxidation of the *benzylidene* derivative, m. p. 265—267°, of III gives the substance, $\text{C}_6\text{H}_4\text{--}\begin{array}{c} \text{N}=\text{C--NHR} \\ \text{NH--S} \end{array}$, m. p. 105°.

H. BURTON.

Nomenclature of alkaloids and alkaloidal derivatives. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. Chem. biol., 1929, 11, 521—530).—Present nomenclature is criticised and reforms are suggested.

F. C. HAPFOLD.

Nicotine tetrachloriodide. F. D. CHATTAWAY and G. D. PARKES (J.C.S., 1929, 1314—1317).—*Nicotine tetrachloriodide*, C₁₀H₁₄N₂·2HICl₄, m. p. 150°, is obtained quantitatively on mixing solutions of nicotine and of iodine trichloride in hydrochloric acid, and may be employed for the preparation of pure nicotine and for its isolation from tobacco, since decomposition with aqueous sodium sulphite, followed by ether extraction, produces the pure base, b. p. 249—250°. Nicotine tetrachloriodide is stable when kept in a closed vessel, but is decomposed by aqueous alkalis and more slowly by water to give mainly nicotine and nicotinic acid together with small quantities of iodate and iodide. The following were similarly prepared: *nicotinic acid tetrachloriodide*, m. p. 137°; *methyl N-methylnicotinate tetrachloriodide*, m. p. 110°; *trigonelline tetrachloriodide*, m. p. 122°.

A. I. VOGEL.

Nicotine and its derivatives. I. Molecular extinction coefficients. T. M. LOWRY and W. V. LLOYD (J.C.S., 1929, 1376—1382).—The absorption spectra of nicotine, the salt C₁₀H₁₄N₂·2HCl·ZnCl₂·H₂O, the *isomethiodide*, m. p. 164°, and its *hydriodide*, m. p. 209°, and of the *dimethiodide*, m. p. 216°, in water and of nicotine in pure *cyclohexane* have been measured. They all exhibit a strong absorption band at 2650 Å. which is twice as strong in the zinc chloride compound as in the *methiodides* but is one tenth as strong when the base is dissolved in water. It is suggested that in aqueous solution a non-ionised hydrate or *ψ*-base is formed by saturation of a double linking of the pyridine ring (cf. Decker and Kauffmann, A., 1911, i, 307).

A. I. VOGEL.

Calycanthine. I. Isolation from *Meratia præcox*. R. H. F. MANSKE (J. Amer. Chem. Soc., 1929, 51, 1836—1839).—The seeds of *Meratia præcox*, Rehd. and Wils., an Asiatic shrub, contain 2.5% of calycanthine (cf. Späth and Stroh, A., 1925, i, 1447), which had previously been isolated only from American *Calycanthaceæ*. The seeds also contain dextrose and small quantities of an *α*-alkaloid, m. p. 197—198°, which contains no phenolic groups, and an oily *β*-alkaloid (*hydrochloride*, m. p. 219—220°), both of which give a positive Ehrlich reaction. Hydrolysis

of the epicarp of the seeds with dilute sulphuric acid yields *l*-xylose.

H. E. F. NOTTON.

Anserine, new constituent of bird muscle-tissue. D. ACKERMANN, O. TIMPE, and K. POLLER (Z. physiol. Chem., 1929, 183, 1—10).—Extraction of goose flesh with water and treatment of the extract with mercuric sulphate and sulphuric acid (cf. Dietrich, A., 1914, i, 1104) affords a precipitate from which 0.12% of *anserine*, C₁₀H₁₆O₃N₄, m. p. 238—239°, [α]_D +11.26° in water [*nitrate*, m. p. 216—218° (decomp.); *chloroplatinate*, decomp. 215—220°; *chloroaurate*, m. p. about 90—95°; *picrate*, decomp. 205—208°], was obtained by removal of mercury with hydrogen sulphide and purification through the *copper oxide* compound, C₁₀H₁₆O₃N₄·CuO, decomp. 230—232° (two modifications, ultramarine blue and reddish-purple, according to solvent used for purification). The new substance is precipitated from solution by alkaloidal reagents, and it gives the ninhydrin reaction. Anserine is not present in the liver, stomach, or heart.

H. BURTON.

Constitution of anserine. W. LINNEWIEH, A. W. KEIL, and F. A. HOPPE-SEYLER (Z. physiol. Chem., 1929, 183, 11—18; cf. preceding abstract).—Anserine contains a carboxyl group, since it furnishes an *ethyl ester* (*chloroplatinate*, m. p. 225—230°). The presence of amino- and NMe groups is also indicated by the Van Slyke and Zeisel methods. Distillation with soda-lime in a current of hydrogen affords 4(5): *N*-dimethylglyoxaline, whilst treatment with barium hydroxide and water at 140° yields *dl-α-amino-β-N-methyliminazolypropionic acid*, decomp. 248—252° (*nitrate*, decomp. 144—146°), and *β*-aminopropionic acid [*α-naphthylcarbimide* derivative, m. p. 230—232° (decomp.)], separable by treatment with phosphotungstic acid. Anserine is, therefore, *α-(β'-amino-propion)amido-β-N-methyliminazolypropionic acid*.

H. BURTON.

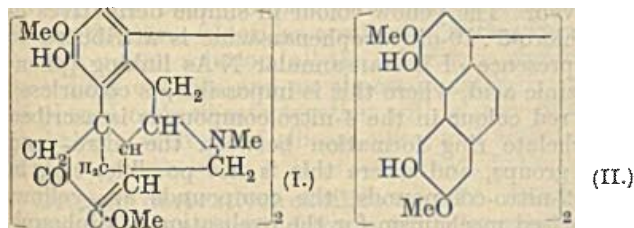
Strychnos alkaloids. II. Oxidation by permanganate of the substances C₁₉H₂₂O₈N₂. C₁₉H₂₂O₈N₂ obtained from Hanssen's acid. H. LEUCHS and A. HOFFMANN (Ber., 1929, 62, [B], 1253—1261).—The acid C₁₉H₂₂O₈N₂ reduces permanganate in faintly alkaline solution at 0° almost instantaneously until about 4 atoms of oxygen have been absorbed giving oxalic acid and an acid, C₁₇H₁₈O₈N₂, which becomes brown without softening at about 300° (also *monohydrate*); the corresponding *hydrochloride*, softening at 250—290° with slight darkening, is described. The acid is not affected by yellow mercuric oxide and hydrobromic acid in water or by bromine and hydrobromic acid. It yields an *oxime*, C₁₇H₁₈O₈N₃ (also *monohydrate* and *dihydrate*), and a *semicarbazone dihydrate*. With methyl-alcoholic hydrogen chloride it affords the *hydrochloride* of the *dimethyl ester*, C₁₉H₂₂O₈N₂Cl₂·H₂O. Boiling acetic anhydride transforms the acid into the compound, C₁₇H₁₄O₆N₂·AcOH, which loses acetic acid when heated and leaves the *dianhydride*, C₁₇H₁₄O₆N₂, converted by water into the original acid. Oxidation of the acid C₁₉H₂₂O₈N₂ by permanganate yields the acid C₁₇H₁₈O₈N₂·H₂O.

H. WREN.

Bimolecular alkaloids. I. Disinomenine and *ψ*-disinomenine. K. GOTO and H. SUDZUKI (Bull.

Chem. Soc. Japan, 1929, 4, 107—111; cf. this vol., 830).—When sinomenine is oxidised by potassium ferricyanide, silver nitrate, or similar mild agents, it gives a mixture of bimolecular products, separable by recrystallisation of the hydrochlorides. One substance, *disinomenine*, ($C_{19}H_{22}O_4N_2$), m. p. 222°, decomp. 245°, $[\alpha]_D +149.98^\circ$, gives a pink colour with formaldehyde and sulphuric acid, and yields a *hydrochloride*, m. p. above 290°, a *methiodide*, m. p. 263° (decomp.), an *oxime*, m. p. 265° (decomp.), and a *semicarbazone*, m. p. above 290°. Its isomeride, ψ -*disinomenine*, $[+MeOH]$, m. p. 228°, decomp. 245°, $[\alpha]_D -127.03^\circ$, gives a yellowish-brown colour, and yields a *methiodide*, m. p. 267—268° (decomp.), and a *hydrochloride*, an *oxime*, and a *semicarbazone*, all of which melt above 290°. Acetic anhydride converts either substance into tetra-acetyl*disinomenol* (cf. A., 1926, 1160; 1927, 146), from which *disinomenol*, m. p. above 310° (blue colour with ammoniacal silver nitrate in acetone), and the tetramethyl, *tetraethyl* (m. p. 184°), and *tetrabenzoyl* (new m. p. 280°) derivatives of the last are prepared; *disinomenol* and its derivatives are distinguished from *sinomenol* and its derivatives by the fact that the former give with sulphuric acid a brown coloration, changing to a purple flocculation on dilution, whilst the latter give a yellow coloration, destroyed on dilution. The absorption curves of *sinomenine*, *disinomenine*, and ψ -*disinomenine* are given.

Since, like *bromosinomenine*, in which the bromine atom is considered to occupy the 2-position, the *disinomenines* give a less intense diazo-coupling reaction than *sinomenine* itself, and since *bromosinomenine* does not yield a bimolecular derivative, it is thought that *disinomenine* and ψ -*disinomenine* have the formula I, the difference between the two compounds lying possibly in the point of attachment of the bridge linking. *Disinomenol* is now formulated as II.



Disinomenine occurs naturally with *sinomenine*, but ψ -*disinomenine* has not been isolated from the plant.
E. W. WIGNALL.

Preparation of phosphenyl chloride. J. A. C. BOWLES and C. JAMES (J. Amer. Chem. Soc., 1929, 51, 1406—1408).—Phosphorus trichloride and benzene vapours were passed over a quartz tube sealed in a glass vessel and heated internally by a nichrome winding. The same apparatus may be used to prepare acetamide from ammonia and acetic acid (yield almost theoretical).
S. K. TWEEDY.

Bromination of *p*-aminophenylarsinic acid. A. LEULIER and Y. DREYFUSS (Compt. rend., 1929, 188, 1416—1418).—Bromination of sodium *p*-aminophenylarsinate with 48% hydrobromic acid and hydrogen peroxide (A., 1924, i, 1297), with varying

proportions of these reagents, yields the mono- (nearly theoretical yield) or di-bromo- (85%) derivatives, or tribromoaniline.
J. W. BAKER.

Reaction between polyhydric alcohols or phenols and arsenic compounds, in particular arsinoacetic acid. B. ENGLUND (J. pr. Chem., 1929, [ii], 122, 121—140; cf. A., 1928, 1364).—A study has been made of the influence of polyhydroxy-compounds on the solubility of arsenic compounds, from which deductions are made as to the spatial arrangement of the hydroxyl groups. The results are compared with the boric acid and acetone methods of Böeseken, and the possibility of studying molecular configuration by this method is discussed.

Methylarsinic, benzylarsinic, and arsanilic acids each react with two molecules of pyrocatechol in acetic acid to yield crystalline compounds containing the group $As \left[\begin{smallmatrix} O & C \\ & \diagdown \diagup \\ & O & C \end{smallmatrix} \right]_2$. Methyl arsinoacetate and resorcinolarsinic acid each react with one molecule of *d*-tartaric acid to yield compounds of another type.

By measurement of the solubility of arsinoacetic acid, arsenic trioxide, and resorcinolarsinic acid in acetic acid in presence of hydroxy-compounds it is found that two adjacent hydroxyl groups generally greatly increase the solubility, and this effect is intensified when three or four hydroxyl groups are in a position favourable to the formation of a five-membered ring, as in ethylene glycol, glycerol, erythritol, pyrocatechol, or pyrogallol. *β*-Glycols, and *m*- and *p*-dihydric phenols, e.g., resorcinol, quinol, and phloroglucinol, have a smaller effect. Stereoisomerides with different spatial configuration of the hydroxyl groups have different effects, e.g., active and *meso*-forms of hydrobenzoin and tartaric acid, *cis*- and *trans*-forms of cyclohexane-, cyclopentane-, and hydrindene-diols. The magnitude of the effect is altered by substitution, e.g., in ethylene glycol, pinacol, and benzpinacol, and in pyrocatechol and protocatechuic acid. The influence of carbonyl or carboxyl groups on the solubility is small, e.g., in succinic acid and benzil. The velocities of the reaction of diols with arsinoacetic acid to form compounds with one and two atoms of arsenic in the molecule have also been investigated both titrimetrically and polarimetrically. Diols with *cis*-hydroxyl groups give consistently greater increases in solubility and higher velocity coefficients than the *trans*-isomerides.
R. K. CALLOW.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. IX. Synthesis of nitromethyldiphenylamine-6'-arsinic acids and their conversion into nitromethyl derivatives of 10-chloro-5 : 10-dihydrophenarsazine. Constitution of 10-chloro-5 : 10-dihydrophenarsazine. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1929, 1229—1262).—The nitromethyldiphenylamine-6'-arsinic acids were prepared by condensing the appropriate bromonitrotoluenes with *o*-aminophenylarsinic acid or the bromonitrobenzenes with aminotolylarsinic acids (potassium carbonate, amyl alcohol, and copper method). Their ring closure has been studied by conversion into the dichloro- or dibromo-arsine, where isolable, by treating a boiling solution of the arsinic

acid in a mixture of alcohol and hydrochloric or hydrobromic acid containing a trace of iodine with sulphur dioxide, followed by boiling in acetic acid solution. The 5 : 10-dihydrophenarsazines formed were oxidised to phenarsazinic acids with hydrogen peroxide in acetic acid. The following compounds were thus prepared: 2-nitro-3'-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 215—217° (decomp.); 2-nitro-3'-methyl-10-dihydrophenarsazine-6'-dichloroarsine, m. p. 129.5—130°; 10-chloro-4-nitro-7-methyl-5 : 10-dihydrophenarsazine, m. p. 201—202°; 4-nitro-7-methylphenarsazinic acid (I), m. p. 300—303° (decomp.) (sodium salt); 4-amino-7-methylphenarsazinic acid (II), unmelted at 310°, from I and ferrous hydroxide; 10-chloro-4-amino-7-methyl-5 : 10-dihydrophenarsazine hydrochloride, m. p. 216—220° (decomp.); 3-nitro-3'-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 191—192°; 10-chloro- and 10-bromo-1(or 3)-nitro-7-methyl-5 : 10-dihydrophenarsazine, m. p. 253—255° (decomp.) and 248—250° (decomp.), respectively; 4-nitro-3'-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 276° (decomp.); 2-nitro-4'-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 226—227°; 10-chloro-4-nitro-8-methyl-5 : 10-dihydrophenarsazine, m. p. 206°; 4-nitro-8-methylphenarsazinic acid, m. p. 297—300° (decomp.) (sodium, ammonium, barium, calcium, and magnesium salts); 3-nitro-2-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 223—224° (decomp.) (sodium, ammonium, barium, and calcium salts); 10-chloro- and 10-bromo-3-nitro-4-methyl-5 : 10-dihydrophenarsazine, both m. p. 216.5°; 3-nitro-4-methylphenarsazinic acid, unmelted at 306° (sodium salt); 4-nitro-2-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 277° (decomp.) (yield 73%) (sodium, ammonium, barium, calcium, magnesium, mercurous, mercuric, silver, and lead salts); 10-chloro- and 10-bromo-2-nitro-4-methyl-5 : 10-dihydrophenarsazine, m. p. 303—305° (also produced by reduction of 2-nitro-4-methylphenarsazinic acid) and 301—302°, respectively; 2-nitro-4-methylphenarsazinic acid, unmelted at 306° (ammonium, barium, calcium, silver, magnesium, mercurous, mercuric, potassium, and sodium salts); 5-nitro-2-methyl-10-dihydrophenarsazine-6'-arsinic acid (III), m. p. 224—226° (decomp.) (sodium, potassium, barium, lead, silver, mercurous, mercuric, and magnesium salts); 5-nitro-2-methyl-10-dihydrophenarsazine-6'-dichloroarsine, m. p. 173°; 10-chloro-1-nitro-4-methyl-5 : 10-dihydrophenarsazine, m. p. 258—260°; 5-nitro-2-methyl-10-dihydrophenarsazine-6'-dibromoarsine, m. p. 164°, and 10-bromo-1-nitro-4-methyl-5 : 10-dihydrophenarsazine, m. p. 272° (decomp.), from III; 1-nitro-4-methylphenarsazinic acid, unmelted at 305°; 2-nitro-6-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 195—197° [from 2-bromo-3-nitrotoluene, m. p. 41—42°, b. p. 135—136°/8 mm. and 157°/22 mm. (prepared in 67% yield from 2-amino-3-nitrotoluene by the diazo-reaction), and o-aminophenylarsinic acid] (ammonium, sodium, and barium salts); 2-nitro-6-methyl-10-dihydrophenarsazine-6'-dichloro- and -6'-dibromoarsine, m. p. 104—105° and 97—98°, respectively; 2-nitro-4-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 227—229° (decomp.) (magnesium salt); 2-nitro-4-methyl-10-dihydrophenarsazine-6'-dichloroarsine, m. p. 91—93°; 10-chloro- and 10-bromo-4-nitro-2-methyl-5 : 10-dihydrophenarsazine, m. p. 187—188° and 186—188°, respectively; 4-nitro-2-methylphenarsazinic acid, m. p. 305° (decomp.) (ammonium,

sodium, silver, barium, and calcium salts); 5-nitro-3-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 228—230° (decomp.) (ammonium, calcium, barium, silver, mercurous, mercuric, lead, sodium, and magnesium salts); 10-chloro- and 10-bromo-1(or 3)-nitro-3(or 1)-methyl-5 : 10-dihydrophenarsazine, m. p. 245—247° (decomp.) and 237—242°, respectively; 1(or 3)-nitro-3(or 1)-methylphenarsazinic acid, unmelted at 300° (sodium salt); 3-nitro-4-methyl-10-dihydrophenarsazine-6'-arsinic acid (IV), m. p. 165—166° (barium salt, 6H₂O); reduction of IV gave two isomeric ring condensation products, C₁₃H₁₀O₂N₂ClAs, m. p. 257—258° (decomp.) and 225—226° (decomp.), respectively, oxidation of which yielded two indistinguishable 1- and 3-nitro-2-methylphenarsazinic acids, unmelted at 297° (barium and sodium salts); 4-nitro-3-methyl-10-dihydrophenarsazine-6'-arsinic acid, m. p. 200° (decomp.) (sodium and ammonium salts); 10-chloro-2-nitro-1(or 3)-methyl-5 : 10-dihydrophenarsazine, m. p. 220—228° (decomp.); 2-nitro-1(or 3)-methylphenarsazinic acid, unmelted at 308° (calcium, barium, and sodium salts).

The following summarises these and previous results: (1) All substituted nitrodiphenylamine-6'-arsinic acids in which the nitro-group is in the *o*-position to the :NH group yield stable dichloroarsines; when the nitro-group is in the *m*- or *p*-position to the :NH group (exception, 5-nitro-2-methyldiphenylamine-6'-arsinic acid) the corresponding cyclic chloro-compounds are formed on reduction in the presence of hydrochloric acid. (2) All substituted 10-chloro-4-nitro-5 : 10-dihydrophenarsazines are crimson and have lower m. p. and greater solubility in organic solvents than the other nitro-10-chloro-5 : 10-dihydrophenarsazines; the m. p. of the 2-nitro-compounds are very high [exception, 10-chloro-2-nitro-1(or 3)-methyl-5 : 10-dihydrophenarsazine]. (3) 10-Chloro-3-nitro-4-methyl-5 : 10-dihydrophenarsazine is yellow, whereas the 1-nitro-compound is deep red. An explanation of the results based on the electronic theory is given. The yellow colour in simple derivatives of 10-chloro-5 : 10-dihydrophenarsazine is attributed to the presence of a transannular N·As linking (phenarsazinic acid, where this is impossible, is colourless). The red colour in the 4-nitro-compounds is ascribed to chelate ring formation between the nitro- and NH groups, and where this is not possible, *e.g.*, in the 2-nitro-compounds, the compounds are yellow. A revised mechanism for the cyclisation of diphenylamine-6'-arsinic acids, including an explanation of the intermediate formation of dichloroarsines, is given and all the results are interpreted on this basis.

A. I. VOGEL.

Meriquinonoid derivatives of dihydrophenarsazine. G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1929, 61, 13—26).—See this vol., 585.

***p*-Bromodiethylaniline and mercuric acetate.** F. C. WHITMORE, A. R. CADE, and G. J. LEUCK (J. Amer. Chem. Soc., 1929, 51, 1952).—Attempts to mercurate *p*-bromodiethylaniline (cf. *p*-bromodiethylaniline, A., 1920, i, 118) under the most varied conditions yielded only ill-defined oxidation products.

H. E. F. NOTTON.

Mercuration of naphthalic acids. G. J. LEUCK, R. P. PERKINS, and F. C. WHITMORE (J. Amer. Chem.

Soc., 1929, **51**, 1831—1836).—Sodium naphthalate and mercuric acetate in boiling aqueous solution give the *anhydride* of 8-hydroxymercuri-1-naphthoic acid (sodium salt), converted by hydrochloric acid into 1-naphthoic acid. 3-Nitronaphthalic acid gives a mixture (I) of the *anhydrides* of 3-nitro- and 6-nitro-8-hydroxymercuri-1-naphthoic acids, the former being the main product. Its sodium salt is converted by sodium iodide in alcohol into the sodium salt of mercury bis-3-nitro-8-naphthyl-1-carboxylic acid ("No. 93"). The mixture, I, gives with hydrochloric acid 3-nitro-1-naphthoic acid, m. p. 270.5—271.5° (*amide*, m. p. 280—280.8°), and 6-nitro-1-naphthoic acid (*amide*, m. p. 216.5°), from which several derivatives were prepared. 4-Nitronaphthalic acid gives on mercuriation a mixture of *anhydro*-4-nitro-8-hydroxymercuri-1-naphthoic acid with a little of the 5-nitro-derivative, identified by conversion into the 4- and 5-nitro-1-naphthoic acids. 3- and 4-Nitro-1-naphthoic acids are conveniently prepared in this way.

H. E. F. NOTTON.

Alizarin and mercuric acetate. F. C. WHITMORE and G. J. LEUCK (J. Amer. Chem. Soc., 1929, **51**, 1951—1952).—Alizarin is converted by excess of (? boiling aqueous) mercuric acetate into (? 1 : 2 : 5 : 8-tetrahydroxy-4-acetoxymercurianthraquinone, which gives with alkali a bluish-red solution and with hydrochloric acid a dye similar to alizarin.

H. E. F. NOTTON.

Organic derivatives of silicon. XXXIX. Action of sodium on phenoxychlorosilicanes. R. A. THOMPSON and F. S. KIPPING (J.C.S., 1929, 1176—1179).—Interaction of phenol (2½ mols.) in benzene solution with boiling silicon tetrachloride (1 mol.) and subsequent heating at 200° for 3—4 hrs. gave, on fractionation, *phenoxytrichlorosilicane*, b. p. 183—186°/60 mm., *diphenoxydichlorosilicane*, b. p. 215—218°/60 mm., 199.5—202°/40 mm., *triphenoxychlorosilicane*, b. p. 252—256°/60 mm., 235—239°/25 mm., and 2—5% of phenyl orthosilicate, m. p. 48°. When the three chlorides are heated with sodium in boiling xylene solution, all the chlorine is eliminated as sodium chloride and an almost quantitative yield of phenyl orthosilicate together with a grey powder, probably a mixture of silicon, silica, and silicoformic acid are produced.

A. I. VOGEL.

Organic derivatives of silicon. XL. Attempts to prepare unsaturated compounds from phenylsilicon trichloride. F. S. KIPPING, A. G. MURRAY, and (in part) J. G. MALTBY (J.C.S., 1929, 1180—1191).—Unsuccessful attempts to prepare unsaturated silicon compounds from phenylsilicon trichloride and sodium are described. In all cases a mixture of complex and probably saturated products was obtained. Phenylsilicon trichloride, b. p. 152—153°/200 mm., reacts slowly with sodium in the absence of a solvent at about 190° with the formation of an insoluble powder (25.1—26.8% Si) which is unaffected by alkali hydroxide; in naphthalene solution, a small quantity of an insoluble product (33.9—34.7% Si), yielding hydrogen with alkali hydroxides and giving a residue (13% Si) after evaporation with hydrofluoric acid, together with a large proportion of a benzene-soluble product (Si, 20.1—22.9; C, 61.6—66.8; H, 4.0—4.9%), probably containing naphthyl radicals

and >SiPh₂ groups, is obtained. Very little interaction occurs in boiling benzene or toluene solutions, but prolonged heating with benzene at about 150° gave an insoluble product similar to that obtained with naphthalene (30—31.5% Si), which gave about 1.35 atoms of hydrogen per atom of silicon on treatment with sodium hydroxide, and a benzene-soluble resin (C, 65.5; H, 4.7; Si, 22.6%) yielding about 2 atoms of hydrogen per atom of silicon when heated with piperidine and sodium hydroxide solution. With boiling xylene as solvent and completion of the reaction by the addition of potassium in a nitrogen atmosphere, a small amount of insoluble product (30.8—33.2% Si) similar to the above, and a xylene-soluble resin, which absorbed about 5% of oxygen on heating at 120° and combined with 1/9—1/4 of its weight of iodine in benzene solution, was obtained. The xylene-soluble resin was systematically fractionated with the aid of acetone and fractions with mol. wts. from about 900 to about 9000 were isolated; the crude product is a mixture of compounds containing from about 6 to at least 50 silicon atoms in the molecule.

A. I. VOGEL.

Tin tetraphenyl as a phenylating reagent. R. W. BOST and P. BORGSTROM (J. Amer. Chem. Soc., 1929, **51**, 1922—1925).—Chlorine, bromine, and iodine monochloride give with tin tetraphenyl high yields of chloro-, bromo-, and iodo-benzenes; alkyl halides give mainly unsaturated hydrocarbons and tin triphenyl halides. *tert.*-Butyl bromide gives a little *tert.*-butylbenzene, and chloroform a little triphenylmethane. Acetyl chloride at 100° gives a little acetophenone, benzoyl chloride at 200° a little benzophenone, and benzenesulphonyl chloride at 200° gives diphenylsulphone (34% of the theoretical). Sulphur and tin tetraphenyl in a sealed tube yield at 170° diphenyl sulphide, at 190° diphenyl disulphide, and at 250° thianthrene. Cold nitric acid gives nitrobenzene, and sulphuryl chloride gives tin triphenyl chloride and tin diphenyl hydroxychloride.

H. E. F. NOTTON.

Irradiated proteins. VI. Spectroscopic and biological evidence of changes in proteins produced by light. M. SPIEGEL-ADOLF and Z. OSHIMA. VII. Ultra-violet absorption of serum- and egg-albumin denatured by heat, ultra-violet, radium-, and X-rays. M. SPIEGEL-ADOLF and O. KRUMPEL (Biochem. Z., 1929, **208**, 32—44, 45—59; cf. this vol., 409).—VI. Egg-albumin and the serum-proteins in feebly alkaline solutions, which prevent visible precipitation, after exposure to a mercury-vapour lamp show increased absorption of the shorter wave-lengths. The absorption increases with the concentration of the alkali (or acid) when this is added before irradiation. Addition of the acid before irradiation produces the same effect as without irradiation, namely an increase in the transparency to ultra-violet rays.

By varying the concentrations of the added electrolytes, the differences in the absorption of serum-albumin and pseudo-globulin can be made to disappear. By the use of irradiated protein solutions or of glass plates of varying transparency as filters for short-wave-length light it is shown that *B. prodigiosus*

and *B. coli* exhibit an optimum growth inhibition at different wave-lengths.

VII. Serum- and egg-albumin (with addition of acid or alkali to prevent coagulation) when heated to 100° show an increase in absorption at the shorter wave-lengths from 274.9 μ . Longer heating of serum-albumin does not increase the absorption, but tends to diminish it. The spectral changes produced by heat are less in amount, but resemble qualitatively those produced by ultra-violet light and by radium irradiation.

J. H. BIRKINSHAW.

Fractionation of partial protein hydrolysates. K. FELIX and A. LANG (Z. physiol. Chem., 1929, 182, 125—140).—The exchange of the sodium of permutoite for certain bases (arginine, histidine, ornithine, clupeine) derived from protein hydrolysis follows the law of Rothmund and Kornfeld and is expressed by $(c_1'/c_2')(c_2/c_1)^2 = K$, where c represents the concentration of the bases in solution and c' that in the permutoite. The temperature coefficient for arginine is 1.8 per 10°. When arginine and ornithine are present together the latter is selectively taken up. All the bases can be set free from the permutoite by ammonia. The method is applied to the partial fractionation of a pepsin hydrolysate of gelatin.

J. H. BIRKINSHAW.

Micro-determination of sulphur, phosphorus, and arsenic in organic compounds by Gasparini's method. K. HELLER (Mikrochem., 1929, 7, 208—212).—A modified form of Gasparini's method (destruction of organic matter by electrolysis in nitric acid solution) and apparatus suitable for micro-determinations is described. Sulphur, phosphorus, and arsenic are eventually determined, according to established micro-methods, as barium sulphate, ammonium phosphomolybdate, and magnesium pyroarsenate, respectively. The method is unsuitable for the micro-determination of halogens.

J. S. CARTER.

Micro-determination of methoxyl and ethoxyl groups. A. FRIEDRICH (Mikrochem., 1929, 7, 185—194).—The Zeisel determination is modified by replacing the stream of carbon dioxide by an air stream and passing the volatile alkyl iodide through a heated tube packed with copper oxide and lead chromate; the resulting carbon dioxide is determined by absorption. A second determination is then carried out in the normal manner. The constitution of the alkoxy-group is calculable from the weights of carbon dioxide and silver iodide. Complete details are given and sources of error are discussed.

J. S. CARTER.

Determination of ethylene by absorption in a solution of silver nitrate. V. N. MORRIS (J. Amer. Chem. Soc., 1929, 51, 1460—1462).—Silver nitrate solution, preferably concentrated, is suitable for the quantitative absorption of ethylene, which may be recovered by diminishing the pressure.

S. K. TWEEDY.

Specific colour reaction for isobutyl alcohol. A. KUTZLNIGG (Z. anal. Chem., 1929, 77, 349—352).—Potassium ferrocyanide solution gives with isobutyl alcohol an orange coloration, especially in the light. The coloration is not produced by ether, methyl ethyl ketone, ethyleneglycol, glycerol, methyl, ethyl,

and isobutyl acetates, chloroform, carbon tetrachloride, trichloroethylene, epichlorohydrin, petroleum, benzene and its homologues, phenol, quinoline, tetralin, hexalin, decalin, methylhexalin, cyclohexanone, and methylcyclohexanone. Amyl acetate gives no coloration on heating, but on irradiation with a quartz-mercury lamp yields a yellow coloration, which, however, may easily be distinguished from that obtained with isobutyl alcohol. Although sodium nitroprusside gives no coloration with the alcohol, sodium aminoprusside and aquoprusside are more satisfactory as reagents than potassium ferrocyanide.

H. F. GILLBE.

Reducing power of polyols towards alkaline solutions of potassium iodomercurate. P. FLEURY and J. MARQUE (Compt. rend., 1929, 188, 1686—1688).—It is found that polyhydric alcohols are able to reduce potassium iodomercurate solution at 100°, the reduction being a function of the alkalinity of the medium and of the duration of the process. With mannitol, dulcitol, inositol, erythritol, glycerol, or glycol the amount of oxygen used is proportional to the number of carbon atoms in the alcohol, and is, in general, a little greater than 1 atom of oxygen per atom of carbon, except in the case of glycerol, where it is nearly 1.5. A similar, but less regular, oxidising action is displayed by potassium iodomercurate towards non-reducing sugars, and becomes less facile with increasing mol. wt. (e.g., towards trioses and tetroses), but is still quite distinct towards a polysaccharide such as glycogen. The activity of the reagent towards acid-alcohols, i.e., the normal products of the oxidation of sugars, is extremely low and in some cases is nil.

Analytical application of the foregoing to the determination of mannitol, inositol, dulcitol, and glycol is described in detail, and compared with the method of Baudouin and Lewin (A., 1927, 476).

The behaviour of the α - and β -glycerophosphoric acid towards potassium iodomercurate is markedly different, and affords a means of distinguishing between them; the α -form is a much more active reducing agent, attributed to the presence of the free secondary alcoholic group, which is not present in the β -form.

C. W. SHOPPEE.

Iodometric determination of dextrose. V. A. TOSCANI (Chemist-Analyst, 1929, 18, No. 2, 7).—Starch paste made by triturating 1 g. of soluble starch with saturated sodium chloride solution, and then adding 100 c.c. of the hot solution, is sensitive and stable. If a reducing sugar is present the solution is made alkaline before adding alkaline ferricyanide solution. To determine dextrose standard potassium ferricyanide solution and 3 c.c. of a mixture of potassium iodide (1 g.), zinc sulphate (2 g.), and sodium chloride (10 g.) in water (40 c.c.) are added, the solution is acidified and titrated with thiosulphate.

CHEMICAL ABSTRACTS.

Micro-potentiometric determination of reducing carbohydrates. J. B. NIEDERL and R. H. MÜLLER (J. Amer. Chem. Soc., 1929, 51, 1356—1359).—The potentiometric method of Daggett, Campbell, and Whitman (A., 1923, ii, 345) has been simplified and made suitable for micro- and semi-micro-determinations.

S. K. TWEEDY.

Reactions of primary arsines. S. S. NAMETKIN and V. NEKRASSOV (*Z. anal. Chem.*, 1929, 77, 285—289).—Hydrogen sulphide produces a white amorphous precipitate of the arsine sulphide in aqueous solutions of primary dichloroarsines; from solutions in 96% alcohol the precipitates are crystalline, but the test is not so sensitive. With mercuric nitrate solution the arsines produce a white precipitate of mercurous chloride which rapidly becomes grey in the cases of methyl- and ethyl-dichloroarsines. A. R. POWELL.

Determination and separation of formaldehyde and acetaldehyde by means of "methone." D. VORLANDER [with C. IHLE and H. VOLKHOLOZ] (*Z. anal. Chem.*, 1929, 77, 321—327).—"Methone" (5:5-dimethyldihydroresorcinol) may be employed for the determination of acetaldehyde and/or formaldehyde by dissolution of the precipitate of methylene- or ethylidene-dimethone in alcohol and titration with sodium hydroxide solution. The methylene compound alone can be dried to constant weight at 90—95°. Alternatively, an excess of standardised methone solution may be added to the aldehyde solution, and the excess of methone titrated with sodium hydroxide solution after removal of the condensation product by filtration. Separation of the two aldehydes may be effected by heating the mixed methone compounds at 100° with four to five times the quantity of acetic acid for 6—7 hrs.; the solution is then precipitated by addition of ice-water, and the precipitate, collected after 12 hrs., is treated with sodium hydroxide solution (*d* 1.095), whereby the formaldehyde compound alone is dissolved, and may be reprecipitated after filtration by acidification with acetic acid. The solubility corrections which must be applied are formaldehydedimethone, 0.001 g., and ethylidenedimethone, 0.008 g. per 100 c.c. of aqueous solution. H. F. GILLBE.

Micro-method for determining semicarbazones and its application to analysis of ketones. R. P. HOBSON (*J.C.S.*, 1929, 1384—1385).—Semicarbazide and semicarbazones (the latter after heating for 7—8 hrs.) when heated with a solution containing 15% of hydrochloric acid and 5% of mercuric chloride react thus: $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 + \text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2 + \text{NH}\cdot\text{NH}_2$; $\text{NH}_2\cdot\text{NH}_2 + 2\text{HgCl}_2 = \text{N}_2 + 2\text{Hg} + 4\text{HCl}$, yielding one third of their nitrogen as ammonia, the latter being determined by Pregl's modified micro-Kjeldahl method ("Quantitative Organic Micro-analysis," 1924, p. 99) with 40% aqueous sodium hydroxide containing an equal volume of a saturated solution of sodium thiosulphate (for the decomposition of the mercury ammonium complex). The application of the method to semicarbazide hydrochloride and the semicarbazones of acetone and *d*-camphor is described. A. I. VOGEL.

Micro-determination of methylimides. A. FRIEDRICH (*Mikrochem.*, 1929, 7, 195—201).—The apparatus differs from that customarily used in that condensed hydriodic acid is continuously removed from the gas stream. J. S. CARTER.

End-point of the titration in Goldenberg's method of tartaric acid determination. A. UHL (*Z. anal. Chem.*, 1929, 77, 328—334).—Litmus and azolitmin are not satisfactory indicators on account of the relatively gradual colour change. Electrometric titration is preferable, the best procedure being to titrate to the approximate end-point using azolitmin as indicator, and then to complete the titration (or titrate back) electrometrically.

H. F. GILLBE.

Alkalimetric micro-determination of amino-acids and peptides. W. GRASSMANN and W. HEYDE (*Z. physiol. Chem.*, 1929, 183, 32—38).—The method of Willstätter and Waldschmidt-Leitz (*A.*, 1922, ii, 169) has been adapted for use with 0.2 c.c. of an amino-acid solution. Phenolphthalein is replaced by 0.1% alcoholic thymolphthalein and the micro-titration is carried out with 90% alcoholic potassium hydroxide (0.01*N*). The end-point is determined by comparison with the blue colour obtained with 0.0025*M*-copper chloride and excess of ammonia. With pure amino-acids and peptides the method is accurate to $\pm 1\%$ even at a concentration of about 0.002*M*, thus agreeing with the macro-method. Determination of the rate of enzymic hydrolysis of peptides and gelatin by the micro-method compares favourably with the macro-method, but the degree of accuracy is less than with the pure amino-acids: this is attributed to the effect of the buffer solutions and protein on the end-point. H. BURTON.

Conditions for the determination of cocaine in physiological material. E. SADOLIN (*Dansk Tidsskr. Farm.*, 1929, 3, 188—196; cf. *A.*, 1927, 264).—Owing to the ease with which cocaine is hydrolysed by alkalis, its extraction by ether should be carried out in a solution the *p_H* value of which is less than 9, e.g., by employing sodium hydrogen carbonate. Of the total cocaine originally present in physiological material 60—80% can thus be recovered, even when a prolonged extraction is necessary on account of emulsification, but with urine a satisfactory determination is practicable only if the urine has an acid reaction. H. F. HARWOOD.

Determination of urobilin. M. ROYER (*Compt. rend. Soc. Biol.*, 1928, 99, 1003—1005; *Chem. Zentr.*, 1929, i, 419).—The fluorescence produced by the addition of zinc salts is compared with that of a solution of trypanflavin (10 mg. per litre corresponding with 0.613 mg. of urobilin per litre of water).

A. A. ELDRIDGE.

Biochemistry.

Chemistry of over-ventilation. G. POPOVICIU and H. POPESCU (*Compt. rend. Soc. biol.*, 1929, 101, 406—408).—In convulsions caused by over-ventilation there is an increase in serum-calcium and a

decrease in the serum-phosphate. The decrease in phosphate is reduced by ergotamine and increased by adrenaline and ephedrine. All these drugs tend to reduce the serum-calcium. E. BOYLAND.

Elimination of carbon dioxide in insects. W. H. THORPE (Science, 1928, 68, 433—434).—The elimination of carbon dioxide by various larvæ has been followed by means of a 1% solution of *o*-chlorophenol-indophenol as indicator, and confirmed by means of barium hydroxide. L. S. THEOBALD.

Determination of the carbon dioxide content of the mixed venous blood. II. Carbon dioxide equilibria between mixed venous blood and re-breathed airs. M. C. G. ISRAELS and F. W. LAMB (J. Physiol., 1929, 67, 315—324).—For accurate determination of the carbon dioxide tension of oxygenated blood, the subject should re-breathe into 4 litres of a mixture containing 3.5% of oxygen and 6.5% of carbon dioxide, for 10—12 sec., and the air finally expired should be analysed.

E. BOYLAND.

Effect of temperature on the equilibrium of carbon dioxide and blood, and heat of ionisation of hæmoglobin. G. S. ADAIR, N. CORDERO, and T. C. SHEN (J. Physiol., 1929, 67, 288—298).—The heat of ionisation of hæmoglobin calculated from the carbon dioxide dissociation curves of blood and hæmoglobin at different temperatures is less than that obtained by calorimetric methods. The heat of ionisation of the carboxyl groups varies with p_{H} ; the calorimetric results are high because the p_{H} at which they are determined is greater than that of the blood.

E. BOYLAND.

Respiratory proteins of the blood. IV. Buffer action of hæmocyanin in blood of *Limulus polyphemus*. A. C. REDFIELD, G. HUMPHREYS, and E. INGALLS (J. Biol. Chem., 1929, 82, 759—773).—Titration curves are given for the blood-serum of *Limulus*, and for solutions of the hæmocyanin in distilled water and in presence of salts. The curve given by the blood-serum is closely imitated by a solution of hæmocyanin in water in presence of an amount of magnesium chloride equivalent to that contained in the blood, the ionic strength of the solution being made up to that of the blood by addition of sodium chloride. It thus appears that the buffer value of *Limulus* blood is almost entirely accounted for by the hæmocyanin. The excess base in the normal blood-serum amounts to $18-37 \times 10^{-5}$ mol. per g. of hæmocyanin. C. R. HARRINGTON.

Glycolytic power of polymorphonuclear leucocytes. P. MAURIAC (Compt. rend. Soc. Biol., 1929, 101, 374—376).—Polymorphonuclear leucocytes are much more effective in utilisation of dextrose than are ordinary leucocytes. This glycolysis is unaffected by insulin.

E. BOYLAND.

Micro-determination of blood-sugar. I. OGAWA and K. KODAMA (J. Biochem. Japan, 1928, 10, 1—4).—The blood is deproteinised with acetic acid and potassium ferricyanide and then boiled with sodium carbonate, when the sugar causes reduction to ferrocyanide. The cooled solution is acidified with acetic acid, ferric chloride is added, and the blue coloration is matched against comparison solutions.

CHEMICAL ABSTRACTS.

Sugar in blood and cerebrospinal fluid. S. KATZENELBOGEN (J. Pharm. Exp. Ther., 1929, 36,

231—234).—The cerebrospinal-fluid-sugar level depends on the level of the blood-sugar. The ratio of the two may vary within wide limits. The meningeal permeability to dextrose may be modified in the same rabbit without apparent change in condition.

F. C. HAPFOLD.

Participation of a phosphorus compound in glycolysis of blood *in vitro*. A. ROCHE and J. ROCHE (Bull. Soc. Chim. biol., 1929, 11, 549—599).—The blood-sugar undergoes rapid glycolysis *in vitro*; blood-phosphate remains constant, but increases rapidly as glycolysis lags or ceases. The addition of dextrose to a system in which glycolysis is complete revives this process and the increase in the free phosphate content of the blood lags temporarily; such addition to fresh blood increases glycolysis and phosphate fixation. The addition of a certain amount of phosphate hastens glycolysis, but further addition is without effect. Simultaneous addition of both dextrose and phosphate increases the rate of glycolysis and lengthens the period during which phosphate is not liberated. The threshold of activation of glycolysis by phosphate is a function of the concentration of dextrose in the blood. Added calcium chloride increases the liberation of phosphate but does not effect glycolysis, sodium citrate effects neither, potassium oxalate retards glycolysis, whilst sodium fluoride stops it and delays the liberation of phosphate. When calcium chloride is added after 30 min. delay to blood treated with sodium fluoride, glycolysis is activated, whilst addition after 24 hrs. causes an abundant liberation of phosphate but no glycolysis. The degradation of dextrose occurs simultaneously with phosphate fixation.

F. C. HAPFOLD.

Determination of chloride in serum and red corpuscles. M. M. LEVY (Bull. Soc. Chim. biol., 1929, 11, 633—634).—To 1 c.c. of serum are added 10 c.c. of silver nitrate (2.906 g. per litre), 1.4 c.c. of saturated potassium permanganate solution, and 4 c.c. of nitric acid. The whole is boiled until the precipitate is white, cooled, and 0.5 c.c. of saturated iron alum solution is added. The excess of silver nitrate is titrated against a standard solution of potassium thiocyanate. The method can be applied to the red corpuscles.

F. C. HAPFOLD.

Micro-determination of chlorides in blood and cerebrospinal fluid. D. S. SCHEFER (Zhur. exp. Biol. Med., 1928, 10, 261—265).—The blood (0.1 c.c.) is treated with (1 : 3) nitric acid (3 c.c.) and hydrogen peroxide solution (1 c.c.), heated to coagulate the protein, and centrifuged, the residue being again treated with nitric acid (2 c.c.) and centrifuged. The united liquids are mixed with 0.01N-silver nitrate (2 c.c.), the solution is centrifuged, and the liquid is titrated with 0.01N-ammonium thiocyanate. In the analysis of cerebrospinal fluid the hydrogen peroxide is omitted.

CHEMICAL ABSTRACTS.

Determination of sulphur in blood and organic products. A. LESURE and A. DUNEZ (Bull. Soc. Chim. biol., 1929, 11, 600—608).—Certain procedures in a previous method are elaborated (A., 1928, 1270). Trichloroacetic acid may be required to remove traces of proteins from serum even after a second

treatment with acetic acid. Benzidine hydrochloride is suggested as more suitable than benzidine in the preparation of the sulphate precipitant. In the determinations of free sulphate and of total oxidised sulphur, the deproteinised serum is first dried and extracted with alcohol at 96°. Sera having total sulphur content exceeding 0.18 part per 1000 and ratios of oxidised sulphur to total sulphur less than 1:2 are definitely pathological. The total sulphur content of some defatted normal and pathological tissues has been determined. F. C. HAPFOLD.

Micelle changes produced by the addition of crystalloids to serum. G. CLUZET (Compt. rend. Soc. Biol., 1929, 101, 458—461).—The viscosity and refractive index of serum have maxima at p_H 5.5, but the maximum conductivity occurs at p_H 7.0. Electrolytes affect these physical properties but sucrose and dextrose do not. E. BOYLAND.

Fractionation of water-soluble proteins of blood-serum. S. GOLDSCHMIDT and H. KAHN (Z. physiol. Chem., 1929, 183, 19—31).—Treatment of ox blood-serum with solid ammonium sulphate to give a concentration of 26% causes the precipitation of the globulin. The ammonium sulphate content of the filtrate is increased to 36%, which precipitates an albumin fraction, and subsequent saturation of the filtrate from this yields a further albumin fraction. Purification of these by electrodialysis and subsequent precipitation within the following limits of concentration of ammonium sulphate, 29—33, 33—36, and 37—41%, affords three fractions, the elementary analyses, nitrogen distributions, and histidine and tryptophan contents of which were determined. The most soluble fraction (precipitated by 37—41% ammonium sulphate; 4% of total albumin) contains no tryptophan and the maximum quantity of histidine. H. BURTON.

Blood chemistry of rattlesnakes. J. M. LUCK and L. KEELER (J. Biol. Chem., 1929, 82, 703—707).—Analytical figures are given for the blood of two species of rattlesnake, *Crotalus atrox* and *C. oregonus*; the blood is chiefly characterised by the almost complete absence of carbamide and by the high content of amino-acids. C. R. HARRINGTON.

Blood coagulation. Retardation and acceleration. E. WALDSCHMIDT-LEITZ, P. STADLER, and F. STEIGERWALDT (Z. physiol. Chem., 1929, 183, 39—59).—The coagulation of goat's blood, in presence of isotonic sodium chloride solution at 37°, is inhibited by hirudin, and a "hirudin unit" is defined as the amount necessary to prolong the normal period of clotting (5 min.) to 25 min. The number of these units in 1 g. of a preparation is termed the "hirudin value." Extraction of leeches' heads with various solvents and subsequent determination of the hirudin values shows that aqueous glycerol is the best medium. Attempted precipitation of hirudin from an extract by heavy metal salts is unsatisfactory, but adsorption on aluminium hydroxide at p_H 4.7 is almost quantitative, and almost complete elution is obtained using ammonium phosphate solution. The activity of a neutral, aqueous solution is only slightly impaired by boiling for several hours, but in presence of sodium chloride solution it undergoes complete loss of activity

after 4 hrs. at 100°. The activity is also destroyed by trypsin-kinase, pepsin, and papain-hydrogen cyanide at their optimum p_H values. Purification of an extract is effected by adsorption of impurities on kaolin, subsequent adsorption on aluminium hydroxide, and elution of the adsorbate. The hirudin is then obtained by precipitation with alcohol and ether.

Heparin (cf. Howell, A., 1925, i, 1346; 1928, 318), obtained from dog liver, affects the coagulation of blood in almost an identical manner to hirudin. It is purified by the above method. The enzymic destruction, however, differs from that of hirudin. Proteolytic substrates (proteoses and peptides) usually retard coagulation, whilst trypsin-kinase causes an acceleration. H. BURTON.

Sensitisation of erythrocytes by amboceptors of specific sera. A. P. KONIKOV (Zhur. exp. Biol. Med., 1928, 10, 357—366).—Combination of erythrocytes with amboceptors is optimal at p_H 6.0—6.7, and at a definite salt concentration; the presence of an electrolyte is essential. The process of sensitisation is interpreted as an ionic reaction resulting in the formation of a complex containing stroma, amboceptor, and salt. CHEMICAL ABSTRACTS.

Behaviour of hæmolytic, complement-free hæmolytic, and normal sera in presence of chemical hæmolysers. K. C. SEN and N. N. MITRA (J. Indian Chem. Soc., 1929, 6, 155—170).—Hæmolysis of sheep's red blood-corpuscles by saponin, potassium oleate, sodium taurocholate, 0.002*N*-hydrochloric acid, and 0.04*N*-sodium hydroxide, in presence of sodium chloride solution, is inhibited by a low concentration of added hæmolytic serum. With larger concentrations of the serum, in presence of saponin and oleate, the time of hæmolysis is practically the same as with the serum alone, the effect of the chemical hæmolyser being inhibited almost entirely. Under similar conditions, hydrochloric acid and taurocholate cause an inhibition, sodium hydroxide an acceleration. Using complement-free serum, the hæmolysis by saponin and taurocholate is inhibited to a greater extent than with hæmolytic serum. The results previously described (Sen and Sen, A., 1928, 1151) on the inhibition of taurocholate hæmolysis by normal serum are confirmed. Using low concentrations of corpuscles and small amounts of serum inhibition also occurs, but with relatively large quantities of serum there is an acceleration (cf. Ponder, A., 1923, i, 975); a similar phenomenon is observed with oleate. The acceleration depends also on the time interval after which the serum is added to the corpuscle-hæmolyte mixture, since addition before or with the hæmolyte causes inhibition. No acceleration of saponin hæmolysis by normal serum was observed under the conditions studied. H. BURTON.

Hæmolysis in sucrose solution and behaviour of normal serum in presence of chemical hæmolysers. A. C. ROY and K. C. SEN (J. Indian Chem. Soc., 1929, 6, 171—180).—The time-dilution curves for the hæmolysis of sheep's red blood-corpuscles by taurocholate, saponin, and oleate in presence of sucrose solution are normal except for high concentrations of taurocholate (cf. this vol.,

589). The inhibiting action of the sugar is confirmed. Inhibition or acceleration of the time of hæmolysis by taurocholate or oleate can be obtained by addition of normal serum, depending on the time interval after which the serum is added to the mixture (cf. preceding abstract). With low corpuscle concentration, an increased amount of serum causes an acceleration. The results are analogous to those obtained in presence of sodium chloride solution.

H. BURTON.

Effect of p_H on saponin hæmolysis. M. BODANSKY (J. Biol. Chem., 1929, 82, 567—577).—The effect of acid on saponin hæmolysis observed by Ponder (A., 1926, 751) is compounded of two effects, (a) the formation of an ionisable compound with the saponin which retards hæmolysis and (b) the action on the blood-corpuscles themselves, which, as their positive charge increases on the acid side of the isoelectric point, become more sensitive to saponin, and, conversely, are more resistant at alkaline reactions. This effect of p_H on the blood-corpuscles themselves is predominant. C. R. HARRINGTON.

Electro-osmosis as the principal factor in specific hæmolysis. A. P. KONIKOV (Zhur. exp. Biol. Med., 1928, 10, 368—383).—The combination between complement and salt is chemical in nature.

CHEMICAL ABSTRACTS.

Relation of chromatin to hæmoglobin and bilirubin. H. H. RIECKER (J. Exp. Med., 1929, 49, 937—943).—The iron content of the spleen and bone-marrow (determined histologically) depends on the chromatin content, being high when hæmoglobin is being formed.

E. BOYLAND.

Structure and composition of hæmosiderin. S. F. COOK (J. Biol. Chem., 1929, 82, 595—609).—Hæmosiderin granules were extracted in an unaltered condition from spleen pulp by digestion of the tissue with dilute potassium hydroxide solution in the cold. Treatment of the granules with hydrochloric acid removed the iron as ferric chloride, leaving colourless stromata. Extraction of the granules with 1% nitric acid gave a brown solution from which, by increasing the acid to 20%, there was precipitated a coloured compound containing only iron (44%), hydrogen, and oxygen; traces of ionised iron were left in the mother-liquor. It appears therefore that the granules consist of a stroma impregnated with a colloidal form of ferric hydroxide, this supposition being confirmed by the fact that the qualitative reactions of the pigment extracted by 1% nitric acid could be imitated by those of a solution of colloidal ferric hydroxide prepared artificially.

C. R. HARRINGTON.

Nature of the sugar residue in the hexose-monophosphoric acid of muscle. J. PRYDE and E. T. WATERS (Biochem. J., 1929, 23, 573—582).—The hexosephosphoric acid of normal muscle press-juice from rabbit, goat, and donkey is a monophosphoric acid, of brucine salt —20.3° in methyl alcohol. The diphosphoric acid, identical with that of yeast fermentation, is obtained only when the fermentative resynthesis using sodium fluoride is employed (cf. Embden and Zimmermann, A., 1925, i, 729; 1927, 749). The carbohydrate

residue of muscle hexosemonophosphoric acid consists of 90% of dextrose and 10% of ketose.

S. S. ZILVA.

Regularity of variation of characters of oils extracted from an animal as a function of the section used. L. MARGAILLAN (Compt. rend., 1929, 188, 1630—1632; cf. Marcelet, B., 1926, 677).—Oils extracted out of contact with air from the fatty tissues of specific sections of the *Delphinus tursio*, Fabr., show a regular increase in their iodine value proceeding from the head to the tail. In order to characterise the oil it is therefore necessary to define rigorously the section of the tissues extracted.

C. C. N. VASS.

Unsaponifiable material. I. Distribution of unsaponifiable matter in the animal body. E. IGARASHI (Sei-I-Kwai Med. J., 1928, 47, No. 9; Abstr. 1—2).—In the rabbit the voluntary muscle contains less cholesterol and more unknown unsaponifiable substance than involuntary muscle; the unknown unsaponifiable substance is present chiefly in the nervous system and endocrine organs. The ratios of fatty acid to cholesterol and to the unknown saponifiable substance are constant in organs of different animals.

CHEMICAL ABSTRACTS.

Behaviour of cholesterol in the animal body. I. Determination of cholesterol in tissue. J. ONIZAWA (J. Biochem. Japan, 1928, 10, 45—61).—The finely-minced tissue is mixed with twice its volume of 2% sodium hydroxide solution; after several hours, the mixture is heated at 100° for 30—60 min. until almost complete dissolution is effected. The liquid and the rinsings (water, acetone, ether) of the vessel are vigorously shaken, the ether layer is separated, and the extraction repeated twice, with careful rinsing (ether). The ethereal solution is washed with dilute alkali, the ether is removed, and the residue dried on a water-bath and then in an oven at 80°. An ethereal solution of the residue is filtered through an asbestos filter; after removal of the ether the substance is treated while warm with acetone and filtered, after 4 hrs., through asbestos. After evaporation of the acetone, the substance is dissolved in chloroform or ether, and the solution is used for the determination, the cholesterol (1—3 mg.) being precipitated with a 1% solution of digitonin in 80% alcohol. After 12 hrs. the mixture is kept for 5—10 min. with acetone (80%) at 40—50°, centrifuged, and the supernatant liquid filtered through asbestos. The precipitate is washed twice with 80% acetone, then transferred to the filter with pure acetone, washed (ether, acetone, water), and dried in a vacuum at 105°. The error for 1 mg. does not exceed 3%. For the determination of cholesterol esters saponification is effected with saturated alcoholic sodium hydroxide for 6 hrs. at 100°, whereby, however, a loss (2—3%) of the digitonin compound occurs.

CHEMICAL ABSTRACTS.

Spectrographic analysis of the ash of blood and organs. P. DUTOIT and C. ZBINDEN (Compt. rend., 1929, 188, 1628—1629).—By means of the arc spectra the following metals have always been observed in the ash of blood, lightly calcined to avoid any loss of volatile chlorides and phosphorus compounds:

silver, aluminium, calcium, copper, iron, potassium, magnesium, manganese, sodium, phosphorus, silicon, titanium, and zinc. In some samples, cobalt, chromium, germanium, lead, nickel, tin, and strontium were observed. The analysis of the ash of tumours and organs showed a selective adsorption or absence of the heavy metals; thus nickel, cobalt, and lead accumulated in the pancreas, the suprarenal glands retained tin, and zinc predominated in the liver and kidney. Copper and silver appear to be absent from tumours.

C. C. N. VASS.

Occurrence of nickel in bones. A. MARTINI (Mikrochem., 1929, 7, 235).—The presence of nickel in gelatin has been traced to the bones used in its manufacture. Nickel is apparently a normal constituent of bones.

J. S. CARTER.

Colostrum of East Friesian milch sheep. A. BURR (Landw. Jahrb., 1928, 68, Suppl. I, 176—178; Chem. Zentr., 1929, i, 163).—The dry matter is high, the lactose at first low, rising later from 2 to 5%, the chlorine low (0.07%), and ash content 1%. Nitrogenous substances immediately after lambing are high (17.89—23.12).

A. A. ELDRIDGE.

Colostrum. A. L. PROVAN (Welsh J. Agric., 1928, 4, 141—147).—Average values, for shorthorn cows, of colostrum from the second and third milkings, 12 hrs. and 24 hrs., respectively, after calving, and of normal milk were: total solids 20.65, 16.68, 12.63; fat 3.31, 3.50, 3.69; solids not fat 18.26, 13.18, 8.94; protein 13.05, 8.15, 3.41; ash 0.937, 0.817, 0.708; CaO 0.2011, 0.1864, 0.1646; P_2O_5 0.3390, 0.3269, 0.2324; K_2O 0.1902, 0.2005, 0.1952; Cl 0.1323, 0.1135, 0.0962%. Samples of colostrum exhibited considerable individual variations. Analyses of samples of colostrum at different periods after calving showed a rapid diminution of the protein and chloride contents, and a slow diminution of the lime and phosphate contents. The fat content of colostrum decreased with increasing age of the cow. Variations with the number of calvings and with the breed of cows are recorded.

CHEMICAL ABSTRACTS.

Inorganic constituents of milk. N. C. WRIGHT and J. PAPISH (Science, 1929, 69, 78).—Spectrographic examination of cow's milk obtained from various localities in Great Britain and the United States showed the presence in small but definite traces of the following elements not previously identified in milk: silicon, boron, titanium, vanadium, rubidium, lithium, and strontium. One sample of dried milk contained more than the usual amount of copper; another sample obtained from cows pasturing near zinc smelters contained an abnormal quantity of zinc.

L. S. THEOBALD.

Physiology of the pancreas. IV. Elimination of dyes in the external secretion of the pancreas. L. A. CRANDALL, E. OLDBERG, and A. C. IVY (Amer. J. Physiol., 1929, 89, 223—229).—Sodium thiocyanate and some dyes (e.g., fuchsin, fluorescein, methylene-blue, rhodamine, and safranin) after intravenous injection are excreted to a slight extent in the pancreatic secretion.

E. BOYLAND.

Inorganic composition of body fluids of the Chelonia. H. W. SMITH [with H. SILVETTE] (J.

Biol. Chem., 1929, 82, 651—661).—The pericardial and perivisceral fluids of turtles contain considerably more hydrogen carbonate and correspondingly less chloride than the blood-serum; the potassium, calcium, and magnesium may also be reduced in comparison with the blood, although the total base content of both fluids remains about the same. A transudate which is sometimes to be found in the infra-cardial spaces has the composition of a simple ultrafiltrate of the blood-serum, and is characterised as lymph. The unequal distribution of hydrogen carbonate between the blood and the tissue fluids is ascribed to a secretory activity on the part of the cell membranes determining the transport of certain ions.

C. R. HARINGTON.

Fat excretion. VI. Excretion by Thiry-Vella fistulas. R. W. ANGEVINE (J. Biol. Chem., 1929, 82, 559—565).—Figures are given for the composition of the lipins excreted by an isolated loop of small intestine in dogs. Both the total amount and the composition of this lipin fraction were independent of the diet of the animal as well as of the level of the small intestine selected.

C. R. HARINGTON.

Loss of water and salts through the skin. W. HANCOCK, A. G. R. WHITEHOUSE, and J. S. HALDANE (Proc. Roy. Soc., 1929, B, 105, 43—59).—Loss of water from the skin in temperate climates is largely due to the evaporation of water passing by osmosis through the skin, and the amount of chloride lost is small. As the loss of water becomes greater due to true sweating the percentage of chloride in the water increases and true sweat contains about nine times as much sodium chloride as potassium chloride. The percentage of chloride in true sweat can increase with duration and rate of sweating from 0.06 to 0.22%.

E. A. LUNT.

Nitrogen excretion of fishes. H. DELAUNAY (Compt. rend. Soc. Biol., 1929, 101, 371—372).—Teleosts like marine invertebrates excrete nitrogen mainly in the form of ammonia but the elasmobranchs excrete urea.

E. BOYLAND.

Biochemical determination of allantoin in urine. R. FOSSE, A. BRUNEL, and P. DE GRAEVE (Compt. rend., 1929, 188, 1632—1634).—In alkaline media, the allantoinase and urease of soya-bean extract transform allantoin into allantoic acid and destroy the urea; subsequent treatment with hydrochloric acid destroys the urease and liberates urea, which is then weighed as dioxanthylcarbamide, from allantoic acid. In order to eliminate the urea formed from uric acid by the soya-bean extract (Nemec, A., 1921, i, 213), the uric acid is first removed by precipitation with acid mercuric sulphate. Preliminary determinations of the allantoin content of some animals' urine are recorded.

C. C. N. VASS.

Ammonia coefficients of urine. R. GOFFON (Bull. Soc. Chim. biol., 1929, 11, 531—542).—The application of the constants of Hasselbalch and others to the study of the renal regulation of the acid-base equilibrium is limited.

F. C. HAFFOLD.

Origin of urinary ammonia. S. R. BENEDICT and T. P. NASH, jun. (J. Biol. Chem., 1929, 82, 673—678).—The work of Bliss (this vol., 339) and of

Embsden and others (*ibid.*, 346) on ammonia formation and utilisation in the organism is criticised. The authors' previous view (A., 1922, i, 191) that urinary ammonia is formed in the kidney is confirmed, carbamide being regarded as the probable precursor.

C. R. HARRINGTON.

Purine bases in urine of dogs. H. LETHAUS (Z. physiol. Chem., 1929, 183, 98—102).—Dogs fed on a diet of meat and rice excrete uric acid, hypoxanthine, adenine, and xanthine.

H. BURTON.

Micro-determinations of carbon and nitrogen in faecal material. A. BOIVIN and J. ROCHE (Bull. Soc. Chim. biol., 1929, 11, 543—548).—A modification of the method of Nicloux is preferred to Pregl's micro-method for the determination of carbon in dried faeces, and the micro-Kjeldahl to the micro-Dumas method for the determination of nitrogen.

F. C. HAPPOLD.

Insulin in acromegalic diabetes. H. ULRICH (Arch. Int. Med., 1929, 43, 785—794).—A review of the literature demonstrates that the view is unfounded that diabetes associated with acromegaly responds to treatment by insulin as well as does pancreatic diabetes.

W. O. KERMACK.

The cholesterol of the blood-plasma in epilepsy. M. GOSDEN, J. T. FOX, and W. R. BRAIN (Lancet, 1929, ii, 12—16).—Epilepsy is accompanied by a decrease in the cholesterol of the blood-plasma.

E. BOYLAND.

Influence of iodine on the excretion of creatine in exophthalmic goitre. W. W. PALMER, D. A. CARSON, and L. W. SLOAN (J. Clin. Invest., 1929, 6, 597—608).—Administration of iodine diminished creatinuria.

CHEMICAL ABSTRACTS.

Optimal hydrogen-ion concentrations in colloidal gold in the Lange test. H. NICOL (J.S.C.I., 1929, 48, 100T).—The author concludes that a slightly alkaline sol is preferable. Dilute oxalic acid may be used to adjust the p_H without affecting the physical condition of the sol.

Early detection of mastitis by examination of milk. G. ROEDER (Fortschr. Landw., 1928, 3, 871—873; Chem. Zentr., 1929, i, 163).—Mastitis is accompanied by a higher, and then by a lower, p_H than that (6.3—6.6) of normal milk. Bromothymol-blue is used as indicator.

A. A. ELDRIDGE.

Experimental dehydration; chemical changes in the blood of the dog contrasted with those following obstruction of the cardiac end of the stomach. R. L. HADEN and T. G. ORR (J. Exp. Med. 1929, 49, 945—953).—In dehydration by intestinal obstruction and administration of sucrose, the blood-chlorides and the urine output are higher than in simple obstruction, whilst the total protein and non-protein-nitrogen are lower.

E. BOYLAND.

Carbohydrate metabolism in parathyroidectomised dogs. C. I. REED (Amer. J. Physiol., 1929, 89, 230—238).—The tetany following parathyroidectomy is relieved by administration of dextrose, but during the tetany the dextrose tolerance is lower than normal.

E. BOYLAND.

Effect of insulin on parathyroidectomised dogs. C. I. REED (Amer. J. Physiol., 1929, 89, 239—242).—Parathyroidectomy does not influence the effect of insulin on the blood-sugar, but insulin produces an increase in the blood-calcium and decrease in the blood-phosphate.

E. BOYLAND.

Prevention of tetany of parathyroidectomised dogs. III. Ammonium chloride. I. GREENWALD (J. Biol. Chem., 1929, 82, 717—725).—Administration of ammonium chloride relieves tetany in parathyroidectomised dogs with coincident increased excretion of phosphorus, sodium, and potassium. The relief of tetany is probably due to diminished reflex excitability associated with the condition of acidosis.

C. R. HARRINGTON.

Absorption of phosphorus in normal and rachitic children. G. MURDOCH (Arch. Dis. Childhood, 1927, 2, 285—301).—Increased serum-phosphate was observed on administration of sodium hydrogen phosphate to normal and rachitic children; addition of calcium lactate diminished the effect.

CHEMICAL ABSTRACTS.

Suprarenal insufficiency. IV. Blood-sugar in suprarenalectomised rats. L. C. WYMAN and B. S. WALKER (Amer. J. Physiol., 1929, 89, 215—222).—Suprarenalectomy produced a marked fall in blood-sugar, but this could be maintained at a normal level by transplanted cortical tissue.

E. BOYLAND.

Serum-calcium of cats during fasting. S. MORGULIS and A. M. PERLEY (Amer. J. Physiol., 1929, 89, 213—214).—The serum-calcium of cats remained fairly constant during fasting.

E. BOYLAND.

Calcium and magnesium relationships in the animal. W. P. ELMSLIE and H. STEENBOCK (J. Biol. Chem., 1929, 82, 611—632).—Administration of magnesium salts was without effect on the metabolism of calcium in rats on normal diets and on diets deficient in calcium; the severity of the rickets produced in rats by diets rich in calcium and low in phosphorus was not increased by simultaneous administration of magnesium. Therapeutic use of magnesium therefore appears to be without danger.

C. R. HARRINGTON.

Metabolism of sulphur. XVI. Diet and composition of hair in the young white rat. H. D. LIGHTBODY and H. B. LEWIS (J. Biol. Chem., 1929, 82, 663—671).—The previous conclusion (this vol., 843) that cystine is utilised primarily for growth requirements and secondarily for the formation of hair is confirmed. The cystine and sulphur content of the hair of young rats was reduced by deficiency of cystine in the diet, no such reduction being observed in cases of retardation of growth by dietary deficiency of other amino-acids.

C. R. HARRINGTON.

Nerve metabolism. V. Phosphates. R. W. GERARD and J. WALLEN (Amer. J. Physiol., 1929, 89, 108—120).—Rest in nitrogen causes a breakdown of the acid-labile and acid-stable forms of combined phosphate, to produce inorganic phosphate. This is reversed in oxygen. Stimulation in oxygen produces the same changes as occur with rest in nitrogen, but the change is not so great.

E. BOYLAND.

Alleged toxicity of galactose. L. RANDOIN and R. LECOQ (Compt. rend. Soc. Biol., 1929, 101, 355—357).—With a suitable diet pigeons are able to utilise galactose satisfactorily, when it forms the only sugar of the food.
E. BOYLAND.

Origin and destination of cell-fat. J. AMAR (Compt. rend., 1929, 188, 1626—1628).—Biochemical, biological, and thermal reactions and clinical data are employed to support the view that lipogenesis takes place in the cytoplasm at rest, glycogenesis during muscular activity.
C. C. N. VASS.

Behaviour of aminobenzoic acid in the body of lower animals. T. KAMEI (J. Biochem. Japan, 1928, 10, 189—195).—In the frog, *o*-, *m*-, and *p*-aminobenzoic acids are excreted (20%) unchanged. Neither uraminobenzoic nor aminohippuric acid was found. In the turtle the *m*- and *p*-compounds behave likewise, but of the *o*-compound only 3% appears in the urine.
CHEMICAL ABSTRACTS.

Basal metabolism of inhabitants of the tropics. P. J. T. VAN BERKHART (Med. Dienst. Volks. Ned.-Indie, Reprint, 1929, 69 pp.).—The basal metabolism of Europeans and Malays living in the tropics is lower than that of Europeans living in temperate climates.
F. C. HAPFOLD.

Basal metabolism of inhabitants of the tropics. C. EYKMAN (Med. Dienst. Volks. Ned.-Indie, Reprint, 1928, 4 pp.).—Polemical: A reply to van Berkhart (preceding abstract).
F. C. HAPFOLD.

Hydrogen-ion concentration of the reproductive organs of the White Leghorn chicken. G. D. BUCKNER and J. H. MARTIN (Amer. J. Physiol., 1929, 89, 164—169).—The mucosa of the upper part of the oviduct of an actively laying chicken has p_H 6.3—6.6 and that of the uterus and vagina has p_H 5.6—5.9. The semen of the vesicles of a cock is at p_H 7.3. The albumin of an egg has p_H 7.4 in the uterus, 8.2 when freshly laid, and 9.8 20 days after laying.
E. BOYLAND.

Effect of p_H on the action of certain poisons. A. A. LJUBUSCHIN (Zhur. exp. Biol. Med., 1928, 10, 277—283).
CHEMICAL ABSTRACTS.

Phosphorus poisoning in rabbits. A. HURUYA (J. Biochem. Japan, 1928, 10, 63—95).—The urinary nitrogen is increased in mild, and decreased in severe, intoxication; the urea fraction decreases, and the ammonia fraction increases, with the degree of intoxication. Injection of phosphorus causes increased excretion of sulphur. Affection of the kidneys is accompanied by high values for the blood-non-protein-nitrogen and -sulphate.
CHEMICAL ABSTRACTS.

Detection of lead in body-fluids and tissues. D. GANASSINI (Arch. Ist. Biochim. Ital., 1929, 1, 105—112).—Addition to serum containing lead of a little 10% sodium sulphite solution gives an immediate precipitate of lead sulphite, insoluble in excess of the reagent. In cases of chronic lead poisoning, however, this test often fails, as the lead is fixed in the coagulum. The blood is then repeatedly treated, at boiling temperature, with a little nitric acid, and

the filtered, slightly coloured liquid mixed with an equal volume of saturated sodium sulphite solution; within 12 hrs. lead sulphite settles. Urine containing lead sometimes deposits lead sulphite when treated with its own volume of saturated sodium sulphite solution. If a negative result is obtained in this way, 100 c.c. of the urine are boiled for a few minutes with 5 c.c. of nitric acid and excess (about 10 g.) of solid sodium sulphite is gradually dissolved in the solution; the appearance of a white precipitate after 12 hrs. renders probable the presence of lead. The washed precipitate should always be identified (1) by treating it with a solution of 1 g. of iodine and 2 g. of potassium iodide in 100 c.c. of water, the iodine converting the lead sulphite into the sulphate, with which potassium iodide gives lead iodide, or (2) by warming it on a microscope slide with hydrochloric acid and treating the dry residue with a crystal of potassium nitrite and a drop of a solution of 4 g. of sodium acetate and 2 g. of copper acetate in 100 c.c. of 10% acetic acid; black or brown cubes of the compound $K_2CuPb(NO_2)_6$ are thus formed. A rapid test for lead in urine consists in shaking 10 c.c. of the urine with 8—10 drops of hydrochloric acid, about 1 g. of powdered sodium sulphite, and a little zinc dust; provided that neither bismuth nor mercury has been administered, the appearance of a black precipitate indicates the presence of lead. Modified conditions are given for Mayençon and Bergeret's electrolytic test, in which the lead is deposited as metal by means of a platinum-zinc or platinum-aluminium couple. T. H. POPE.

Detection of bismuth in the inflammatory nodules after intramuscular injections. J. LEBOUCC (J. Pharm. Chim., 1929, [viii], 9, 524—525).—Bismuth has been detected in the greyish nodules occurring in the gluteal region of a patient after intramuscular injection.
E. H. SHARPLES.

Bismuth in the animal body. R. VAURS (Bull. Soc. Chim. biol., 1929, 11, 609—619).—Methods used for the detection of bismuth in urine are criticised. A method is described in which the urine is concentrated and organic matter destroyed by treatment with nitric and sulphuric acids. Calcium sulphate is removed, the filtrate neutralised with ammonia and acidified with hydrochloric acid, and bismuth precipitated as the sulphide. To remove copper the sulphides are redissolved in nitric acid and the bismuth is precipitated as basic carbonate.
F. C. HAPFOLD.

Standardisation and stabilisation of mydriatics and myotics. E. E. SWANSON, H. E. THOMPSON, and C. L. ROSE (J. Amer. Pharm. Assoc., 1929, 18, 446—450).—Atropine sulphate, homatropine sulphate, scopolamine hydrobromide, hyoscyamine sulphate, ephedrine and β -ephedrine and their sulphates have been biologically assayed by the cat's-eye method of Munch (J. Assoc. Off. Agric. Chem., 1927, 10, 383). The results agree with those reported by Munch. Five tinctures of belladonna, all of which gave similar results by chemical assay, showed a variability of 1.5—8 times by the above method. This is probably due to the presence of more active alkaloids.
E. H. SHARPLES.

Rate of absorption of cocaine hydrochloride when injected subcutaneously into rabbits. H. SANDQUIST and W. HÖK (Svensk Farm. Tid., 1928, 32, 649).
CHEMICAL ABSTRACTS.

Influence of ergotamine on the blood-sugar. G. EDA (J. Biochem. Japan, 1928, 10, 101—114).—Experiments on normal man and dogs do not justify the conclusion that ergotamine has a hypoglycaemic action, whereas in diabetes, or in depancreatised dogs, the blood-sugar is diminished.

CHEMICAL ABSTRACTS.

Creatine. I. Effect of creatine on blood-sugar. R. M. HILL and I. H. MATTISON. II. Effect of creatine on rabbits. W. A. PEABODY and R. M. HILL (J. Biol. Chem., 1929, 82, 679—685, 687—692).—I. Subcutaneous or oral administration of creatine reduces the blood-sugar of fasting dogs and diminishes the rise in blood-sugar which would normally follow ingestion of dextrose. No toxic effects of creatine were observed, and it was impossible, by its use, to reduce the blood-sugar so much as to produce hypoglycaemic convulsions.

II. Creatine failed to produce hypoglycaemia in rabbits, nor did it exercise any toxic effect on the liver, as indicated by the power of this organ to deaminate glycine (cf. Blatherwick and others, A., 1928, 199).

C. R. HARRINGTON.

Creatine and creatinine. I. N. SATO (Sei-I-Kwai Med. J., 1928, 47, No. 10).—Creatine, when administered to rabbits, is partly retained, partly converted into creatinine, and partly excreted in the urine. After oral administration, the creatine contents of the kidneys and liver are increased; that of the muscle at first increases and then decreases. Retention of creatine or creatinine is diminished when intravenous injection is substituted for oral administration.

CHEMICAL ABSTRACTS.

Effect of diguanide and its derivatives on sugar metabolism. E. HESSE and G. TAUBMANN (Arch. exp. Path. Pharm., 1929, 142, 290—308).—Certain derivatives of diguanide when administered to normal or hyperglycaemic animals cause a lowering of the blood-sugar level. These compounds in their physiological behaviour resemble "synthalin" and in certain respects differ from insulin. In particular the curative effect of the administration of adrenaline or of dextrose is much less effective against the toxic action of these compounds than against that of insulin.

W. O. KERMACK.

Possible decomposition of 5-iodo-, 5-bromo-, 5-chloro-, and 3:5-dibromo-salicylic acids in the animal organism. C. GIROD (J. Pharm. Chim., 1929, [viii], 9, 513—520).—The above acids, after oral administration to rabbits, are eliminated unchanged in the urine. They promote the production of glucuronic acid and are probably eliminated in association with this compound, as is salicylic acid. The following are described: 4-chloro-2:6-di-iodophenyl acetate, m. p. 127.5°; 4-chloro-2:6-di-iodophenetole, m. p. 69°; 2:4-dichloro-6-iodophenol, m. p. 63°; 2:4-dichloro-6-iodophenyl acetate, m. p. 65—66°; 2:4-dichloro-6-iodophenetole, b. p. 290—294°; 4-bromo-2:6-di-iodophenol, m. p. 128°; 4-bromo-

2:6-di-iodophenyl acetate, m. p. 135°; 4-bromo-2:6-di-iodophenetole m. p. 75°; 2:4-dibromo-6-iodophenol, m. p. 104°; 2:4-dibromo-6-iodophenyl acetate, m. p. 106.5—107°; 2:4-dibromo-6-iodophenetole, m. p. 54°.

E. H. SHARPLES.

Excretion of picric acid in the urine after different methods of injection into animals. V. J. LESZCZYNSKI (Russ. J. Physiol., 1929, 12, 205—210).—The daily output of picric acid through the urine following injection into the stomach subcutaneously, intravenously, or intraperitoneally in dogs, cats, and rabbits was determined by Gumbert's reaction. The excretion of picric acid by the animals, even when doses of 100—150 g. were injected, did not continue for so long a time as that recorded for man. The duration of the excretion depended not only on the method of injection, but also on the animal species. With dogs the longest period was observed after injection into the stomach, in cats after subcutaneous and intravenous injection, in rabbits after subcutaneous injection. Cats excreted picric and picramic acids over the longest period, rabbits over the shortest. Rabbits did not excrete picramic acid after intravenous and intraperitoneal injections, 5-gram doses of picric acid given intravenously to dogs and intraperitoneally to cats were rapidly transformed into picramic acid, whereas rabbits following intraperitoneal injection excreted a derivative of picric acid other than picramic acid.

C. C. N. VASS.

Preparation of diastase. F. WINKLER and F. KOOK (Chem.-Ztg., 1929, 53, 457).—Green malt or the kernels of sunflower seeds are thoroughly bruised in a mortar and treated with chlorinated organic compounds until thoroughly disintegrated. The mass is digested with water and glycerol or a dilute "yaten" solution, the mixture sterilised and centrifuged, and the liquor siphoned off and filtered. The filtrate is treated with acetone, the precipitate separated after 24 hrs. by centrifuging, and the solution evaporated at 40° under reduced pressure. The resulting yellowish-white substance has a higher diastatic power than that obtained by the usual alcohol method.

A. R. POWELL.

Lactic acid formation in muscle extracts. IV. Comparison between dextrose and glycogen in respect of lactic acid formation and phosphoric ester accumulation. D. STIVEN (Biochem. J., 1929, 23, 583—586).—The accumulation of phosphoric ester from dextrose is very small compared with that from glycogen in the muscle of the cat, even when the rate of lactic acid formation from the former is greater than that from the latter. Both the rate and extent of the lactic acid formation from dextrose are greater than from glycogen; there is, however, a great variation from one extract to another. This variation is not due to faulty technique, but to some factor as yet uncontrolled.

S. S. ZILVA.

Hydrolysis of *d*-glucosides of *d*- and *l*-methyl-*n*-hexylcarbinol with emulsin. S. MITCHELL (J. Biol. Chem., 1929, 82, 727—730).—Tetra-acetyl- β -methyl-*n*-hexylcarbinyl-*d*-glucoside, from acetobromo-

glucose and methyl-*n*-hexylcarbinol with silver carbonate, has m. p. 95°, and yields, when hydrolysed with barium hydroxide, β -methyl-*n*-hexylcarbinyl-*d*-glucoside. The glucosides prepared thus from the *d*- and *l*-carbinols had $[\alpha]_{D}^{25}$ -37.8° and -46.6°, respectively; the former was hydrolysed by emulsin 8.4 times as rapidly as the latter. C. R. HARRINGTON.

Asymmetric hydrolysis of esters by enzymes.

II. Configuration specificity of liver esterase of different animals and its dependence on concentration of the substrate. R. WILLSTATTER, R. KUHN, and E. BAMANN (Ber., 1929, 62, [B], 1538—1548; cf. A., 1928, 755).—The relative activities of the different liver esterases towards methyl butyrate are: dog 18.8, ox 18.8, man 24.5, sheep 49.5, horse 78.8, and rabbit 274.0. The substrates used are ethyl *r*-, (+)-, and (-)-mandelates. The initial rates of hydrolysis are measured at 25°. In the most concentrated solutions (0.096*M*), hydrolysis occurs to 1% or less, in 0.012*M* solution 1—4%, and in 10 times more dilute solution 4—30%. Reaction is directly proportional to the time and the change is zero-molecular. With esterase of sheep, dog, man, and rabbit the optimal substrate concentration of the (-)-ester is 0.024*M*; with increasing concentration the amount of acid formed decreases; with ox and horse esterase, maximum reaction is not attained in 0.096*M*-solution. Except in the case of sheep-liver esterase, maximal action towards the (+)-ester is not developed in 0.095*M*-solution. Only in the case of sheep-liver esterase is it possible to calculate the dissociation constants of the esterase-(-)-ester and esterase-(+)-ester from the maximal rates of reaction; the values agree nearly with those observed for pigs (*loc. cit.*). The optical activities of the mandelic acids obtained by partial hydrolysis of ethyl *r*-mandelate are determined for the various esterases with differing periods and substrate concentrations; the most striking observation is the dependence of the sign of rotation of the acid on the substrate concentration with the esterases of man and rabbit.

H. WREN.

Disappearance of histamine from autolysing lung tissue. C. H. BEST (J. Physiol., 1929, 67, 256—263).—Lung tissue in the presence of toluene is able to destroy both naturally occurring and added histamine. This property is lost on heating at 90° for 4 min.

E. BOYLAND.

Proteolytic enzymes in green malt. C. K. MILL and K. LINDERSTRØM-LANG (Compt. rend. Trav. Lab. Carlsberg, 1929, 17, No. 10).—There are at least two proteolytic enzymes in an extract of green malt. The first, which is a protease, acts on gelatin, edestin, and egg-albumin peptone, and has in the decomposition of edestin at 40° an optimum p_H of 4.3, measured at 18°. The second enzyme is a peptidase which decomposes leucylglycine, and at 40° has its optimum action at p_H 7.6—7.9, measured at 18°. The peptidase is inhibited by phosphates and decomposes readily when the malt extract is kept at its natural reaction (p_H 5.9) at the ordinary temperature.

C. RANKEN.

Action of trypsin on caseinogen. H. W. WAHL-TEICH (J. Biol. Chem., 1929, 82, 737—749).—The

digestion of caseinogen by trypsin has been studied at three different temperatures with varying concentrations of enzyme. Under all conditions, the appearance of the maximum proteose-nitrogen (*i.e.*, nitrogen precipitable with zinc sulphate) coincided with disappearance of the original substrate, and with an increase in the amino-nitrogen to about 10% of the total. The time taken to convert 10—12% of the total nitrogen into amino-nitrogen gives a useful measure of tryptic activity. Between 20° and 40° the rate of tryptic action is approximately doubled for 10° rise in temperature. C. R. HARRINGTON.

Influence of chemical reagents, especially of metallic salts, on the tyrosinase reaction. S. TAKAOKA (Keio J. Med., 1928, 8, 165—190).—Zinc chloride accelerates the tyrosinase reaction. Salts which shift the p_H value to the acidic side generally inhibit the reaction. Salts which shift the p_H value to the alkaline side generally accelerate the second reaction (formation of black substance). In dilute solution, oxidising and reducing agents accelerate the first reaction (red coloration) and have an inhibiting effect, respectively. Inhibition is observed with alcohols and diamines. The first reaction is accelerated by pilocarpine and inhibited by brucine; the second is accelerated by morphine hydrochloride, quinine hydrochloride, or strychnine nitrate.

CHEMICAL ABSTRACTS.

Enzymic inactivation of co-zymase. H. VON EULER, K. MYRBACK, and E. BRUNIS (Z. physiol. Chem., 1929, 183, 60—66).—The inactivation of co-zymase by castor-bean lipase (*cf.* Buchner and Klatte, A., 1908, i, 380) is not dependent on the enzyme, since inactivation also occurs with the enzyme-free preparation. Similarly, inactivation by pancreas is not due to pancreatic lipase. Inactivation is also brought about by dry liver powder (obtained by washing liver with acetone and alcohol) at p_H about 8 but not at p_H 4—5. Similar dry preparations from the stomach, intestine, and pancreas exert an analogous influence. The inactivation appears to be related to the fission of phosphate from the co-zymase preparation. The results of Raymond (A., 1928, 1402) on the extraction of co-zymase from yeast with water and toluene were not confirmed.

H. BURTON.

Alcoholic fermentation of amino-acids. E. PARISI [with B. BERNARDI and F. DE MEICHSNER] (Annali Chim. Appl., 1929, 19, 234—239; *cf.* B., 1926, 169).—As the amount of amino-acids in molasses (beet) distillery slop is only slightly lower than that originally present in the molasses, these compounds cannot be utilised to any great extent by the yeast during fermentation. This conclusion is confirmed by Ehrlich (A., 1907, ii, 383). Experiments on the fermentation of sugar in solutions containing nitrogen as glycine, alanine, valine, leucine, isoleucine, α - or β -phenylalanine, glutamic acid, tryptophan, or asparagine show that, in the transformation of 15—16 g. of sugar into alcohol, at most 0.02 g. of amino-nitrogen is consumed by the yeast. T. H. POPE.

Nitrogen content of growing cultures of *Mycoderma* and of *Saccharomyces cerevisiae*. L. M. CHRISTENSEN (Plant Physiol., 1928, 3, 61—

69).—The apparent nitrogen content of cultures on molasses depends on the p_H , time, and method of analysis. The true amount of nitrogen fixed is probably greater than that indicated.

CHEMICAL ABSTRACTS.

Metabolism of *Aspergillus oryzae*. III. H. TAMIYA (Acta Phytochim., 1929, 4, 227—295; cf. A., 1928, 1063).—An apparatus is described by means of which the respiration of fungi in gaseous systems of known composition can be measured. Maximum growth and respiration of *A. oryzae* on Pfeffer's medium at p_H 5.5 was obtained in a mixture of 17% of nitrogen and 83% of oxygen, the oxidation quotient being 0.5—1.0. Removal of sugar from the medium caused an inhibition of growth, a decrease in the intensity of respiration, and a still larger decrease in fermentation, whilst the oxidation quotient rose to 1.3—2.0. Addition of more than 7.5×10^{-3} mol. of potassium cyanide to the medium resulted in diminished growth and inhibition of respiration and fermentation in 15% of nitrogen and 85% of oxygen, whilst the oxidation quotient reached an abnormally high value. Under anaerobic conditions in the presence of potassium cyanide the mould showed no change in weight, but whilst the fermentation was diminished a stronger resistance against this inhibition was observed than under similar but aerobic conditions. The presence of carbon monoxide always caused an inhibition of growth under aerobic conditions, whereas the intensities of the respiration and fermentation processes were not inhibited. Under anaerobic conditions carbon monoxide neither activated nor inhibited fermentation. The synthetic quotient, which is measured by the ratio of the increase in weight of the mould (in g.) to the sugar used (in mg.), was in normal cultures 0.4—1.0; on removal of sugar or addition of carbon monoxide it was decreased.

Cytochrome was always observed in aerobic cultures, whereas in anaerobic cultures it was absent or only faintly detectable, the rate of its disappearance being retarded in the presence of potassium cyanide.

C. C. N. VASS.

Dehydrase and glutathione in moulds. H. TAMIYA (Acta Phytochim., 1929, 4, 297—311).—*Aspergillus oryzae* grown on Pfeffer's medium containing 0.025% of methylene-blue caused a decolorisation at the commencement, but with the onset of autolysis the colour returned. Individual examination at p_H 7.6 of the dried mould, an extract of the mould obtained after boiling for 1 hr., a mould which had been washed with water for 24 hrs., and the medium freed from the mould showed that the reduction was not due to the mould alone. The strongest reduction was obtained when the dried mould and the medium were used together. Whilst the extract showed no reduction and the washed mould a diminished reduction, together these gave an increased reduction. Anaerobiosis caused a decrease in the reducing power of the mould which, however, fell less rapidly with age, whereas that of the culture medium varied with age, increasing to a maximum on the eighth day. The glutathione content of the dried mould determined by the method

of Tunncliffe (A., 1925, i, 752) was found to be 0.2—0.5%. Aerobic cultures showed a maximum glutathione content after 4 days, which gradually decreased, and no positive sodium nitroprusside reaction was obtained at the end of 5 months. Anaerobic cultures contained approximately one half of the glutathione content of aerobic cultures, but its rate of disappearance was much slower, glutathione being detectable at the end of 5 months. The glutathione content of the medium increased up to the eleventh day in aerobic cultures, when it reached the recorded glutathione content of blood (0.01—0.02%), whilst under anaerobic conditions, although the amount of glutathione formed was smaller, it remained unchanged for a longer period.

C. C. N. VASS.

Influence of carbon monoxide on the metabolism of moulds. H. TAMIYA (Acta Phytochim., 1929, 4, 313—326).—The growth and intensity of respiration of *Aspergillus oryzae* have been observed in varying concentrations of oxygen, nitrogen, and carbon monoxide. During short periods of growth, e.g., 4 days, carbon monoxide does not inhibit respiration, but causes slight destruction of the living cells.

C. C. N. VASS.

Biochemical synthesis of fumaric from pyruvic acid. A. GOTTSCHALK (Z. physiol. Chem., 1929, 182, 311—312).—Contrary to the results previously described (A., 1926, 545; 1928, 804), and in agreement with Ehrlich and Bender's observations (A., 1928, 95, 804), the author has been unable to obtain fumaric acid during the growth of *Rhizopus nigricans* on a pyruvic acid—mineral salt or a levulose—mineral salt medium.

H. BURTON.

Fungicidal action of sulphur. III. Toxicity of hydrogen sulphide and the interaction of sulphur with fungi. R. W. MARSH (J. Pomology, 1929, 7, 237—250).—Experiments are described showing the high toxicity of hydrogen sulphide to germinating spores of several species of fungi. The addition of powdered sulphur to spores of *Monilia fructigena* inhibits germination, whereas *Botrytis cinerea* is unaffected by this treatment. The same effect can be obtained when sulphur is placed on a flowering plant bearing these spores. These experiments are thought to indicate that sulphur is toxic to these fungi only by virtue of the hydrogen sulphide produced and that a fungus sensitive to sulphur is one which can reduce sulphur.

E. A. LUNT.

Type III pneumococci. A. STULL (J. Biol. Chem., 1929, 82, 641—650).—The specific soluble carbohydrate of Heidelberger and Goebel (A., 1927, 77, 1114) could be isolated from an unbuffered culture medium after 18 hrs.' growth of type III pneumococci. The organisms were separated, dried, and extracted successively with a variety of solvents. The whole of the specific soluble carbohydrate (the only specific precipitating material found) was contained in the distilled-water extract of the fat-free material.

C. R. HARRINGTON.

Effect of tin on tubercle bacillus. N. DOS SANTOS (Compt. rend. Soc. Biol., 1929, 101, 383—384).—Stannous chloride in concentrations of 1 to

5000 does not affect the growth of the tubercle bacillus. E. BOYLAND.

Colorimetric and biological determination of the adrenaline content of the suprarenals of rabbits. M. WATANABE and H. SATO (Tohoku J. Exp. Med., 1928, 11, 433—448).—With the cortical suprarenal substance of rabbits, the method of Folin, Cannon, and Denis gave a positive reaction, whilst the biological methods did not. For the total gland, this method gave higher values than did the biological or Suto and Inouye's method.

CHEMICAL ABSTRACTS.

Determination of adrenaline in the suprarenal extract from oxen, pigs, cats, dogs, and rabbits. T. SUGAWARA (Tohoku J. Exp. Med., 1928, 11, 410—432).—Biological and colorimetric methods were compared. The values obtained were, apparently, not related to the method of extraction. Adrenaline diffuses from the medulla to the cortex after extirpation of the gland, particularly on manipulation of the capsule.

CHEMICAL ABSTRACTS.

Adrenaline and hyperglycæmia. G. S. EADIE (Amer. J. Physiol., 1929, 89, 46—49).—The increased blood-sugar in adrenaline hyperglycæmia is derived from the liver, not from the muscles.

E. BOYLAND.

Hormone content of the urine of the pregnant female. M. M. MAINO (Arch. Ist. Biochim. Ital., 1929, 1, 95—104).—Allen and Doisy's biological test shows that the ovarian hormone appears in the urine in amounts sufficient to cause œstrus in castrated experimental animals only at about the middle of the fourth month of pregnancy. During the first months of pregnancy the urine contains a hormone acting mainly on the ovary, in which it determines the appearance of mature follicles, hæmorrhage, and atresic corpora lutea. This hormone is undoubtedly different from the ovarian hormone and as it does not occur in appreciable proportions during non-pregnancy, its presence serves for the early diagnosis of pregnancy.

T. H. POPE.

Dextrose-insulin equilibrium. J. P. BOUCKAERT, P. DENAYER, and R. KREKELS (Compt. rend. Soc. Biol., 1929, 101, 511—512).—The amount of dextrose necessary to maintain the blood-sugar after insulin administration is relatively much less for large doses of insulin.

E. BOYLAND.

Action of insulin on the carbamide of the blood. A. C. MARIE (Compt. rend. Soc. Biol., 1929, 101, 445—447).—Insulin reduces the high carbamide concentration produced by administration of adrenaline.

E. BOYLAND.

Modification of insulin action in medullary-adrenal-inactivated cats by post-pituitary extracts. E. M. K. GEILING, S. W. BRITTON, and H. O. CALVERY (J. Pharm. Exp. Ther., 1929, 36, 235—241).—Simultaneous injection of pituitary extract and insulin prevents, diminishes, or retards the hypoglycæmia and convulsions produced when insulin is administered in adequate doses to normal and medullary-adrenal-inactivated unanæsthetised cats. Medullary-adrenal-inactivated animals are the more sensitive to insulin and require larger doses of pituitary

any extract than normal animals to protect them equally against the insulin. Pituitary extract administered during insulin hypoglycæmia may abolish severe convulsions and muscular weakness without an appreciable rise in blood-sugar. Post-pituitary liquid and adrenaline produce hyperglycæmia in cats when the adrenal medulla was evacuated and the hepatic nerves were severed. This effect was much less than with normal animals. F. C. HAPFOLD.

Action of extract of pituitary on the blood-sugar after pancreatectomy. C. G. IMRIE (J. Physiol., 1929, 67, 264—269).—The injection of pituitrin up to 44 hrs. after administration of insulin to a depancreatized dog causes a rise in blood-sugar. If the pituitrin is given 70 hrs. after the insulin this rise does not occur. The extra sugar is derived from liver, not from muscle-glycogen.

E. BOYLAND.

Standardisation of thyroid preparations. J. R. MÖRCH (J. Physiol., 1929, 67, 221—241).—The value of thyroid preparations is determined by their effect on the carbon dioxide production of white mice under special conditions. It is claimed that the results are significant to within 33%.

E. BOYLAND.

Occurrence of vitamin-A in blood and blood-serum of domestic animals, cow's milk, milk products, and foodstuffs. B. ROSIO (Z. physiol. Chem., 1929, 182, 289—304).—The vitamin-A colour reaction (antimony chloride) has been applied to the blood-serum from the horse, cow, sheep, and goat. Quantitative measurements (obtained by matching the colour produced in a Lovibond tintometer) show that with increase in the age of the horse and cow the vitamin content decreases. Pregnant cows and mares show generally an increased value; this appears to depend somewhat on age. For cows the mean vitamin content is about three times as high as for horses. The vitamin content of cow's blood is one half that of the serum. The vitamin-A content of cow's milk increases with increase in the amount of fat present; a similar relationship is found for butter. Swedish turnip (rutabaga), white mangold, and soya meal give colour reactions, whilst turnip does not.

H. BURTON.

Vitamin-B from brewer's yeast. A. SEIDELL (J. Biol. Chem., 1929, 82, 633—640).—On treatment of an aqueous solution of the antineuritic concentrate previously described (A., 1926, 644) with benzoyl chloride and sodium carbonate, followed by extraction with chloroform, much of the nitrogenous material passed into the chloroform, whilst most of the physiological activity remained in the aqueous solution. The latter was poured into 4 vols. of acetone, yielding a precipitate of salts together with 90% of the active principle; in this form, 0.15 mg. of nitrogen represents the daily protective dose for a pigeon.

C. R. HARRINGTON.

Antineuritic and water-soluble B vitamins in beef and pork. R. HOAGLAND (J. Agric. Res., 1929, 38, 431—446).—Dried lean pork, fresh and smoked hams, and dried lean beef have been tested on pigeons with respect to their contents in antineuritic and water-soluble B vitamins. The results

indicate that dried lean pork is a good source of the antineuritic vitamin. E. A. LUNT.

Physiology of vitamins. VII. Hæmoglobin, solids, sugar, and chloride changes in the blood of vitamin-B-deficient dogs. C. J. STUCKY and W. B. ROSE (Amer. J. Physiol., 1929, 89, 1—17).—The blood-sugar of vitamin-B-deficient dogs remained normal, whilst the blood-chloride fell sometimes to a marked extent; anhydramia developed accompanied by an increase in the hæmoglobin content of the blood. Starvation occurs on account of inefficient utilisation of food and reduced water consumption. E. BOYLAND.

Vitamin action and surface activity. II. Antiscorbutic action of plant juices and their surface activity. N. E. SCHEPILEVSKAJA (Biochem. Z., 1929, 208, 334—351).—The antiscorbutic action of a number of plant juices (of turnip, beet, radish, carrot, cabbage, etc.) is shown to run approximately parallel with their surface activities. P. W. CLUTTERBUCK.

Effect of drying and of sulphur dioxide on antiscorbutic property of fruits. A. F. MORGAN and A. FIELD (J. Biol. Chem., 1929, 82, 579—586).—Sun-drying or dehydration of untreated peaches caused destruction of their antiscorbutic properties; the latter were, however, not affected by drying if the fruit were first treated with sulphur dioxide. C. R. HARINGTON.

Vitamin-D and faecal reaction. A. L. BACHARACH and H. JEPHCOTT (J. Biol. Chem., 1929, 82, 751—758).—A reply to the criticisms of Shohl and Bing (A., 1928, 1288) and Oser (this vol., 210) of the authors' method (A., 1928, 332) for the determination of vitamin-D. C. R. HARINGTON.

Spectrographic examination of lipins. V. BRUSTIER and L. BUGNARD (Compt. rend. Soc. Biol., 1929, 101, 420—421).—The total lipins extracted from a rabbit apparently contained ergosterol. E. BOYLAND.

Composition of bone. VI. Effect of massive doses of irradiated ergosterol. B. KRAMER, M. J. SHEAR, and M. R. MCKENZIE (J. Biol. Chem., 1929, 82, 555—557; cf. A., 1928, 1271).—No deviation from the normal was observed in the residual Ca : P ratio of the bones of growing rats as the result of administration of massive doses of irradiated ergosterol. C. R. HARINGTON.

Antirachitic action of certain cholesterolic lipins of the snail (*Helix pomatia*). G. MOURIQUAND and A. LEULIER (Compt. rend., 1929, 188, 1701—1702).—An irradiated mixture of cholesterol and lipins derived from *Helix pomatia* possesses powerful antirachitic properties. C. W. SHOPPEE.

Vegetable assimilation and respiration. XX. Photosynthesis in green plants. G. E. BRIGGS (Proc. Roy. Soc., 1929, B, 105, 1—35).—Experiments have been carried out on the determination of photosynthetic efficiency in the following portions of the visible spectrum: 4300—5100, 5100—5600, 5700—6400 Å., the efficiency for comparative purposes being defined as the volume of carbon dioxide reduced per unit of energy absorbed. For the plants

tested, *Phaseolus vulgaris*, *Sambucus nigra*, yellow and green elm, the efficiency decreased with decreasing wave-length. Comparison is made of these with existing data and theoretical considerations are advanced showing that, contrary to Warburg and Negelein's conclusions, the number of quanta required for the reduction by the plant of a molecule of carbon dioxide increases discontinuously with increasing wave-length. E. A. LUNT.

Permeability of plant cells in relation to the action of mercury on seeds. A. NIETHAMMER (Z. physikal. Chem., 1929, 142, 309—319).—The occurrence of mercury in plants grown from seed which has been in contact with various organic mercury compounds has been investigated. In general inappreciable quantities of mercury appear in the plant. H. F. GILLBE.

Protochlorophyll. W. H. EYSTER (Science, 1928, 68, 569—570).—The work of Liro (Ann. Acad. Scient. Fennicæ, 1909, 1) and others indicates that protochlorophyll is not a decomposition product, but is a pigment which develops independently of light and changes to chlorophyll on insolation, probably in the presence only of a specific enzyme. L. S. THEOBALD.

[Detection of germinable seeds by] determination of acetaldehyde [content] by Griebel's micro-method. A. NIETHAMMER (Mikrochem., 1929, 7, 227—230).—The acetaldehyde content is determined approximately, preferably after a preliminary swelling in water, by Griebel's method (A., 1928, 82). Non-germinable seeds contain little or no acetaldehyde. J. S. CARTER.

Translocation of potassium in tomato plants and its relation to their carbohydrate and nitrogen distribution. G. JANSSEN and R. P. BARTHOLOMEW (J. Agric. Res., 1929, 38, 447—465).—Tomato plants grown on a nutrient solution with low potassium content show an increase in the percentage of dry matter, and high total and soluble nitrogen contents. There appears to be an optimum potassium concentration conducive to the normal assimilation of carbohydrate compounds. E. A. LUNT.

Determination of inorganic nitrogen in plant extracts. A. C. SESSIONS and J. W. SHIVE (Plant Physiol., 1928, 3, 499—511).—The aqueous extract is deproteinised with 10% acetic acid and concentrated to 500 c.c.; ammonia is determined in 50 c.c. by Folin's aspiration method after addition of saturated sodium carbonate solution (50 c.c.) and sodium chloride (5 g.). Sodium hydroxide (to 0.125N) and Devarda's alloy are added, and the ammonia is determined by aspiration. CHEMICAL ABSTRACTS.

[Moisture in] wheat grown under constant conditions. I, II. H. L. VAN DE SANDE-BAKHUYZEN (Plant Physiol., 1928, 3, 1—30).—Moisture determinations suggest that the imbibition capacity of the plasma-colloids, which is maintained by the growth hormones as long as a vegetative point is present, decreases, by the act of fertilisation, as soon as the growing point is virtually lost to the vegetative plant. CHEMICAL ABSTRACTS.

Influence of the malting process on the fat of barley. K. TAUFEL and M. RUSCH (Biochem. Z., 1929, 209, 55—61).—The fat of barley is composed chiefly of glycerides of palmitic, stearic, oleic, linoleic, and linolenic acids. During the process of germination of the grain there is a loss of almost 11% of dry material, about 12% of this loss being in the fat. It is chiefly the oleic acid which disappears from the fat. There is probably also some conversion of the oleic acid into stearic acid. Special biological significance is attached to the fact that there is formation and accumulation of unsaponifiable matter in the fat during the process of germination.

W. MCCARTNEY.

Cytological study of water-soluble and fat-soluble constituents of *Citrus*. J. DUFRENOY (J. Agric. Res., 1929, 38, 411—429).—The natural colouring process of the *Citrus* fruit is concomitant with starch transference from the chloroplasts in the cells of the three upper layers in the peel. The fat bodies then develop in the chloroplasts and the orange pigment that gives the fruit its colour dissolves in the fat bodies. The same process can be effected artificially by treatment with ethylene. Excitation of the epidermal cells of the fruit by light freezing results in permanent injury of the cell and hence of the fruit.

E. A. LUNT.

Catalase and oxidase of the tomato as influenced by the soil reaction. E. S. HABER (Iowa State Coll. J. Sci., 1928, 3, 29—39).—The catalase was lowest with soil of 6.5—7; soil reaction had no effect on oxidase. Catalase was highest in green mature fruits, and oxidase in ripe fruits.

CHEMICAL ABSTRACTS.

Composition of pineapple plants. F. G. KRAUSS (Ernähr. Pflanze, 1928, 24, 398—400; Chem. Zentr., 1929, i, 662).—Results of analyses of the pineapple plant at various stages of growth are recorded. The ash is high in potassium and silica.

A. A. ELDRIDGE.

***Phytolacca*.** G. E. JENKINS (J. Amer. Pharm. Assoc., 1929, 18, 573—576).—Alcoholic extract of air-dried poke root (*Phytolacca Americana*, Linné) (moisture content about 9.0%; ash 9.4%) contains a small amount of an essential oil, 0.21% of potassium nitrate, and 0.16% of a gum which gives characteristic tests for alkaloids.

C. C. N. VASS.

Constituents of *Caesalpinia Bonducella* nut (Flem.). I. Bonducella nut oil. S. N. GODBOLE, D. R. PARANJPE, and J. G. SHRIKHANDE (J. Indian Chem. Soc., 1929, 6, 295—302).—Extraction of the dried kernels with light petroleum yields 20% of a pale-yellow oil, d_{20}^{25} 0.9215, n_D^{25} 1.4750, saponification value 199.5—200.5, iodine value (Winkler) 127, Hehner value 93. The oil-free kernels on further extraction with alcohol give saponin and a bitter glucoside, containing almost all the sulphur in the nut: when extraction is carried out with 2% hydrochloric acid, a substance (chars without melting at 295°) is obtained. Hydrogenation of the oil is possible with a nickel-pumico catalyst at 180°; poisoning of the catalyst occurs frequently as with mustard oils. As saturation of the oil proceeds the values of n decrease in almost a linear function.

The percentage composition of the acids isolated from the oil is linoleic (61.4), oleic (21.6), palmitic (10), and stearic (5.79). Sitosterol is present in the unsaponifiable matter (1.5% of original oil). The oil has an inhibiting action on castor-seed lipase.

H. BURTON.

Lobeline-like substance isolated from the roots of *Lobelia sessilifolia*, L. S. KUBOTA, S. NAKASHIMA, and R. ITO (Chinese J. Physiol., 1929, 3, 278—286).—A crystalline hydrochloride, m. p. 180—190°, possessing alkaloidal properties, has been isolated. Like that of lobeline, with which it may be identical, it acts as a respiratory stimulant.

C. C. N. VASS.

L-Asparagine in the fresh flowers of *Ulex europaeus*, L. M. BRIDEL (J. Pharm. Chim., 1929, [viii], 9, 112—113).—See this vol., 477.

isoSakuranetin from the flowers of *Pseudaegle trifoliata*. S. HATTORI (Acta Phytochim., 1929, 4, 219—226).—When the dried flowers of *P. trifoliata*, Makino, are extracted with 50% alcohol, concentrated, and then boiled with 3% hydrochloric acid for 30 min., a dark brown substance separates on keeping. Purification from alcohol affords isosakuranetin, m. p. 194—195° (Shinodo and Sato, this vol., 189), which gives a purplish-red colour with alcoholic ferric chloride. The following derivatives have been prepared: methyl ether, m. p. 117—118° (*loc. cit.*); ethyl ether, m. p. 115°, by the action of diazoethane; acetyl derivative, m. p. 114—115°; benzoyl derivative, m. p. 143°. Fusion with potassium hydroxide gives phloroglucinol and anisic acid.

C. C. N. VASS.

Proteins of the ginkgo. M. FURUICHI (Bull. Tottori Higher Agric. Sch., 1928, 1, 105—132).—Ginkgo contains starch 69.6, protein 12, fat 3%; the ash of the seed contains K_2O 40.6, Na_2O 8.4, CaO 4.8, $Fe_2O_3 + Al_2O_3$ 3.7, P_2O_5 21.6, SO_3 8.3, SiO_2 4.9%. Of the total nitrogen, 60% is present as a globulin, ginkgoin. The point of maximum surface tension observed when hydrochloric acid is added to an alkaline solution of the globulin, albumin, protamine, or glutelin corresponds approximately with that of maximum turbidity.

CHEMICAL ABSTRACTS.

Proteins of the soya bean. T. TADOKORO and K. TOSHIMURA (Hokkaido J. Agric., 1928, 20, 355—362).—The ash and phosphorus contents decrease, and the nitrogen content increases, in the order legumelin, glycinin, glutelin. The free amide-nitrogen decreases in the order glycinin, glutelin, legumelin. The melanin-nitrogen is highest in glycinin, the histidine-nitrogen in legumelin, and the lysine-nitrogen in glutelin. Glycinin is the most highly condensed protein present. CHEMICAL ABSTRACTS.

Special constituents of the soya bean. S. MURAMATSU (Mem. Pub. Morioka Agric. Coll., 1928, 1—15).—The following compounds were isolated: 1. *hydroxy-acid*, $C_{50}H_{50}O_{20}$, m. p. 240°; lecithin (from the oil from skin and cotyledons, 0.64%; from the residue after extraction with ethyl alcohol, skin 0.07%, cotyledons 0.78%); a *sterol*, and an *alcohol*, $C_{24}H_{32}O_8$, m. p. 235°.

CHEMICAL ABSTRACTS.

Phyto-pharmacology of leucines and cystines. D. I. MACHT (J. Pharm. Exp. Ther., 1929, 36, 243—

250).—The effects of leucine and cystine on the growth of *Lupinus albus* seedlings in nutrient solutions have been studied. The *l*-acids were pharmacologically more active than the *d*-acids in their action on growth. Combination of the stereoisomeric forms of both acids produced an effect on growth which could not be explained as a mean effect of the two components. F. C. HAPFOLD.

Occurrence of chlorates in a tomato soil. O. OWEN (J. Pomology, 1929, 7, 270—275).—A case of disease similar in symptoms to the mosaic disease of the tomato was shown to be due to the presence of a toxic amount of chlorates in the soil. E. A. LUNT.

Pigments of red algæ. R. LEMBERG (Naturwiss., 1929, 17, 541).—The pepsin method of obtaining the pigment in a protein-free state is unsuitable because the chromoprotein from red algæ is less readily broken down than in the case of hæmoglobin. The pigment is best obtained by brief treatment with hot concentrated hydrochloric acid followed by extraction of the diluted solution by means of chloroform, air being excluded throughout the operations. Oxidation results in the formation of phycocyan from phycoerythrin pigments. The phycocyan pigment has been isolated in crystalline form from "Nori," a Japanese delicacy, but the phycoerythrin pigment has not yet been obtained pure. It is proposed to call the new pigments *phycobilins*. They are amphoteric, relatively strongly acidic, and easily esterified. With hydrogen chloride in chloroform, salts are formed which are readily hydrolysed by water. The phycobilins and their esters resemble the magnesium-free derivatives of chlorophyll in forming complex zinc and copper salts, soluble in organic solvents and characterised by intense fluorescence. Phycocyanobilin resembles biliverdin in spectroscopic properties. The ease with which it is oxidised indicates the presence of a hydroxypyrrole ring. Phycocyanobilin crystallises from chloroform-benzene, in an atmosphere of carbon dioxide, as dark blue prisms reflecting red light. Provisionally, the formula $C_{34}H_{43}O_8N_4$ is given; methoxyl determinations on the methyl ester indicate the presence of two carboxyl groups. The pigments represent about 2% of the chromoprotein. R. A. MORRIS.

Dispersoid analysis by means of a diffusion apparatus. A. NISTLER (Kolloidchem. Beih., 1929, 28, 296—313).—The determination of particle size in a sol by means of diffusion analysis is recommended for biochemical purposes. A new diffusion apparatus for this purpose is described in detail and some results are given for a number of dyes. E. S. HEDGES.

Micro-determination of protein. K. SAMSON (Biochem. Z., 1929, 208, 262—273).—The centrifuge method for the determination of protein (precipitation in a graduated centrifuge tube and determination in terms of the volume of protein after centrifuging) is examined theoretically and a number of examples are given using different precipitating agents, times of centrifuging, etc., and the method is applied to the separate determination of albumin and globulin fractions of cerebrospinal fluid. P. W. CLUTTERBUCK.

Van Slyke's method [for the determination of amino-acids]. L. ROSENTHALER.—See this vol., 713.

Oxidation of dixanthhydrylcarbamide by dichromate; determination of carbamide. F. W. ALLEN and J. M. LUCK (J. Biol. Chem., 1929, 82, 693—701).—Luck's method (A., 1928, 1229) for the determination of carbamide is modified by oxidising the xanthhydryl compound with excess of potassium dichromate, the excess of oxidising agent being determined iodometrically. The method is applicable to urine, blood, and tissues, in the last case after clarification of the protein-free filtrate with copper sulphate and barium hydroxide.

C. R. HARRINGTON.

Determination of nitrates and nitrogen [in organic material]. E. M. EMMERT (Science, 1928, 68, 457—458).—Nitrogen present as nitrate is determined by treating 1 g. of plant or animal tissue or 10 g. of soil with 25 c.c. of cold, 75% sulphuric acid and gradually distilling into 50 c.c. of chlorine dioxide solution kept yellow by bubbling through it a stream of this gas. The distillate is then boiled until colourless, neutralised, evaporated to dryness, and the nitrate determined by means of phenoldisulphonic acid. The remaining nitrogen in the sample is determined by the addition of 5 g. of potassium or sodium chlorate, distillation, and treatment as above. The final residue is neutralised with sodium hydroxide and the inorganic constituents are determined. The precautions necessary to avoid harmful explosions in the above method are detailed.

L. S. THEOBALD.

Van Slyke's method for determination of chlorides. A. J. EISENMANN (J. Biol. Chem., 1929, 82, 411—414).—Contrary to the statement of Wilson and Ball (A., 1928, 1269), Van Slyke's method for the determination of chlorides in its original form (A., 1924, ii, 271) gives accurate results.

C. R. HARRINGTON.

Determination of chlorine ions in organic fluids. R. CALATRONI and E. TSCHOPP (Biochem. Z., 1929, 208, 274—278).—The hot deproteinised fluid is treated with excess of standard silver nitrate and, after separating the insoluble chloride by centrifuging, the excess of silver in the supernatant fluid is determined by treating an aliquot part with an aqueous solution of hydrogen sulphide in presence of gelatin as protective colloid. The silver sulphide formed is a very stable colloid and may be determined colorimetrically. The results agree fairly closely with those obtained on the same solution by Van Slyke's method, the variations being from ± 0.5 to 1.5%.

P. W. CLUTTERBUCK.

Determination of chlorine in organs and foods. M. BIRNER (Z. ges. exp. Med., 1928, 61, 700—706; Chem. Zentr., 1928, ii, 2582—2583).—The organic material is covered in a tall, narrow nickel crucible with 2—3 times the quantity of sodium hydroxide, and the mass is heated on the water-bath, the temperature being raised to 120° after addition of a small amount of potassium nitrate, and finally to a temperature not above 450°. After cooling, the mass is dissolved in water, filtered, and the chlorine determined by Volhard's method. Nitrite is removed by boiling after addition of silver nitrate, the last traces being oxidised with a few drops of permanganate solution. A. A. ELDRIDGE.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1929.

General, Physical, and Inorganic Chemistry.

Ultra-violet bands of the hydrogen molecule. A. SCHAAFSMA and G. H. DIEKE (*Z. Physik*, 1929, 55, 164—186).—The hydrogen spectrum has been investigated over the region 1250—1700 Å., and almost all lines have been arranged in the *B*—*A* band system. Oscillation levels up to $n=12$ have been found for the *A* state and up to $n=9$ for the *B* state. By applying combination conditions the terms have been isolated and the constants calculated. No lines belonging to other band systems lie in this region.
J. W. SMITH.

Some peculiar hydrogen bands. C. J. BRASEFIELD (*Physical Rev.*, 1929, [ii], 33, 925—931).—Photographs of the secondary spectrum of hydrogen as excited by an electrodeless ring discharge were taken at pressures from 0.08 to 0.001 mm. A number of lines were found to be more intense at low than at high pressures, and were arranged into bands assumed to be $0 \rightarrow 0$, $1 \rightarrow 0$, $0 \rightarrow 1$, and $1 \rightarrow 1$ bands. The values of the moments of inertia are $I_0' = 3.8 \times 10^{-40}$, $I_1' = 5.5 \times 10^{-40}$, $I_0'' = 2 \times 10^{-40}$, and $I_1'' = 2.3 \times 10^{-40}$. The corresponding values of the nuclear separations are $r_0' = 2.14 \times 10^{-8}$, $r_1' = 2.57 \times 10^{-8}$, $r_0'' = 1.55 \times 10^{-8}$, and $r_1'' = 1.66 \times 10^{-8}$ cm. The emitter of these bands is thought to be either H_2^+ or doubly excited hydrogen.
N. M. BLYTH.

Intensity problem in the Stark effect in hydrogen. H. MARK and R. WIERL (*Z. Physik*, 1929, 55, 156—163).—The intensity distribution in the Stark effect components of the H_α and H_β lines of hydrogen is different in collision excitation from that in resonance excitation with a field direction perpendicular to the direction of the positive rays. An analogy is drawn with the polarisation of light emitted by a moving hydrogen atom. The *p*-intensity (the electrical vector of the light parallel to the electric field and perpendicular to the velocity direction) is greater for collision excitation than for resonant excitation.
J. W. SMITH.

Asymmetry in the radiation from the hydrogen atom in the electric field. J. STARK (*Nature*, 1929, 124, 125—126, and *Naturwiss.*, 1929, 17, 568—569).—Observations on the hydrogen lines H_α , H_β , H_γ , and H_δ for the case of emission along the axis of a superposed electric field have revealed differences in the intensities for the two sides of the plane perpendicular to the axis. The asymmetry of radiation of the hydrogen atom in the electric field is incompatible with the Bohr—Epstein—Kramers theory, with the Heisenberg—Schrödinger theory, and with Sommer-

feld's theorem on the symmetry of the hydrogen atom.
A. A. ELDRIDGE.

Second order Stark effect in the Balmer series of hydrogen. II. H. R. VON TRAUBENBERG and R. GEBAUER (*Z. Physik*, 1929, 56, 254—258; cf. this vol., 734).—The shifts of the higher components of H_γ towards the red end of the spectrum observed experimentally agree with the values now calculated from Schrodinger's theory, but not with Epstein's calculations from the old quantum theory.
J. W. SMITH.

Continuous spectrum of the hydrogen atom. D. CHALONGE and N. T. ZE (*Compt. rend.*, 1929, 189, 243—245).—The capacity of the discharge in the experiments of Chalonge and Lambrey (this vol., 616) has been varied, and the form of the resulting intensity-wave-length curves indicates that the new spectra obtained are probably due to the superposition of the molecular and continuous atomic spectra of hydrogen. The latter accompanies (and its maximum intensity is produced before the limit of) the Balmer series, and a progressive enlargement of the lines of the latter, due to the Stark effect, is produced by a displacement of the maximum towards the higher wave-lengths.
J. GRANT.

Hydrogen atom-rays. I. Technical production of hydrogen atom-rays and the action of hydrogen atoms on the Schumann plate. II. Reflexion of hydrogen atoms at crystals and passage of the atoms through thin foils. H. KERSCHBAUM (*Ann. Physik*, 1929, [v], 2, 201—212, 213—220).—I. The technique has been improved by the use of celluloid divisions in the tube for generating the hydrogen atom stream, and the use of Schumann plates for detection of the rays.

II. Reflexion experiments on thermally generated streams of hydrogen atoms impinging in two different angular regions (45 — 50° and 5 — 10°) on mica, gypsum, and celluloid show that the angle of incidence is equal to the angle of reflexion, with respect to the normal to the crystal. When the stream passed through very thin celluloid and mica foil no selective scattering could be observed. The passage of hydrogen atoms through neon has been studied in a preliminary way.
R. A. MORTON.

Detection of atomic scattering by measurement of the ionisation produced by a single *H*-particle. G. HOFFMANN and H. POSE (*Z. Physik*, 1929, 56, 405—415).—A new method of detecting atomic scattering is described in which the ionisation

produced by each *H*-particle can be measured by means of a Duanten electrometer, which must be used in conjunction with a special type of ionisation chamber. The method is illustrated by measurements for *H*-particles produced by the bombardment of aluminium with α -particles from polonium.

J. W. SMITH.

Properties of the He_2 rotation terms. W. E. CURTIS and A. HARVEY (*Nature*, 1929, 124, 12).—Certain regularities exhibited by the rotation term differences of the various electronic states render possible the prediction (within a few cm^{-1}) of most of the rotation terms at present missing; conversely, the interpretation of new bands is facilitated. Thus, two new branches of *P*- and *Q*-form (Dieke, Imanishi, and Takamine, this vol., 732) are recognised as *Q*- and *R*-branches of the $6X$ level of ortho- He_2 .

A. A. ELDRIDGE.

Fine structure in the helium band lines. G. S. MONK and R. S. MULLIKEN (*Nature*, 1929, 124, 91).—Fine structure has been observed in the lines of a number of ortho- He_2 bands having $2^3\Sigma^-$ as their lower electronic state, but the $2^3\Sigma^- \rightarrow 3^3\Pi$ band at 4650 \AA . shows no evidence of fine structure. The bands at 6400 , 5733 , and 4546 \AA . show qualitatively the same fine structure for all band lines which end on any given rotational level; other bands show a similar relation. An interpretation of the $2^3\Pi$ fine structures is offered.

A. A. ELDRIDGE.

Analysis of the fine structure of D_3 line of helium. H. R. WEI (*Astrophys. J.*, 1928, 68, 246—256).—By using gratings of high resolving power and large dispersion in the high orders, the D_3 line of helium has been resolved into a triplet, a result which has been confirmed with an echelon spectrograph. The ratio of intensity is $4.5 : 3 : 1$ and the separation ratio $10.3 : 1$.

L. S. THEOBALD.

Regularities in the band spectrum of helium. Vibration quanta of He_2 and He_2^+ . W. WEIZEL and E. PESTEL (*Z. Physik*, 1929, 56, 197—214).—The fine structures of twelve bands in the spectrum of helium have been determined. Deductions are drawn concerning the vibration quanta and their dependence on the electron terms.

J. W. SMITH.

Isotope effect in the spectrum of neon. H. NAGAOKA and T. MISHIMA (*Proc. Imp. Acad. Tokyo*, 1929, 5, 200—202).—In order to study the effect of the two isotopes of neon and to compare results with Bohr's theory on the change of Rydberg constant, the interference fringes of neon, cooled in liquid air to obtain sharpness, were observed, and the lines measured and classified. The spectrum differed from the ordinary close doublets, and deviations from the calculated wave-length values were attributed to the isotope effect, and were in good agreement with calculated values of the shift to shorter wave-length based on the change of Rydberg constant.

N. M. BLIGH.

High-pressure carbon bands and the Swan system. R. C. JOHNSON and R. K. ASUNDI (*Proc. Roy. Soc.*, 1929, A, 124, 668—688).—Photographs of the high-pressure carbon bands have been obtained in the first order of a 21-foot grating, using large discharge tubes filled with carbon monoxide at a

pressure of 20—40 mm. and having at least one of the electrodes made of carbon. With tubes having a life of 4—6 hrs. the high-pressure bands were emitted strongly, and found to bear an exceptionally close resemblance in their fine structure to the Swan bands as developed under low-temperature conditions. Impurities such as hydrogen, carbon dioxide, and water vapour inhibit formation of the bands. The Swan system and the high-pressure carbon system are shown to have a common final state, hence the emitter responsible for both systems is a C_2 molecule. The inhibiting effect of hydrogen on the high-pressure system is definitely against a hydrocarbon emitter (cf. Johnson, A., 1927, 395). Four new high-pressure bands have been found in the near ultra-violet and two more in the near infra-red which, with the six known bands, form a single n'' progression ($n''=0$). The bands consist of *P* and *R* branches only and the electronic transition involved is $3P_n^D \rightarrow 3P_f^P$. A detailed examination of the structure of the *R* branches shows several anomalies and perturbations of an unusual type. The methods used by Hund and by Mulliken for the elucidation of the structure of diatomic molecules (cf. A., 1928, 105, 1166) are discussed, and Mulliken's application to the C_2 molecule is extended to cover the initial state of the high-pressure system. This is believed to be a normal $3f$ level and different in this respect from the two lower $3P$ levels, which are believed to be inverted.

L. L. BIRCUMSHAW.

Spectrum of carbon. D. S. JOG (*Indian J. Physics*, 1929, 3, 451—461).—The wave-lengths of the carbon spectrum as given by a number of investigators being somewhat discordant, and a number of lines being unaccounted for, a re-examination was undertaken and the results are fully tabulated and discussed. The results of a search for inner transitions in the spectrum of C I of the type ($2L_1L_2M \rightarrow L_12L_2M_1$) are also given.

N. M. BLIGH.

Molecular binding and low 5S terms of N^+ and carbon. L. A. TURNER (*Proc. Nat. Acad. Sci.*, 1929, 15, 526—528).—Herzberg's analysis (cf. A., 1928, 808, 1165) of the negative bands of nitrogen suggests that the dissociation of the excited molecular ion produces a normal atom and a normal atomic ion, whereas the dissociation of the normal molecular ion produces an atom and an ion, one of which is excited. The energy difference is 2.4 volts. Fowler's tables (cf. A., 1927, 489) show two lines for the excited state of nitrogen corresponding with 3P_2 and 3P_1 levels and 2.4 volts, indicating that the N^+ ion rather than the nitrogen atom is excited. The correct fixation of the 5S terms of nitrogen and carbon is discussed.

N. M. BLIGH.

Ultra-violet band spectrum of nitrogen. R. T. BIRGE and J. J. HOPFIELD (*Astrophys. J.*, 1928, 68, 257—278; cf. A., 1928, 1294).—A more detailed examination of previous spectrograms together with recent spectrograms shows that the ultra-violet emission spectrum of nitrogen consists of a clearly-defined system of more than 60 bands, degraded towards the red. The weighted average wave-lengths of these bands are tabulated, together with the vibrational quantum analysis of the system. The

absorption spectrum of nitrogen also contains this system. Numerous additional emission and absorption bands are reported, and three new systems presumably are represented among the emission bands. Four new electronic levels in the neutral nitrogen molecule are thus evaluated, although one of these may be doubtful, since the corresponding system occurs only with commercial, partly-purified nitrogen and not with chemically pure nitrogen. The two most probable values of the heat of dissociation of nitrogen calculated from the vibrational constants of the several electronic levels are 11.9 and 9.5 volts, respectively.

L. S. THEOBALD.

Spectrum of ionised nitrogen (N II). L. J. FREEMAN (Proc. Roy. Soc., 1929, A, 124, 654—667).—The second group of terms based on the $2p'$ terms of N III (cf. Fowler and Freeman, A., 1927, 489) has now been investigated. Nine quintuplet multiplets have been observed, resulting in the identification of all the $3s'$, $3p'$, and $3d'$ terms. The deepest term, $2p'^5S$, has not been found. The term separations of O III are all about 2.3 times as great as those for N II. The differences in the energy levels when the series electron occupies various orbits is not much affected by the disposition of the inner electrons, since the two systems of N II quintuplets and triplets run nearly parallel, both in relative magnitudes and relative separations. Six new triplet combinations have been found, resulting in the identification of two new terms. For corresponding terms of the N II triplets and N III quadruplets, the separations are very similar in the two systems. About 75 N II lines are newly classified.

L. L. BIRCUMSHAW.

Simultaneous ionisation and dissociation of oxygen and intensities of the ultra-violet O_2^+ bands. E. C. G. STUECKELBERG (Physical Rev., 1929, [ii], 34, 65—67).—The formation of O^+ from the neutral molecule by a single impact of about 20 volts (cf. Hogness, A., 1926, 768; Smyth, this vol., 113) is explained from potential energy curves of the molecule and ion. The intensities of the ultra-violet O_2^+ bands were calculated from the same curves and found to be in good agreement with experiment.

N. M. BLIGH.

Spectra of phosphorus and arsenic in the extreme ultra-violet. Multiplets of As IV and As V. P. QUENEY (Compt. rend., 1929, 189, 158—159).—The principal lines of As V and As IV have been obtained by extrapolation, according to Millikan and Bowen's laws of regular and irregular doublets, from the homologous lines of Zn II, Ga III, and Ge IV, and of Zn I, Ga II, and Ge III, respectively. The results were confirmed experimentally.

J. GRANT.

Second spark spectrum of sulphur, S III. S. B. INGRAM (Physical Rev., 1929, [ii], 33, 907—913; cf. Gilles, this vol., 225).—With experimental data previously obtained (cf. A., 1928, 1068) the spectrum of S III is analysed. Most of the triplet terms predicted by the Hund theory are found and the strongest in the visible and extreme ultra-violet are classified. The ground term $3s^23p^2P_0$ gives the ionisation potential as 34.9 ± 0.4 volts. Complete term tables and a list of classified lines are given. The term $3s^23p.4s^3P$ is anomalous, having a total separation

of 450, whilst the p doublet of the ion is 950. The interval ratio of this term is 10 : 1, instead of 2 : 1 as given by Lande's rule. Combinations of this term with the ground term in the extreme ultra-violet are very weak.

N. M. BLIGH.

Excitation of visible "red" and "blue" argon spectra by electron collision. B. SCHULZE (Z. Physik, 1929, 56, 378—393).—The excitation of the arc and first spark spectra of argon in the visible region by electron collision has been investigated, the successive appearance of the different lines with increasing accelerating voltage being observed photographically. In contradiction to previous work the arc spectrum in the visible and near infra-red regions can be excited in seven stages between 13.3 and 15.7 volts. In all cases good agreement is obtained with the excitation potentials calculated from the series terms, thus affording a direct confirmation of the analysis of the "red" spectrum given by Meissner (A., 1926, 1186; 1927, 177). The excitation potentials of a series of lines of the first argon spark spectrum (the "blue" spectrum) were measured in a similar way, good agreement being obtained with the values calculated from the spectroscopic measurements of de Bruin (A., 1928, 450; this vol., 3). J. W. SMITH.

Possibility of observing an emission spectrum of the calcium substratum in the galaxy. Y. OHMAN (Nature, 1929, 124, 179—180).

Intensities in the calcium spark spectrum. A. ZWAAN (Arch. Neerland, 1929, [üia], 12, 1—76).—Mathematical. The potential function is considered, the central field of the Ca^{++} ion being investigated, and the "Eigenfunktion" is calculated, the approximation method of Kramers being used. The probability of switch is also calculated, the doublet structure of the Ca^{++} spectrum being neglected. The following values were obtained for A and f : $4_2 \rightarrow 3_3$, $A = 1.3 \times 10^7$; $f = 0.09$; $4_2 \rightarrow 4_1$, $A = 1.55 \times 10^8$; $f = 1.08$. These values are high compared with those of Milne, and indicate that the calcium in the highest layers of the chromosphere is not in equilibrium. A. J. MEE.

New series in the iron spectrum produced by a highly condensed spark. M. KAHANOWICZ (Atti R. Accad. Lincei, 1929, [vi], 9, 761—764).—Three doublets (5937.5, 5928; 5677.5, 5666.5; 5003, 5001 Å.), which may be regarded as due to a modification of the second Stark effect, are observed in the iron spectrum produced by a highly condensed spark. They belong to the series $\nu = R[1/2^2 - 1/(n/32)^2]$, where $n = [(4 \times 26) - 1]$, $[(4 \times 27) - 1]$, and $[(4 \times 31) - 1]$, respectively.

F. G. TRYHORN.

Spectral relations between certain iso-electronic systems and sequences. III. Ti I, V II, Cr III, Mn IV, and Fe V. H. E. WHITE (Physical Rev., 1929, [ii], 33, 914—924; cf. this vol., 734).—With the help of the irregular doublet law these spectra were analysed and wave-lengths, relative intensities, and designations are tabulated. About 40 lines for the electron transition $3d^34p - 3d^34s$ and about 12 lines for the transition $3d^34d - 3d^34p$ were traced through the first three elements, and in the former transition the multiplet $^5F' - ^5G'$ was traced as far as Fe V. The systematic increase in term separations

is given for the ${}^5F'$ and ${}^5G'$ terms arising from the electron configurations $3d^34s$ and $3d^34p$, respectively; the Lande interval rule and Hund's rule for relative term positions are found to be satisfied. A new type of Moseley energy level diagram for these and other elements is considered.

N. M. BLIGH.

Vector coupling in the nickel-, palladium-, and platinum-like spectra. J. E. MACK (Physical Rev., 1929, [ii], 34, 17—34).—The structure of the atomic states in which the outer electrons occur in configurations of nine d electrons and one s or p electron is chiefly considered. The $3d^96s$ and $5d^96p$ configurations are identified among the known levels of Pt I, and partly identified in Tl IV and Pb V. The lines observed in the condensed spark discharge of thallium $\lambda 868$ —1070 and lead $\lambda 477$ —1280 are tabulated. The relative energies, line intensities, and g -values of the levels of the d^9s and d^9p configurations of the sequences Ni I—Ge V, Pd I—Sn V, and Pt I—Pb V show a transition from LS or Russell-Saunders coupling to jj coupling with increasing atomic number and net charge. In the pure jj coupling the levels are arranged in groups, two in d^9s and four in d^9p . The positions of the d^9p groups observed for Hg III, Tl IV, and Pb V agree well with the positions calculated for jj coupling by Sommerfeld's regular doublet law. In the d^9p configuration of Tl IV and Pb V, only levels built upon $d^92D_{5/2}$ are observed.

N. M. BLIGH.

Spectra of Cu I, Cu II, and Mn II by means of a vacuum tungsten furnace. O. S. DUFFENDACK and J. G. BLACK (Physical Rev., 1929, [ii], 34, 35—43).—A high-temperature vacuum tungsten furnace for the study of the spectra of elements of high $b.p.$ is described. All previously observed absorption lines of Cu in the range of the quartz spectrograph were found and also six new lines from the $3d^94s$ level, 2618.381, 2824.375, 2882.81, 2961.177, 3010.84, 3194.103. CuH bands were also observed in absorption. The emission spectrum of Cu I was excited by resonance radiation from the furnace walls, the atoms being excited to the 2P state with emission of the lines 3247, 3274, 5106, 5700, and 5782. The excitation of Cu II and Mn II spectra by collisions of the second kind with ions of argon, neon, and helium was studied with reference in each case to the possible excess energy for excitation after ionisation; theoretical results were confirmed.

N. M. BLIGH.

Second spark spectrum of selenium (Se). D. K. BHATTACHARJYA (Nature, 1929, 124, 229).— PD , PP , and PS groups of $N_2O_1 \leftarrow N_2O_2$ have been located graphically at 24000, 28000, and 28400, respectively. Leading lines of these multiplets in the same transition are: ${}^3P_0 \rightarrow {}^3D_3$ 23979 (4169.16 Å.), ${}^3P_2 \rightarrow {}^3P_2$ 27482.6 (3639.6 Å.), ${}^3P_2 \rightarrow {}^3S_1$ 28210.0 (3643.8 Å.).

A. A. ELDRIDGE.

Series spectrum of Se IV. P. PATTABHIRAMAYYA and A. S. RAO (Indian J. Physics, 1929, 3, 531—535).—An analysis of the spectrum of Se IV is tabulated showing: a classification of the identified lines with the terms and term values; the variation of the logarithms of doublet separations and the logarithms of the net nuclear charge; the comparative positions of some of the prominent members in the spectra of Ga I,

Ge II, As III, and Se IV; the progression of the terms in the spectra of these elements; and some unclassified pairs with their probable classification.

N. M. BLIGH.

Spectrum of trebly-ionised bromine. S. C. DEB (Nature, 1929, 123, 981).—The chief lines of the group $N_2(O_1 \leftarrow O_2)$ have been located, as follows: ${}^3P_2 {}^3D_3$ at ν 36675.2, ${}^3P_2 {}^3P_2$ at ν 40130.8, at ν 42247; also ${}^1P_1 {}^1P_1$ is at ν 42177.

A. A. ELDRIDGE.

Complexity of the terms of the resonance spectrum of tellurium vapour. W. KESSEL (Compt. rend., 1929, 189, 94—96; cf. Rosen, A., 1927, 608).—The author's method for the excitation of intense resonance radiation resulted in a well-developed series for tellurium vapour in which the fundamental element of each term was a doublet composed of lines of unequal intensities $\Delta\lambda = 0.5$ Å. apart, the frequencies being related by the formula $\nu = 0.53n^2 - 246.7n + 2294.3 \pm \Delta\nu$. The fundamental doublets were λ 4358.5, 4358.9 ($n=0$), and 4452.8, 4453.3 ($n=2$).

J. GRANT.

Temperature classification of the stronger lines of cerium and praseodymium. A. S. KING (Astrophys. J., 1928, 68, 194—245).—The furnace spectra of cerium and praseodymium obtained between 2000° and 2700° and at 1900°, respectively, have been examined, and lines arising from neutral and ionised spectra have been segregated by a comparison of furnace, arc, and spark spectra. This was facilitated by the addition of caesium, which suppresses the ionised lines normally appearing in the furnace spectrum. The furnace spectrum is especially effective in revealing lines of the neutral atom unrecognised in the arc and spark spectra. The prominent lines of cerium and praseodymium in the arc and spark spectra belong to the ionised atom, whilst at greater wave-lengths the neutral lines are stronger and form a large part of the arc spectrum. Tables of 1362 lines for cerium and of 1018 for praseodymium are given, the lines being selected for their prominence and suitability as a means of identification in either the neutral or ionised condition. Praseodymium is notable for the large number of complex lines which it shows both in the neutral and in the ionised spectra.

L. S. THEOBALD.

M-Series of rhenium. E. LINDBERG (Z. Physik, 1929, 56, 402—404; cf. A., 1928, 1078).—The discrepancies between the measurements of the author and those of Beuthe (*ibid.*, 1294) are discussed. New measurements have been made in which the previous observations have been confirmed and new lines measured.

J. W. SMITH.

Spectrum of trebly-ionised thallium (Tl IV). P. PATTABHIRAMAYYA (Indian J. Physics, 1929, 3, 523—529).—Tables are given of the scheme of multiplets formed by the combination of terms; the progression of the regular doublet law in the homologous spectra of Pt I, Au II, Hg III, and Tl IV; the progression of the difference in sub-levels in the spectra of the homologous series of elements; the progression of the ${}^3s^1P$, ${}^3s^1D$ multiplet in the sequence of the spectra, and a list of lines classified.

N. M. BLIGH.

Notation for atomic spectra. H. N. RUSSELL, A. G. SHENSTONE, and L. A. TURNER (*Physical Rev.*, 1929, [ii], 33, 900—906).—Suggestions and recommendations are made for adapting existing spectral notations to a standardised form suitable for designating multiplet, configuration, and series analyses.

N. M. BUGH.

Possible origin of faint Fraunhofer lines. D. S. KOTHARI (*Nature*, 1929, 124, 90—91).—Many of the lines are ascribed to the combined effect of Raman scattering and ordinary absorption. It does not appear that the coronal spectrum is due to modification of strong Fraunhofer lines by Raman scattering.

A. A. ELDRIDGE.

Spectrum of the [solar] corona. E. M. LINDSAY (*Nature*, 1929, 124, 94).—The possibility that the unknown lines of the solar corona might be due to the occurrence of forbidden transitions between terms in the spectra of ionised iron (Fe II), calcium (Ca II), titanium (Ti II, Ti III), and argon (Ar II), and of the neutral titanium atom has been examined and dismissed. There is no evidence that they arise in second type collisions involving the metastable 18 terms of ionised calcium (Ca II).

A. A. ELDRIDGE.

Spectrum of the solar corona. I. M. FREEMAN (*Astrophys. J.*, 1928, 68, 177—193).—Thirty-three of the 38 lines of undisputed coronal origin have now been identified with emission lines in the spectrum of argon.

L. S. THEOBALD.

Measurement of the strength of sunlight. J. E. MOSS and A. W. KNAPP (*Analyst*, 1929, 54, 334—335; cf. Bagnall, this vol., 407).—It is suggested that Bagnall's reaction should be carried out in quartz vessels, since glass absorbs radiations shorter than 320 μ , and bottle glass probably absorbs still more of the ultra-violet spectrum. If it is known which wavelengths decompose the potassium iodide the value of any actinometer test is increased. Unless one unit of ultra-violet radiation liberates the same quantity of iodine from the nearly colourless potassium iodide solution as from the orange-coloured mixture of solutions of iodine and potassium iodide, the quantity of iodine liberated will not be directly proportional to the amount of ultra-violet radiation incident in the solution.

D. G. HEWER.

Black body [radiation] at the m. p. of palladium by the tube method. G. RIBAUD and S. NIKITINE (*Ann. Physique*, 1929, [x], 11, 451—482).—A more detailed account of work already published (this vol., 366).

Abnormal broadening of spectral lines. A. W. PORTER (*Trans. Faraday Soc.*, 1929, 25, 389—391).—The most probable origin of an abnormal broadening of spectral lines is considered to be the lack of uniformity in the distribution of the illumination falling on the working crystal. Consideration of a simple case illustrates the general nature of the effect of such illumination. A stationary mechanical oscillation in the crystal would also produce a broadening of the spectral lines.

L. L. BIRCUMSHAW.

Hyperfine structure in doublets and its use for the determination of nuclear moments. H. SCHULER and H. BRUCK (*Z. Physik*, 1929, 55, 575—

580).—Theoretical. Examination of the hyperfine structure of the doublet spectrum of thallium leads to a value, $\nu = \frac{1}{2}$, for a new momentum which is constant for all atomic states. From considerations of the intensities in the hyperfine structure it is concluded that the new momentum is a nuclear one.

W. E. DOWNEY.

Hyperfine structures in triplet spectra and their use for the determination of nuclear moments. H. SCHULER and H. BRUCK (*Z. Physik*, 1929, 56, 291—296; cf. preceding abstract).—Triplet spectra are examined under the assumption that for a single isotope the nuclear moment is constant for all atomic states and forms a new quantum number i . In the case of cadmium the isotopes fall into two groups with $i=0$ and $i=1$ respectively. Data so far available are tabulated and discussed.

J. W. SMITH.

Ultra-violet spark spectra in liquids. A. CAMPETTI (*Nuovo Cim.*, 1928, 5, 291—306; *Chem. Zentr.*, 1929, i, 480).—The spark spectra of cadmium, zinc, magnesium, calcium, copper, silver, gold, aluminium, lead, bismuth, and antimony under water and, in some cases, under petroleum or carbon tetrachloride have been studied. The continuous background arises chiefly from the central zone of the spark. The number of reversed lines generally increases as the far ultra-violet is approached. Usually lines corresponding with the first and second resonance potentials of an element are strongly reversed.

A. A. ELDRIDGE.

Spectral reflectances of common materials in the ultra-violet region. M. LUCKIESH (*J. Opt. Soc. Amer.*, 1929, 19, 1—6).—Using the photographic method spectral reflectance data are recorded graphically as a function of the wave-length for the following substances in separate groups: fabrics—linen, bleached wool, pongee silk, white blotting paper, and bleached cotton, the last-named having the highest reflectance; dry white pigments—white lead, stannic oxide, lithopone, titanium pigment, and zinc oxide; other dry powders—magnesium carbonate, slaked lime, wall plaster, kaolin, alumina, silica, opal glass, and graphite; some commercial paints, and the polished metals silver, aluminium, chromium, nickel, zinc, steel, tin; and porcelain enamel.

N. M. BUGH.

Reflecting power of some substances in the extreme ultra-violet. P. R. GLEASON (*Proc. Nat. Acad. Sci.*, 1929, 15, 551—557; cf. Pfund, A., 1926, 649).—The reflecting power was investigated quantitatively for the extreme ultra-violet region 585—1850 Å. A vacuum spectrograph was incorporated, the light analysed by and reflected from a concave speculum grating falling on a photographic plate directly or after reflexion from the surface. Curves showing the reflecting power as a function of the wave-length are given both for fresh and old surfaces sputtered or deposited and polished and of known opacity, in the case of aluminium, beryllium, brass, chromium, gold, nickel, platinum, silicon, silver, speculum, steel, stellite, fluorite, glass, and quartz. Platinum was easily the best reflector at the shortest wave-lengths, whilst nickel, crystalline quartz, and gold were the only others reflecting more than 10% at 585 Å.

N. M. BUGH.

Sparking potential in hydrogen. E. MEYER (Helv. phys. Acta, 1928, 1, 14—17; Chem. Zentr., 1929, i, 970).—Progressive drying of hydrogen continuously diminishes the sparking potential. Small quantities of water in nitrogen depress the sparking potential. An explanation is offered.

A. A. ELDRIDGE.

Critical potentials and low tension-arcs in hydrogen. S. VENCOV (Compt. rend., 1929, 189, 27—30).—Different means of excitation and decomposition of the hydrogen molecule by electronic shock were obtained by various combinations of electric fields supplied by a potentiometric device. The principal critical potentials observed were due to molecular resonance (11.5 ± 0.5 volts), atomic ionisation resulting from thermal ionisation of H_2 molecules into atoms (13.6 ± 0.2 volts), molecular dissociation (16.5 ± 0.5 volts), and dissociation followed by double ionisation (29.7 ± 0.6 volts). The work of molecular dissociation of hydrogen is 3 volts. Examination of the corresponding spectra indicates a combination of the cumulative absorption of the radiations and the successive shocks necessary for ionisation (cf. Witmer, A., 1926, 552).

J. GRANT.

Photo-electric cells of alkali metals. S. ASAO (Mazda, 1928, 3, 155—165).—Cells in which the anode was a glass bulb bearing sodium, potassium, or their hydrides on the inner wall, and the cathode was a metallic ring, did not give reproducible results. Sodium was superior to potassium and the hydride increased the sensitivity. By filling the bulb with argon the anode current was considerably increased.

CHEMICAL ABSTRACTS.

Maximum excursion of the photo-electric long-wave limit of the alkali metals. H. E. IVES and A. R. OLPIN (Physical Rev., 1929, [ii], 34, 117—128).—The photo-electric long-wave limit, as the metals are deposited on platinum, moves from the short to the long wave-length of the spectrum, reaching a maximum and then receding. For sodium this maximum is in the visible region, but for potassium, rubidium, and caesium it lies in the infra-red, and for these a monochromatic illuminator was used by adapting a spectrometer with a "thalofide" cell. The photo-electric current was plotted against wave-length, and the maximum was found in each case to coincide with the first line of the principal series, or the resonance potential. This relation was found to hold for lithium, the maximum long-wave limit of which is thus shown to be greater than that of sodium. The special technique necessary for preparing and dealing with pure lithium metal is described. It is concluded that photo-electric emission is caused when sufficient energy is given to the atom to produce its first stage of excitation, and that atomic excitation is also the initial process in thermionic emission.

N. M. BLIGH.

Photo-electric effect of molten tin and two of its allotropic modifications. A. GOETZ (Physical Rev., 1929, [ii], 33, 373—385).—See this vol., 482.

Emission of electrons from cold metals. T. E. STERN, B. S. GOSSLING, and R. H. FOWLER (Proc. Roy. Soc., 1929, A, 124, 699—723).—The original formula of Fowler and Nordheim for the "auto-

electronic" current density (A., 1928, 681) is corrected, the numerical factor 6.8×10^7 being introduced in place of 2.1×10^8 . The nature of the comparison possible between the theory, which states a relation between the current density and the surface field, and the quantities actually observed—i.e., the total current passing between the electrodes and the applied voltage—is discussed. To derive the fullest information from the comparison, the emitting area A and the ratio of the surface field to the applied voltage are determined. This ratio depends not only on the large-scale geometry of the apparatus, but also on the micro-geometry of the irregularities of the cathode surface. The comparison yields fairly satisfactory results, except for the surprisingly small values of A derived. The theory is extended to include an examination of the space charge effect, which is found to be negligible, and an examination of the effect of surface films on the emission coefficient. If the cathode is of clean tungsten a much higher field must be applied to obtain a given auto-electronic emission than if it is covered with a layer of sodium, barium, caesium, or other electro-positive impurity. A formula is obtained for the emission through a surface layer under an applied field.

L. L. BIRUMSHAW.

Connexion between spark potential and Volta-effect. R. BAR (Helv. phys. Acta, 1928, 1, 186—192; Chem. Zentr., 1929, i, 725—726).

Experiments on the explanation of the selective outer photo-electric effect. III. Selective photo-electric effect with potassium films adsorbed on a platinum plate. R. SUHRMANN and H. THEISING (Z. Physik, 1929, 55, 701—716; cf. A., 1928, 680, 1068; this vol., 114, 229).—The electron sharing per unit of energy was investigated for linearly polarised light in both the principal vector positions up to 300 m μ , and with unpolarised light up to 240 m μ , for variations of the thickness of potassium films adsorbed on a platinum surface. Only a very little of the potassium was distributed in the atomic state on the surface, but this possessed a normal sensitivity curve for the electric vector parallel to the plane of incidence, of which the long-wave limit was in the visible spectrum. With somewhat more potassium atoms than are necessary to make up a unimolecular layer a high spectral maximum is reached about 340 m μ , and the vector ratio is strongly selective. With increasing thickness of the potassium layer the maximum is displaced towards the red and becomes small. The selectivity is retained as long as the layer is thin.

A. J. MEE.

Photo-electric and thermionic properties of molybdenum. M. J. MARTIN (Physical Rev., 1929, [ii], 33, 991—997).—The variation of the photo-electric sensitivity of a molybdenum surface during prolonged heat treatment was studied over 300 hrs. Thin molybdenum ribbons were heated at 1325° in a high vacuum and the photo-currents produced by the light from a quartz-mercury arc were measured with a quadrant electrometer. The sensitivity increased with time of heating, to a limiting value, and was accompanied by a shift in the long wave-length limit from 2600 to 3800 Å. approx. The value 3.22 ± 0.16 volts was found for the photo-electric work function,

and the value 3.48 ± 0.07 volts for the thermionic work function as found from a graph of the emission as a function of the temperature. The photo-electric sensitivity decreased with rise of temperature by about 30% between 0° and 1000° . N. M. BLIGH.

Dependence of ionisation potential on atomic number. R. PEIERLS (Z. Physik, 1929, 55, 738—743).—The relationship between ionisation potential and atomic number recently discussed by Alexander (this vol., 487) is further investigated, and it is found that there are no deviations from theoretical expectations. A. J. MEE.

Influence of plastic deformation on the internal photo-electric effect in rock-salt crystals. M. PODASCHEWSKY (Z. Physik, 1929, 56, 362—369; cf. A., 1928, 1076).—Plastic deformation produces a marked influence on the primary photo-electric current in rock-salt crystals coloured by X-rays. On loading, the photo-electric current falls at first very rapidly, but finally comes asymptotically to a constant value, depending on the load applied. On removing the load, the preparation retains permanently the effect possessed at the time of unloading. The photo-electric sensitivity diminished in this way may be restored by prolonged illumination with X-rays. Ordinary elastic deformation produces no change in the photo-electric effect. J. W. SMITH.

Effects of a crystallographic transformation on the photo-electric and thermionic emission from cobalt. A. B. CARDWELL (Proc. Nat. Acad. Sci., 1929, 15, 544—551).—With the method previously used for iron (cf. A., 1928, 808) the photo-electric and thermionic emission from very carefully outgassed cobalt was investigated. Curves are given showing the change in photo-electric emission with rising temperature for a sample which, through supercooling from a critical temperature of about 850° , existed in the face-centred cubic form, and for a sample in the hexagonal close-packed form, obtained by very slow cooling from the same temperature. A more complex curve shows the effect with falling temperatures. Curves are given similarly to show the values of the thermionic current for rising and falling temperatures. During the transition process from one crystal lattice to another an intermediate structure is shown to exist, more sensitive photo-electrically and thermionically than the initial or final form. As contrasted with platinum and iron (cf. DuBridge, A., 1927, 391) the photo-electric sensitivity of cobalt is at no time independent of the temperature, and it is suggested that this is due to a change in the reflective power of the surface with temperature. N. M. BLIGH.

Ionisation by collision in monatomic gases. J. S. TOWNSEND and S. P. MACCALLUM (Proc. Roy. Soc., 1929, A, 124, 533—545; cf. A., 1928, 567, 1300).—A reply to Atkinson's criticisms and a discussion of his theories of ionisation (A., 1928, 809; this vol., 368). A number of contradictions are indicated. Examples, taken from the authors' work on helium and neon (*loc. cit.*), are given to show that the principles on which the theory of collisions of the second order is based are not supported by experiment. If the hypothesis which states that

very few electrons attain energy above that corresponding with the first critical potential were accepted, it would be impossible to obtain a consistent explanation of many simple phenomena observed in electric discharges in monatomic gases. Atkinson's second theory of conductivity includes many of the principal hypotheses forming the basis of Townsend's original theory of ionisation by collision.

L. L. BIRCUMSHAW.

Electrode function and ionic and electronic charges. F. KLINGELFUSS (Z. Physik, 1929, 55, 778—788).—Mathematical. The additional term to the sparking potential due to the free charge in air at atmospheric pressure causes a dielectric displacement. The calculations show that there is a difference in the size of the ionic and the electronic charges.

A. J. MEE

Thermionic "A" and "B." E. H. HALL (Proc. Nat. Acad. Sci., 1929, 15, 504—514).—Experimental and thermodynamic evidence is reviewed, and shown to be consistent with views previously stated (cf. this vol., 482, 618) on the theory of conduction by electrons in two different states, free electrons or thermions, and associated or valency electrons. The possible identity of the thermionic and photo-electric work-functions is discussed. N. M. BLIGH.

Theory of electron scattering in gases. A. C. G. MITCHELL (Proc. Nat. Acad. Sci., 1929, 15, 520—525).—The scattering of electrons in gases is treated using the Born collision theory in connexion with the Fermi statistical potential for atomic fields.

N. M. BLIGH.

Diffraction of electrons. P. TARTAKOVSKY (Z. Physik, 1926, 56, 416—420).—The diffraction by aluminium foil of electrons with velocities up to 1500 volts has been investigated. Diffraction rings were observed, corresponding with the Debye X-ray diagrams. J. W. SMITH.

Mobility of ions in gases. R. J. VAN DE GRAAFF (Nature, 1929, 124, 10—11).—The author's method (A., 1928, 932) is improved. A. A. ELDRIDGE.

Oscillations in ionised gases. L. TONKS and I. LANGMUIR (Physical Rev., 1929, [ii], 33, 990; cf. this vol., 367).—A correction. N. M. BLIGH.

Simultaneous ionisation and excitation of diatomic molecules by impacts with positive ions and excited atoms. O. S. DUFFENDACK and H. L. SMITH (Physical Rev., 1929, [ii], 34, 68—80).—A study of mixtures of helium, neon, and argon with carbon monoxide and nitrogen, using a low-voltage arc and two separately controlled filaments, shows that impacts occur between a rare gas ion and a diatomic molecule leading to ionisation and excitation of the latter, and impacts of the second kind between excited helium and neon atoms and neutral carbon monoxide molecules leading to simultaneous ionisation and excitation of the latter. Several effects in similar mixtures in glow discharges are explained. Two new bands in the system due to ionised carbon monoxide and six new edges and a new band in the comet-tail system were found. Wave-lengths and a system analysis are given. From a study of the intensity distribution of the negative band systems of carbon

monoxide excited in mixtures with helium or neon a number of deductions on the degree of excitation of the CO ion in the two mixtures is made. The spectrum of carbon dioxide observed by Fox (cf. A., 1927, 916) is shown to be due to the carbon dioxide ion.

N. M. BLIGH.

New method of positive-ray analysis and its application to the measurement of ionisation potentials in mercury vapour. W. BLEAKNEY (Physical Rev., 1929, [ii], 34, 157—160).—The uniform magnetic field of a large solenoid is used to concentrate a narrow beam of electrons into a long straight path and at the same time to effect the separation of ions having different values of e/m . Preliminary values found for the ionisation potentials of Hg^{2+} , Hg^{3+} , and Hg^{4+} are 30, 71, and 143 volts, respectively.

N. M. BLIGH.

Velocity of formation of molecules from free atoms. V. KONDRATJEV and A. LEIPUNSKY (Z. Physik, 1929, 56, 353—361).—From the previously recorded intensity measurements in the continuous spectrum emitted by the reaction $\text{Br}' + \text{Br} = \text{Br}_2 + h\nu$ (A., 1928, 1075) the probability of molecule formation on collision between an active and a normal bromine atom is calculated. Another, independent, value of this magnitude is also deduced from the absorption coefficient in the region of continuous absorption. The probabilities calculated are of the order of magnitude of 10^{-8} — 10^{-10} , indicating that the formation of molecules in this manner is a very slow process.

J. W. SMITH.

Emission of anode rays of sodium and of chromium. A. POIROR (Compt. rend., 1929, 189, 150—151).—Morand's work on lithium (A., 1927, 492) indicates that a stable emission is obtained from metals of low at. wt., and particularly from easily dissociable halogen salts. By an analogous method, however, a stable emission of long duration of anode rays of sodium and chromium was obtained from pure sodium dichromate. Emission commences at a temperature below the m. p. of the salt; strict control of the potential and of the temperature of the anode is essential.

J. GRANT.

Production of molecular rays of uniform velocity. B. LAMMERT (Z. Physik, 1929, 56, 244—253).—An apparatus by means of which molecular rays of mercury with velocities between certain limits can be separated is described. By measuring the intensities of the radiation over various velocity bands, a direct proof has been obtained of the applicability of the Maxwell distribution law to this case.

J. W. SMITH.

Ion rays. M. ZENTGRAF (Ann. Physik, 1929, [v], 2, 313—332; cf. Schmidt, A., 1926, 877; 1927, 397).—The relations between the current strength of ion rays and voltage have been studied at various temperatures and pressures. Apart from an irreversible decrease in emission with time, there is also an effect connected with impoverishment and subsequent recovery of the emitting surface. The effect is most marked with higher voltages and lower temperatures, whilst recovery is most rapid at the lowest voltages and the highest temperatures practicable. Emission of ion rays reaches saturation (a) with very

small voltages when the pressure is low, (b) more definitely at low temperatures than at high, (c) more markedly for the less volatile silver halides than for the more volatile thallium salts and cadmium iodide. The onset of emission depends on the pressure, the first ions appearing with lower voltages when the pressure is lower, but a small positive potential is always necessary. Visible discharge for the salts occurs at 300—400, 600—800, and 1600—2000 volts at pressures of 1, 10, and 100 mm., respectively. In a high vacuum no visible discharge occurs below 1900 volts. Experiments with cells filled with vaporised salts gave greatly increased currents, varying in the same sense as the voltage. Saturation is evident only at the lower pressures, and the discharge becomes luminous at lower voltages.

R. A. MORTON.

Passage of slow cathode rays through metals. II. A. BECKER (Ann. Physik, 1929, [v], 2, 249—263; cf. *ibid.*, 1927, [iv], 84, 779).—In the velocity range 4500—100 volts the following relations between the amount and velocity of the transmitted electrons have been found for thin metal foil. Apart from slow secondary electrons which reach a maximal fraction of the total electrons at a few hundred volts, the primary electrons are made up of (a) a very small fraction of unretarded electrons, (b) electrons more or less retarded, (c) electrons in a definite velocity region, corresponding with selective permeability to electrons. This last property decreases at first rapidly, then more slowly as the electron velocity decreases, and finally at voltages of the order of 100 volts the change becomes very small. Extension of the work to the smallest velocities consistent with adequate intensity shows that with thicknesses of nickel of 0.02 and 0.04 μ data can be obtained over the range 0.5—100 volts. From 2 to 10 volts the transmission-velocity curve increases rapidly, but beyond this point the rate of increase with increasing velocity is considerably reduced, the curve showing a flatter linear portion from 20 to 100 volts. Between 20 and 100 volts, there is evidence of selective distribution of electrons. True absorption of electrons contributes but little (compared with reflexion losses) to the total loss in intensity effected by the nickel foil; e.g., at 20 volts the transmission of a 0.02 μ thickness is 1.12×10^{-4} , whilst at 0.04 μ it is as high as 0.047×10^{-4} . The scattering of electrons occurs preferentially in certain directions.

R. A. MORTON.

Isotope of carbon, mass 13. A. S. KING and R. T. BIRGE (Nature, 1929, 124, 127).—A new, faint band, observed by the use of the vacuum electric furnace, corresponds with an assumed molecule $\text{C}^{13}\text{C}^{12}$. Six individual lines have been distinguished in the band.

A. A. ELDRIDGE.

Isotope of carbon, mass 13. R. T. BIRGE (Nature, 1929, 124, 182—183).—Evidence of the existence of the molecule $\text{C}^{13}\text{O}^{16}$ is presented by Hopfield's absorption spectrograms of carbon monoxide, and of the existence of the molecule $\text{C}^{13}\text{N}^{14}$ by King's furnace (emission) spectrogram of the CN band 3883 Å. It is also concluded that if isotopes of nitrogen exist, they are much less abundant in comparison with N^{14} than is C^{13} in comparison with C^{12} .

A. A. ELDRIDGE.

Atmospheric oxygen bands, and the relative abundance of the isotopes O^{16} and O^{18} . H. D. BABCOCK (Proc. Nat. Acad. Sci., 1929, 15, 471—477).—It has been pointed out by Giauque (this vol., 369) that the A' band described by Dieke (cf. A., 1927, 1005) indicates the existence of two oxygen isotopes of masses 16 and 18. Data for the A' band are revised and extended and by a special method of comparing intensities with the A band the relative proportion of O^{18} to O^{16} is deduced as 1:1250. A series of very weak doublets in the A and B bands has been detected; comparison with calculation indicates that they may be affected by some slight perturbation.

N. M. BLIGH.

Isotopes of oxygen. R. T. BIRGE (Nature, 1929, 124, 13—14).—Correction of an arithmetical error in the equation given by Dieke and Babcock (A., 1927, 1005) for the upper level of the atmospheric bands of oxygen [the corrected equation being $E_n = 13120.97 + 1418.69n - 13.925n^2 - 0.02n^3$ ($n=0, 1, 2, 3$)] reduces the magnitude of discrepancies recorded by Giauque and Johnston (this vol., 369, 736).

A. A. ELDRIDGE.

At. wt. of antimony from different sources. R. K. McALPINE (J. Amer. Chem. Soc., 1929, 51, 1745—1750).—The density and at. wt. of antimony are independent of the geographical source of the metal (cf. Muzaffar, A., 1923, ii, 771).

S. K. TWEEDY.

Mass numbers of the elements. Element formation. F. H. LORING (Chem. News, 1929, 139, 1—3).—Aston has pointed out (cf. this vol., 622) that there are no elements with mass numbers of 2, 3, 5, 8, etc. If a series of the type $2 \times 1/(2+1)$, $2 \times 2/(2+2)$ be worked out most terms give recurring decimals but a few do not. The latter correspond with the missing mass numbers, but there are numerous exceptions, e.g., sodium (23) gives a non-recurring decimal. It is suggested that these exceptions are due to the absorption of an atom of hydrogen.

A. R. POWELL.

Helicoidal classification of the elements. C. JANET (Chem. News, 1929, 138, 372—374, 388—393).—A new diagram of the classification of the elements, based on Moseley's law, has been derived by arranging the elements spirally around a cylinder.

H. F. GILLBE.

Evaluation of the α -radiation of the active deposit of actinium by measuring its β -radiation. M. NAHMLAS (J. Chim. phys., 1929, 26, 319—326).—A more detailed account of work already noted (this vol., 621).

Capture of electrons by swiftly-moving α -particles. B. DAVIS and A. H. BARNES (Physical Rev., 1929, [ii], 34, 152—156).—A stream of electrons from a thermionic source was superposed on a beam of α -particles from polonium, and the number of captures determined by subjecting the beam to a magnetic field and counting the scintillations due to the deflected α -particles for various electron velocities. As the latter increases the decrease in scintillations due to the smaller deflexion of α -particles which have captured an electron gives the percentage of captures. It was found that captures take place only at definite electron velocities which are related to those in the

Bohr orbits of ionised helium by the relations $v-u-w$ and $v-w'-u$, where u is the velocity of the α -particle, w and w' are two velocities of the electron at which capture takes place, and v is any circular Bohr orbit electron velocity. The number of captures plotted against voltage impressed on the electron stream gives a series of maxima on each side of the equivalent velocity of the α -particles corresponding with the energy levels of ionised helium.

N. M. BLIGH.

Spectrography by crystal diffraction of γ -rays of the radium group. M. FRILLEY (Ann. Physique, 1929, [x], 11, 483—568).—A summary is given of the nature and origin and the theory of the lattice spectroscopy of the γ -rays. A complete investigation was made of the spectrum of γ -rays from the radium group, and extended for the first time to the higher frequencies, to a wave-length of 16×10^{-11} cm., by a crystal-diffraction method using an adapted X-ray rotating-crystal spectrograph. Owing to the very short wave-length the reflexion angle of the highest frequency rays is less than 10° . Results were in good agreement with those for corpuscular radiation except in the region of the K fluorescence rays of radium- B and - C , where strong γ -rays were detected which had not previously been observed. The wave-lengths of these support the theory attributing the emission of β - and γ -rays to the atom resulting from radioactive disintegration. The high intensity of the K radiation seemed to be due to the influence of nuclear γ -rays in the same region. Einstein's photo-electric law and Bragg's diffraction law were confirmed for these frequencies, and the evidence supported the electromagnetic wave-nature of the radiation.

N. M. BLIGH.

Heat of β - and γ -radiation of radium. A. DORABIALSKA (Bull. Acad. Polonaise, 1928, A, 459—470).—See this vol., 116.

Temperature coefficient of radioactive disintegration. O. K. RICE (Proc. Nat. Acad. Sci., 1929, 15, 593—595).—It is shown that the low temperature coefficients found for radioactive changes are to be expected from the known sizes of atomic nuclei, on the basis of the new quantum-mechanical explanation of radioactivity (cf. Gamow, this vol., 7; Gurney and Condon, this vol., 374). A single quantum level is proved to be responsible for an ordinary radioactive decomposition up to or above 5000° .

N. M. BLIGH.

Detection of atomic disintegration of aluminium by means of the Hoffmann electrometer. H. POSE (Naturwiss., 1929, 17, 624).—Disintegration experiments with aluminium foil 30μ thick, using polonium as a source of α -particles, show that the Hoffmann electrometer serves for the detection of liberated H -particles. A relatively large number of H -particles have ranges below 30 cm. of air, a second, smaller group range from 30 to 47 cm., whilst a third, much smaller group extend to 62 cm., when the number becomes very small.

R. A. MORTON.

A Wilson apparatus for convenient low pressures. J. PETROVA (Z. Physik, 1929, 55, 621—627).—An apparatus is described which shows the tracks of both α - and β -rays at pressures down to 30 mm.

W. E. DOWNEY.

Range of β -rays from radium-*D* by the Wilson method. J. PETROVA (Z. Physik, 1929, 55, 628—645).—Using the new apparatus (cf. preceding abstract), the distribution curve of the range of the β -rays from radium-*D* has been obtained. The curve shows two maxima corresponding with mean ranges, at normal pressure and 20°, of 0.80 and 1.58 cm. The maximum ranges are 1.3 and 2.4 cm., respectively. Some tracks between 2 and 4 cm. in length were observed.

W. E. DOWNEY.

Detection of atomic disintegration of aluminium by means of the tube electrometer. E. A. W. SCHMIDT (Naturwiss., 1929, 17, 544—545).—Preliminary. Earlier work (A., 1927, 494) is confirmed and extended.

R. A. MORTON.

Striations in high-frequency discharges. K. A. MACKINNON and J. K. ROBERTSON (Nature, 1929, 124, 55).

Luminous discharge in gases at low pressures. H. PETTERSSON (Nature, 1929, 123, 978—979).—A method for increasing the luminosity of the discharge in electrodeless tubes by electric oscillations of high frequency, and of causing the discharge to pass through narrow capillary tubes, has been applied to nitrogen, neon, carbon monoxide, and carbon dioxide. The last two undergo rapid dissociation. In spectrograms from the oxides of carbon all the Deslandres bands belonging to the first negative carbon spectrum between 2300 and 2900 Å. have been identified, and fainter bands of similar structure have been observed. The origin of the double bands near 2896 and 2883 Å. is probably different from that of the other bands of the series.

A. A. ELDRIDGE.

Stark effect of higher atoms and its interpretation in terms of the quantum theory. R. LADENBURG (Physikal. Z., 1929, 30, 369—383).—A summary. Present-day quantum theories account satisfactorily for all the more important observations, and indeed partly for the very complicated phenomena arising from the action of electric fields on the series lines of the higher elements. Certain intensity anomalies (cf. Stark and Liebert, Ann. Physik, 1918, [iv], 56, 547, 589) concerning the changes in relative intensities with increasing field strength, observed with successive terms of the P — P' series of orthohelium and lithium, remain to be explained. Neon, argon, oxygen, and some of the heavier elements exhibit effects which need investigation before a theoretical explanation can be arrived at. The interpretation of the Stark effect for the helium series provides support for the validity of the wave-mechanics quite as convincing as that given to the Bohr theory by the data for the Stark effect on hydrogen lines.

R. A. MORTON.

Paths of charged particles in electric and magnetic fields. W. BARTKY and A. J. DEMPSTER (Physical Rev., 1929, [ii], 33, 1019—1022).—Mathematical. The velocity and directional focussing of a beam of charged particles, and a combination of electric and magnetic fields, are considered, suitable for positive-ray analysis experiments, or for determinations of the ratio of charge to mass.

N. M. BLIGH.

Dependence of ultra-violet reflexion of silver on plastic deformation. H. MARGENAU (Physical Rev., 1929, [ii], 33, 1035—1045).—The behaviour of the minimum reflecting power of silver in the near ultra-violet was examined for surfaces under varying degrees of strain produced by polishing, etching, and electroplating. Reflexion curves were obtained by measuring incident and reflected intensities directly by means of two quartz photo-electric cells. Minima for different surfaces were found in the region 3160 Å., shifting to lower wave-lengths by about 20 Å. for unstrained surfaces. The results are explained as due to a change in the number of free electrons and hence in the index of refraction of the metal.

N. M. BLIGH.

Nature of the ultra-penetrating rays (cosmic rays). P. AUGER and D. SKOBELZYN (Compt. rend., 1929, 189, 55—57).—Evidence is advanced in favour of the hypothesis that cosmic rays are not primary but secondary radiations, and are produced from an "ultra- γ " radiation which will not itself ionise directly (cf. Skobelzyn, this vol., 737).

J. GRANT.

Momentum distribution in hydrogen-like atoms. B. PODOLSKY and L. PAULING (Physical Rev., 1929, [ii], 34, 109—116).—Mathematical.

N. M. BLIGH.

Problem of the ionised hydrogen molecule. C. Y. CHAO (Proc. Nat. Acad. Sci., 1929, 15, 558—565; cf. Niessen, A., 1927, 808; Wilson, A., 1928, 574).—Mathematical. The energetics of the ionised hydrogen molecule are treated by the method of wave mechanics, with the introduction of approximations. The adiabatic transition of the energy levels when H_2^+ is dissociated into a nucleus and a H-atom is investigated.

N. M. BLIGH.

Molecular structure and properties of homopolar compounds. II. Structure of the carbon atom and isomerism in homologous series. A. DIBROVA (Ukraine Chem. J., 1928, 3, 435—443; cf. A., 1928, 827).—Assuming with Main Smith and others that all four valency electrons of the carbon atom are in orbit L but two are of quantum number 2, and the other two of quantum number 2, the differences in b. p. and density between primary, secondary, and tertiary saturated and unsaturated hydrocarbons are discussed both from the point of view of their probable molecular structure and polarisation.

A. FREIMAN.

Effect of a nuclear spin on the optical spectra. J. HARGREAVES (Proc. Roy. Soc., 1929, A, 124, 568—591).—Mathematical. The motion of a single electron in a Coulombian field due to a nucleus possessing a $\frac{1}{2}$ quantum of spin is considered, and the results are compared with Jackson's recent work on the hyperfine structure of the optical spectrum of caesium (cf. this vol., 1). It is found that each of the electron spin fine structure levels splits up into two. The problem is dealt with on the lines of Pauli's treatment (cf. A., 1927, 807), introducing, in addition to the electronic spin variables, similar ones for the nuclear spin. The method does not give the correct S levels, but empirical equations are constructed which give two levels. The calculated intensities of the Zeeman components of the transitions are found to be independent of the central field. A determination

of the numerical intensity ratios of the *D* and *P* series shows that the strongest lines are those in which there is no change in the spin configuration, whilst the next strongest are those in which there is one change, either that of the nucleus or that of the electron. So far as the energy levels are concerned, the results obtained are substantially the same as those of Jackson. L. L. BIRCUMSHAW.

Electro-dynamics of the rotating electron. I. TAMM (Z. Physik, 1929, 55, 199—220).—Mathematical. J. W. SMITH.

Heisenberg's indetermination principle and the quantum. G. E. M. JAUNCEY (Nature, 1929, 124, 57).

Distribution of charge in the carbon atom. G. W. BRINDLEY (Proc. Leeds Phil. Soc., 1929, 1, 402—411).—The distribution of charge in the carbon atom can be arrived at theoretically by a consideration of the *F* curve for carbon, *F* being the scattering power of the atom for X-rays, and a function of the glancing angle θ and the wave-length λ . The *F* curve for diamond is compared with the theoretical curve derived from the usual model of the carbon atom. The two curves do not agree well, the disagreement being greatest for large values of $\sin \theta$, where the calculated curve is known most accurately. In any investigation to determine the asymmetry of the carbon atom experimentally by X-ray methods, spectra which occur between $\sin \theta = 0.10$ and 0.30 will be specially important, as over this range the contributions of the *L* electrons to the *F* curve are varying most rapidly. Very little information can be derived about *L* electrons from a study of spectra at values of $\sin \theta$ greater than 0.40 . A. J. MEE.

Forces between atoms and between molecules.
I. Periodicity of interatomic forces. D. AVDALIAN (Ukraine Chem. J., 1929, 4, 95—98).—The force *D* acting between atoms is calculated for the elements in the periodic table from Lindemann's formula $D = T_s/V^{2/3}$, *T*, being the absolute m. p. and a measure of the intensity of the atomic energy and $V^{2/3}$ the square of the amplitude of the vibration at the m. p. which is proportional to the energy of the vibration. The curve connecting *D* with the atomic numbers shows a series of minima and maxima, the minima separating the periods in the periodic tables. A. FREIMAN.

Modern developments of wave mechanics and their bearing on the understanding of crystal structure. P. P. EWALD (Trans. Faraday Soc., 1929, 25, 402—409).—The general principles which have been advanced for the elucidation of the structure of atoms and atomic forces are reviewed and applied to problems of chemical action and of crystal chemistry. These include the Schrödinger picture of the atom, the Pauli exclusion principle and electron spin, the principle of energy shift by resonance, and the London-Heitler application to exchange energy. An account is given of Unsöld's and of Pauling's work on polar crystals and of recent work in connexion with exchange phenomena in metals. It is emphasised that the principle of exchange energy is important, not only for the homopolar, but also for the polar chemical linking. L. L. BIRCUMSHAW.

Diatomic molecules according to the wave mechanics. I. Electronic levels of the hydrogen molecular ion. P. M. MORSE and E. C. G. STUECKELBERG (Physical Rev., 1929, [ii], 33, 932—947).—Mathematical. N. M. BLIGH.

Scattering coefficient of hydrogen according to wave mechanics. J. A. STRATTON (Helv. phys. Acta, 1928, 1, 47—74; Chem. Zentr., 1929, i, 968).—A study of the intensity and spatial distribution of the unmodified component. A. A. ELDRIDGE.

Structure of atomic nuclei. M. F. SOONAWALA (Indian J. Physics, 1929, 3, 489—492).—A table is constructed on the hypothesis that atomic nuclei are formed by the synthesis of protons, electrons, and rare gas nuclei, and its features are examined for evidence as to why the most favoured condensation of protons and electrons should give rise to the nuclei constituting matter. It is shown that the isotopes of the rare gases may, with the protons and electrons, give rise to the known groups of elements. N. M. BLIGH.

Possible cause for the transformation of energy into matter. G. I. POKROVSKI (Z. Physik, 1929, 55, 771—777; cf. this vol., 623).—Mathematical. The gravitation effect of energy is discussed as a cause of the formation of new protons, and the determination of the upper limit of the elementary mass, i.e., the mass of the proton, is mentioned. The value obtained is 1.67×10^{-24} g. A. J. MEE.

Possibility of an experimental proof of the reciprocal annihilation of electrons and protons. C. LÖNNQVIST (Z. Physik, 1929, 55, 789—800).—The reciprocal annihilation of protons and electrons by collision is a hypothetical source of energy, the cosmic importance of which has been stressed by Eddington. Some indications of methods which could be used for the experimental proof of the occurrence of such annihilation are given. It is suggested that hydrogen nuclei, i.e., free protons, are completely unprotected against electron bombardments, and hence they will be neutralised at their first encounter with an electron. Means for testing this are discussed. A. J. MEE.

Relative masses of the proton, electron, and helium nucleus. E. E. WITMER (Nature, 1929, 124, 180—181).—Numerical relationships, possibly of a fundamental nature, are indicated, and the possibility that the helium nucleus is an ultimate particle is considered. A. A. ELDRIDGE.

Effect of the addition of hydrogen and water on the radiation emitted from the carbon monoxide flame. W. E. GARNER and F. ROFFEY (J.C.S., 1929, 1123—1140; cf. A., 1928, 375).—The addition of hydrogen or water vapour diminishes the emission of radiation and increases the speed of flame of mixtures of carbon monoxide and oxygen under conditions of rapid cooling. This confirms Helmholtz's view that the radiation from flames is largely chemiluminescence. The emitters of the radiation are freshly formed activated molecules of carbon dioxide. The radiation is diminished in three stages: (1) from 0 to 0.04% H_2 , where the decrease is proportional to $[H]^{1/2}$, (2) at 0.04%, where a marked step occurs, and (3) from 0.04 to 2%, where the decrease is

continuous but less rapid than in (1). Measurements of the speeds of the flame have been made, and the radiation-speed curves show a step at 0.04% H_2 . The speed increases with the addition of hydrogen or water. The general inference drawn from the results is that the decrease in radiation is due partly to chemical and partly to physical causes, the latter being mainly collisions of the second kind between activated carbon dioxide molecules and atomic hydrogen or protons. The occurrence of the step supports Bone's view that there are two distinct chemical mechanisms in the flame, one being dominant above 0.04% H_2 and the other below this concentration. The increase in speed of flame on the addition of hydrogen up to 0.04% can be interpreted as due to a rise of temperature consequent on the diminished radiation. F. L. USHER.

Formation, pre-dissociation, and dissociation of molecules determined by vibration spectra. Sulphur monoxide. V. HENRI and F. WOLFF (J. Phys. Radium, 1929, [vi], 10, 81–106).—It follows from the principles of wave mechanics that a molecule is not necessarily formed when two atoms approach one another, but that combination depends on the mutual orientation of the magnetic moments of their valency electrons. Generally, the distribution of the valency electrons of two atoms the nuclei of which have been made to coincide should conform with Pauli's principle. In the case of nitrogen two kinds of diatomic molecule should be possible, one dissociating at 11.4 volts and the other at 3.8 volts, the latter kind being, in the author's view, identical with Rayleigh's active nitrogen. Analysis of the vibration spectrum makes it possible to calculate the energy of dissociation of a diatomic molecule into atoms of which neither, or one, or both may be activated. A new spectrum has been obtained by sparking dried sulphur dioxide at a pressure of 20–30 mm. It consists of a large number of bands at intervals of 40–60 Å. and extending to 2549 Å. The general character of the spectrum is that typical of a diatomic molecule, but differs greatly from the spectra of oxygen or sulphur. An analysis of the vibration spectrum shows that the molecules responsible for it are those of SO. The energy of dissociation of this compound into normal atoms has been calculated to be –148 kg.-cal., in striking agreement with the figure obtained from thermochemical data, viz., –146.2 kg.-cal. The moment of inertia of the molecule has been found to be 32×10^{-40} , giving 1.34 Å. as the distance between the oxygen and sulphur atoms. F. L. USHER.

Effect of volume changes on the infra-red vibrations of simple crystals. E. O. SALANT (Proc. Nat. Acad. Sci., 1929, 15, 533–537).—Using the formula of Carpenter and Stoodley (cf. A., 1928, 694) it is shown how to calculate the effect of changing the distance apart of neighbouring ions in the crystal, and also the effect of volume changes on the wave-length of maximum reflecting power as given by the Havelock equation. The latter calculation is shown to require a knowledge of the change with volume of the dielectric constant and of the wave-length corresponding with the vibration frequency. The calcu-

lated results in the two cases are given for sodium chloride and for potassium chloride, bromide, and iodide. N. M. BLIGH.

Near infra-red absorption spectra of calcite and strontianite. E. K. PLYLER (Physical Rev., 1929, [ii], 33, 948–951).—Thick specimens (2 cm.) cut at right angles to the optic axis were used, and for calcite bands were observed at 1.76, 1.9, 2.0, and 2.2 μ , similar to those found by Schaefer (cf. A., 1927, 5) in the near infra-red. Combination relationships were found to exist between these two sets of bands, with fair agreement of observed and calculated values. For strontianite the bands were at 1.89, 2.01, and 2.19 μ and of a similar type to those of calcite. The value 9.2 μ was calculated for the inactive fundamental, in good agreement with Nielsen's value 8.98 μ (cf. this vol., 119). N. M. BLIGH.

Combination bands in the infra-red spectra of carbon tetrachloride and silicon tetrachloride. H. H. MARVIN (Physical Rev., 1929, [ii], 33, 952–953).—Assuming that the six Raman bands of carbon tetrachloride (cf. Pringsheim and Rosen, A., 1928, 1307) give the fundamental absorption frequencies, it is shown that their simple combinations account for almost all the absorption bands between 1 and 16 μ . The absorption bands of silicon tetrachloride are accounted for by similar combinations of six fundamental frequencies, the two systems and their combinations being very similar. N. M. BLIGH.

Absorption spectrum of hydrogen chloride. C. F. MEYER and A. A. LEVIN (Physical Rev., 1929, [ii], 34, 44–52).—The vibration-rotation spectrum of hydrogen chloride consists of a fundamental band at 3.46 μ and a harmonic at 1.76 μ . Using a new spectrometer and very narrow slits, the lines of the fundamental were resolved, each into two lines due to the existence of the isotopes Cl^{35} and Cl^{37} . The relative intensities of the lines in the two series agrees with the accepted proportion of the isotopes, 3:1 approximately. In the harmonic, good separation of the lines arising from the isotopes was obtained. Wave-number and intensity results for the two series of lines in each band are given. N. M. BLIGH.

Analysis of the hydrogen chloride bands. W. F. COLBY (Physical Rev., 1929, [ii], 34, 53–56; cf. preceding abstract).—Wave-numbers for the two isotopes in the bands are fitted to a cubic formula of the rotational quantum number derived from Fues' energy expression (cf. A., 1926, 881), and tables are given of the wave numbers thus computed. From the formula the constants of the molecule were determined in accordance with the energy expression for the rotating dipole as derived by wave mechanics. N. M. BLIGH.

Effect of temperature on the absorption bands of fused quartz in the infra-red. W. A. PARLIN (Physical Rev., 1929, [ii], 34, 81–91).—The absorption bands of thin quartz films, of thickness 2 mm. for the 3 μ region to 4×10^{-4} mm. for the 8 μ region, were investigated at the ordinary temperature and at 850°. The band in the region of anomalous dispersion at 9 μ shifted towards longer wave-lengths with rise of temperature. With higher resolution fine-structure

bands were found which did not shift with change of temperature, but underwent marked intensity changes. Several sharp bands between 2 and 4 μ did not change with temperature. A broad double band was found at 12.5 μ .
N. M. BLIGH.

Diatomic molecules according to the wave mechanics. II. Vibrational levels. P. M. MORSE (Physical Rev., 1929, [ii], 34, 57—64).—An exact solution is obtained for the Schrödinger equation representing the motions of the nuclei in a diatomic molecule, a simple form for the potential energy function being assumed, satisfying certain specified conditions. A formula is obtained for the allowed vibrational energy levels, and is found to satisfy experimental values. The normal molecular separation r_0 and the classical vibration frequency ω_0 are shown to be related by the empirical law $r_0^3\omega_0 = K$, to a close approximation; K is the same constant for all diatomic molecules and all electronic levels. By the above results experimental data for various levels and molecules are analysed and a table of constants is obtained from which the potential energy curves can be plotted.
N. M. BLIGH.

Investigations in the spectral region 20—40 μ . L. KELLNER (Z. Physik, 1929, 56, 215—234).—Owing to its good transmission at wave-lengths of 20 μ and upwards, paraffin wax is a very suitable material for windows for a micro-radiometer for use in the long-wave infra-red region. It is gas-tight and owing to its selective absorption in the shorter-wave region up to about 16 μ it filters this out of the radiation.

The transmission of thin sheets of rock-salt over the range 20—37 μ has been measured and the extinction coefficient at different wave-lengths over this range calculated. The "residual rays" of fluor-spar have been measured over a similar range. In contradiction to previous observations (Rubens and Hettner, A., 1916, ii, 463), only one maximum was found, between 26 and 30 μ , the reflecting power rising to a maximum at about 32.8

J. W. SMITH.

Method of obtaining the optical constants of metallic reflecting substances in the infra-red. C. BOECKNER (J. Opt. Soc. Amer., 1929, 19, 7—15).—The method described, which is applicable to amorphous substances and to uniaxial crystals, consists in measuring the reflecting power of light, polarised in the plane of incidence, at two angles of incidence, and calculating the refractive index and the extinction coefficient by the Fresnel formula. The change of reflecting power with change of angle of incidence was also investigated. Curves are given for the reflecting power for angles of incidence of 5° and 68°, and for the refractive index and extinction coefficient of fused and crystalline quartz, plotted against wave-lengths. Experimental and calculated values of the reflecting power show good agreement.

N. M. BLIGH.

Infra-red emission bands under high dispersion. M. NEUNHOEFFER (Ann. Physik, 1929, [v], 2, 334—349).—The infra-red emission of burning hydrogen and carbon monoxide has been studied by means of a reflexion grating and thermopile, and quantitative absorption curves have been obtained

for the principal bands. The water bands exhibit rotation frequencies clearly, but the carbon dioxide bands show no sign of resolution at the same dispersion. The water band at 2.7 μ exhibits a single constant frequency difference of 24 ± 0.5 cm.⁻¹, indicating one definite moment of inertia 2.3×10^{-40} at the temperature of the flame. When the temperature of the carbon monoxide flame is raised by inserting an electrically heated platinum spiral, the maxima near 4.3 μ are not changed in wave-length, but the percentage change in intensity is greater on the long-wave than on the short-wave sides of the bands. Addition of argon to the carbon monoxide does not shift the maxima, but the changes in intensity occur in a manner consistent with the fall in flame temperature. The bands near 2.7 μ for both water and carbon dioxide are similarly affected by variations in the environment, although the broadening of the short-wave band for water is more symmetrical when the gas is preheated.
R. A. MORTON.

Fluorescence and infra-red absorption. V. POSEJPAL (Compt. rend., 1929, 189, 159—161).—A generalisation of the author's theory (this vol., 120) in which it is shown that an effect analogous to the Raman and Cabannes-Daure effects exists for fluorescence spectra. The calculated and observed values of the wave-lengths of the fine bands of the fluorescence spectrum of benzene (liquid or vapour) are in close agreement. The theory also provides confirmation of the Haber-Lindemann formulae.
J. GRANT.

Infra-red registering spectrometer. P. LAMBERT and J. LECOMTE (Compt. rend., 1929, 189, 155—158).—The spectrometer consists of two 30° rock-salt prisms, one of which is fixed and receives the original source of light, whilst the other is supported on a movable platform which also carries a thermo-electric cell on to which the ray emerging from the second prism is directed. Wave-length-percentage transmission curves are obtained directly by passing a spot of light from a galvanometer (connected to the thermo-couple) across a light-sensitive paper held on a plate which travels in unison with the platform carrying the second prism. A wave-length range of 15 μ is obtainable.
J. GRANT.

Quantum theory of the Raman effect. E. AMALDI (Atti R. Accad. Lincei, 1929, [vi], 9, 876—881).

Incoherent scattering in gases. F. RASETTI (Nature, 1929, 124, 93).—A purely electronic transition has been observed in the scattering process with nitric oxide. By the use of apparatus permitting ultra-violet excitation of gases at 10 atm., good Raman spectra of hydrogen have been obtained.

A. A. ELDRIDGE.

Raman effect in diatomic gases. II. F. RASETTI (Proc. Nat. Acad. Sci., 1929, 15, 515—519; cf. this vol., 627).—With an improved experimental arrangement permitting the use of the 2536 mercury line as exciting light to obtain stronger scattering, experiments were conducted on nitrogen, oxygen, and hydrogen showing more clearly the relation between Raman transitions and band spectrum structure. Sharp, well-resolved Raman lines corresponding with

rotational transitions were obtained and photographed and their frequencies measured. The molecules are all in the *S* states, and the lines are discussed theoretically from the point of view of the new quantum mechanics. Oxygen gives a pattern of equally spaced lines, nitrogen presents a spectrum of alternating intensities, and the previously unknown moment of inertia of the nitrogen molecule in the normal state is found to be $(14.0 \pm 0.1) \times 10^{-40}$. The vibrational-rotational Raman spectra should give a *Q*-form branch and *PP*- and *RR*-form branches, but only the unresolved *Q*-form branch has been observed.

N. M. BLIGH.

Influence of temperature on Raman lines. Y. FUJIOKA (Nature, 1929, 124, 11).—Experiments with benzene, toluene, and carbon tetrachloride show that when the temperature of the scattering substance is raised, certain Raman lines become very diffuse. It is supposed that the diffuseness of Raman lines is due to molecular rotation, rise of temperature accelerating the rotation and causing broadening of the lines. The effect is most noticeable for close doublets.

A. A. ELDRIDGE.

Raman effect in carbon disulphide. A. S. GAVESAN and S. VENKATESWARAN (Nature, 1929, 124, 57).—The scattered spectrum of carbon disulphide gives two prominent frequency shifts, corresponding with 15.27 and 12.50 μ , respectively. None of the infra-red absorption bands observed by Coblentz are represented in the scattered spectrum.

A. A. ELDRIDGE.

Relation between Raman spectra and ultra-violet absorption. A. LANGSETH (Nature, 1929, 124, 92).—On the assumption that the strongest band in the absorption spectrum of chlorobenzene is due to the electronic transition from the lowest level in the normal state to the lowest level in the excited state, a general analysis of the spectrum by means of the Raman frequencies has been made. The strongest frequencies of vibration in the excited state are: 318.8, 519.0, 523.9, 929.8, and 962.6 cm^{-1} .

A. A. ELDRIDGE.

Raman effect in carbon dioxide. P. N. GHOSH and P. C. MAHANTI (Nature, 1929, 124, 92–93).—The results of Rasetti (this vol., 241) support the linear model of the carbon dioxide molecule.

A. A. ELDRIDGE.

Raman effect in gases and liquids. P. N. GHOSH and P. C. MAHANTI (Nature, 1929, 124, 230).—Optically inactive vibrations are postulated.

A. A. ELDRIDGE.

Raman effect. A. DADIEU and K. W. F. KOHLRAUSCH (Physikal. Z., 1929, 30, 384–391).—The Raman frequencies for 25 aliphatic and aromatic compounds are given, and their classification with respect to groupings of the type C–C, C=O, etc. is discussed. The classification is by no means unequivocal; e.g., benzene exhibits not only the frequency $\nu = 3050$ which is characteristic of the aromatic C–H linking, but also shows the frequency $\nu = 2940$ which is ascribed to the aliphatic C–H linking. Anti-Stokes lines are recorded only with halogen derivatives. Investigation of mixtures of benzene and carbon tetrachloride and of solutions of naphthalene in carbon tetrachloride shows no reciprocal effects as regards

shifting of the Raman spectra. The acetic acid–water system disclosed no frequencies capable of indicating the occurrence of dissociation. The influence of temperature on the intensities of the Raman lines and the scattered (undisplaced) exciting lines has been studied for carbon tetrachloride. R. A. MORTON.

Raman effect of water. A. DADIEU and K. W. F. KOHLRAUSCH (Naturwiss., 1929, 17, 625–626).—The Raman frequency for water has been variously recorded as 3280 to 3450 cm^{-1} , the mean of all the determinations being 3338 cm^{-1} . Repetition has resulted in the observation that the Raman lines corresponding with three mercury lines are all double, the frequencies being 3324 and 3513 cm^{-1} , respectively. The mean, 3419 cm^{-1} , corresponds with 129 g.-cal./mol. for the energy necessary for the rupture of the O–H linking, whilst observed values are given as 120 and 147 g.-cal./mol. The observed Raman lines are shown to be not inconsistent with theory.

R. A. MORTON.

Raman spectra of *p*-, *o*-, and *m*-xylenes. (Mlle.) W. CZAPSKA (Compt. rend., 1929, 189, 32–33).—The Raman spectra excited by the mercury lines λ 4047 to 4359 are different for the xylenes, but the frequencies $\Delta\nu$ 1371 and 2918 are common to all three. The *o*- or *p*- and *m*-, but not the *o*- and *p*-isomerides have frequencies in common.

J. GRANT.

Raman spectra of sulphuric acid and the sulphates. S. K. MUKHERJEE and P. N. SENGUPTA (Indian J. Physics, 1929, 3, 503–505).—To investigate characteristic infra-red frequencies of salts in solution Wood's method (A., 1928, 1306) was used, involving only short exposure periods, and spectrograms were obtained of magnesium, sodium, and copper sulphates and of sulphuric acid. In the case of the sulphates modified lines were found at 4552.2 and 4213.7 \AA . The wave-number difference between the exciting and excited lines corresponds with infra-red absorption at 10.2 μ . Sulphuric acid shows five modified lines corresponding with absorption at 11.01, 10.96, 17.9, and 18.4 and 4.68 μ . Each solution gave always the same frequency for the scattered components and this infra-red frequency is attributed to the SO_4 ion.

N. M. BLIGH.

Scattering of light in quartz and solid amorphous substances which contain the SiO_2 group. E. GROSS and M. ROMANOVA (Z. Physik, 1929, 55, 744–752).—The spectra of radiations scattered by crystalline quartz, amorphous quartz, crown and flint glasses were investigated. It was found that in amorphous quartz and the glasses there were displacements in the spectra. For quartz, besides the already known but weak lines corresponding with wave-lengths 19.9 and 8.2 μ , the very weak lines corresponding with wave-lengths 31.3, 19.0, 17.1, 15.8, 13.4, 10.6, and 9.8 μ , were found. Amorphous substances containing the SiO_2 group have faded bands in their scattered spectra, instead of the lines found in the spectrum of crystalline quartz.

A. J. MEE.

Vibrational quantum analysis of red cyanogen bands. R. K. ASUNDI and J. W. RYDE (Nature, 1929, 124, 57).—The band at ν 14430 is not the true

0—0 band of the system. Six new bands have been fitted in the existing n'/n'' table for the red cyanogen bands. Assuming ν 10937 to be the 0—0 band, the vibrational equation is: $\nu_{\text{head}} - 10937 + (1782n' - 13.5n'^2) - (2055n'' - 13.3n''^2)$. A. A. ELDRIDGE.

New bands in the spectrum of lanthanum oxide. G. PICCARDI (*Nature*, 1929, 124, 129).—The oxide has been completely vaporised by the use of the oxy-hydrogen flame; the spectrum then consists of bands only. Between 7000 and 2400 Å. 18 groups of bands have been recorded.

A. A. ELDRIDGE.

Absorption spectra of phthaleins of trihydric phenols. R. C. GIBBS and C. V. SHAPIRO (*J. Amer. Chem. Soc.*, 1929, 51, 1755—1766).—Data and curves are given for the absorption spectra of pyrogallolbenzein, gallein, sulphongallein (cf. Orndorff, A., 1925, i, 277; 1926, 949; 1927, 671), hydroxyquinolphthalein and -sulphonphthalein (cf. this vol., 822), and phloroglucinolsulphonphthalein, in (a) absolute alcohol, (b) concentrated sulphuric acid, and (c) aqueous potassium hydroxide. The results are interpreted along lines now familiar (cf. A., 1928, 570, 1019, 1374). In alcoholic solution pyrogallolbenzein is quinonoid, gallein mainly lactonoid, and sulphongallein and its dimethyl ether are internal complex salts. In sulphuric acid the first three compounds show closely related absorptions, as they do in aqueous potassium hydroxide. Phloroglucinol-sulphonphthalein is quinonoid in neutral solution; its orange-yellow alkaline solutions remain unchanged for some months. The quinonoid phthaleins, unlike those of lactonoid structure, show considerable differences in absorption with changes in the number and position of the hydroxyl groups.

H. E. F. NOTTON.

Absorption spectra of halogenated fluoresceins. R. C. GIBBS and C. V. SHAPIRO (*J. Amer. Chem. Soc.*, 1929, 51, 1769—1773).—The absorption curves of dibromo- (I), tetrabromo- (II, eosin), and tetrachloro- (III) -fluoresceins in alcohol and in sulphuric acid have been measured. Introduction of halogen produced no radical change in the absorption spectrum of fluorescein (cf. A., 1928, 526). The bands are displaced towards the region of longer wavelengths, the order of magnitude of the displacement being for the ultra-violet bands, $II > I > III$, and for the visible band, $II > III > I$. Accordingly, the halogen derivatives have, like fluorescein, a quinonoid and not an internal salt structure (cf. Orndorff, A., 1914, i, 542; 1927, 671). The results are compared with those previously obtained (cf. preceding abstract; Holmes, A., 1925, i, 255).

H. E. F. NOTTON.

Tautomerism of hydroxytriarylcabinols. II. L. C. ANDERSON (*J. Amer. Chem. Soc.*, 1929, 51, 1889—1895; cf. A., 1928, 219, 285).—Data and curves are given for the absorption spectra of ethereal solutions of the following triphenylmethane derivatives: diphenyl-5-chloro-*o*-tolylmethane, diphenyl-5-bromo-*o*-tolylmethane, *p*-hydroxy-*m*-methoxytriphenylmethane, *p*-hydroxytriphenylmethane, and diphenyl-*o*-tolylmethane, and of the fuchsone and benzenoid and quinonoid carbinols derived from each, also of triphenylmethane and triphenylcarbinol. The

results are similar to those obtained in alcoholic solution (Orndorff and others, A., 1927, 764), and they afford further evidence for the existence of the quinonoid forms of the carbinols.

H. E. F. NOTTON.

Ferrous nitroso-compounds. H. I. SCHLESINGER and H. B. VAN VALKENBURGH (*J. Amer. Chem. Soc.*, 1929, 51, 1323—1331).—The absorption spectra of the complexes formed between ferrous phosphate and nitric oxide in phosphoric acid solutions and between ferrous chloride and nitric oxide in alcohol solutions are almost identical with the spectra of the ferrous sulphate-nitric oxide complex in sulphuric acid. The shift of the absorption bands towards the violet which occurs on dilution of the solution indicates a transition between two compounds. This transition appears to be determined by the activity of the water in the solution. The results support the views of Kohlschütter and Sazanoff (A., 1911, ii, 730). The spectra of numerous other salt solutions saturated with nitric oxide yielded no evidence of the existence of complex ions in these solutions. S. K. TWEEDY.

Absorption spectra of halogens and inter-halogen compounds in solution in carbon tetrachloride. A. E. GILLAM and R. A. MORTON (*Proc. Roy. Soc.*, 1929, A, 124, 604—616).—Measurements have been made of the absorption of solutions of chlorine, bromine, and iodine in carbon tetrachloride, using a Hilger quartz spectrograph in conjunction with a sector photometer. Summation curves are constructed on the assumption that solutions containing different halogens in stoichiometric proportions would obey the simple mixture law, and these are compared with experimental absorption curves obtained with solutions of definite inter-halogen compounds, and with experimental curves for mixtures in proportions corresponding with known compounds and with compounds the existence of which is doubtful. The results are in good agreement with those of previous investigators, whose work is summarised. It is shown that iodine chloride, iodine bromide, and bromine chloride (cf. Hanson and James, A., 1928, 1004; Barratt and Stein, this vol., 411) possess absorption bands of which the maxima are accurately measurable at 464, 487, and 380 μ , respectively. At the dilutions necessary for the investigation of absorption spectra all three compounds are to some extent dissociated; with iodine chloride the dissociation is scarcely detectable, with iodine bromide it remains slight, whilst with bromine chloride it is considerably greater. Solutions containing halogens in the proportions necessary for the formation of iodine trichloride, iodine tribromide, and bromine trichloride were found to contain the monohalide and free halogen only.

L. L. BIRCUMSHAW.

Effect of gases on the colour of iodine vapour, and the solvent action of various vapours on solid iodine. R. WRIGHT and T. MCGREGOR (*J.C.S.*, 1929, 1364—1367).—It has been observed that the colour of iodine vapour is not so deep in a vacuum as in air (cf. Dewar, *Proc. C.S.*, 1898, 241), nitrogen, oxygen, carbon dioxide, or argon. A qualitative spectroscopic examination showed increased absorption in presence of gases and a shifting of the head of

the absorption band towards the red. The spectra were identical whichever of the gases mentioned was present, and whether excess of iodine was used or less than would saturate the available space with vapour. The colour change is therefore not due to solubility of the iodine in the gas used or to chemical interaction between the gas and iodine. The vapour pressure of iodine has been found to be slightly less in air than in a vacuum. Experiments on the solubility of iodine in the vapours of several organic solvents have given indefinite results. F. L. USHER.

Ultra-violet absorption curves of terpene alcohols. J. SAVARD (Bull. Soc. chim., 1929, [iv], 45, 398—402; cf. A., 1928, 1252).—The ultra-violet absorption of rhodinol, citronellol, linalool, and geraniol in hexane solution has been determined. The accepted constitutional formulæ for linalool and geraniol, and probably also for rhodinol and citronellol, are in agreement with the results of spectral analysis. C. W. GIBBY.

Molecular absorption of iodine in the vacuum ultra-violet. H. SPONER and W. W. WATSON (Z. Physik, 1929, 56, 184—196).—Iodine vapour shows three distinct absorption series in the ultra-violet region. At very low pressures (the vapour pressure at -24°) there occurs only one series of bands at about 1750 Å. At higher pressures these bands broaden and become more intense, and new members appear. It has not yet been found possible to classify these bands. At about -4° a strong series of close, narrow bands begin to appear in the region 1950—1780 Å. Two possible systems for arranging this series are discussed. Strong absorption also occurs in the region 1600—1500 Å., but this could be observed only qualitatively. J. W. SMITH.

Absorption of a crystal of dialogite. P. LEROUX (Compt. rend., 1929, 189, 162—163).—The pleochroic absorption phenomena observed for tourmaline (A., 1928, 934) have been shown to occur in the case of Colorado dialogite (MnCO_3) for the wave-lengths 3655—5790 Å., slight anomalies being due probably to small inclusions in the crystal which are absent from the purer tourmaline. The pleochroism of dialogite is most marked in the ultra-violet region. J. GRANT.

Chlorides of sulphur. II. Molecular extinction coefficients. T. M. LOWRY and G. JESSOP (J.C.S., 1929, 1421—1435; cf. A., 1927, 505).—An account is given of observations of the extinction coefficients of chlorides of sulphur of compositions between that of the monochloride and that of the tetrachloride. Since the colour of sulphur chloride mixtures reaches a maximum at the approximate concentration of the dichloride and not of the tetrachloride, the deep red colour of these solutions is to be attributed to dichloride. Sulphur dichloride absorbs all wave-lengths less than 6200 Å. Sulphur monochloride has a maximum of selective absorption in the ultra-violet at 2660 Å. A colorimetric analysis of the system was made, using the wave-lengths 5220 and 5400 Å., to which chlorine and sulphur monochloride are completely transparent. Sulphur tetrachloride is not formed in appreciable quantities in the liquid chlorides of sulphur, which

behave as ternary equilibrium mixtures, to which the law of mass action can be applied in accordance with the equation $2\text{SCl}_2 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{Cl}_2$. F. J. WILKINS.

Comparative spectrum analysis of *o*-, *m*-, and *p*-isomerides of certain benzene derivatives. J. SAVARD (Ann. Chim., 1929, [x], 9, 287—350).—The ultra-violet spectral absorption of the vapours of phenol, *o*-, *m*-, and *p*-cresols has been investigated at various temperatures. Except in the case of *p*-cresol two spectra, separated by definite intervals and corresponding, respectively, with the normal and activated state of the molecule, are found, their superposition giving rise to doublets and certain abnormalities in intensity. Vibration frequencies are greater in the normal than in the activated state. At the ordinary temperature *p*-cresol has a spectrum consisting of four regularly spaced groups between 2644 and 2848 Å., the intensity of lines in any particular series decreasing towards the extreme ultra-violet. The spectrum of *o*-cresol consists of a group of bands seemingly irregularly distributed between 2748 and 2784 Å. and a doublet at 2692 Å., whilst that of *m*-cresol consists of two groups, one consisting of seven bands and a doublet between 2642 and 2794 Å. and another group between 2750 and 2630 Å. Certain similarities exist between the spectra of the *o*- and *m*-compounds, which, however, are sharply differentiated from that of the *para*, these differences persisting with rise of temperature until absorption becomes total (at 31° for the *o*-, 43° for *m*-, and 41° for the *p*-compound). The spectra in the vapour state are similar to those in hexane solution (Klingstedt, A., 1923, ii, 201), but are shifted about 360 cm^{-1} towards the violet. The spectra are represented by the following relationships: *ortho*, $1/\lambda = 36248$ (or 36412) + $704(p' - p_0) - 69p_0 + 245(q' - q_0) - 48q_0$; *meta*, $1/\lambda = 35983$ (or 36100) + $693(p' - p_0) - 76p_0 + 270(q_1 - q_0) - 48q_0$; *para*, $1/\lambda = 35339 + 808(p' - p_0) - 55p_0 + 209.5(q_1 - q_0) - 41q_0$, where p_0 and q_0 , p_1 and q_1 are whole numbers in the normal and activated molecules, respectively. The spectra of toluene (cf. Henri and Walter, A., 1923, ii, 275) and of phenol are represented, respectively, by $1/\lambda = 37421(37484) + 932(929)(p' - p_0) - 178p_0 + 263(q' - q_0) - 21(34) - q_0$, and $1/\lambda = 36350(37286) + 784(p_1 - p_0) - 62p_0 + 152(q_1 - q_0) - 38q_0$. On the basis of these results and those for dihalogenobenzenes (Errera and Henri, this vol., 377) the energy of activation, quantification of vibrations, degrees of vibrations, activation energy levels, and deformability of molecules are discussed. In each case similar differences between *o*-, *m*-, and *p*-positions are found. J. W. BAKER.

Behaviour of various organic vapours in the high-frequency glow discharge. E. HIEDEMANN (Ann. Physik, 1929, [v], 2, 221—232).—Hydrogen passed through a heated palladium tube in a vacuum apparatus is perfectly pure even when various impurities are introduced into the surroundings of the palladium tube. The discharge phenomena in the vapours of ether, ethyl alcohol, acetone, acetic acid, chloroform, carbon tetrachloride, and benzene have been investigated qualitatively using a high-frequency discharge. In all cases decomposition was observed, a precipitate of carbon or a carbon com-

pound of high mol. wt. being formed. The product formed with benzene contains diphenyl, diphenylene, and higher isomerides. The kind of discharge used does not appear to determine the nature of the product, although composition varies with the current strength and potential gradient in the tube.

R. A. MORTON.

Quantum theory of fluorescence. E. SEGRÉ (Atti R. Accad. Lincei, 1929, [vi], 9, 887—892).

Thermophosphorescent radiations of hiddenite and kunzite. O. STUELMAN, jun. (J. Opt. Soc. Amer., 1929, 18, 365—369).—These minerals are lithium aluminium silicates differing in colour on account of various traces of impurities. The presence of traces of chromium and iron and the absence of potassium in hiddenite was confirmed by an examination of its visible and arc spectra. Spectrograms obtained showed that the thermophosphorescence of hiddenite consisted of an orange band from 0.7 to 0.589 μ and a faint green band with its maximum near 0.54. The emission colours for kunzite were recorded over a temperature range of 210—420°. Attempts to obtain spectrograms were unsuccessful. Examination with colour filters indicated at 300° a yellowish-green band from 0.515 to 0.528 μ and an orange band from 0.570 to 0.650 μ , both widening with rise of temperature.

N. M. BLIGH.

Thermoluminescence excited by high-voltage cathode rays. (Miss) F. G. WICK and (Miss) E. CARTER (J. Opt. Soc. Amer., 1929, 18, 383—392).—The thermoluminescence produced by penetrating cathode rays was studied for Franklin fluorite, Ingleside calcite, and calcium sulphate plus manganese. After exposure of the specimens to the cathode rays observations were made of the maximum brightness and decay rate of the thermoluminescence (cf. A., 1927, 397), effects of varying the time of exposure, cathode tube voltage, and temperature. The effects produced are generally similar to those produced by X-rays, but in the latter case a higher subsequent excitation temperature is necessary, the saturation time is greater, and the effect is less permanent.

N. M. BLIGH.

Time-lags in fluorescence and in the Kerr and Faraday effects. E. GAVIOLA (Physical Rev., 1929, [ii], 33, 1023—1034).—Reports of time-lags (cf. Beams and others, A., 1926, 1069; 1927, 83, 610, 1007) are examined critically, and it is shown that the assumption of such time-lags cannot be sustained. Probable explanations of the causes of the erroneous views are given.

N. M. BLIGH.

Luminous effect in electrolysis at mercury electrodes. A. DUMANSKI, Z. CESCHEVA, and A. BANOV (Z. physikal. Chem., 1929, B, 3, 440—442).—When aqueous solutions of sodium chloride, sulphate, carbonate, oxalate, or phosphate, potassium bromide or iodide, aluminium chloride, or hydrochloric or sulphuric acid are electrolysed at 12—70 volts with a mercury anode, the latter becomes luminous, the colour of the light emitted depending on the nature of the electrolyte. No luminosity is observed with sodium nitrate, sulphite, acetate, or borate, potassium hydroxide or chlorate, or nitric acid. The intensity of the

light increases with the applied *P.D.*, and with the electrolyte concentration up to 0.1*N*. The material of the cathode exercises no influence on the appearance. The phenomenon is dependent on the formation of an insoluble compound at the surface of the anode.

F. L. USHER.

Fluorescing power of solutions. Effect of concentration. Action of antioxygens. (MLLE.) F. VITTE (J. Chim. phys., 1929, 26, 276—287).—The variation of the fluorescing power of solutions with the concentration of the fluorescent substance has been investigated for fluorescein and erythrosin in alkaline solutions of constant p_H . For solutions of fluorescein the fluorescing power decreases exponentially with the concentration above a certain small concentration, below which the fluorescence is constant. The fluorescing power of erythrosin solutions increases with the concentration at first exponentially, then more rapidly, and finally remains practically constant. The fluorescing power of fluorescein in alkaline solution decreases rapidly with the concentration of added antioxygen (potassium iodide or resorcinol). A special form of fluorometer, in which the relative fluorescing powers of two solutions can be directly compared, is described.

O. J. WALKER.

Measurement of luminescence. J. PLOTNIKOV (Z. Elektrochem., 1929, 35, 432—434).—A method of measuring the intensities of various luminescent radiations has been devised by making use of Kruss' polarisation colorimeter.

H. T. S. BRITTON.

Influence of a magnetic field on the fluorescence of mercury vapour. H. NIEWODNICZANSKI (Z. Physik, 1929, 55, 676—689).—The increase in the intensity of the fluorescence of mercury vapour, excited by the line 2537 Å., reported by Franck and Grotrian (*ibid.*, 1921, 4, 89) is not confirmed. A magnetic field acting on the region where excitation takes place produces a periodic variation in the intensity of the fluorescence with increasing field strength. This behaviour is explained in terms of the Zeeman effect and the hyperfine structure of the line 2537 Å. to the effect that excitation of not too dense mercury vapour by the 2537 Å. line results first in the excitation of mercury atoms and not of mercury molecules.

W. E. DOWNEY.

Sodium chloride phosphor containing cuprous salt. (FRL.) M. FORRÓ (Z. Physik, 1929, 56, 235—243).—Sodium chloride phosphor containing 0.03—0.3% of cuprous salt shows an absorption band at 255 $m\mu$, the position of which is independent of the cuprous salt concentration. The breadth of this band varies in different specimens and is considered to depend on the degree of distortion of the crystal lattice ("internal temperature"). This conclusion is supported by the fact that the principal change in the absorption spectrum over the temperature range —193° to 500° is the gradual broadening of the band as the temperature rises. With 1% Cu, large changes are observed in the intensities in the absorption band after heating to 400° (cf. MacMahon, this vol., 239), but these revert to the previous values on keeping. Irreversible disturbance of the lattice occurs first on prolonged heating at about 600°.

J. W. SMITH.

Heterodyne null method of measuring dielectric constant. P. N. GHOSH and P. C. MAHANTI (*Nature*, 1929, **124**, 13).—Sources of error are discussed. The dielectric constant of dry air, free from carbon dioxide, is $1.000579_{\pm 4}$ at *N.T.P.*

A. A. ELDRIDGE.

Dielectric polarisation of liquids. V. Atomic polarisation. C. P. SMYTH (*J. Amer. Chem. Soc.*, 1929, **51**, 2051—2059).—The atomic polarisations, *P*, of numerous liquids are tabulated. In general, *P* is greater the greater is the number of atomic nuclei or groups in the molecule. The valency forces between these nuclei or groups, however, are insufficient to explain the differences in *P* in homologous and other series. The presence of electric doublets in the molecule, and dissymmetry of their arrangement, are conducive to higher values of *P*. In calculating the electric moment of a molecule *P* may be disregarded if the moment is high and the molecule is small and contains only one or two electric doublets.

S. K. TWEEDY.

Dipole moment as a characteristic property of a group. K. HOJENDAHL (*Physikal. Z.*, 1929, **30**, 391—397).—From Pohrt's measurements (*Ann. Physik*, 1913, **42**, 569) of the dielectric constants of a series of organic vapours, dipole moments have been calculated. The results show that for monosubstituted homologues the dipole moment is roughly constant. Each polar group is thus apparently characterised by a constant "group moment" which can be regarded as a vector possessing a definite direction. Measurements have been made on the dielectric constants and refraction of 24 organic compounds dissolved in benzene. Experimental dipole moments can thus be obtained and compared with the data calculated from the vector-sum of the group moments. The results support the classical regular benzene structure in one plane and are not consistent with any of the alternatives. The experimental data for dinitro-, chloronitro-, and bromonitro-benzene, dinitronaphthalene, and nitrotoluene are in good agreement with the calculated values, but in the case of the nitroanilines, anisole, and nitroanisole considerable deviations occur. Substituent groups are divided into three classes: (a) those with positive poles pointing outwards, (b) those with negative poles pointing outwards, (c) those in which the group moment is oblique to the group. The groups NO_2 , Cl, Br belong to one of (a) and (b) and Me, NH_2 to the other, but it is not possible to decide which set is positive and which negative.

R. A. MORTON.

Dielectric constant of desiccated oxygen. H. L. RILEY (*J.C.S.*, 1929, 1026—1028).—With a view to determine whether the change in its chemical and electrical properties observed on intensive drying of oxygen is accompanied by some fundamental change in the structure of the gaseous molecule such as would alter its dielectric constant, two precisely similar condensers were constructed, one containing oxygen dried over calcium chloride, the other oxygen intensively dried over phosphoric oxide, which was also placed in the condenser. Comparison over a period of 10 months showed no change in capacity

of the condenser attributable to the intensified drying.

C. A. SILBERRAD.

Additivity of molecular dipole moments. Constitution of C_α compounds. A. EUCKEN and L. MEYER (*Physikal. Z.*, 1929, **30**, 397—402).—From the moments C—C, 0; H—O, 1.6; C=O, 2.3; Me—C, 0.4; H—C, 0.4; C—O, 0.7, and C—Cl, 1.5 the principle of additivity is found to apply satisfactorily to a variety of compounds with and without the capacity for free rotation. Stereochemical rotation of some groups accounts for the apparent moment of many C_α compounds.

R. A. MORTON.

Explanation of the orientation polarisation found in C_α derivatives. A. SCHLEEDÉ, G. JUNG, and A. HETTICH (*Z. physikal. Chem.*, 1929, **B**, **3**, 479—480).—The conclusions reached by Ebert, Eisenschitz, and Hartel (cf. A., 1928, 1308) regarding molecular polarisation in methane derivatives do not necessarily follow from their experimental results. A study of the dependence of molecular polarisation on temperature is being undertaken in order to decide between two possible interpretations.

F. L. USHER.

Electric moment of primary alcohols. P. C. MAHANTI and R. N. DASGUPTA (*Indian J. Physics*, 1929, **3**, 467—475).—The electric moments of a number of primary alcohols have been calculated from measurements of the dielectric constants and densities of their solutions in benzene. To obtain a sharp null point the Nernst bridge method was used. The value obtained for each alcohol is nearly the same, indicating that the oxygen atom of the hydroxyl group in alcohols is similarly polarised.

N. M. BLIGH.

Electric moment and structure of derivatives of diphenyl. E. BRETSCHER (*Helv. phys. Acta*, 1928, **1**, 355—361; *Chem. Zentr.*, 1929, **i**, 725).—*pp'*-Derivatives of diphenyl would have no electric moment only if the partial moments of the two rings were anti-parallel; the observation of an electric moment would admit a choice between various configurations. *pp'*-Difluoro-, -dichloro-, and -dibromo-diphenyl, and diphenyl itself have no electric moment, whilst the upper limits for the dipole moments of *pp'*-dimethoxy- and -diamino-diphenyl are reconcilable with a considerable value of the moment.

A. A. ELDRIDGE.

Dipole moment of antimony trichloride. O. WERNER (*Z. anorg. Chem.*, 1929, **181**, 154—158).—The dipole moment calculated from measurements of the dielectric constant in benzene solution is $\mu = 3.64 \times 10^{-18}$, a value much greater than that for the corresponding iodide, 0.4×10^{-18} . Reasons for this are discussed.

J. S. CARTER.

Glass. III. Dielectric constants of glassy and liquid dextrose. F. R. CATTOIR and G. S. PARKS (*J. Physical Chem.*, 1929, **33**, 879—882; cf. A., 1928, 1189).—The dielectric constants for glassy and liquid dextrose have been measured over the range 200—423° Abs. by a resonance method. For glassy dextrose, the value of ϵ increases from 3.8 to 5.4 with a rise in temperature; between 293° and 310° Abs. the glass softens and ϵ rises; it reaches a

maximum of 23.9 at 378° Abs. and then slowly falls to 21.0 at 423° Abs. The values for glassy dextrose are similar to those of inorganic glasses and non-polar liquids, whilst those for liquid dextrose are similar to those of polar liquids. L. S. THEOBALD.

Kinetics of the change of optical properties [of crystals] with temperature. W. SCHMIDT and E. BAIER (Z. Krist., 1928, 68, 477—502; Chem. Zentr., 1929, i, 496).

[Optical properties of] potassium, rubidium, caesium, ammonium, and thallium tartrates. M. W. PORTER (Z. Krist., 1928, 68, 531—542; Chem. Zentr., 1929, i, 503).

Existence of liquid racemates. A. N. CAMPBELL (J.C.S., 1929, 1111—1123; cf. A., 1928, 1083).—The physical properties of liquid esters of racemic acid have been compared with those of corresponding esters of *d*-tartaric acid, to decide the question of the existence of liquid racemates. The following have been prepared: *n*-propyl racemate, m. p. 25°, b. p. 167°/11 mm., 286°/765 mm., d_{20}^{25} 1.1256, n_D^{25} 1.4413; isopropyl racemate, m. p. 34°, b. p. 154°/12 mm., 275°/765 mm., d_{20}^{25} 1.1214, n_D^{25} 1.4374; *n*-butyl racemate, b. p. 185°/12 mm., 320°/765 mm., d_{20}^{25} 1.0879, n_D^{25} 1.4451; isobutyl racemate, m. p. 58°, d_{20}^{25} 1.0160. The m. p. of *n*-propyl, isopropyl, and methyl dipropionyl-racemates are higher than those of the corresponding *d*-tartrates, and the inactive forms are therefore, in the solid state, true racemates. The f.-p. and solubility curves of the isobutyl tartrates have been determined, and lead to a similar conclusion. A little below 0° isobutyl racemate passes to the *dl*-conglomerate. Differences in b. p. and d of a number of racemates and *d*-tartrates have been established. The active forms have usually a higher refractive index, a lower dispersion, and a higher viscosity than the inactive. Determinations of the surface tensions show that the association of the active form is greater than that of the racemic. The conclusion is reached that there is a marked difference between the active and racemic forms of the liquid esters of tartaric acid. F. L. USHER.

Natural optical activity. W. KUHN (Z. physikal. Chem., 1929, B, 4, 14—36).—Mathematical. For very strongly rotating substances the refractive index for left circular light is very nearly the same as that for right circular light, the difference being only 1 in 10^6 . The parts of different spectral ranges concerned in optical activity are investigated. In many cases very weak absorption bands play an important part. Mathematically, the problem is investigated by obtaining qualitative and quantitative results for two coupled resonators oscillating perpendicular to each other. The results thus obtained can be applied to systems of more resonators. A quantitative relationship between circular dichroism and optical rotation inside and outside the absorption bands is obtained. A. J. MEE.

Elliptical polarisation produced by reflexion at the surface of solutions of fatty acids in water. C. BOUHET (Compt. rend., 1929, 189, 43—45).—The author's results (cf. this vol., 503) show that the curves relating the concentration/concentration of

saturated solution and ellipticity are all of the same form, although not completely superposable, and are displaced in general towards the smaller ellipticities when the number of carbon atoms increases. In all cases a constant ellipticity was obtained, and the surface area occupied by each acid molecule is then approximately 25×10^{-16} cm.² Conclusions reached from X-ray examination of the solid acids (Morrow, A., 1928, 224) were confirmed by these results and support Gibbs' hypothesis of the orientation of molecules perpendicular to the surface. J. GRANT.

Rotation-dispersion of optically active ammonium salts. E. WEDEKIND and G. L. MAISER (Z. Elektrochem., 1929, 35, 438—440).—The optical activity of *d*- and *l*-phenylbenzylallylmethylammonium *d*-camphorsulphonates, nitrates, and hydroxides was measured in various solvents using light of the wave-lengths 6650, 5770, 4920, and 4360 Å., respectively. In no case was the rotation, compared with the dispersion of the light used, anomalous, neither had the solvent any marked effect on the rotation-dispersion. Measurements were also made in acetone of the rotations of 1-methylallyltetrahydroquinolinium iodide and *l*-menthyl 2-isopropyltetrahydroisoquinolinium iodide acetate using the same sources of light. The results were anomalous. H. T. S. BRITTON.

Optical properties of amino-acids. II. Arginine and histidine. G. L. KEENAN (J. Biol. Chem., 1929, 83, 137—138).—*Arginine dihydrate* crystals are strongly doubly refracting and have n_a 1.528, 1.549, n_y 1.579; the anhydrous crystals have n_a 1.548, n_B 1.562, n_y 1.610. Crystals of histidine have n_a 1.520, n_B indeterminate, n_y 1.610. C. R. HARRINGTON.

Microscopical study of electric double refraction in liquids. M. IWATAKE (Tech. Rep. Tôhoku, 1929, 8, 399—410).—A photomicrographic study has been made of the Kerr effect in nitrobenzene, *o*-nitrotoluene, pyridine, and carbon disulphide. Electrodes of various shapes were used, with a field intensity of 6000—7500 volts/mm. With the two Nicols crossed a bright layer, very close to the anode surface, appears with increasing potentials in nitrobenzene and pyridine. Under the same conditions with *o*-nitrotoluene a bright layer appears momentarily close to the cathode and subsequently disappears, to be followed by the appearance of a bright layer at the anode. With carbon disulphide the space between the electrodes is uniformly bright. The results suggest that the field in the gap is not uniform, due perhaps to the stratified settling of a non-homogeneous liquid substance in the gap. An explanation analogous to that of chromatic polarisation of uniaxial crystals, assuming the optical axis to be coincident with the electric field, is applicable. The effect is not shown by carbon disulphide. F. G. TRYHORN.

Measurement of optical activity in the extreme ultra-violet. W. KUHN (Ber., 1929, 62, [B], 1727—1731).—An apparatus is described and figured. H. WREN.

Paramagnetic rotation of the plane of polarisation in the neighbourhood of absorption lines.

R. MINKOWSKI (Naturwiss., 1929, 17, 568—569).—Paramagnetic rotation in the neighbourhood of the caesium lines $1^2S_{\frac{1}{2}}-2^2P_{\frac{1}{2}}$ (8944 Å.) and $1^2S_{\frac{1}{2}}-2^2P_{\frac{3}{2}}$ (8521 Å.) has been detected. Quantitative experiments in the latter case show that within the limits of error ($\pm 15\%$) the paramagnetic effect in the neighbourhood of the line is in satisfactory agreement with calculations based on the Ladenburg-Kramers-Heisenberg dispersion formula. R. A. MORTON.

Quantum theory of valency. W. HEITLER (Naturwiss., 1929, 17, 546—547).—Theoretical.

R. A. MORTON.

Demonstration of the direct and reverse transformations of both forms of hydrogen. H. SENFTLEBEN (Z. physikal. Chem., 1929, B, 4, 169—173).—An apparatus which makes it possible to demonstrate the changes of one form of hydrogen into the other to large classes is described. A. J. MEE.

Para- and ortho-hydrogen. K. F. BONHOEFFER and P. HARTECK (Z. physikal. Chem., 1929, B, 4, 113—141; cf. this vol., 479).—The preparation of pure para-hydrogen is described, together with systematic experiments on the conversion of one type into the other, the results of which have already been published. The pure para-form has m. p. 13.83° Abs., vapour pressure 787 ± 1 mm. at 20.39° Abs., the temperature at which the normal gas boils. The saturation pressure at the triple point is 53.0 ± 0.1 mm., whereas that for the normal gas is 53.9 ± 0.1 mm. The chemical and electrochemical properties of the two forms were also investigated. It is not to be expected that there will be any noticeable difference at ordinary temperatures. The strong lines in the para-hydrogen emission spectrum are the weak ones in the emission spectrum of ordinary hydrogen. The preparation of para-hydrogen provides proof of the accuracy of the new quantum theory. A. J. MEE.

Pseudo-components of hydrogen. A. SMITS (Physikal. Z., 1929, 30, 425—427).—The work of Bonhoeffer and Harteck (this vol. 479) and of Eucken (*ibid.*, 497) is an experimental realisation of certain aspects of the author's theory of allotropy. The implications of the discovery of ortho- and para-hydrogen are discussed. R. A. MORTON.

Structure of the molecules of N_2 , O_2 , and F_2 . A. T. WILLIAMS (J. Chim. phys., 1929, 26, 327—330).—A critical examination is made of certain consequences of the Lewis-Langmuir theory and particularly of the more recent theory of Niven (cf. A., 1927, 714) concerning the structure of the diatomic gaseous elements. It is concluded that these molecules are asymmetric. O. J. WALKER.

Anomaly in the diamagnetism of gases. IV. Oxygen addition. A. GLASER (Ann. Physik, 1929, [v], 2, 233—248; cf. this vol., 628).—The pressure-diamagnetic susceptibility curves for argon-oxygen mixtures are linear, the susceptibility, however, decreasing with increasing concentration of paramagnetic oxygen and decreasing concentration of diamagnetic argon. Argon does not show the anomaly. The curves for carbon dioxide-oxygen mixtures show straight-line portions in certain higher-pressure regions, but in the pressure range

of the diamagnetic anomaly with pure carbon dioxide the oxygen content of mixtures plays a decisive part. With 0.1% O_2 the curve is a straight line, whilst with 0.15, 0.2, and 0.3% the anomalous behaviour increases progressively, but in the reverse sense to that encountered with pure carbon dioxide. Traces of oxygen as an impurity appear therefore to be extremely important in studying the diamagnetic anomaly. Hammar's results (A., 1926, 1197) are discussed from this point of view.

R. A. MORTON.

Paramagnetism through ions subjected to molecular forces. R. BRUNETTI (Atti R. Accad. Lincei, 1929, [vi], 9, 754—760).—Theoretical. The consequences of the severing of the bond existing between the vectors corresponding with the quantum numbers l and s in the case of atoms or ions in a strong force field are discussed. F. G. TRYHORN.

Paramagnetic properties of the rare earths. B. CABRERA and A. DUPRIER (Compt. rend., 1929, 188, 1640—1642; cf. A., 1925, ii, 618).—The Curie-Weiss law is satisfied by the sulphates and oxides of gadolinium, terbium, dysprosium, holmium, and erbium to a first approximation, but for those of praseodymium, thulium, yttrium, neodymium, europium, and probably of samarium the equation $(\chi + k)(T + \Delta) = C$ accords better with the experimental results. The constant k represents a susceptibility independent of temperature, paramagnetic and diamagnetic for the elements near samarium and yttrium, respectively, and due to deformation of the atom. J. GRANT.

Diamagnetism and space-charge distribution of atoms and ions. E. C. STONER (Proc. Leeds Phil. Soc., 1929, 1, 484—490).—The diamagnetic susceptibilities corresponding with the space-charge distributions obtained by the self-consistent field method of Hartree (A., 1928, 216) have been calculated for helium and for the ions Li^+ , Na^+ , K^+ , Rb^+ , and Cl^- . The experimental values for ionic susceptibilities are critically discussed and the calculated values are considered to be in good agreement with the experimental values for the positive ions. The calculated and experimental values for helium agree to within 1%, but the calculated value for the free chlorine ion is much greater than that observed for the ion in solution. The difference is discussed in relation to the space-charge distribution of an ion in a crystal. L. S. THEOBALD.

Mean square angular momentum and diamagnetism of the normal hydrogen molecule. J. H. VAN VLECK and (MISS) A. FRANK (Proc. Nat. Acad. Sci., 1929, 15, 539—544; cf. A., 1928, 572).—Using the wave function found by Wang (*ibid.*), the mean square electronic angular momentum is calculated for the normal hydrogen molecule and found to have the value $0.394\hbar^2/4\pi^2$. Taking account of the summation over the various excited states, a simple method is found of calculating the correction to Pauli's formula or to Wang's calculation of the diamagnetism of the hydrogen molecule, and the value -4.2×10^{-6} is obtained. N. M. BLYTH.

Magnetic anisotropy of naphthalene crystals. S. BHAGAVANTAM (Proc. Roy. Soc., 1929, A, 124,

545–554).—Naphthalene crystals show a marked degree of magnetic and optical anisotropy. Two of the magnetic axes coincide with two of the crystallographic axes (*b* and *c*), whilst the third is a line perpendicular to both. The values -710 , -390 , and 1590×10^{-7} , respectively, were found for the principal susceptibilities along the *b* axis, along the *c* axis, and along a line perpendicular to both. Two of the axes of the optical ellipsoid also coincide with the *b* and *c* axes to within about 3° , and the values 1.775 , 1.932 , and 1.442 , respectively, have been found for n_D along the *b* axis, the *c* axis, and a line perpendicular to both. The fact that the direction of the maximum diamagnetic susceptibility coincides with that of the minimum refractive index explains the strong positive birefringence shown by aromatic liquids in a magnetic field. The experimental results indicate that the two molecules in the unit cell are oriented with their planes parallel to the *bc* plane, and not, as suggested by Bragg, to the *ac* plane. L. L. BIRCUMSHAW.

Chemical combination as an electrostatic phenomenon. IX. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 386–389; cf. this vol., 867).—Methods of calculating the deformation constant α of an ion are described, and the results compared. The influence of the size of a cation on the extent of deformation produced is discussed, especially with regard to hydrogen and to organic compounds. H. F. GILLBE.

Valency of sulphur in dithionates. R. E. WINGER and D. M. YOST (Proc. Nat. Acad. Sci., 1929, 15, 462–464).—The shift in the *K*-absorption edges of various compounds of certain elements including sulphur is known to depend chiefly on the valency of the element in a given compound, shifting to smaller values with increasing valency. The *K*-absorption edge was examined for potassium dithionate and found to lie at 4992.8 , between the values for quadri- and sexa-valent sulphur, indicating an equal valency of five for the two sulphur atoms in the dithionate in accordance with the usual view. N. M. BLIGH.

Effective strength of linking in polyatomic molecules. G. SCHWARZENBACH (Helv. Chim. Acta, 1929, 12, 820–821).—The conclusion of Ebel and Bretscher (this vol., 744, 745), that it cannot be assumed from thermochemical evidence that the strength of a C–C and a C–H linking is the same within narrow limits, is criticised. The view that the energy of fission of linkings of the same kind and nature has a constant value independently of the position and presence of other linkings and atoms in the molecule is discussed. L. S. THEOBALD.

Double sulphates and their components. V. Aluminium and chromium alums. F. KRAUSS, A. FRICKE, and H. QUERENGASSER (Z. anorg. Chem., 1929, 181, 38–54; cf. this vol., 665).—Measurements of the densities and isobaric dehydration curves and derived calculations of the heats of formation of the various hydrates of caesium, rubidium, and potassium aluminium alums and potassium chromium alum indicate that two types of alums must be distinguished. Potassium chromium alum exists with 0, 2, 6, and $12H_2O$. The aluminium salts exist with 0, 3, and $12H_2O$. J. S. CARTER.

Formation of associated or additive compounds in the crystalline state. W. KRINGS (Z. anorg. Chem., 1929, 181, 298–308).—From considerations based on the theory of polar compounds the heat of addition of 1 mol. of ammonia to 1 mol. of sodium chloride has been calculated and shown to be somewhat higher than, but of the same order of magnitude as, that determined experimentally. The mechanism of the formation of additive compounds with 5, 7, 9, and 10 and with fractional numbers of molecules of ammonia or water of crystallisation is discussed from the point of view of the co-ordination and polar theories. A. R. POWELL.

Quantum mechanics of chemical reaction. R. M. LANGER (Physical Rev., 1929, [ii], 34, 92–108).—The failure of classical mechanics applied to chemical phenomena and the difficulties of the “activation” hypothesis are discussed. Starting from the wave equation, it is shown that quantum mechanics can describe a typical chemical reaction, and that this can be generalised. It is found that a system may change from one configuration to another when a quantum level of the one has the same energy as a quantum level of the other. Examples of molecular rearrangements and decompositions are discussed and illustrated by *cis-trans*-isomerism, and the racemisation of pinene. The theory is also applied to catalysis and radioactive disintegration. The essential requirement is found to be that a molecular system should be capable of existing in physically distinguishable states of equal energy; the special problem is to find the perturbing potential causing the reactants to go over into the reaction products. N. M. BLIGH.

Parachor and chemical constitution. XI. Arsenic and selenium compounds. W. J. R. HENLEY and S. SUGDEN (J.C.S., 1929, 1058–1065).—The parachor of selenium (62.5) has been determined from those of five compounds in which it is bivalent (diphenyl selenide 445.6, diphenyl diselenide 506.5, phenylselenium bromide 321.4, *p*-bromophenyl selenocyanate 366.1, and *p*-chlorophenyl selenocyanate 349.3); that of arsenic (50.3) from those of the trichloride 212.0, the tribromide 253.5, phenyldichloroarsine 348.3, and diphenylchloroarsine 487.1. These values are in conformity with those of elements adjacent to them in the periodic table. The parachors of several higher valent compounds of selenium have also been determined (diphenyl selenoxide 461.6, phenylseleninic acid 299.5, and selenium oxychloride 181.1). All of these are in agreement with the values calculated on the assumption that the double linking is semipolar (460.9, 308.0, 189.5, respectively, as against 485.7, 332.8, and 214.3 for non-polar linkings). The two last are even lower than required for semipolar linkings. This is due to association. Thus the mol. wt. of a 20% solution of selenium oxychloride in benzene is 195.7 (theory 166.1); the parachor of the monohydrate of this compound is in favour of the structure $Se(OH)_2Cl_2$ with two singlet linkings. C. A. SILBERRAD.

Parachor and chemical constitution. XII. Fused metals and salts. S. SUGDEN and H. WILKINS (J.C.S., 1929, 1291–1298).—The parachors

of conducting liquids have been found to show both positive and negative anomalies. The parachor of a salt involves the constant for a polar linking, estimated at -1.6 units (cf. A., 1927, 714). Salts of organic bases which are dissociated in the fused state and in which all the atomic parachors are known with certainty afford a means of checking this value. Parachors of six out of ten such salts support the value -1.6 within the limits of experimental error, whilst those of the remaining four show considerable positive and negative anomalies. Thallous nitrate, stannous chloride, lead chloride, and the metals aluminium, tin, lead, and antimony showed positive parachor anomalies, too large in most cases to be accounted for by association of atoms or ions, and due apparently to some special condition of the metal atom not considered in the calculation. Approximate values for the atomic parachors of the alkali metals have been deduced from the observed parachors of various salts. The salts of the alkali metals, especially the fluorides, show large negative anomalies in their parachors.

F. L. USHER.

Parachor and chemical constitution. XIII. Some compounds of titanium and tin. F. B. GARNER and S. SUGDEN (J.C.S., 1929, 1298—1302).—The value 56.7 for the atomic parachor of tin has been deduced from the observed parachors of tin tetrachloride, tetrabromide, and tetraethyl. $[P]=45.3$ for titanium has been obtained from the parachor of titanium tetrachloride. These results harmonise with the values hitherto found for other elements of the fourth group. An additive compound, $\text{SnCl}_4 \cdot 2\text{POCl}_3$, m. p. 54.5° , b. p. 118 — 119° , has been isolated. This substance showed little conductivity in the fused state and is probably non-polar. A structure containing four singlet linkings is suggested, but the value of the parachor calculated on this assumption is lower than that experimentally observed ($[P]_{\text{obs.}}=691.6$, $[P]_{\text{calc.}}=665.5$). The explanation suggested is that the fused compound is partly dissociated into its components.

F. L. USHER.

Molecular volumes at absolute zero. III. Zero volumes, parachors, and molecular diameters. S. SUGDEN (J.C.S., 1929, 1055—1058; cf. A., 1927, 920).—A comparison of the author's work with that of Biltz (Nachr. Ges. Wiss. Göttingen, 1926, 45; A., 1927, 498) shows substantial agreement in the values of the atomic constants arrived at. The mean distances between molecules in 17 substances have been calculated, (a) at 0° Abs. (from zero volumes), (b) at unit surface tension (from parachors), and (c) at the critical temperature, and compared with molecular diameters as deduced from gas viscosity by Chapman's equation (cf. A., 1918, ii, 416). Results from (a) average 1.32 times the molecular diameter (except for $\text{H}_2=1.71$ and $\text{He}=1.92$); from (b) 1.78 with no marked variations; and from (c) about double (except for $\text{He}=2.64$, $\text{Cl}_2=1.60$, and $\text{Br}_2=1.69$).

C. A. SILBERRAD.

Theory of the equilibrium figures of small drops growing by diffusion in relation to the problem of form in physics. N. VON RASCHEVSKY (Z. Physik, 1929, 56, 297—307; cf. A., 1928, 474,

690; this vol., 509).—Since a slowly growing drop of the type previously considered is not spherical, the concentration varies along the surface, and hence also the surface tension. It is shown that the product of the surface tension and the curvature is constant for any point on the surface. This is discussed in connexion with the problem of shape determination in pure physical phenomena.

J. W. SMITH.

Wave-length of the K lines of copper using ruled gratings. J. A. BEARDEN (Proc. Nat. Acad. Sci., 1929, 15, 528—533).—A glass grating of 600 lines per mm., and a glass and speculum-metal grating each with 50 lines per mm. were used. The values obtained were $K\alpha=1.5422 \pm 0.0002$ and $K\beta=1.3926 \pm 0.0002 \text{ \AA.}$, differing appreciably from measurements using crystals, but probably more trustworthy. From the new results the following values of constants are calculated: the grating space of calcite 3.035 \AA. , $N=6.022 \times 10^{23} \text{ g.-mol.}$, $e=4.804 \times 10^{-10} \text{ e.s.u.}$, $6.604 \times 10^{-27} \text{ erg sec.}$, the fine structure constant $1/\alpha=136.6$ (cf. Eddington, this vol., 231).

N. M. BLYTH.

Optical line gratings for X-ray spectral analysis in the region 1—2 \AA. H. SEEMAN and K. F. SCHOTZKY (Z. Physik, 1929, 55, 252—272).—The applicability of various types of line gratings with 100—1000 lines per mm. for different wave-lengths of X-radiation is discussed.

J. W. SMITH.

Iron, cobalt, nickel, and copper as deflexion lattices for the corresponding X-rays. S. PASTORELLO (Nuovo Cim., 1928, 5, 284—289; Chem. Zentr., 1929, i, 722).

New X-ray effect. C. V. RAMAN and P. KRISHNAMURTI (Nature, 1929, 124, 53).—X-Ray diffraction patterns of graphite show a notable amount of scattered radiation in the area surrounding the primary beam, terminating sharply at the first diffraction ring and reappearing with diminished intensity in the area between the first and second diffraction rings. The effect is ascribed to mobile electrons loosely associated with the crystal lattice.

A. A. ELDRIDGE.

Diffraction of X-rays by two-dimensional crystal lattice. W. L. BRAGG (Nature, 1929, 124, 125).—The effect observed by Linnick (this vol., 492), and attributed by that author to the effect of very thin layers of the mica crystal as independent two-dimensional gratings, is ascribed to ordinary diffraction by a three-dimensional grating, provided that the mica is assumed to consist of a number of flakes not quite parallel. The mechanism of diffraction is considered in relation to the simulation of a two-dimensional grating effect.

A. A. ELDRIDGE.

An X-ray effect of slow fracture. U. DEHLINGER (Naturwiss., 1929, 17, 545).—Strongly rolled sheet copper or silver was bent backwards and forwards until fracture occurred. Photographs of the last Debye lines taken at a place close to the fracture showed the K doublet of copper separated with great sharpness, no grains being recognised in the specimen. The lines shown at the unbent end of the sheet exhibited the usual diffuse effect.

R. A. MORTON.

Emission of soft X-rays by different elements, with reference to the effect of adsorbed gas. U. NAKAYA (Proc. Roy. Soc., 1929, A, 124, 616—641).—An extension of the work of Richardson and Robertson (A., 1927, 804). A more detailed investigation has been made of the effect of polishing the surface, the state of degassing of the photo-electric plate, and the conditions of oxidation of the target faces. The presence of adsorbed gas molecules on the photo-electric plate and target plays an important part in the absorption and excitation of soft X-radiation. The efficiency of liberation of photo-electrons is increased, the amount of increase being greater the more adsorbed gas molecules there are in the surface. The relative change in the value of i_p/i_i for different states of the adsorbed molecules on the plate is the same for the radiations produced by different targets. The excitation of soft X-rays for a given amount of thermionic current appears to be decreased by the presence of gas molecules on the target. A number of facts support this conclusion, such as the increase in i_p/i_i when the target is subjected to a heavy bombardment compared with the value for a long bombardment at low temperature, the increase when the oxide film on the target is reduced with hydrogen, and the variation of the value with time observed at high voltages. When all the targets and photo-electric plates are well degassed and the oxide films reduced with hydrogen, consistent values of i_p/i_i are obtained with an error of less than 3% up to 1000 volts. Curves plotted for 11 elements show that i_p/i_i does not vary proportionally with the voltage, as hitherto assumed. Measurements were also made at higher voltages, chromium, iron, and copper being examined from 1500 to 2000 volts, and manganese, nickel, and cobalt from 1500 to 4500 volts. The ratio i_p/i_i increases at first, but gradually approaches a constant value, and the curves showing the relation of i_p/i_i to voltage take the form of saturation curves.

L. L. BIRCUMSHAW.

Determination of particle size by the use of X-rays. H. MARK (Trans. Faraday Soc., 1929, 25, 387—389).—The factors influencing the experimental data in the determination of particle size are discussed, with special consideration of the cases of parallel and divergent radiation and of transparent and absorbing material. The fact that different crystals of a powder are not all of the same size and the possibility of lattice defects lead to serious difficulties. It is found that the intensity of reflexion from a distorted lattice differs from that from an undistorted lattice.

L. L. BIRCUMSHAW.

Intensity, sharpness, and reproducibility of Debye-Scherrer lines. H. MÖLLER and A. REIS (Trans. Faraday Soc., 1929, 25, 386).—A procedure has been developed whereby the intensity distribution of the lines in a Debye-Scherrer photograph can be deduced from the conditions of the experiment. A parallel beam is used and the intensity distribution in one line is determined for all angles of refraction, using the cross-section and absorption of the block. For high intensities and sharp lines, the cross-section must be accurately adjusted, varying with the absorption coefficient of the preparation. Conditions are

favourable when the cross-section of the line and the aperture width approximate respectively to the line given by an infinitely small focal spot and by an infinitely small preparation. L. L. BIRCUMSHAW.

Change of frequency of X-rays scattered by bound electrons. D. P. MITCHELL (Physical Rev., 1929, [ii], 33, 871—878).—With the high resolution obtainable by the use of the two-crystal X-ray spectrometer (cf. Davis and Purks, A., 1927, 804) the fine structure of scattered X-rays (cf. A., 1928, 1168) was investigated. Molybdenum X-rays were scattered by graphite, aluminium, and beryllium. Lines from graphite were shifted 0.0013, 0.0023, and 0.0113, and from aluminium 0.0023, 0.0055, and 0.069 Å. to the long-wave side of Mo- $K\alpha_1$. From beryllium the shifts were 0.0048 and 0.00065 Å. to the long- and short-wave side, respectively. The scattering electrons are shown to be ejected with zero kinetic energy, and the critical potentials obtained are 32, 57, and 279 volts for carbon, 57, 136, and 1550 volts for aluminium, and 16 and 119 volts for beryllium.

N. M. BLIGH.

Raman effect for X-rays. D. COSTER, I. NITTA, and W. J. THIJSEN (Nature, 1929, 124, 230).—It is impossible to account for the order of magnitude of the intensity of the anti-Stokes line for beryllium quoted by Mitchell (preceding abstract).

A. A. ELDRIDGE.

Effect of chemical combination on the absorption of X-rays at wave-lengths on each side of the K discontinuity. C. L. COTTRELL (Physical Rev., 1929, [ii], 33, 879—888).—The difference in the absorption of X-rays by free as compared with chemically combined iodine was investigated for wave-length bands on each side of the K absorption limit of this element, using the double ionisation chamber method. The reacting solutions were an alcoholic solution of iodine and an aqueous solution of sodium thiosulphate (cf. Morehouse, A., 1927, 707), the reaction being $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$. The results show that on the long wave-length side of the K limit the absorption coefficient of the free iodine is about 0.3% greater, and on the short wave-length side 0.5% smaller, than for the combined atom. Silver was also investigated.

N. M. BLIGH.

Diffraction of X-rays in liquids: benzene, cyclohexane, and certain of their derivatives. G. W. STEWART (Physical Rev., 1929, [ii], 33, 889—899).—With the apparatus and procedure previously reported (A., 1928, 465, 1079) an examination by the X-ray diffraction ionisation method was made of benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, ethyl- and isopropyl-benzene, cyclohexane, methyl- and 1:2-, 1:3-, and 1:4-dimethyl-cyclohexane, phenol, aniline, cyclohexanol and cyclohexanone, *m*-2- and -4-, *o*-4-, and *p*-2-xylene, *o*-, *m*-, and *p*-toluidine, and *o*-, *m*-, and *p*-tolyl methyl ether. The experiments give the effective thicknesses of the benzene and cyclohexane rings, the changes in these thicknesses with substitutions, and information on the orientation of molecules in the liquid state in support of the cybotactic theory. The benzene and cyclohexane rings show a flattened structure, having a

thickness of 4.7 and 5.1 Å., respectively, and the thickness is shown to depend on the relative positions of the substituents, *para*-substitutions giving the least thickness of ring, and the *meta*- usually giving less thickness than the *ortho*-position. All the hydroxy-compounds studied showed double molecules.

N. M. BLIGH.

X-Ray absorption limits and the distribution of electrons round the atom. B. B. RAY (Indian J. Physics, 1929, 3, 477—488).—Theoretical. Kossel's view of the absorption process and the fine-structure lines is developed to explain the secondary edges in compounds, and a general relation is found that for different elements in compounds of similar structure the separation of the *K* edge in the elementary atoms from that of corresponding edges of the same atoms in the compound is the same. The discontinuities in the curve for $\Delta(v/R) - K - K\beta_1$ and the atomic number from aluminium to zinc supports the Saha electronic distribution scheme rather than that of Stoner and Main Smith.

N. M. BLIGH.

Fine structure in the Compton effect. B. DAVIS and H. PURKS (Physical Rev., 1929, [ii], 34, 1—6; cf. A., 1928, 1168).—Using the double X-ray spectrometer (cf. A., 1927, 804) and a special X-ray tube with molybdenum target and large scattering angles of 155° and 163°, the displaced scattered radiation (Compton effect) from carbon and beryllium was investigated. The fine structure found for carbon was a relatively strong line, 0.0421 from Mo- $K\alpha_1$ position, and three weaker lines at 0.0012, 0.002, and 0.0109 Å. from the strong line. The displacement is 9% less than the theoretical. For beryllium a strong line was found at 0.0446 from Mo- $K\alpha_1$ position, a line at 0.0051 towards the long wave-lengths, and a weak line at 0.0009 towards the short wave-lengths.

N. M. BLIGH.

Experimental evidence for the filling of electron levels from the relative intensity of X-ray spectrum lines. S. K. ALLISON (Physical Rev., 1929, [ii], 34, 7—16).—The double line $L\beta_5$, representing the transitions $5_{32}, 5_{33} \rightarrow 2_{22}$, had been found much more intense in the uranium than in the tungsten *L* series (cf. A., 1928, 938). Intensity measurements involving this line are given for osmium, iridium, platinum, gold, thallium, lead, and bismuth, keeping high vacua in the X-ray tubes to avoid difficulties due to deposition of tungsten on the targets from the filaments. The curve showing the intensity ratio β_5/β_1 against atomic numbers rises with increasing atomic number and takes an upward jump between platinum and gold, indicating that gold is the first element in which 10 electrons occupy the 5_3 orbits approximately undisturbed in the solid state.

N. M. BLIGH.

Dependence of the number of crystal nuclei on the temperature. G. TAMMANN (Z. anorg. Chem., 1929, 181, 408—416).—A theoretical discussion on the dependence of formation of crystal nuclei in a liquid on the temperature and viscosity.

H. F. HARWOOD.

Diagram of the physical properties of crystals. J. KUNZ (Physikal. Z., 1929, 30, 463—464).—Theoretical.

R. A. MORTON.

Lattice determination in polycrystalline aggregates. K. WEISSENBERG (Trans. Faraday Soc., 1929, 25, 391—392).—Two methods have been developed which are of special value for investigating organic compounds of high mol. wt. In the first method a growth or deformation structure is obtained in which only a few distinct crystallite orientations occur in statistical preponderance. In the second, the preparation is made as long as possible in the direction of the beam and the interferences of the planes with the greatest spacing are strengthened.

L. L. BIRCUMSHAW.

Allotropy and the determination of densities by means of X-rays. N. H. KOLKMEIJER (Trans. Faraday Soc., 1929, 25, 392—397).—The difficulties of the X-ray and pycnometer methods of determining densities are discussed, and numerous examples are given of the discrepancies between the values obtained by the two methods, and also of those obtained by different observers using the same method. Since both methods are capable of giving values correct to within $\pm 0.1\%$, the discrepancies are probably mostly due to the presence of "physical impurities" in the material used. They may also be ascribed partly to the formation of mixed crystals. The possibility of testing the "physical purity" of a material by means of X-rays is illustrated by the determination of the densities of hexagonal (d_4^{25} 5.681) and cubic (d_4^{25} 5.683) silver iodide by the spectrographic method. A new precision camera is described.

L. L. BIRCUMSHAW.

X-Ray investigation of the structure of annealed carbon steel. G. KURDJUMOV (Z. Physik, 1929, 55, 187—198).—The changes which the crystal structure of hardened carbon steel undergoes on annealing have been investigated by the Debye-Scherrer method. The three steps in the process which have been observed by other methods are confirmed by the X-ray investigation. At the first change, which occurs at an appreciable velocity at 100—150°, the tetragonal structure breaks down; the second step, obtained by heating to 250°, is caused by the breakdown of the austenite; the third, which occurs only slowly at 300—400°, is associated with the formation of an α -iron-cementite mixture.

J. W. SMITH.

Lattice constants of quenched steels. S. SEKITO (Sci. Rep. Tohoku, 1929, 18, 69—77).—The axial ratio of the tetragonal lattice which appears on the surface layers of quenched carbon steels (cf. Honda and Sekito, B., 1928, 753) diminishes with increasing depth until it reaches the value 1.00. The maximum value of this ratio is 1.07 with hypereutectoid steels; the value decreases with decreasing carbon content and with decreasing quenching temperature.

A. R. POWELL.

X-Ray investigation of iron-nitrogen alloys. A. ŌSAWA and S. IWAIZUMI (Sci. Rep. Tohoku, 1929, 18, 79—89).—Röntgenographic examination of the substances obtained by passing ammonia over finely divided iron at various temperatures has confirmed the existence of the compounds Fe_3N and Fe_2N . The former has a cubic lattice, $a = 3.86$ Å., in which the iron atoms have a face-centred distribution and one nitrogen atom is present in the elementary cube,

d_{calc} , 6.57. Fe_2N has a close-packed hexagonal lattice, $a=2.743 \text{ \AA}$, $c/a=1.59$, one nitrogen atom being present in every elementary parallelepiped, d_{calc} , 5.02. Both compounds appear to form limited series of solid solutions with one another and with iron.

A. R. POWELL.

Röntgenographic investigations on aluminium at high temperatures. A. J. ALICHANOV (Z. Metallk., 1929, 21, 127).—X-Ray examination of aluminium of 99.5% purity at temperatures up to 593° showed that no change in the lattice structure takes place other than the normal expansion due to heating, and hence that aluminium does not undergo allotropic modification, at least up to 593° .

A. R. POWELL.

Intermetallic compound having a simple cubic lattice. A. ŌSAWA (Nature, 1929, 124, 14).—Antimony-tin alloys containing 43, 50, and 5.5% Sb, respectively, annealed for 200 hrs. at 240° , 270° , and 290° , slowly cooled to 240° , maintained at that temperature for 25 hrs., and then slowly cooled to the ordinary temperature, showed an X-ray spectrum indicating a simple cubic lattice.

A. A. ELDRIDGE.

X-Ray studies on alloys. A. F. WESTGREN and G. PHRAGMEN (Trans. Faraday Soc., 1929, 25, 379—385).—A comparative study is made of the results of X-ray analyses of alloys, with the object of tracing the regularities governing the phenomena in this field of research. The structural analogies of intermetallic phases and their connexion with the concentration of valency electrons are considered (cf. A., 1926, 1084), and a graphical representation is given of the regularities found in some binary copper and silver alloys. Special reference is made to the unique crystal structure of manganese and to the fact that in some alloys where the ratio of valency electrons to atoms is 3:2 (e.g., Ag_3Al , Cu_5Si) the atoms are grouped as in β -manganese. The terms "solid chemical compound" and "solid solution" are discussed, and a short account is given of the change of the average volume of the atoms in alloys with varying composition. A marked contraction takes place in all cases where chemically unrelated metals are alloyed with each other, the contraction being too pronounced to make the linear dimensions additive. This is illustrated by reference to the system silver-cadmium.

L. L. BIRCUMSHAW.

Metallic state. J. D. BERNAL (Trans. Faraday Soc., 1929, 25, 367—379).—From the point of view of crystal chemistry, metallic substances occupy a position intermediate between ionic and homopolar substances, the transition from one state to the other being almost continuous. It is proposed to classify metals into metallic ionic, metallic homopolar, and truly metallic substances. One of the most important characteristics of the metallic state is the close-packed structure observed by X-ray analysis; the closeness is more marked in the truly metallic substances, decreasing in the direction of homopolar or ionic structures. The results of X-ray studies on intermetallic compounds are shown schematically, and the fact is stressed that, although the actual structures are mostly complicated, nearly all are

variants of the close-packed structure. The criteria for the existence of distortion in a metal crystal not only enable solid solutions to be distinguished from true metals, but also establish the existence of true intermetallic compounds. The electrical properties of intermetallic compounds indicate that they are to be considered as true metals, but the majority tend more to the homopolar or ionic types. The differences between metals in respect of their dissolving power is thought to have an important bearing on the theory of electrical conduction. A hypothesis as to the nature of superconductivity (cf. Kapitza, this vol., 632) is advanced, based on the assumption that a sudden freezing out of impurities occurs at the threshold temperature. A metal in the superconductive state is postulated as being extensively cracked but with an undistorted lattice. The importance of magnetic measurements is emphasised, and the structures of certain diamagnetic intermetallic compounds which follow the Hume-Rothery rules are explained in terms of homopolar linking. The empirical requirements of the metallic linking and their possible theoretical meaning are discussed.

L. L. BIRCUMSHAW.

X-Ray examination of the system Au-Hg. A. PABST (Z. physikal. Chem., 1929, B, 3, 443—455).—An investigation of the crystal structure of gold amalgams by the powder method. It was found necessary to anneal amalgams containing less than 20% Hg at temperatures up to 300° for 18—90 hrs. in order to develop the crystals. Amalgams containing up to 15% Hg gave diagrams showing a series of mixed crystals (cubic), the side of the unit cell increasing regularly with mercury content from 4.070 \AA . (pure gold) to 4.107 \AA . With more than 15% Hg a hexagonal phase appears along with the mixed crystals, the latter vanishing at 25% Hg. The constants for this phase are $a_0=2.908$, $c_0=4.791 \text{ \AA}$, approximating closely to those of a hexagonal close-packed cell containing $\text{Au}_3\text{Hg}/2$. With increasing mercury content a number of new lines appear in the diagrams, those relating to the hexagonal phase finally disappearing at 60% Hg. The new lines are probably due to two crystalline phases of undetermined structure, containing 60% and 66—68% Hg, respectively.

F. L. USHER.

Crystal structure of solid nitrogen. L. VEGARD (Naturwiss., 1929, 17, 543).—The X-ray spectrum of solid nitrogen indicates a complicated cubic lattice. The edge of the elementary cube is 11.3 \AA . long and the cell contains 64 atoms. The spectrum shows only lines satisfying the condition $\Sigma h=2n$, corresponding with a body-centred lattice. The space-group is probably O^8 .

R. A. MORTON.

Crystal structure of bismuth fluoride. O. HASSEL and S. NILSEN (Z. anorg. Chem., 1929, 181, 172—176).—The structure is based on a face-centred lattice. The unit cube has $a=5.853 \pm 0.004 \text{ \AA}$, and contains 4 mols.; d_{calc} , 8.75.

J. S. CARTER.

Crystalline structure of thorium boride. G. ALLARD (Compt. rend., 1929, 189, 108—109).—The powder method indicated a simple cubic structure with $a=4.32 \text{ \AA}$. and one mol. of ThB_6 per unit cell. The six boron atoms are assumed to be situated at the

points of an octahedron with the thorium atoms at the centre which coincides with that of the lattice.

J. GRANT.

Crystal form of calcium sulphate. L. S. RAMSDALE and E. P. PARTRIDGE (Amer. Min., 1929, 14, 59—74).—"Soluble anhydrite" is identical in crystal structure with the hemihydrate, which is zeolitic in character. The transition temperature of gypsum to anhydrite in contact with water is 38° (?), and from gypsum to hemihydrate 98°.

CHEMICAL ABSTRACTS.

Crystal structure of dimethyldiethylammonium chlorostannate. R. W. G. WYCKOFF and R. B. COREY (Amer. J. Sci., 1929, [v], 18, 138—144).—Laue and oscillation spectral photographs have been taken of crystals of dimethyldiethylammonium chlorostannate; they have tetragonal holohedral symmetry. The unit cell has $a_0=9.065$, $c_0=14.12$ Å., and contains two molecules. It belongs to the space-group $4Di-6$, the tin and chlorine atoms having the positions: tin (a) 000; ; chlorine (e) 00 u ; 00 u ; etc., (h) $wv0$; $wv0$; etc., where $u=0.177\pm0.01$, w =about 0.23, and v =about 0.13. The structure is probably a distorted calcium fluoride arrangement. The nitrogen atoms are probably at (d) of $4Di-6$ (D_{3h}^6); the distribution of the carbon atoms is not determined.

C. W. GIBBY.

Structure of sillimanite and mullite. W. H. TAYLOR (Z. Krist., 1928, 68, 503—521; Chem. Zentr., 1929, i, 497—498).—A dark brown specimen of sillimanite had $a:b:c=0.980:1:0.757$; a 7.43 \pm 0.03, b 7.58 \pm 0.04, c 5.74 \pm 0.02 Å. The space-group V_6^6 is preferred to C_{2v}^2 . The unit cell contains 4 mols. of Al_2SiO_5 . Crystallographically and optically, mullite is almost identical with sillimanite; the unit cell contains 1.5 mols. of $3Al_2O_3 \cdot 2SiO_2$. Kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, monoclinic prismatic, reveals in its X-ray diagram no similarity with mullite or sillimanite. The appearance of mullite lines in the diagram of ignited kaolin may be due to the formation of $Al_2O_3 \cdot 2SiO_2$, which would have a structure similar to that of sillimanite and mullite. A. A. ELDRIDGE.

Enargite group. Structure of sulvanite, Cu_3VS_4 . W. F. DE JONG (Z. Krist., 1928, 68, 522—530; Chem. Zentr., 1929, i, 497).—Enargite, Cu_3AsS_4 , and famatinitite, Cu_3SbS_4 , give almost identical Debye diagrams. Sulvanite, Cu_3VS_4 , containing Cu 51.20, V 14.20, S 34.60%, is cubic, a 10.750 \pm 0.005 Å., with 8 mols. in the unit cell, space-group O_h^2 .

A. A. ELDRIDGE.

X-Ray study of microcrystalline ferric hydroxide minerals. J. BOHM (Z. Krist., 1928, 68, 567—585; Chem. Zentr., 1929, i, 498—499).— α - $Fe_2O_3 \cdot H_2O$, rhombic holohedral, has a 4.60, b 10.01, c 3.04 Å., $a:b:c=0.459:1:0.303$, d 4.195; the γ -form has a 3.85, b 12.5, c 3.07 Å., $a:b:c=0.308:1:0.246$, d 3.97. Most of the ferric oxide minerals examined afforded the Debye diagram of the α -form, together, in some cases, with lines arising from impurities, particularly silica. The varying water content is ascribed to adsorption. γ - $Fe_2O_3 \cdot H_2O$ was not observed in minerals. Haematites are of two types according to the direction of fibrillation.

A. A. ELDRIDGE.

Is the lattice of tetragonal mercuric cyanide a molecular or a radical lattice? O. HASSEL (Z. anorg. Chem., 1929, 180, 370—373).—The author maintains the interpretation put forward in a previous paper (cf. Z. Krist., 1926, 64, 217). F. L. USHER.

Is the lattice of tetragonal mercuric cyanide a molecular or a radical lattice? R. FRICKE (Z. anorg. Chem., 1929, 180, 374—376; cf. A., 1928, 821).—A reply to Hassel (preceding abstract).

F. L. USHER.

Lattice dimensions and phase range of the magnetic substance Fe_2Sb_3 . I. OFTEDAL (Z. physikal. Chem., 1929, B, 4, 67—70; cf. A., 1927, 924).—The previous determination of the lattice constants of a member of the ϵ -phase in the system iron-antimony has been repeated with a new preparation, as Hagg's results (cf. this vol., 749) were not in agreement. The new result fully confirms the previous one. Some explanation of the difference is given.

A. J. MEE.

X-Ray analysis of solid carbon disulphide. J. DE SMEDT (Physica, 1929, 9, 5—8).—For a tetragonal structure, $a=b=8.12$ Å., $c=3.77$ Å.; the unit cell contains 3 mols.; d_{calc} 1.51, d_{obs} 1.55.

CHEMICAL ABSTRACTS.

Crystal structure of cis-ethylene oxide-dicarboxylic acid. A. REIS and W. SCHNEIDER (Z. Krist., 1928, 68, 586—594; Chem. Zentr., 1929, i, 474—475).—The substance is monoclinic, $a:b:c=3.118:1:0.998$, $\beta=91^\circ 10'$; the unit cell contains 8 mols. of $C_4H_4O_5$; space-group C_{2h}^2 .

A. A. ELDRIDGE.

Crystal structure of indigotin and fumaric acid. A. REIS and W. SCHNEIDER (Z. Krist., 1928, 68, 543—566; Chem. Zentr., 1929, i, 473—474).—Indigotin is monoclinic, $a:b:c=1.897:1:1.741$, $\beta=107^\circ 30'$; the unit cell, a 11.00, b 5.8, c 10.1 Å., contains 2 mols. of $C_{16}H_{10}O_2N_2$; space-group C_{2h}^2 . Fumaric acid is monoclinic, $a:b:c=0.503:1:0.438$, $\beta=111^\circ 5' \pm 5'$; the unit cell, a 7.6, b 15.1, c 6.65 Å., contains 6 mols. of $C_4H_4O_4$; space-group C_{2h}^2 . Yardley's results (A., 1925, ii, 1126) are criticised.

A. A. ELDRIDGE.

Crystal structure of pentaerythrityl tetraacetate. H. MOLLER and A. REIS (Z. Krist., 1928, 68, 385—386; Chem. Zentr., 1929, i, 192).—The results of Knaggs (A., 1928, 464) are supported.

A. A. ELDRIDGE.

X-Ray examination of insulin, edestin, and hæmoglobins. W. H. GEORGE (Proc. Leeds Phil. Soc., 1929, 1, 412—415).—The powder method was used with soft X-rays from a copper or iron anticathode. No traces of crystalline diffraction effects could be obtained with insulin, edestin, or pure, freshly-prepared hæmoglobins of sheep or horse blood. It was found, however, that an old sample of methæmoglobin gave Laue diagrams, but these were probably due to decomposition products or impurities. The extreme importance of blind experiments when powder methods are used is stressed.

A. J. MEE.

Translation lattice of cellulose hydrate. K. WEISSENBERG (Naturwiss., 1929, 17, 624).—Preliminary.

R. A. MORTON.

X-Ray diffraction in liquids and solutions and the molecular structure factor. P. KRISHNAMURTI (Indian J. Physics, 1929, 3, 507—522; cf. this vol., 751).—An examination was made of substances consisting of symmetrical molecules, in the liquid state and in solutions of different concentrations. Tetranitromethane gave two rings for the liquid, of spacings 5.49 and 3.02 Å., and gave in dilute benzene or cyclohexane solution a strong scattering at small angles and a faint maximum at 3.02 Å. The strong inner ring in the liquid is due to diffraction by neighbouring molecules and is intermolecular; the faint outer ring is due to the structure factor of the molecule and is intramolecular. Hexamethylenetetramine gave in concentrated aqueous solution a broad inner maximum and an outer one at 2.86 Å.; in more dilute solutions the water ring was superposed on the latter, shifting its position to smaller angles. Dilute solutions of carbon tetrachloride in cyclohexane gave faint outer maxima in approximately the same position as in the pure liquid. The calculation of the distance between planes containing the maximum number of molecules per unit area, rather than the distance between neighbouring molecules, is discussed.

N. M. BLIGH.

What circumstance conditions the solidification in the plastic deformation of solid isotropic bodies? H. HENCKY (Z. Physik, 1929, 55, 145—155).—Theoretical.

J. W. SMITH.

Electromotive behaviour of single zinc crystals. M. STRAUMANIS (Nature, 1929, 124, 56).—No variations in the potentials of different, artificially prepared, planes of single crystals of zinc against a neutral zinc sulphate solution could be observed (cf. Anderson, this vol., 127), although the potential varied with the composition of the electrolyte and with the previous treatment of the metal. A similar equality was observed with zinc-cadmium alloys containing up to 0.2% Cd.

A. A. ELDRIDGE.

Determination of crystal potentials by diffraction of high-voltage electrons. A. G. EMSLIE (Nature, 1929, 123, 977—978).—Preliminary experiments with calcite, galena, and antimony, in which $\sqrt{V} \sin \theta$ varied rapidly with ϕ , where V is the energy of the electrons in volts and ϕ is the inner potential of the crystal, indicated that the method may be of importance for precise measurement of ϕ .

A. A. ELDRIDGE.

Effect of gases on the electric charges developed by heated metals. D. H. BANGHAM and D. R. LEWIS (J.C.S., 1929, 1140—1149; cf. A., 1914, ii, 330).—The rate of development of the charge on a cylinder of gold gauze suspended in a Jena glass tube after successive earthings, when heated at 468° and 497°, has been studied in the presence of oxygen, nitrogen, and hydrogen. With oxygen, increase of pressure caused a marked shift of the equilibrium potential towards the positive side, and the rate of attainment of the final potential, even at low pressures, was considerably slower than in a vacuum. The ions responsible for the current are not charged atoms or molecules of oxygen, but are similar to those shown by Richardson to be emitted by "new" wires, probably

sodium and potassium ions. Nitrogen gave results similar to those with oxygen. Hydrogen, on the other hand, caused a displacement of the equilibrium potential toward the negative side, and facilitated the emission of ions, the saturation current at a pressure of 0.0238 mm. being nearly four times its normal value in a vacuum.

F. L. USHER.

Magnetostriction of diamagnetic substances in strong magnetic fields. P. KAPITZA (Nature, 1929, 124, 53).—Change of shape due to distortion produced by a magnetic field on the binding forces between atoms (atomic magnetostriction) has been observed with bismuth and other diamagnetic substances. It appears probable that the linkings between the atoms which lie further apart are weakened, whilst those between the closer atoms are strengthened.

A. A. ELDRIDGE.

Magnetic permeability of nickel in feeble oscillatory fields. R. G. LOYARTE (Univ. Nac. La Plata, Estud. Cien., 1928, 209—216).—Israel's observation of complicated permeability of nickel for oscillations of wave-lengths 28—60 cm. is attributed to the dependence of damping on the period.

CHEMICAL ABSTRACTS.

Determination of magnetic permeability of iron wires at high frequency by means of Wheatstone's bridge. K. KREIELSHEIMER (Z. Physik, 1929, 55, 753—770).—A method is described for the determination of the high-frequency resistance of iron wires by direct bridge measurements. From this the magnetic permeability may be obtained. With copper wire the resistance obtained agreed with the theoretical value to within $\pm 4\%$; this relatively large error is due to the comparatively small value of the resistance to be measured. For the permeability of iron the error is $\pm 1.7\%$.

A. J. MEE.

Theory of the plasticity of metals. H. SHŌJI (Sci. Rep. Tohoku, 1928, 18, 1—9).—Mathematical; modifications of the expression previously deduced to define plasticity (Z. Physik, 1928, 51, 728) are introduced.

A. R. POWELL.

Strength and plasticity of rock-salt crystals. E. SCHMID and O. VAUPEL (Z. Physik, 1929, 56, 308—329).—In agreement with the views of Sohncke (Ann. Phys. Chem., 1869, 137, 177) the breaking strength of rock-salt crystals is characterised by a limiting stress which can be withstood perpendicular to the cubic faces. The various possible slip mechanisms are discussed. Tempering produces a lowering of the elastic limit and of the tensile strength of rock-salt crystals. Experiments carried out with crystals stressed under water have led to results conflicting with the theory of the Joffé effect (A., 1924, ii, 384).

J. W. SMITH.

Heat effect in the stretching of brass crystals. M. MASIMA and G. SACHS (Z. Physik, 1929, 56, 394—396).—The amount of work dissipated in heat during the stretching of brass crystals has been followed by measuring the rise of temperature during the process. It was found that considerably more heat was liberated on each change in the slip mechanism than during simple slip on one slip plane.

J. W. SMITH.

Specific resistance of cupric sulphide and its temperature coefficient. K. FISCHBECK and O.

DORNER (Z. anorg. Chem., 1929, **181**, 372—378).—The specific resistance of cupric sulphide has been determined, using a spiral of the material prepared by immersing a copper spiral 70 cm. long and 0.1 mm. in diameter in sulphur vapour. Three series of experiments under varying conditions gave values for the specific resistance ranging from 36.76 to 42.33 microhm per cm., and a temperature coefficient of 0.0037; this latter is markedly higher than the value found by Bädcker (cf. A., 1907, ii, 327). The resistance is proportional to the temperature over the whole range investigated, between -80° and $+400^{\circ}$.

H. F. HARWOOD.

Influence of extension and contraction of the surface in the phenomenon of triboelectricity of mercury. V. POLARA (Nuovo Cim., 1928, **5**, 127—136; Chem. Zentr., 1929, i, 203).

Photo-*E.M.F.* in selenium. R. L. HANSON (J. Opt. Soc. Amer., 1929, **18**, 370—382).—Three types of selenium cells and the arrangements for a detailed study of photo-*E.M.F.* are described, and this was found over a wide range of applied *E.M.F.* to be independent of the current through the cell and to be related linearly to the intensity of illumination. The photo-*E.M.F.* sensitivity has a maximum for the visible spectrum in the region 490 m μ . It is shown that the photo-*E.M.F.* cannot be a thermal *E.M.F.*; the former was found to have no direct relation with the photo-electrical conductivity effect.

N. M. BLIGH.

Electrical conductivity of vapours of salts. H. QUERENGASSER (Z. Elektrochem., 1929, **35**, 459; cf. this vol., 634).—The work of Schmidt (A., 1927, 397), Kahra (this vol., 229), and Birkenberg (*ibid.*) is acknowledged.

H. T. S. BRITTON.

Contact potential measurements with adsorbed films. I. LANGMUIR and K. H. KINGDON (Physical Rev., 1929, [ii], **34**, 129—135).—Contact *P.D.* were measured between a clean unheated tungsten filament, and the same filament coated with an adsorbed film of thorium, caesium, oxygen, or a mixture of caesium and oxygen. The method used was intended to minimise surface contamination errors. The values found for the contact potentials between cold surfaces are, Cs,O,W—W, 3.1; Cs,W—W, 2.8; Th,W—W, 1.46; W—O,W, 0.8 volts. These values do not agree with those calculated from the thermionic emission constants. N. M. BLIGH.

Specific heats of para-hydrogen in the solid, liquid, and gaseous states. K. CLUSIUS and K. HILLER (Z. physikal. Chem., 1929, **B**, **4**, 158—168).—A method for obtaining para-hydrogen in large quantities is described. The specific heats of the liquid and solid para-form and its m. p. were determined; within the experimental error, the values obtained agree with those for ordinary hydrogen. The specific heat of para-hydrogen exceeds the classical value for a diatomic molecule at 115° Abs., and at 160° Abs. has the value 2.79 g.-cal. The possibility of obtaining the pure ortho-form is discussed.

A. J. MEE.

Detection of a transformation of ortho- into para-hydrogen by determinations of specific heat. A. EUCKEN and K. HILLER (Z. physikal. Chem., 1929, **B**, **4**, 142—157).—See this vol., 497. A. J. MEE.

Determinations of the specific heat of [air,] nitrogen, and carbon dioxide at high temperature. M. CHOPIN (Compt. rend., 1929, **188**, 1660—1662).—The author's methods (this vol., 44) show that for 200—1000° $C_p = 6.82 + 0.00058t$ for nitrogen and $8.9 + 0.61(t/100)^{0.63}$ for carbon dioxide. Air has C_p equal to that of nitrogen at 500° but 1% higher than that at 1000° . The results are compared with those of other workers.

J. GRANT.

Specific heats, heats of formation, and decomposition pressures of strontium halide hydrates. G. F. HUTTIG and C. SLONIM [in part with L. TRIP and O. MAIER] (Z. anorg. Chem., 1929, **181**, 65—77).—The above quantities have been experimentally determined and the molecular heats and total energy contents at temperatures between 50° and 350° Abs. calculated therefrom. Measurements on the dehydration of barium halide hydrates are included.

J. S. CARTER.

Lithium. VII. Specific heats, heats of formation, decomposition, pressures, and densities of lithium halide hydrates. C. SLONIM and G. F. HUTTIG [with O. MAIER] (Z. anorg. Chem., 1929, **181**, 55—64).—Determinations of the above quantities have enabled calculations to be made of the molecular heats and total energy contents at temperatures between 50° and 350° Abs.

J. S. CARTER.

Thermal data on organic compounds. V. Revision of the entropies and free energies of nineteen organic compounds. G. S. PARKS, K. K. KELLEY, and H. M. HUFFMAN (J. Amer. Chem. Soc., 1929, **51**, 1969—1973).—From experimental measurements made at sufficiently low temperatures, it is found that the molal heat capacity (*C*)—temperature curves fall into two not dissimilar classes, one for aliphatic and one for cyclic compounds. In each class the various curves are essentially similar and a standard curve has been constructed which holds up to 90° Abs. In either class the equation $C_p = (A + BT)C_p$ holds quite accurately, where *A* and *B* are constants characteristic of each substance (determined by substituting known values of *C* and *T* in the equation) and C_p is the heat capacity on the standard curve at *T*. The entropy values at 25° of several organic compounds are revised, and revised values for the free energies of the compounds are calculated therefrom with an accuracy which is limited almost entirely by the accuracy of the heats of combustion involved in the calculation. The general principle that the entropy of an organic compound changes in a definite, additive manner with changes in its constitution is confirmed.

S. K. TWEEDY.

Specific heats of important metallurgical substances. W. A. ROTH and W. BERTRAM (Z. Elektrochem., 1929, **35**, 297—308).—Two new types of calorimeter, designed to eliminate errors caused by evaporation of the calorimeter water on introducing the heated substance undergoing test, were used, viz., the "buffer-calorimeter" (cf. Roth, A., 1925, ii, 949) and an all-metal calorimeter in which the heated body is inserted in a silver vessel, fitted into a block of aluminium which is surrounded by a water-jacket (cf. Jaeger and Rosenbohm, A., 1928, 469).

The following data were obtained: α -Quartz,

transition point 575° , mean specific heats, at 96° , 0.1911; at 455° , 0.2325; at 503° , 0.2330. β -Quartz, $c = 0.1794 + 0.0001645(t - 20) - 0.000000085(t - 20)^2$ for $t = 575^\circ$ to 898° . Amorphous silica obtained by hydrolysing silicon tetrachloride, $c = 0.1782 + 0.000104(t - 20) - 0.0000000403(t - 20)^2$ for $t = 50^\circ$ to 933° . Quartz-glass (d^{18} 2.2058), $c = 0.1782 + 0.0001231(t - 20) - 0.00000004937(t - 20)^2$ for $t = 96.5^\circ$ to 855° . Calcium oxide, $c = 0.1823 + 0.0000879(t - 20) - 0.0000000366(t - 20)^2$ for $t = 417^\circ$ to 852° . Calcium metasilicate (d^{18} 2.9163), $c = 0.1749 + 0.0001107(t - 20) - 0.0000000485(t - 20)^2$ for $t = 50^\circ$ to 884° . Alumina, $c = 0.1930 + 0.0001382(t - 20) - 0.0000000705(t - 20)^2$ for $t = 96^\circ$ to 914° . Cryolite (artificial, d^{18} 2.9482) α -modification: transition point 565° , $c = 0.2251 + 0.0001977(t - 20) - 0.0000001086(t - 20)^2$, β -modification: from 565° to m. p., 1000° , $c = 0.2359 + 0.0001977(565 - 20) - 0.0000001086(565 - 20)^2 + 0.000100(t - 565)$. Calculation gave 1.24 kg.-cal. as the heat of transition and 16.64 kg.-cal. as the heat of fusion per mol. Sodium chloride, $c = 0.2066 + 0.00007024(t - 20) - 0.0000000375(t - 20)^2$ for $t = 99^\circ$ to 785° , m. p. 800° ; calculated heat of fusion 7.41 kg.-cal./mol. Iron (chief impurities, 0.18% P and 0.39% Mn), for temperatures up to 750° (transition point) $c = 0.1060 + 0.00006003(t - 20)$; calculated heat of transition 0.324 kg.-cal./g.-atom.

The specific heats of several iron ores were measured; the heats of formation of calcium metasilicate at temperatures varying from 20° to 900° were calculated.

H. T. S. BRITTON.

Thermal conductivity of copper, nickel, and some alloys of nickel. W. C. ELLIS, F. L. MORGAN, and G. F. SAGER (Rensselaer Polyt. Inst. Bull., 1929, 21, 1—23).—One end of a wire (0.25 cm. diam.) of the metal was heated by a coil through which a periodic current was passed so that a sinusoidal variation of temperature was produced in that end. At two points on the wire, separated by 2.3—4.69 cm., the temperatures were continuously recorded by thermocouples. The velocities (V_1 , V_2) of two heat waves of different periods (T_1 , T_2) were deduced from the time lag determined as the time elapsing between similar indications (passing through the zero) of the two galvanometers connected with the thermocouples. The thermal conductivity q ($=$ g.-cal./cm./sec./ $^\circ$ C.) is given by an equation, for which mathematical proof is furnished. The chief results are ($\kappa \times 10^5 =$ electrical conductivity = mhos/cm., $c =$ specific heat): copper (electrolytic) q 0.919, κ 5.58; nickel (Driver Harris R—12), q 0.168, κ 0.966; "Climax" (Fe 70, Ni 30), d 8.01, c 0.116, q 0.0329, κ 0.1052; "Climax 193" (Fe 68, Ni 29, Cr 2, Mn 1), d 8.01, c 0.114, q 0.0324, κ 0.1071; "nichrome IV" (Ni 80, Cr 20), d 8.39, c 0.104, q 0.0358, κ 0.0939; nichrome (Ni 62, Cr 12, Fe 26), d 8.40, c 0.107, q 0.0325, κ 0.0911; "Advance" (Cu 55, Ni 45), d 8.78, c 0.094, q 0.0546, κ 0.2032; Monel (Ni 70, Cu 28, Fe 2), d 8.94, c 0.132, q 0.0832, κ 0.2346. The results for copper and nickel show the accuracy of the method. The figures for the ratio thermal conductivity/electrical conductivity show that the Wiedemann-Franz law does not apply to these alloys.

C. A. SILBERRAD.

Specific heat of pure iron at high temperatures. S. UMINO (Sci. Rep. Tohoku, 1929, 18, 91—107).—The mean specific heat of iron increases abruptly at the A3, A4, and m. p., but between these points it increases linearly with rise of temperature. The true specific heat remains constant between the A2 and A3 points, where it decreases suddenly, then rises linearly to the A4 point, where there is a sudden increase to a value which remains constant to the m. p., after which it increases rapidly with further rise of temperature. The portions of the true specific heat-temperature curve just below and just above the γ -iron range fall on the same straight line. The heats of transformation at the A3 and A4 points and the latent heat of fusion are 5.60, 1.86, and 65.65 g.-cal./g., respectively. The ratio of the heats of transformation at the A3 and A4 points, namely 3 : 1, is the same as the ratio of the changes of length at the same points.

A. R. POWELL.

Calculation of latent heats of vaporisation of hydrocarbons and alcohols. J. W. SCHULTZ (Ind. Eng. Chem., 1929, 21, 557—559).—By the use of a Duhring line giving vapour pressures with a molal entropy line constructed from known latent heats, values have been determined for the latent heats from 0° to their respective critical temperatures for benzene, *n*-heptane, *n*-hexane, *n*-octane, ethyl and propyl alcohols. Comparison with determined results shows good agreement except in the region of the critical temperature, but this can be corrected graphically by making the latent heat-temperature curve intersect the abscissa at zero for the critical temperature. With ethyl and propyl alcohols it was found that by constructing the Duhring and entropy lines using methyl alcohol for reference instead of water as with the hydrocarbons, the points fell on a straight line over a much wider range of temperature.

H. S. GARLICK.

Supercooled water. L. HAWKES (Nature, 1929, 124, 225—226).—Water cooled at -17° to -22° may remain isotropic, and possibly hard. A deposit on cooling pipes at -22° consisted of a mixture of water drops and ice.

A. A. ELDRIDGE.

Properties of some very dry organic substances. J. TIMMERMANS (Bull. Soc. chim. Belg., 1929, 38, 160—162).—Benzene, *p*-xylene, and cyclohexane, dried in sealed tubes with phosphoric oxide for 35 months, failed to show the marked alterations in f. p. and surface tension observed by Baker. The views of Smits (A., 1928, 1189) are cited as an explanation of this apparent contradiction (cf. Lenher, this vol., 872).

B. W. ANDERSON.

Theoretical basis of the kinetic theory of gases. V. GLUMAC (Z. Physik, 1929, 56, 432—434).—The fundamental equation of the kinetic theory of gases is shown to follow directly from the Bernoulli formula $p/p + P + c^2/2 = \text{constant}$.

J. W. SMITH.

Extension of Avogadro's law. Application to the liquid state. I. N. LONGINESCU (J. Chim. phys., 1929, 26, 312—313).—The equation $P_i/n = \text{constant}$ is derived as a general statement of Avogadro's law for fluids. The total pressure (P_i) is equal to the sum of the external (P_e) and internal (P_i) pressures, and n is the number of molecules in unit volume. For gases

$P_i - P_e$, for liquids $P_i = P_e$. In the case of different liquids having the same internal pressure it follows that $M/D = \text{constant}$, i.e., that the density is a measure of the mol. wt. O. J. WALKER.

Relation between the internal pressure of fluids and some physico-chemical properties. I. N. LONGINESCU (J. Chim. phys., 1929, 26, 314—316).—An expression is obtained for the internal pressure of fluids assuming that the forces between the molecules can be represented by m^2/d^x , where d is the distance between two g.-mols., x is a constant ($=5$), and m is the "attractive mass" of a g.-mol. The latter quantity is additive and independent of temperature, pressure, and volume, but depends on the nature of the linking. The additivity of the attractive mass has been verified in 40 cases, and from it several formulæ involving the critical data of fluids can be derived. O. J. WALKER.

Effect of a gas on the pressure of a vapour. L. A. SAYCE and H. V. A. BRISCOE (J.C.S., 1929, 1302—1307).—The unsaturated vapour pressure exerted by a given concentration of ether is considerably lower in the presence of an indifferent gas (carbon dioxide at 500 mm.) than in a vacuum. The effect is even more marked with pentane vapour. The results disagree with Campbell's view (cf. A., 1915, ii, 516) that the diminution of the saturated vapour pressure of a liquid in the presence of a gas is to be attributed solely to the adsorption of gas in the liquid surface. F. L. USHER.

Saturated vapour pressures and the latent heat of evaporation. N. A. KOLOSOVSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 681—684).—Levalt-Ezerski's attempt (A., 1928, 1083) at generalising and extending the applicability of Magnus' equation for vapour pressures to all types of liquid is discussed and criticised. It is shown that his equation $\lambda = 2.3026aRT_0 = \text{constant}$, where λ is the latent heat of evaporation, is impossible and the agreement obtained between calculated and observed data is attributed to a confusion between λ , the total latent heat of evaporation, and λ_0 , the internal latent heat of evaporation. A. FREIMAN.

Vapour-pressure constant of neon. K. CLUSIUS (Z. physikal. Chem., 1929, B, 4, 1—13).—The specific heats of solid and liquid neon from 11° Abs. were determined. The heat of vaporisation of neon at 0° Abs. is found to be 447.6 g.-cal. From this the vapour-pressure constant of neon is calculated to be 0.39 ± 0.04 , which is in good agreement with the theoretical value of 0.37. It is shown that the assumption of different quantum weights for neon is not justified, as it is not also for argon and hydrogen. A. J. MEE.

Generalisation of the third law of thermodynamics for the case of gases. B. A. MESTSCHERSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 775—779).—Polemical against Kolosovski (this vol., 387). A. FREIMAN.

Change of coefficient of expansion of normal liquids with temperature. K. M. STACHORSKI (Ukraine Chem. J., 1928, 3, 457—462).—The expression $\alpha = 0.17T_c/(T_c - T)$ permits the calculation of the coefficient of expansion (α) of normal liquids for

temperatures between the b. p. and f. p. Using the data in Landolt-Bornstein tables, α is calculated for *n*-pentane, *n*-hexane, benzene, ether, ethyl acetate, ethyl propionate, fluorobenzene, chlorobenzene, carbon tetrachloride, and stannic chloride. For temperatures near the b. p. α can be assumed to be 0.18. The equations of Thorpe and Rucker (J.C.S., 1884, 45, 135), Oswald (A., 1912, ii, 230), and Davies (*ibid.*, 426) are shown to be incorrect, whilst the equations of Herz (cf. 1917, ii, 441) and of Kolosovski (A., 1927, 302) are simply limiting cases of the author's equation. For the case of associated liquids the "metacritical" temperatures (A., 1911, ii, 189) are calculated by means of the equation $T_m - T/(1 - 0.17/\alpha T)$ for ethyl alcohol, ether, and acetic acid. The results suggest that the degree of association of acetic acid does not change between its b. p. and its critical temperature. A. FREIMAN.

Vapour pressure of isopropyl acetate. C. J. HAGGERTY and J. F. WEILER (J. Amer. Chem. Soc., 1929, 51, 1623—1626).—The vapour pressures, measured between 0 and 90° by the method of Smith and Menzies (A., 1910, ii, 1037), are given by the equation $\log p(\text{mm.}) = 14.2517 - 2.0972 \log T - 2170.1/T$. The calculated b. p. is 88.2° and the calculated molal heat of vaporisation 7900 g.-cal. Determinations of the entropy of vaporisation indicate that isopropyl acetate is a normal liquid. S. K. TWEEDY.

Vapour pressure of ethylene chloride between -30° and 100°. J. N. PEARCE and P. E. PETERS (J. Physical Chem., 1929, 33, 873—878).—The vapour pressure of ethylene chloride between -30° and 100° has been determined; between -30° and 90° it can be represented, with an accuracy of less than 1 mm., by $\log p = -4481.12/T - 52.3092 \log T + 0.07153T - 0.000041847T^2 - 128.756$. Interpolation from the vapour pressure-temperature curve gives b. p. 84.1°/760 mm.; the molal heat of vaporisation at the b. p. is 7745 g.-cal.; the molal entropy of vaporisation is 21.68 g.-cal. and t_c (calc.) is 321.9°. L. S. THEOBALD.

Hydrocyanic acid. II. H. SINOSAKI and R. HARA (Tech. Rep. Tohoku, 1929, 8, 297—342).—Measurements of the vapour density of hydrogen cyanide have been made at temperatures between 0° and 190°, and at pressures between 100 and 830 mm. The relation between PV/T and P , for 1 g. of hydrogen cyanide, is given for the 0°, 30°, and 60° isotherms by $PV/T = R - bP - cP^2$, and for the 100° and 189° isotherms by $PV/T = R - bP$. The relationships between b and c and T are given respectively by $(\log b)^2 = -2.6393 + 0.010449T$, and $\log c = 4.4533 - 0.029123T$. At constant volume the relation between P and T is not linear, but is represented by a curve, of which the curvature increases as the volume diminishes. Taking into account the association of its molecules, the behaviour of hydrogen cyanide may be expressed with an accuracy of 0.1% by an equation of the Keyes type $P = [2308.61T(1 - \eta/2)]/[V - 12.82e^{-78.12/T} - 10^6 \times 28.235/[v^2 + 10^6 \times 0.290] \log(V - 8)]y = 15.33363 - 226.026/T - 5.7511 \log T$. The association factor of hydrogen cyanide was calculated from Keyes' equation at a series of temperatures and volumes. The value in general is small, the maximum recorded being 0.06549 at 30° and a volume of 1000 c.c./g. From

measurements of the density of liquid hydrogen cyanide between 0° and 30°, the following equation, having a probable accuracy of 2 in 150,000, was derived: $V_t = V_0(1 + 0.00200201t + 10^6 \times 6.175t^2)$.

F. G. TRYHORN.

Densities of single crystals of iron, nickel, and aluminium. S. KAYA (J. Study Met., 1928, 5, 385—386).—The densities of single crystals exceed those of polycrystals by 0.037, 0.110, and 0.034%, respectively.

CHEMICAL ABSTRACTS.

Density measurements at high temperatures. IX. Densities of molten gold, gold-silver, and silver-copper alloys. W. KRAUSE and F. SAUERWALD (Z. anorg. Chem., 1929, 181, 347—352).—Determinations of the densities by the buoyancy method at temperatures ranging from 18° to 1300° show that in all these cases the specific volumes have a linear relationship to the temperature and the composition of the alloy.

H. F. HARWOOD.

Density of molten metals and alloys. Y. MATUYAMA (Sci. Rep. Tohoku, 1929, 18, 19—46).—The density of tin, copper, cadmium, lead, and zinc and of seven binary alloys and six ternary alloys of these metals has been measured at temperatures between the m. p. and about 500°. The values of d for the molten metals at the m. p. found by extrapolation are: tin 6.986, bismuth 10.067, cadmium 8.017, lead 10.667, and zinc 6.562; these figures agree closely with those calculated from the expansion of the solid metal and the change of volume during melting. The coefficient of expansion of all the metals tested in the liquid state is almost independent of the temperature, having only a small tendency to decrease with rising temperature. The atomic volume of the molten alloys tested is somewhat greater than that of the mean atomic volume of the constituents; the maximum deviation of about 1% occurs with alloys containing a little more than 50 at.-% of the constituent of lower d . The equation of van Laar and Lorenz connecting the heat of mixture and volume change in alloys holds good for tin-cadmium, lead-cadmium, tin-zinc, and cadmium-zinc alloys.

A. R. POWELL.

Densities of co-existing liquid and gaseous nitrous oxide. E. L. QUINN and G. WERNIMONT (J. Amer. Chem. Soc., 1929, 51, 2002—2008).—The densities of liquid nitrous oxide (D) and of the saturated vapour (d) were determined by a modification of the method of Young (J.C.S., 1891, 59, 929) over the range of -50° to 40°. The results above 0° agree with those of Villard (A., 1894, ii, 379). The law of rectilinear diameter is accurately obeyed. The critical density is 0.459 and the molecular volume at 0° Abs., calculated by Sugden's equation, is 28.1 c.c. The equations for D and d deduced for carbon dioxide by Lowry and Erickson (A., 1928, 11) do not hold satisfactorily when applied to nitrous oxide.

S. K. TWEEDY.

Densities of liquid potassium and sodium. E. RINCK (Compt. rend., 1929, 189, 39—41).—Determinations of density from the pressure exerted on a nickelled copper plunger suspended in the doubly fractionated liquid metal gave results between the m. p. and 65° represented to within 1/500 by the straight lines $d_{Na} = 0.9835 - 0.000260(t - 96.5)$ and

$d_K = 0.826 - 0.000222(t - 62.4)$. Extrapolation to 900° enabled the constant of the Lorenz law (A., 1924, ii, 761) to be calculated for the system $Na + KCl \rightleftharpoons K + NaCl$.

J. GRANT.

Limiting volume of molecules. W. HERZ (Z. Elektrochem., 1929, 35, 457—458).—The ratios molecular refraction: $b_c (-RT_c/8p_c)$, the value of the characteristic constant in van der Waals' equation at the critical point) calculated for numerous liquids, vary from 1.75×10^3 to 6.98×10^3 . Several of the liquids which gave values lower than 3×10^3 had a low b. p. or were strongly associated, whilst those corresponding with values higher than 5×10^3 either had high b. p. or contained sulphur, bromine, or iodine.

H. T. S. BRITTON.

Volume changes in the softening range of glassy substances. G. TAMMANN and W. JELLINGHAUS (Ann. Physik, 1929, [v], 2, 264—284).—Selenium, salicin, and colophony have been investigated in the glassy condition. The determination of volumes in relation to temperature and pressure in the softening range disclosed that the isotherms for lower temperatures and for higher temperatures intersect at pressures below 1000 kg./cm.² Hence the volume of the material at high constant pressure at first decreases with rising temperature and then increases. Thus the volume isobars at high pressures exhibit weakly marked minima in the softening range. The results are interpreted theoretically.

R. A. MORTON.

Compressibility of carbon monoxide at 0° and various other temperatures, from 50 to 130 atm. S. GOIG BOTELLA (Anal. Fis. Quím., 1929, 27, 315—350).—A new series of determinations has been made of the isotherms of carbon monoxide at 0°, 12.44°, and 20.22°, in an apparatus resembling that of Amagat but with refinements whereby an error of not more than 0.02% is obtained. The isotherms, which have in each case been carried beyond the minimum on the pv - p curve, show that as regards its compressibility carbon monoxide comports itself normally, its behaviour resembling that of nitrogen. Amagat's results are confirmed substantially. Minimum values of pv were found at about 90, 80, and 70 atm. for 0°, 12.44°, and 20.22°, respectively. Full details are given for correcting the observations, for determining the normal volume of the gas taken, and for the use of the compressibility of hydrogen as a reference standard.

H. F. GILLBE.

Compressibility of carbon monoxide at 0° above 50 atm. S. GOIG (Compt. rend., 1929, 189, 246—248).—A summary of the methods and results of observations at 0° between 53.58 and 127.67 atm. (cf. preceding abstract).

J. GRANT.

Viscosity of vapours of organic compounds. I. T. TITANI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 433—460).—A new capillary viscosimeter has been devised which can be used with small quantities of gases at various temperatures; it is based on the resistance offered to a mercury column in passing through a narrow glass tube. The viscosities of 16 organic vapours, sulphur dioxide, and air have been determined at several temperatures between 20° and 120°, the results agreeing with Sutherland's formula.

The molecular diameters calculated from the kinetic theory of gases are in general agreement with those deduced from van der Waals' constant b calculated from the critical data. Except in a few cases, notably acetylene and allylene, the cube roots of the molecular volumes at the b. p. are proportional to the molecular diameters. The viscosities at 0°, Sutherland's constant, and the molecular diameters for the gases investigated are tabulated.

J. W. SMITH.

Viscosity of ether at low temperatures. E. VAN AUBEL (J.C.S., 1929, 1111).—The author shows that his relation between fluidity (ϕ) and temperature, $\phi = m + n \log(t_c - t)$, where m and n are constants (A., 1921, ii, 575), is, down to -92.2° , in agreement with the results of Archibald and Ure for ether (A., 1927, 404), the values used in the calculation being: $t_c = 193.8^\circ$, $m = 4003.46$, and $n = -1599.7$.

C. A. SILBERRAD.

Dielectric constant of binary mixtures. I. Methylene and ethylidene halides in benzene. P. C. MAHANTI and R. N. DAS-GUPTA (J. Indian Chem. Soc., 1929, 6, 411—417; cf. this vol., 242).—The dielectric constants of solutions of methylene and ethylidene chlorides, bromides, and iodides in benzene have been measured by the modified Nernst bridge method and the dipole moments calculated. The following values for the latter are given in electrostatic units: methylene chloride 1.61×10^{-18} , bromide 1.89×10^{-18} , iodide 2.12×10^{-18} ; ethylidene chloride 1.95×10^{-18} , bromide 2.12×10^{-18} , iodide 2.30×10^{-18} . The results afford further support for the mechanism of the molecular model previously suggested.

F. L. USHER.

Dielectric polarisation of liquids. IV. Dependence of molar refraction on concentration in mixtures. C. F. SMYTH, E. W. ENGEL, and E. B. WILSON, jun. (J. Amer. Chem. Soc., 1929, 51, 1736—1744).—The values of n_D^{20} were measured for several liquid pairs. The molecular refractivities of the components of a mixture are independent of the concentration to within 0.07%, indicating that the contribution to the polarisation of the electronic shifts induced in a molecule is practically independent of the surrounding molecules. This result does not support Sidgwick's views on the nature of molecular association in hydroxyl compounds. The fact that, e.g., alcohols, which according to Sidgwick are associated, fail to show a change of refraction on evaporation greater than that shown by supposedly unassociated substances also affords evidence that actual sharing of electrons between molecules during association of hydroxyl compounds does not occur.

S. K. TWEEDY.

Viscosity of binary systems with guaiacol as a component. N. A. PUSCHIN and T. PINTER (Z. physikal. Chem., 1929, 142, 211—226).—The authors discuss the trustworthiness of viscosity-concentration diagrams in their application as criteria for the existence of association or dissociation in binary systems. The viscosity and density of the binary mixtures of guaiacol with phenylhydrazine, quinoline, pyridine, aniline, o-toluidine, acetone, benzene, toluene, and mono- and di-methylaniline have been determined at 30°. The viscosity-composition and density-com-

position curves have been compared with the m. p.-composition curves. It is shown that the compounds of guaiacol with the first five amines as indicated by the thermal analysis are characterised by a maximum in the viscosity-composition curve. The position of the maximum shows that, except in the case of phenylhydrazine, the compounds are largely dissociated at 30°. The viscosity-composition curves of guaiacol with the other five substances are convex to the concentration axis. It is suggested that in these systems the association of guaiacol is less.

F. J. WILKINS.

Viscosity formula for binary mixtures, association of the constituents being taken into consideration. III. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1929, 4, 149—152; cf. this vol., 500).—The equation of Dunstan and Wilson (J.C.S., 1907, 91, 90) connecting η and mol. wt. can be written in the form $\log \eta = a - bM$. Data for the paraffins and their simpler derivatives show a to have the mean value of -3.22 , almost independent of temperature, whilst b varies with temperature and from one homologous series to another. For various liquids at 25° the values of b and of the field-constant k (*loc. cit.*) are practically the same when both are compared with those for benzene.

L. S. THEOBALD.

Lowering of the vapour pressure in concentrated solutions of two volatile components. E. KORDES (Z. anorg. Chem., 1929, 181, 203—224).—From Raoult's law it is deduced that the relative lowering of the vapour pressure of two volatile liquids in concentrated solutions may be expressed: $(P_b - p_b)/P_b : (P_a - p_a)/P_a = a.b$, where P_a and P_b are the vapour pressures of the two components in the pure state, p_a and p_b the corresponding partial pressures in the solution, and a and b the concentration in mol.-% of the respective liquids. If P_x is the total vapour pressure of the solution, it follows that $p_b/p_a = (b + a[(P_x - P_a)/P_a]) / (a + b[(P_x + P_b)/P_b])$. Thus if the composition of the liquid phase and the values of P_a and P_b are known, the composition of the vapour phase can be calculated if the total vapour pressure of the solution is determined. The calculated values for the systems nitrogen-oxygen at 74.7° Abs., water-formic acid at 80°, water-acetic acid at 80.09°, and acetone-chloroform at 55.1° agree reasonably well with those found experimentally. In the case of acetone-chloroform mixtures at 28° the calculated values are lower than the experimental values owing to the formation of the 1:1 compound. Molecular association in the vapour phase has no appreciable effect on the validity of the equations. The second equation may be modified to give the composition of the vapour phase at the b. p. of the mixture by substituting the relative molecular proportions of the compounds, b'/a' , for the relative partial pressures on the left-hand side. If c is the equilibrium constant of the system, then $a'/b' - p_a/p_b = (a/b)(P_a/P_b)^c$; for an ideal system c should equal 1, and the extent of its deviation from this value indicates the extent by which the system deviates from the ideal. For oxygen-nitrogen the deviations are very small, but for chloroform-acetone mixtures the value of c rises from -2 to $+4$ with increasing acetone concentration and for water-acetic acid mixtures from 0.2 to 2.3

with increasing acidity, although for mixtures containing 20–80 mol.-% of acid the value of c is approximately 1. The form of the various equations deduced for the lowering of the vapour pressures of the components of mixtures is similar to that of the equations previously deduced for the position of the eutectic point (cf. A., 1927, 1132). A. R. POWELL.

Determination of the b.-p. diagrams of high-boiling liquid mixtures. E. KORDES and F. RAAZ (Z. anorg. Chem., 1929, **181**, 225–236).—The apparatus of Ruff and Korschak (A., 1927, 102) has been used to determine the b. p. and vapour pressure of the systems mercury–cadmium and sodium chloride–potassium chloride and the composition of the vapour phase has been calculated by the method described in the preceding abstract. In the metal system the b. of the mixture rises in a smooth curve convex to the axis of composition, whereas the curve giving the composition of the saturated vapour phase is concave to this axis. In the salt system the curve is slightly concave to the axis of composition, joining the b. p. of the two constituents, 1411° for potassium chloride and 1430° for sodium chloride, and passing through a maximum at 1437° with 50–70 mol.-% of sodium chloride. The saturated vapour curve is almost identical with the b.-p. curve.

A. R. POWELL.

Binary azeotropes. XIV. M. LECAT (Ann. Soc. Sci. Bruxelles, 1929, **49**, B, ii, 109–118; cf. this vol., 756).—A further list is given of 81 positive azeotropes and 47 negative azeotropes, of 10 which are almost positive and 8 which are almost negative. The list includes 58 non-azeotropic pairs in which the isobar is convex towards the concentration axis, 34 in which it is concave, and 23 in which it is practically rectilinear; also 20 other non-azeotropic systems, and 10 in which rapid reaction takes place.

C. W. GIBBY.

Azeotropism in binary systems containing a phenol. M. LECAT (Ann. Soc. Sci. Bruxelles, 1929, **49**, B, ii, 119–143).—467 binary systems in which one constituent is phenolic have been investigated. Negative azeotropism is shown with alcohols (except glycol), ketones, and esters, positive azeotropism with glycol, acids, nitro-derivatives, halogen derivatives, and hydrocarbons, whilst amides, amines, and ethers generally exhibit no azeotropism. C. W. GIBBY.

Concentrated solutions. V. P. SCHISCHOKIN (Z. anorg. Chem., 1929, **181**, 137–153; cf. Mortimer, A., 1923, ii, 299).—Investigation of the f.-p. curves of a large number of binary systems has shown that the individual branches are represented by the equation $S = ke^{-a/T}$, where S is the concentration of the crystallising constituent, T the absolute temperature of the commencement of crystallisation, and k and a are constants, provided that the heat of fusion of the constituent derived from thermodynamic considerations is not greatly different from the actual value. Deviations from the exponential relation are indicative of reaction between the constituents. If binary mixtures of a substance A with substances B and C conform to the requirements of the exponential relation, this relation will also hold for mixtures of B and C . If the system $A-B$ obeys the relation and

the system $A-C$ does not, the relation will not apply to the system $B-C$.

J. S. CARTER.

Liquid mixtures of tellurium and sodium telluride. I. Specific resistance as a function of composition and temperature. II. Phase diagram of the system tellurium–sodium telluride. C. A. KRAUS and S. W. GLASS (J. Physical Chem., 1929, **33**, 984–994, 995–999).—I. The specific resistances of liquid mixtures of tellurium and sodium telluride have been measured at concentrations up to 54 at.-% Na and at temperatures between 300° and 500°, using a fused quartz cell of the type previously described (Kraus and Johnson, A., 1928, 1181). Mixtures rich in tellurium conduct well and behave as metallic conductors, whilst those rich in sodium telluride approximate to fused salts and conduct electrolytically. In all cases, the specific resistance decreases almost exponentially with a rise in temperature. Contrary to Pellini and Quercigh (A., 1910, ii, 1062), sodium telluride and tellurium appear to be completely miscible in the liquid state and the curves indicate the formation of the compound Na_2Te_6 with a congruent m. p. at 436°. A method for the preparation of these alloys by the addition of tellurium to sodium dissolved in liquid ammonia is described.

II. The equilibrium diagram for the system tellurium–sodium telluride has been determined by thermal analysis and shows complete miscibility of the components (see above). In addition to the normal telluride Na_2Te , the compounds Na_2Te_2 and Na_2Te_6 exist, the former showing a transition point at 355° and the latter a congruent m. p. at 436°, in agreement with the temperature found by the electrical method. Eutectics corresponding with the solid phases Na_2Te_2 and Na_2Te_6 , and Na_2Te_6 and tellurium, occur at 319° and 43 at.-% Na and 402.5° and 12.5 at.-% Na, respectively.

L. S. THEOBALD.

Copper–aluminium [alloys] containing tin or cobalt. E. MORLET (Compt. rend., 1929, **189**, 102–104).—Manganese (1–6%) increases the hardness and electrical resistance of copper–aluminium alloys containing 80–90% Cu and dissolves in the α - and γ -constituents without formation of a special constituent. Less than 6% of tin is dissolved when the aluminium content is below 80%, but otherwise a special δ -constituent is produced. Tin induces fragility. Cobalt dissolves in the α - and ($\alpha + \gamma$ -eutectic)-constituents to the extent of 1.27% and 1.66%, respectively, but higher proportions produce special constituents in each case.

J. GRANT.

Constitution of copper–beryllium alloys. G. MASING and O. DAHL (Wiss. Veroff. Siemens-Konz., 1929, **8**, [1], 94–100).—The system beryllium–copper has been investigated by microscopical and conductivity methods up to 12% Be. The saturated α -solid solution contains 2.8% Be at the peritectic temperature 865°, 1.72% at the eutectoid temperature 578°, and 0.75% at 400°. The eutectoid composition is 6% Be and the ($\alpha + \gamma$)-field extends from 1.72 to 11% at 578°. The β -field is bounded by slightly convex lines joining the eutectoid point with the peritectic at 4.2% and the solidus at 10.5%,

respectively. Numerous photomicrographs showing the characteristics of the various phases in copper-beryllium alloys are included. A. R. POWELL.

Magnetic measurements on iron-beryllium alloys. O. VON AUWERS (Wiss. Veroff. Siemens-Konz., 1929, 8, [1], 236—247).—The saturation value, coercivity, remanence, and permeability of beryllium-iron alloys containing up to 4% Be have been determined before and after heat treatment. With more than 3% Be the coercivity and wattage losses increase very rapidly, especially when carbon is also present; these alloys are therefore of no value for electrical apparatus. Alloys with less than 3% Be and some silicon have similar properties to silicon-iron alloys. The maximal permeability, remanence, B_r , and coercivity, H_c , are related by the expression $\mu_{\max} = 0.488B_r/H_c$. A. R. POWELL.

Changes in the etching structure of beryllium-copper alloys during ageing. G. MASING and O. DAHL (Wiss. Veroff. Siemens-Konz., 1929, 8, [1], 149—153).—During the ageing of beryllium-copper alloys at 350° the α - and β -crystals on etching with ammoniacal copper sulphate solution show a series of crystallographically regularly oriented lines which gradually increase in number and intensity. This phenomenon is ascribed to the gradual precipitation of γ from supersaturated α and from the breakdown of the β -phase. The lines are most intense when the hardness is at a maximum; further heating results in their slow disappearance.

A. R. POWELL.

Changes during the ageing of beryllium-copper alloys observed by roentgenographic methods. O. DAHL, E. HOLM, and G. MASING (Wiss. Veroff. Siemens-Konz., 1929, 8, [1], 154—186).—The α -solid solution phase in beryllium-copper alloys has a face-centred cubic lattice which in the case of the alloy with 2.5% Be has a parameter of 3.564 Å. compared with 3.619 Å. for pure copper. The γ -phase has a body-centred cubic lattice, $a = 2.70$ Å., in which the copper and beryllium atoms are regularly distributed, corresponding with the compound CuBe. On ageing the alloy with 2—2.5% Be at 350° the presence of γ is shown in the roentgenograms after 10 min.; at 150° the (331) line of the α -phase begins to become fogged after 4 hrs., indicating the beginning of the separation of γ , which causes a certain amount of internal stress. Wire which has been drawn after quenching hardens on ageing more rapidly and at lower temperatures than unworked wire. The crystals of the γ -phase after ageing have the same fibrous structure as the original α -crystals but are differently oriented, the (110) planes instead of the (111) planes being parallel to the direction of rolling.

A. R. POWELL.

Aluminium and its solid solutions with silicon. W. KOSTER (Z. anorg. Chem., 1929, 181, 295—297).—A criticism of the work of Anastasiadis (this vol., 501), the results of which are considered to be erroneous owing to insufficient annealing. The most probable boundary of the α -solid solution phase in the aluminium-silicon system is that found by Dix and Heath (B., 1928, 126). A. R. POWELL.

Germanium. XXXI. Alloys of germanium: silver-germanium. T. R. BRIGGS, R. O. McDUFFIE, and L. H. WILLISFORD (J. Physical Chem., 1929, 33, 1080—1096).—The equilibrium diagram for the system silver-germanium has been determined from thermal and metallographic data for temperatures between 600° and 1000°. The solid phases in equilibrium with the fused mass are pure germanium and a solid solution of germanium in silver. When saturated, this solid solution contains 6—7 at.-% Ge at 650°. No stable compounds are formed in the range investigated and the alloys form a simple eutectic series; the eutectic temperature is 650° and the eutectic composition 74 at.-% Ag. The specific conductances of the alloys from pure silver to the eutectic are low when compared with the values calculated from the mixture rule and lead to the conclusion that in the fine-structure of these particular alloys germanium predominates as the continuous phase. Comparison of this system with the silver-silicon and silver-tin systems shows it to be intermediate between silver and tin as regards the properties of the silver alloys. Photomicrographs are reproduced.

L. S. THEOBALD.

Crystalline form in the formation of solid solutions. V. Thermal and X-ray analyses of the systems $\text{CoCl}_2\text{--FeCl}_2$ and $\text{MnCl}_2\text{--FeCl}_2$. A. FERRARI, A. CELERI, and F. GIORGI (Atti R. Accad. Lincei, 1929, [vi], 9, 782—789).—No decomposition of the mixed crystals in these systems could be detected by the thermal method. An X-ray examination of the system $\text{CoCl}_2\text{--FeCl}_2$ shows that with increasing percentage of ferrous chloride the cobalt chloride lattice is increased in size (a , 7.05—7.155 Å.), whilst the rhombohedral angle remains constant at 60°. In the second system, a doubling of lines was observed due to the occurrence in the mixed crystals of a rhombohedral lattice with an angle different from 60° which is peculiar to pure ferrous chloride. In this case with increasing manganese chloride content a increases from 7.16 to 7.20 Å., α from 60° 17' to 61° 25', and c/a decreases from 2.434 to 2.370.

F. G. TRYHORN.

X-Ray study of the formation of zinc silicates. A. PABST (Z. physikal. Chem., 1929, 142, 227—232).—Mixtures of zinc oxide and silica in the proportions required for the formation of zinc ortho- and meta-silicates were heated at varying temperatures and powder photographs of the products were prepared. Zinc metasilicate is not formed, the orthosilicate being always obtained even when the composition corresponds with the metasilicate. Further, the results support the statement of Tammann (A., 1926, 921) that the reaction between zinc oxide and silica begins at 775°.

F. J. WILKINS.

Miscibility of phenol with aqueous salt solutions. G. CLAXTON and H. M. DAWSON (Proc. Leeds Phil. Soc., 1929, 1, 416—420).—The solubility of phenol in aqueous solutions containing varying amounts of salts is determined. In all cases the exponential formula $S - S_0 = e^{-km}$ is obeyed, where S_0 and S are the concentrations in pure water and in the aqueous solution, respectively, m is the molar concentration of the salt, and k is a constant. The

salts used were sodium chloride, sodium sulphate, and calcium chloride. It would be expected, however, that S_0 would be independent of the nature of the dissolved salt. This is not the case. The deviation is probably connected with the interionic forces which are responsible for the deviations shown by electrolytes in dilute solutions. The constant k also varies with the nature of the salt. A. J. MEE.

Solubility of calcium carbonate (calcite) in certain aqueous solutions at 25°. G. L. FREAR and J. JOHNSTON (J. Amer. Chem. Soc., 1929, **51**, 2082—2093).—The solubility of calcite at 25° is recorded for various partial pressures (p) of carbon dioxide. The solubility product (in terms of activity) is 4.82×10^{-9} . The concentration of calcium hydrogen carbonate in solution varies approximately as the cube root of p . The solubility of calcite in solutions of gypsum and of sodium chloride at values of p up to 1 atm. was also measured. No solid solution or double salt formation occurs when these salts are present in solid phase. The ratio of the solubility of calcite in a dilute salt solution of constant concentration to that in water is independent of p . The activity coefficients of calcium hydrogen carbonate are calculated; they are higher than usual for salts of the uni-bivalent type. S. K. TWEEDY.

Solubility of magnesium carbonate (nesquehonte) in water at 25° and pressures of carbon dioxide up to 1 atm. W. D. KLINE (J. Amer. Chem. Soc., 1929, **51**, 2093—2097).—The solubility at 25° of magnesium carbonate trihydrate is recorded for pressures of carbon dioxide up to 1 atm. At high pressures the trihydrate is the stable solid phase, but below $p=0.0004$ atm. magnesium hydroxide becomes the stable salt. There is no evidence of definite basic carbonates. The solubility product (in terms of activity) is 1×10^{-5} for magnesium carbonate and about 5×10^{-12} for magnesium hydroxide. S. K. TWEEDY.

Solubility of the phosphates of calcium in aqueous solutions of sulphur dioxide. W. M. MEBANE, J. T. DOBBINS, and F. K. CAMERON (J. Physical Chem., 1929, **33**, 961—969).—The system lime-phosphorus pentoxide-sulphur dioxide-water has been investigated analytically at 0° and 25° in relation to the possibility of a technical process for the manufacture of monocalcium phosphate or superphosphates. The addition of sulphur dioxide to aqueous suspensions of the phosphates of calcium increases the solubility of both the lime and the phosphoric acid, the former to a greater extent than the latter. Three solubility curves have been obtained. For small concentrations of phosphoric acid the solubility of sulphur dioxide in the liquid phase rises to a maximum and then falls, the solid phases being calcium sulphite and a series of solid solutions of which dicalcium phosphate is a limiting member. For medium concentrations of phosphoric acid the solubility of sulphur dioxide again reaches a maximum and the solid phases consist of the mono- and di-phosphates. For high concentrations of phosphoric acid the solubility of sulphur dioxide is approximately constant and negligible, and the solid phase is monocalcium phosphate. Treatment of a

phosphatic rock with sulphur dioxide yields a solution in which the ratio P_2O_5/CaO is only slightly greater than in the dicalcium salt, and the large percentage of water to be removed makes the process impracticable on a large scale. L. S. THEOBALD.

Germanium. IV. Solubility of germanium dioxide in acids and alkalis. W. PUGH (J.C.S., 1929, 1537—1541).—The solubility at 25° of germanium dioxide has been determined in hydrochloric acid solutions (up to 7.62*N*), in sulphuric acid solutions (up to 95%), and in sodium hydroxide solutions (up to 0.1*N*). As an acid oxide its solubility is repressed by hydrochloric acid, reaching a minimum of 0.074 g./100 c.c. at an acid concentration of 5.3*N*. In sulphuric acid the solubility falls steadily with increase of acidity, no evidence occurring of the formation of germanium sulphate. Solutions in sodium hydroxide solution are colloidal and may contain salts of condensed germanic acid. F. G. TRYHORN.

Oxidisability of silicon and its solubility in hydrofluoric acid. C. BEDEL (Compt. rend., 1929, **189**, 180—182).—The author has failed to repeat Sanfourche's experiments (this vol., 1030), which suggested that the solubility of silicon in hydrofluoric acid is the result of previous oxidation in air. The catalytic effect of impurities is regarded as a more likely explanation (cf. this vol., 756). J. GRANT.

Solubility of arsenic tri- and penta-sulphides. R. HÖLTJE (Z. anorg. Chem., 1929, **181**, 395—407).—The solubility of the two sulphides in pure water and hydrogen sulphide solution at 0° has been determined by an analytical method, the sulphide being digested with the solvent for several days, the solution filtered through a Zsigmondy ultra-filter, and the dissolved arsenic determined iodometrically in the filtrate. One litre of water at 0° dissolves 0.89 mg. of arsenic trisulphide and 1.36 mg. of the pentasulphide, but in the presence of 0.002% of hydrogen sulphide these amounts are reduced to 0.23 mg. and 0.27 mg., respectively. Higher concentrations of hydrogen sulphide increase the solubility of the sulphides, but this effect is offset by the presence of hydrochloric acid, being probably due to the formation of small amounts of arsenic thio-acids. For analytical purposes the precipitation of arsenic trisulphide by hydrogen sulphide from a solution containing hydrochloric acid is complete as soon as the solution has become saturated with the gas, but in the case of the precipitation of the pentasulphide by the addition of acid to a thioarsenate solution it is preferable to keep the liquid over-night before filtration; removal of the excess of hydrogen sulphide is unnecessary. H. F. HARWOOD.

Solubilities of the soluble electrolytes. I. Relationships between the temperature coefficients. A. F. SCOTT (J. Physical Chem., 1929, **33**, 1000—1014).—A theoretical paper in which certain relationships between the temperature coefficients of solubility are deduced and an explanatory theory is outlined. The ratio of the temperature coefficients for a pair of salts which fulfil certain conditions is independent of the temperature. The

ratio at different temperatures is identical for all salts with the same dominant ion, *i.e.*, an ion which, in a saturated solution of a very soluble salt, controls the water molecules to the exclusion of the weaker ion. The solubilities of potassium chloride, bromide, and iodide and of rubidium and caesium chlorides are represented by the equation $N_{\text{salt}} = aN_{\text{KCl}} + b$, where N is number of mols. of water per mol. of salt and a and b are specific constants. Between 0° and 100° the ratio of the temperature coefficients for any of these salts is determined by the characteristic constant a . The significance of the discontinuities now revealed in the solubility curves of various salts is also discussed. L. S. THEOBALD.

Factors affecting solubility. L. J. WEBER (Z. anorg. Chem., 1929, **181**, 385—394).—Correlation of Rothmund's solubility determinations for lithium carbonate, silver sulphate, and potassium bromate in the presence of various non-electrolytes with Traube's surface tension values for the latter shows that the diminution of solubility increases in inverse ratio to the surface tension of the added non-electrolyte. Experiments with potassium sulphate also indicate a relationship between solubility and surface tension, but the results are less easily interpreted than those preceding. Similar data for potassium hydrogen tartrate, sodium oxalate, potassium chlorate, and lead chloride in the presence of 21 non-electrolytes agree with the first series in the case of the alkali salts, but the results for lead chloride are untrustworthy owing to the formation of compounds. Conversely, salts which lower the surface tension of water increase the solubility of certain non-electrolytes, *isoamyl* alcohol, for example, being 275 times as soluble in a 30% solution of sodium cinnamate as in pure water. H. F. HARWOOD.

Solubility and dissolution velocity of solids. N. E. GAPON (J. Russ. Phys. Chem. Soc., 1929, **61**, 369—374).—Regarding the process of dissolution of a solid in a liquid as a gradual change and applying the ideas developed by Richardson for the emission of electrons from hot bodies, it is deduced that the critical increment of solution is given by $E - Q' + RT/2$, where Q' is the heat of dissolution of the dissolving substance, and that $K/C\sqrt{T} = \text{const.}$, where K is the dissolution coefficient and C the solubility. On the other hand, the diffusion theory of dissolution leads to $E = W + RT$, where W for most of the solids investigated is identical with the latent heat of fusion, and $d \log_e K/dT = d \log_e \phi/dT + 1/T$, where ϕ is the fluidity.

Experiments on the solubility of benzoic acid at 20° , 40° , and 60° according to Wilderman's method (Z. physikal. Chem., 1908, **66**, 445) support the conclusions of the author's theory rather than those of the diffusion theory. A. FREIMAN.

Solubilities of inorganic salts. S. S. URAZOVSKI (Ukraine Chem. J., 1929, **4**, 7—12).—Fajans' theory (Naturwiss., 1923, **11**, 1165) which attempts to explain the different solubilities of inorganic salts by the different degrees of deformation of their outer electronic shells is shown to be incorrect. It is suggested that the solubilities are determined by the difference in the atomic numbers between the cation

and anion and that the solubility is lowest when the difference is a minimum, and *vice versa*.

A. FREIMAN.

Distribution of trichloroacetic acid between water and organic solvents. L. M. ANDREASOV (Ukraine Chem. J., 1928, **3**, 463—465).—The distribution of trichloroacetic acid between water and benzene, water and nitrobenzene, water and chloroform, water and carbon disulphide, and water and carbon tetrachloride has been determined. In benzene, nitrobenzene, chloroform, and carbon disulphide double molecules are formed, whilst in carbon tetrachloride the acid exists in single molecules. These results disagree with those found by ebullioscopic and cryoscopic methods by other workers.

A. FREIMAN.

Attempted measurement of the partition coefficient of a colloid, gelatin, between two liquids. R. M. WOODMAN and P. H. GALLAGHER (J. Physical Chem., 1929, **33**, 1097—1106; cf. A., 1926, 676).—Measurements of the distribution of gelatin between water and cresol have been attempted, and a partition hypothesis relating to the mechanism of the formation of the emulsions and of the dual types (*loc. cit.*) which complicate the system is advanced. The gelatin is said to be in the colloidal state in both solvents, but the large experimental errors preclude the possibility of determining whether any difference in partition accounts for the formation of two types of emulsion. The partition coefficient, calculated on the simple law, largely favours the cresol. The hypothesis that cresol extracts the gelatin completely from the aqueous solution is untenable, and on the assumption that the partition is mainly determined by the mutual solubility of the two solvents the value 66.6 in favour of the cresol is obtained. This agrees with the experimental values of 73 and 69 found for two different concentrations of gelatin at 13.5° . The stability of the water-in-cresol and the instability of the cresol-in-water emulsions are explained by the fact that the partition coefficient favours the cresol layer. L. S. THEOBALD.

Adsorption with active charcoal. E. ENGEL (Svensk Kem. Tidskr., 1929, **41**, 157—168).—The nature of the adsorption of gases by charcoal is discussed. The "resistance time" of a charcoal, *i.e.*, the length of time required for a definite amount of charcoal to remove a substance from a current of air charged with the vapour of the materials, is given by Mecklenburg's equation, $R = k/vC(V - Qh)$. The values of R , k , and h have now been determined for four different varieties of charcoal, using chlorine, carbonyl chloride, and chloropicrin as the substances to be removed. The results show that for one and the same charcoal adsorption takes place most readily with the substance of greatest mol. wt., but no regularity between the different samples is traceable. Only one of the samples gave results conforming to Freundlich's formula for adsorption isotherms, the other three showing marked divergences. In the removal of a constituent from a gas current by passage through charcoal, the speed of the gas current, the size of the charcoal particles, and the presence of moisture all have a marked influence

on the efficiency of the adsorption, and these factors must therefore be taken into account in technical applications.

H. F. HARWOOD.

Sorption of water vapour by activated charcoals. II. Isothermals in presence of air. A. J. ALLMAND, R. CHAPLIN, and D. O. SHIELDS (J. Physical Chem., 1929, 33, 1151—1160; cf. A., 1928, 471).—Data relating to the rates of sorption and desorption of the charcoals previously described (*loc. cit.*) show that the rates, in general, are less than 0.5 mg. of water vapour per g. of charcoal per mm. pressure difference per hr., that sorption is less rapid than desorption at low and medium pressures but more rapid at higher pressures, that the three charcoals investigated show little difference between each other or when evacuated at 270° or 800°, and, finally, that for any given isotherm the maximum rate of sorption or desorption occurs in the intermediate pressure range over which a small pressure difference corresponds with a large change in the amount of water vapour sorbed. All the isotherms studied show considerable hysteresis and those given by the different charcoals previously evacuated under practically identical conditions differ considerably from each other. Lastly, the effect of the temperature of outgassing is quite definite, for charcoals outgassed at 800° compared with those outgassed at 270° show a larger increase in weight on saturation with air, a higher saturation value, more marked hysteresis, and a greater tendency to retain water after passing dry air at 25°. A discussion of results is reserved.

L. S. THEOBALD.

Sorption of water vapour by activated charcoals. III. Isothermals in presence of nitrogen. A. J. ALLMAND and P. G. T. HAND (J. Physical Chem., 1929, 33, 1161—1166).—A repetition of previous work (cf. preceding abstract) with a current of nitrogen replacing that of air shows that oxygen has no retarding effect on the processes concerned with the adsorption of water vapour by charcoal. The rates of sorption and desorption and the isotherms are similar to those obtained in the presence of air; the hysteresis is of the same magnitude, and the effect of a higher outgassing temperature is even more marked.

L. S. THEOBALD.

Heat of adsorption of oxygen on [coconut] charcoal. M. J. MARSHALL and H. E. BRAMSTON-COOK (J. Amer. Chem. Soc., 1929, 51, 2019—2029).—The differential heat of adsorption, Q , was measured down to very low oxygen concentrations. The Q - c curves, c being the concentration of the oxygen in the charcoal, tend to flatten near $Q=70,000$ g.-cal. (Keyes and Marshall, A., 1927, 207) and then rise abruptly, so that at $c=0$ Q is about 89,600 g.-cal. A curve constructed from the results shows the apparent distribution of activities of the elementary spaces on the carbon surface; the curve does not, as a whole, resemble the probability curve, and three possible explanations of the shape of the curve are discussed. At least 85% of the total elementary spaces have heats of adsorption below 8000 g.-cal. The results are best explained by the multimolecular layer theory of Keyes and Marshall. The specific

surface of the carbon is estimated to be $3-6 \times 10^4$ cm.² per g.

S. K. TWEEDY.

Interferometric investigation of adsorption by pure carbon from non-aqueous binary systems. F. E. BARTELL and C. K. SLOAN (J. Amer. Chem. Soc., 1929, 51, 1637—1643).—The adsorption of 1-bromonaphthalene, benzene, and ethyl carbonate from dilute solution in ethyl alcohol conforms to Freundlich's adsorption isotherm at the low solute concentrations investigated. The order of adsorption from dilute solutions is the same as that of the adhesion tension of the pure solutes against carbon, a result which would probably be universal if external factors did not interfere.

S. K. TWEEDY.

Adsorption by pure carbon from non-aqueous binary systems over the entire concentration range. F. E. BARTELL and C. K. SLOAN (J. Amer. Chem. Soc., 1929, 51, 1643—1656).—The work described in the preceding abstract is extended to the entire concentration range, additional binary systems also being investigated. The component with the higher adhesion tension against carbon is adsorbed to the greater extent, although the other component when it is present at very low concentration is preferentially adsorbed, which causes the adsorption curves to be S-shaped. The adsorption is represented by an equation similar to that used by Ostwald (A., 1923, ii, 128); this equation is derived on the assumption that the adsorption of each component follows Freundlich's adsorption isotherm. Gibbs' adsorption principle is restated in terms of adhesion tension, which restatement indicates the importance of many factors usually ignored in the formulation of the principle, *e.g.*, electrical properties of the boundary layer etc. Adsorption from binary systems by silica, as in the case of carbon, depends on the adhesion tension of the adsorbed component against silica.

S. K. TWEEDY.

Charcoal as an adsorbent. II. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1929, 61, 587—594).—The adsorption of organic and inorganic acids on sugar charcoal prepared by carbonisation at 500° increases with the capillary activity of the acid. In the case of charcoal similarly prepared at 800°, the adsorption follows the reverse order. This difference is due to the presence of amorphous carbon in the first and of microcrystalline carbon in the second product. Neither of these charcoals adsorbs alkalis if they are previously freed from adsorbed carbon dioxide. Similar effects are obtained with wood charcoal, provided that this has previously been freed from inorganic salts. The inactivation of charcoal by prolonged heating at high temperatures appears to be due to the coating of its surface with graphite.

R. TRUSZKOWSKI.

Adsorption and volume of solution. A. RABINERSON (Kolloid-Z., 1929, 48, 231—237).—Measurements of the adsorption of succinic and acetic acids by vegetable charcoal show that when the amounts of adsorbent and adsorbed material are kept constant the degree of adsorption decreases with increasing volume of solution. Over a fairly wide region, the following equation was found to be valid: $x = kv^{-1/n}$,

where x is the amount adsorbed, v is the volume, and k and n are constants. The exponent $1/n$ is not identical with that of the ordinary adsorption equation: it has a lower value. Comparison of the curves relating the amount adsorbed to the amount of adsorbent and the curves relating the amount adsorbed to the amount of substance before adsorption shows that in each case the former curve passes through higher values, and leads to an explanation of the variation of the amount of adsorption with the volume. In regions of high concentration or low volume the x - v curve changes its sign, and the complete curve consists of two branches, the first rising and the second falling.

E. S. HEDGES.

Influence of hydrogen-ion concentration on the adsorption of weak electrolytes by pure charcoals. H. J. PHELPS and R. A. PETERS (Proc. Roy. Soc., 1929, A, 124, 554—568).—The importance of this subject with respect to enzyme chemistry is emphasised, and previous work is briefly reviewed. Commercial norit charcoal, purified by Miller's method (A., 1926, 898) and activated by heating to redness in a vacuum, was used, and various p_H values were obtained, in the case of simple acids and bases, by partial neutralisation with strong acids and bases, and in the case of other substances by the addition of small amounts of buffer solutions. The equilibrium

values were determined by the bubbling hydrogen electrode except in the case of very dilute histidine and histamine solutions, where the colorimetric method was made. The analytical methods adopted for the determination of propionic and hexoic acids, succinic acid, n -propylamine and n -butylamine, and glycine, alanine, glutamic acid, aspartic acid, histidine, and histamine are described. Propionic, hexoic, and succinic acids are decreasingly adsorbed with increasing alkalinity between the limits p_H 3.0 and 7.0, and the change follows approximately the ionisation curves of the acids. In the case of n -propylamine and n -butylamine adsorption increases with increasing alkalinity, but the effect is not directly correlated with the ionisation of the base. In accordance with the observations of Michaelis, no pronounced adsorption is found for glycine, alanine, or aspartic acid at any p_H . The adsorptions of histidine and histamine are compared. They give similar adsorptions from p_H 4.0 to 7.3, after which that of histidine slightly decreases with increasing alkalinity, whilst that of histamine rises to completion at p_H 10.0. The results with histidine can be explained by the classical theory of the dissociation of the amino-acids, but those with glycine, alanine, and aspartic acid require further explanation. It is inferred that adsorption proceeds through the medium of the non-ionised molecule, in contradiction to the theory of Bartell and Miller that adsorption takes place through the medium of the ion (cf. A., 1924, ii, 734). The results are considered to be consistent with Langmuir's theory of adsorption from solution.

L. L. BIRCUMSHAW.

Adsorption of iodine, bromine, and some halides by carbon in different organic liquids. J. TRIVIDIC (Rev. gen. Colloid., 1929, 7, 14—24, 67—73).—Measurements have been made of the

adsorption of iodine and bromine by two kinds of activated vegetable charcoals in a number of different organic liquids including alcohols, saturated chlorinated hydrocarbons, and aromatic hydrocarbons. Contrary to the result obtained by Davis (J.C.S., 1907, 91, 1666), the adsorption of iodine and bromine by activated charcoal proceeds in accordance with the formula of Freundlich. For a series of liquids of similar chemical constitution there appears to be a relation between the quantities of iodine fixed by the carbon and the mol. wt. and densities of the liquids. There also exists a relation between the quantities of iodine or bromine adsorbed by carbon in mixtures of two solvents and the quantities adsorbed in each of the pure liquids, and in these mixtures the adsorption is again in accordance with the Freundlich formula. Measurements of the adsorption of alkali halides in aqueous-alcoholic solution by charcoal gave inconclusive results because of the small degree of adsorption.

E. S. HEDGES.

Adsorption of sulphur dioxide by platinised asbestos. D. O. SHIELDS (J. Physical Chem., 1929, 33, 1167—1174).—The sorption of sulphur dioxide by platinised and ordinary asbestos has been determined at 25° and at pressures up to 40 mm. Sorption is reversible, without the occurrence of hysteresis, and the isotherm is represented in both cases by Langmuir's equation $q = abp/(1 + ap)$, where q is the quantity of gas adsorbed per gram of adsorbent, p is the equilibrium pressure (mm.), and a and b are constants. The adsorption by platinised asbestos is much the greater.

L. S. THEOBALD.

Adsorption of sulphur dioxide by platinum-black. D. O. SHIELDS (J. Physical Chem., 1929, 33, 1175—1183).—The adsorption of sulphur dioxide by platinum-black has been measured at 25° and at pressures from 0 to 175 mm. The process is irreversible, 84 volumes of gas at N.T.P. per unit volume of platinum being adsorbed, and 54 volumes being retained even after 8½ hrs. at 250°. There appears to be a strong, irreversible adsorption accompanied by a weaker and more nearly reversible effect which shows some hysteresis. This last may be due to oxidation of sulphur dioxide to the trioxide at active centres of the platinum-black. The curve obtained on subsequent adsorption follows a course parallel to the desorption curve and not to the first adsorption curve, indicating that adsorbed impurities are not responsible for the hysteresis.

L. S. THEOBALD.

Low-pressure adsorption on a washed glass surface. H. S. FRANK (J. Physical Chem., 1929, 33, 970—976).—The adsorption of water vapour by a surface of pyrex glass washed by hot chromic acid solution has been measured at 25° over the range 5.2×10^{-3} to 8.7×10^{-2} mm. by means of a new form of all-glass manometer. A high-frequency ultramicro-meter method was used to follow the movement of the diaphragm. The results indicate that the adsorption is a slow but reversible process and that an acid-washed glass surface is not plane, but is covered by a layer of silica gel (cf. Frazer, Patrick, and Smith, A., 1927, 722; Latham, this vol., 134).

L. S. THEOBALD.

Adsorption on glass and determination of the adsorbing surface. N. S. SCHENKER (J. Russ. Phys. Chem. Soc., 1929, 61, 413—421).—The adsorption of methyl-violet BB, diamond-fuchsin, and brilliant-safranin on glass-wool has been studied. The total adsorbing surface was found by measuring the length and thickness of each separate thread. The thickness of a thread was determined by means of a precision micrometer screw which had a total internal reflexion prism attached to its head so as to facilitate the taking of readings and make them more accurate. The concentration of dye in the 0.2 c.c. of solution used was determined by means of a specially adopted König-Martens spectrophotometer. The adsorption of methyl-violet BB was found to be 1.78×10^{-7} g./c.c. and of diamond-fuchsin 1.79×10^{-7} g./c.c., agreeing closely with the values found by Schmidt and Durau (A., 1924, ii, 238). The author also determined by the method of Paneth and Thimann (A., 1924, ii, 612) the thickness of the adsorbed layer and found it to be unimolecular in the case of methyl-violet BB and of diamond-fuchsin and to cover about 83% of the glass surface, whilst the layer of the brilliant-safranin is assumed to be unimicellar.

A. FREIMAN.

Adsorption of certain acids by wool. W. W. PADDON (J. Physical Chem., 1929, 33, 1107—1108).—Wool adsorbs tartaric acid less readily than hydrochloric or sulphuric acid from boiling aqueous solutions. In concentrations up to 2 mg.-mol. of acid/250 c.c. sulphuric acid is more readily adsorbed than hydrochloric acid, but at higher concentrations the reverse is the case. No evidence of compound formation between the wool and the acid has been obtained.

L. S. THEOBALD.

Adsorption of electrolytes by crystalline surfaces. II. (MLLE.) L. DE BROUCKERE (Bull. Soc. chim. Belg., 1929, 38, 212—222).—See this vol., 757.

Influence of ammonia on the adsorption of copper or nickel salts. M. GELOSO and (MLLE.) L. S. LEVY (Compt. rend., 1929, 189, 175—177).—Known volumes of a standard solution of iron alum were added to ammoniacal solutions of ammonium sulphate and copper or nickel sulphate and the precipitated ferric oxide was analysed after 3 hrs. at 22°. The adsorption of the copper or nickel salt is influenced considerably by the concentration of ammonia which is not itself detectable in the precipitate, but may have been adsorbed and subsequently removed by washing. Alternatively it may exert its effect simply by an increase of the p_H value.

J. GRANT.

Adsorption of gases and vapours and the Langmuir theory. H. ZEISE (Z. Elektrochem., 1929, 35, 426—431).—The Langmuir adsorption isotherm is discussed, and new interpretations are given to the coefficients involved therein (cf. A., 1928, 1182). The contentions of Pólanýi (this vol., 256) are criticised.

H. T. S. BRITTON.

Potential theory of adsorption. M. PÓLANÝI (Z. Elektrochem., 1929, 35, 431—432).—A reply to Zeise (preceding abstract) and a statement of the principles underlying the author's purely physical theory.

H. T. S. BRITTON.

Shapes of drops, and the determination of surface tension. B. B. FREUD and W. D. HARKINS (J. Physical Chem., 1929, 33, 1217—1234).—A theoretical paper in which the drop-weight method is discussed under the three heads: the hanging, detached, and detaching drop. The theory of the first is treated mathematically. Profiles of hanging and detaching drops taken by a motion-picture camera are reproduced.

L. S. THEOBALD.

Capillary phenomena in non-circular cylindrical tubes. W. O. SMITH and P. D. FOOTE (Ind. Eng. Chem., 1929, 21, 567—568).—Expressions are deduced relating the surface tension of a liquid with the rise in capillary tubes of rectangular and elliptical cross-section. Comparison of theoretical with experimental values shows agreement within the limits of accuracy of the measurements. It is pointed out that the vapour pressure over the surface of a liquid is different for circular and non-circular capillaries of the same cross-sectional area.

H. INGLESON.

Surface tension of fused metals and alloys. III. Gold, zinc, gold-copper, silver-copper, and iron alloys. W. KRAUSE and F. SAUERWALD [with M. MICHALKE] (Z. anorg. Chem., 1929, 181, 353—371).—The surface tension of various gold-copper and silver-copper alloys, zinc, and alloys of iron with carbon, silicon, and phosphorus has been measured by the maximum bubble pressure method (cf. A., 1926, 790); in the case of zinc and the iron alloys the apparatus must be somewhat modified. The noble metals and their alloys and the above-mentioned iron alloys all exhibit a high surface tension in the fused state; a noteworthy feature of the iron alloys is their positive temperature coefficient. Some of the silver and gold alloys also show a maximum surface tension dependent on the temperature.

H. F. HARWOOD.

Dependence of surface tension and latent heat of vaporisation on the density and temperature up to the critical temperature. W. HERZ (Z. anorg. Chem., 1929, 181, 280—284).—Polemical against van Laar (this vol., 641).

A. R. POWELL.

Surface properties of soap solutions. W. C. PRESTON and A. S. RICHARDSON (J. Physical Chem., 1929, 33, 1142—1150).—Simultaneous measurements of surface viscosity (rotating-disc method), surface tension (drop method), and foaming power of soap solutions of distinct types, before and after exposure to air, have failed to reveal any simple correlation of these three properties. Low surface tension does not necessarily involve tendency to foam, and the combination of low surface tension with high surface viscosity or plasticity does not invariably confer high foaming power. Unknown factors determine this.

L. S. THEOBALD.

Surface varnishes on water and molecular dimensions. A. MARCELIN (Compt. rend., 1929, 189, 236—238).—If V is the volume of surface varnish on water in a state of maximum extension, S the area covered, l the length of the molecules, E the extension coefficient of the varnish, and C the coefficient of surface reduction necessary to compress the surface solution to the saturation point, then $l = VC/SE$. This formula gives results in good agreement with

X-ray spectrographic methods for oleic, myristic, palmitic, and stearic acids and for cetyl alcohol, whilst those obtained by Langmuir's method are low on account of decrease in the re-extension coefficient with increasing dilution of the benzene solution used for the production of the varnish. A surface film increases in solubility with increase in surface pressure and temperature (cf. following abstract).

J. GRANT.

Surface solutions and molecular varnishes. Determination of the lengths of their molecules. F. ÉMIR (Compt. rend., 1929, 189, 239—240; cf. this vol., 876).—Marcelin's formula (cf. preceding abstract) gives results in good agreement with X-ray spectrographic methods for palmitic and stearic acids and for cetyl alcohol.

J. GRANT.

Surface solutions of oleic acid. Measurement of very low pressures. J. GUASTALLA (Compt. rend., 1929, 189, 241—243; cf. preceding abstracts).—Marcelin's determinations of the pressure of surface solutions (A., 1926, 120) have been extended to very low pressures by means of a more sensitive modification of the apparatus used, a feature of which is the collection of impurities on the liquid surface by means of a jet of filtered compressed air, and their removal by aspiration. The extension curves of oleic acid on 0.01*N*-hydrochloric acid at 19° correspond with Mariotte's law for surface areas of 60—500 Å.², the value of the coefficient *K* being *R*/20. From 500 to 5000 Å.² the fall of pressure is only 0.007 dyne/cm., but beyond this it decreases considerably, and a Mariotte hyperbola in which *K*—*R* is obtained (cf. Adam and Jessop, A., 1926, 468). J. GRANT.

Orientation of molecules at solid surfaces and the range of action of the orienting forces. D. TALMUD (Z. physikal. Chem., 1929, 142, 233—236).—When an aqueous suspension of a hydrophilic powder such as calcium carbonate or barium sulphate, containing a drop of oleic acid, is shaken with a liquid which is insoluble in and less dense than water, a considerable quantity of this liquid becomes adsorbed on the powder. Addition of an excess of oleic acid sets the liquid free. Further, a suspension in water of a hydrophobic powder such as lead sulphide will adsorb a considerable quantity of benzene which is set free on addition of one drop of oleic acid. In explanation, it is suggested that oleic acid is adsorbed on hydrophilic powders by its hydrophilic groups. The hydrophobic groups are free and able to attach benzene to themselves. With the hydrophobic lead sulphide, the hydrophilic groups of the oleic acid remain free and these are unable to adsorb benzene. Calculations made on the results of experiments with calcium carbonate suspensions and amyl alcohol show that the thickness of the adsorbed layer of amyl alcohol decreases with increase in the amount of oleic acid present.

F. J. WILKINS.

Optical investigation of metallic films rendered active and passive by electrochemical means. L. TRONSTAD (Z. physikal. Chem., 1929, 142, 241—281).—The nature of the polarisation of the light reflected from iron and nickel mirrors which have been rendered passive by various means has been investigated. The change of the optical properties of iron

and nickel films made passive in alkaline solution and of nickel films treated in acid solution resembles that which results when a clean iron surface is brought from vacuum into contact with air. Characteristic limiting values of the optical properties are exhibited in each case. Re-activation of a passive surface produces a reversion of its optical behaviour, but even on prolonged activation the initial state of the surface is never re-attained. Repeated changes from the active to the passive state, and *vice versa*, result in much greater changes taking place in the optical properties than result from passivity produced by one operation extending over a prolonged period. The passive state is regarded as being due to the presence of an unbroken surface of oxide film, which, on activation of the surface, is fractured and rendered porous, without, however, being destroyed. A theory of the passive state has been developed by consideration of the electric charge of the oxide film and the cataphoretic movement of the latter during the passage of the current. The theory is in close agreement with the observed behaviour of nickel film in acid solutions both at low and at relatively high current densities.

H. F. GILLBE.

Interference effect at the disturbed surface of a liquid and surface tension. Z. V. VOLKOVA and V. S. TIROV (Z. physikal. Chem., 1929, B, 4, 71—82).—The effect of variation of surface tension on the interference effect obtained with a beam of light at the disturbed surface of a liquid was studied by using solutions of inorganic substances which increase the surface tension of water. The substances used were such as to increase the surface tension according to a linear law, viz., calcium, magnesium, and lithium chlorides, and sodium and potassium hydroxides. The addition of these substances made the interference effect more stable and lasting. The concentration of the dissolved substance and the deviation of the rays are linearly connected. An attempt is made to explain this phenomenon on the hypothesis that there is a layer of particles which stands out a certain height from the level of the disturbed surface.

A. J. MEE.

Heat of wetting of powders by solutions of interfacially active substances, and heats of adsorption in solutions. Heat effect of the formation of dispersed systems. II. P. REHBINDER and L. KRAJUSCHKINA (Z. physikal. Chem., 1929, 142, 282—288; cf. A., 1927, 193).—Microcalorimetric measurements have been made of the heats of adsorption of isoamyl alcohol from aqueous solution by carbon, and of *n*-butyric acid from aqueous and *n*-hexane solutions by silica powder and by carbon. The heat of wetting of a hydrophilic powder (silica) by a solution increases with increase of dielectric constant of the pure solvent, whereas the reverse holds for hydrophobic powders. The heat of adsorption from a solution is, in accordance with theory, a minimum for those cases in which the heat of wetting is a maximum. The relationships between the differential and integral heats of adsorption and the concentration of the solution are discussed.

H. F. GILLBE.

Temperature at the liquid-solid interface during the crystallisation of supercooled sub-

stances. H. POLLATSCHKE (Z. physikal. Chem., 1929, 142, 289—300).—A method has been devised for the determination of the temperature prevailing at the liquid-solid interface of a crystallising super-cooled liquid. Measurements with salol indicate that, in contradiction to Tammann's assumption, the temperature at the boundary during the process of crystallisation does not reach the m. p. of the substance.

H. F. GILLBE.

Electrokinetic potential of gold in very dilute solutions of electrolytes. P. A. THIESSEN and J. HEUMANN (Z. anorg. Chem., 1929, 181, 379—384).—The electrokinetic potential of gold in very dilute (10^{-8} to $10^{-5}N$) solutions of potassium sulphate and of the chlorides of potassium, caesium, and lithium has been investigated, using a modification of Coehn's apparatus (cf. A., 1927, 420). The negative electrokinetic potential exhibits a maximum value at a concentration of about $10^{-7}N$, and this result can be explained satisfactorily in terms of Debye's theory of a diffuse double layer.

H. F. HARWOOD.

Micelles and membrane equilibria. J. DUCLAUX and R. TITEICA (Compt. rend., 1929, 189, 101—102).—The composition of the liquid removed by ultra-filtration of hydrosols of iron (produced by hydrolysis of ferric chloride at 100°), copper ferrocyanide, Congo-red, and caramel is independent of the nature of the membrane (cellulose, or its nitrate or acetate) and of the pressure employed, and does not change as the micelles become concentrated. Such equilibria are therefore heterogeneous and the intermicellar liquid is that actually removed by ultra-filtration.

J. GRANT.

Polarisation of membranes due to metallic plates. J. LOISELEUR (Compt. rend., 1929, 189, 170—171).—When a metal plate is placed in a solution of an electrolyte containing an animal membrane (bladder), the latter is polarised to an extent which depends on the nature of the metal and its surface, and also on the electrolyte. The effect decreases with time and with increase in concentration of the electrolyte. A modification of the ionic distribution in the different parts of the septum is suggested as an explanation.

J. GRANT.

Diffusion experiments with sugar-protein solutions. D. KRÜGER (Biochem. Z., 1929, 209, 119—127; cf. Loeb and Krüger, A., 1928, 786).—Diffusion experiments carried out with the systems dextrose-egg-albumin, dextrose-caseinogen, dextrose-glycine, and dextrose- α -alanine indicate that, at neutral reaction, no appreciable condensation between the sugar and the protein or amino-acid takes place.

W. MCCARTNEY.

Preparation, analyses, and lead-ion concentration of solutions of colloidal lead. H. S. KEELAN, R. B. SMITH, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1929, 18, 586—589).—The solutions were prepared by sparking lead electrodes dipped in a slowly agitated mixture of water containing gelatin, potassium chloride, and lead, covered with liquid paraffin. The materials used were oxygen-free. Such preparations are non-toxic. The amount of lead in the solution was determined

colorimetrically as lead sulphide. The lead-ion concentrations varied between 1.8×10^{-9} and 5.3×10^{-11} and were not altered by sterilisation. These values are probably due to a small amount of a very insoluble unidentified lead salt. The partition coefficient of lead acetate between water and liquid paraffin varies with the degree of agitation of the mixture.

C. C. N. VASS.

Tartaric acid method for the synthesis of electronegative sols. IV. A. DUMANSKI and A. JAKOVLEV (J. Russ. Phys. Chem. Soc., 1929, 61, 213—215).—See A., 1928, 1321.

Molecularly dispersed silicic acid. H. BRINTZINGER and B. TROEMER (Z. anorg. Chem., 1929, 181, 237—248).—The state of dispersion of silicic acid, prepared by the decomposition of alkali silicate with hydrochloric acid, by hydrolysis of silicon tetrachloride by ice-cold water alone and in the presence of silver oxide, by hydrolysis of methyl silicate by water and by $0.001N$ -, $0.01N$ -, and $0.1N$ -hydrochloric acid, and by hydrolysis of ethyl silicate by $0.01N$ -hydrochloric acid has been determined by measuring its rate of diffusion through parchment and cellophane. The results are expressed by plotting the logarithm of the concentration in the dialyser against the time; for an ionic or a molecularly dispersed substance this is a straight line inclined downwards, whereas for silicic acid solutions the line is curved more or less upwards from the ideal straight line, indicating a certain amount of polymerisation and the presence of two or more states of aggregation. Silicic acid produced by hydrolysis of alkyl silicates is in the most highly dispersed form, the $\log C-t$ curve approximating to a straight line; high acidity of the hydrolysing liquid favours polymerisation, whereas a small acidity favours the production of the molecularly dispersed form. The p_H value of both molecularly dispersed and colloidal dispersed silicic acid solutions is 4.7. The ageing of silicic acid solutions is accelerated by the absence of electrolytes and by the presence of alcohol; in feebly acid solutions the formation of di- and tetra-silicic acid may be detected during ageing, whereas the acid produced by hydrolysis of alkyl silicates rapidly condenses to large molecules.

A. R. POWELL.

Preparation of finely-dispersed colloidal gold. M. DOMANICKI (Ukraine Chem. J., 1929, 4, 1—6).—Amylene, hexylene, diisobutylene, diallyl, and some other unsaturated hydrocarbons have been used in the preparation of colloidal gold sols from alkaline solutions of sodium and potassium aurate. The conditions to be observed and the properties of the sols are described. Although a colloidal palladium sol can be prepared by this method from an alkaline solution of palladium chloride, this is not the case for silver and platinum.

A. FREIMAN.

Germanate gels of the alkaline earths. J. H. MÜLLER and C. E. GULEZIN (J. Amer. Chem. Soc., 1929, 51, 2029—2042).—Rapid and thorough mixing of a solution of germanic acid with suitable excess of calcium hydroxide solution produces precipitation of transparent (or translucent) homogeneous gels of calcium germanate of extremely high dispersion ("solid" gel). The acid and base concentrations

may vary between wide limits, but the temperature should be between 15° and 25°. The lime is responsible for the gelation phenomena. The gel is readily destroyed by mechanical means (agitation, suction-filtration), leaving practically pure calcium metagermanate; however, it is permanent if protected from dry air and carbon dioxide, and is not affected by temperatures up to 95°. The water present, which appears simply to be trapped in the form of lime water by minute fibres of the dispersed calcium salt, may be mechanically replaced by ethyl or methyl alcohol, ether, and benzene, usually with decrease in size and increase in firmness. Addition of lime water forms a characteristic test for germanium dioxide in solution, since the presence of the latter produces an extraordinarily bulky hydrogel.

Strontium gels, which are opaque, are obtained as above, but the reagents must be of higher concentration. Barium germanate forms octahedral, isotropic, crystals, soluble to the extent of 0.07536 g. in 100 g. of solution at 25°. S. K. TWEEDY.

Organo-gels. E. DA FANO (Giorn. Chim. Ind. Appl., 1929, 11, 199—203).—Confirmation is obtained of the fact that certain sodium soaps are dispersed by hot organic solvents, giving coherent gels on cooling. This phenomenon is general and many new gels have been prepared in this way. Small additions of certain substances, mostly fatty acids, act as protective colloids, facilitating the formation of sols and gels, for instance, with formates, acetates, propionates, butyrates, valerates, etc. in various organic solvents, and with other sodium soaps in dense mineral oils, tars, and bitumens. T. H. POPE.

Refractive index of colloidal solutions of sulphur. G. ROSSI and A. MARESCOTTI (Gazzetta, 1929, 59, 309—313).—The refractive index of a solution containing sulphuric acid and sodium sulphate is increased by the presence of sulphur in colloidal suspension. For a given concentration of electrolytes the increase in refractive index is proportional to the sulphur content, but the relative increase becomes smaller as the concentration of the electrolytes increases. F. G. TRYHORN.

Osmometer for measuring the osmotic pressure of colloids. A. GRIGAUT and A. BOUTROUX (J. Pharm. Chim., 1929, [viii], 10, 9—15).—See this vol., 761.

Structure and electrification of smoke particles. H. S. PATTERSON, R. WHYTLAW-GRAY, and W. CAWOOD (Proc. Roy. Soc., 1929, A, 124, 523—532).—The microscopic methods employed previously for large aggregates (cf. A., 1927, 17) have been improved so as to allow of the examination of the so-called ultramicroscopic particles present in dilute smokes. The type of particle appears to depend mainly on the method used to produce the smoke. High-temperature reactions and the arc discharge favour the formation of loose aggregates with a high degree of complexity, whilst volatilisation at a lower temperature gives rise to larger particles of a more compact structure composed of relatively few units. Of the former type the smokes of cadmium oxide, magnesium oxide, silver, and gold have been examined,

and of the latter arsenious oxide, mercuric chloride, and a number of organic substances. In the case of *m*-xyleneazo- β -naphthol a remarkable effect was observed after the particles had been deposited by sedimentation, some of the crystalline particles developing very long, hair-like tails of extreme tenuity; these grew at the expense of the crystal aggregates, until finally, in many cases, very long hairs only were left. Experiments were carried out to determine the influence of electrification on the rate of coagulation, a horizontal electric field being applied to the particles in a special ultramicroscopic cell and the proportion of electrified particles at different periods during the life of the smoke being obtained by direct counting. The results indicate that the electrification of a smoke depends largely on the way in which it is produced. The particles in smokes volatilised from a heater are initially but slightly charged, although the charge increases as the cloud ages; on the other hand, smokes made by the arc or by burning magnesium ribbon are highly charged. In smokes of ammonium chloride, about 70% of the particles finally become charged, the numbers of positively and negatively charged particles being equal, within the limits of error. Magnesium oxide smokes are also electrically neutral as a whole, about 90% of the particles being charged. No marked difference is observed in the coagulation rates of comparable smokes differing greatly in electrical character. L. L. BIRCHUMSHAW.

Structure of colloids. P. P. VON WEIMARN (Rev. gen. Colloid., 1929, 7, 153—158).—A reiteration of the author's views on the colloidal state.

E. S. HEDGES.

Pectography of colloidal solutions of metallic sulphides. P. BARY and J. V. RUBIO (Compt. rend., 1929, 189, 294—296).—Pectographs (patterns obtained by spontaneous evaporation of colloidal solutions in warm air or over sulphuric acid) of the sulphides of antimony, arsenic, zinc, mercury, cadmium, molybdenum, and copper are described. With the exception of copper sulphide the sulphides are deposited in thin layers of gel which gradually lose their imbibed water and crack in patterns.

J. GRANT.

Gel structure. Gels obtained with salts of quinine, optoquin, and eucupine. P. THOMAS and (Mlle.) M. SIBI (Compt. rend., 1929, 189, 292—294).—Gels prepared from mixtures of solutions of the hydrochlorides of quinine, optoquin, or eucupine (*isoamylhydrocupreine*) with saturated sodium acetate solution deposit long, fine, hair-like crystals after 15 min., several hrs., and some months, respectively. The mean diameters are 1—3 μ in all cases, including lithium urate, sodium oleate, and sorbitol acetal, and the mixtures rendered homogeneous by warming will redeposit gels with unchanged properties.

J. GRANT.

Chemistry of "tiles," and the plastic state. ZACHARIAS (Rev. gén. Colloid., 1929, 7, 201—205).—The nomenclature of colloid systems is discussed. The term "tile" (Gr. $\tau\iota\lambda\eta$) is introduced to designate an ultramicroscopic or microscopic particle. The term "solution" is used to comprise all liquid

mixtures, such as molecular solutions, "tilous" solutions, suspensions, and emulsions. "Absorption" denotes any penetration of one substance into another, such as a gas or other substance in a liquid, a jelly, or a porous body. It is pointed out that the idea of "tilous" solutions and jellies as two-phase systems is inconsistent, the notion of a surface of separation ceasing to be applicable below certain sizes of particles.

E. S. HEDGES.

Velocity function of the viscosity of disperse systems. G. W. S. BLAIR (*Kolloid-Z.*, 1929, 48, 283).—Polemical (cf. this vol., 262).

E. S. HEDGES.

Stability of colloidal solutions. A. BOUTARIC (*Rev. gen. Colloid.*, 1929, 7, 49—52).—Electrical charge is not the only factor determining the stability of a colloidal micelle. If the micelles are placed in a very feeble concentration of electrolyte, the ions cannot be adsorbed in sufficient numbers to neutralise the charge and those that are adsorbed will produce slow transformations within the micelle which may alter its whole character. Flocculation will take place only when so great a concentration of ions is present that they are adsorbed more quickly than the micelle can undergo the necessary transformations to resist their action.

E. S. HEDGES.

Factors of stability of colloidal systems. S. I. DIATSKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 423—440).—Two criteria for the stability of colloidal systems are assumed. First, their stability with time, *e.g.*, the persistence of the Brownian movement, the constancy of the electrical conductivity and of other physico-chemical properties, and, secondly, their stability towards electrolytes. The present investigation covers the negatively-charged sol of tungstic acid and positively-charged sol of ferric hydroxide, and the negatively-charged suspension of tungstic anhydride and positively-charged suspension of ferric hydroxide. To five separate quantities of 50 c.c. of a *N*-solution of sodium tungstate were added calculated amounts of hydrochloric acid, so that the solutions should contain $\text{Na}_2\text{O}, 2\text{WO}_3$, $\text{Na}_2\text{O}, 3\text{WO}_3$, $\text{Na}_2\text{O}, 4\text{WO}_3$, $\text{Na}_2\text{O}, 5\text{WO}_3$, and $\text{Na}_2\text{O}, 6\text{WO}_3$, respectively. To a further 100 c.c. of the sodium tungstate solution was added an excess of concentrated hydrochloric acid so that the solution should contain $\text{Na}_2\text{O}, 8\text{WO}_3$. A 0.1*N*-solution of potassium chloride was used as coagulator, and in each case the p_H , the velocity of coagulation, and the ultramicroscopic appearance were observed. The stabilising factors in this case are partly chemical and partly electrostatic in nature. So long as hydration of the colloidal particle continues the system is chemically unstable, but as soon as hydration is completed the system becomes chemically stable and stable towards electrolytes and the size of the electrical double layer becomes of the greatest importance. Since the presence of sodium and hydrogen ions affects the stability of the system the author investigated the effect of their removal on the stability, by determining the p_H of the suspension formed, its electrical conductivity, its ultramicroscopic appearance, the cataphoretic velocity of the particles, their rate of sedimentation, and from this, by applying Stokes' law, their radius, and,

finally, their density by several different methods. In this case the electrical double layer is of utmost importance. As soon as it becomes steady, the stability of the system and the degree of dispersion begin to increase and the system becomes chemically stable. The iron hydroxide sol was prepared by Graham's method, whilst the suspension was prepared by washing the iron hydroxide obtained by treating a ferric chloride solution with ammonia. The sol was dialysed for 150 days, when a shock was sufficient to gelatinise it. The p_H of the dialysed sol was determined by means of the quinhydrone electrode and its electrical conductivity was found to decrease continuously with dialysis. The suspension was decanted 20 times, when its electrical conductivity, its p_H , its cataphoretic velocity, and its coagulation velocity, both with a 0.1*N*-solution of potassium sulphate and with a 0.1*N*-solution of potassium chloride, and the rate of settling of the particles were determined. In contradistinction to the observation of other workers (*e.g.*, Handovsky, A., 1926, 23) it is found that the colloidal micelles of the iron hydroxide on prolonged dialysis do not show any trace of losing chlorine ions. It is concluded that the stability of the system is to a very large extent determined by its degree of hydration. Finally, the author points out that his results do not agree with von Weimarn's views.

A. FREEMAN.

Surface tension and stability of colloidal solutions. G. ROSSI and A. MARESCOTTI (*Gazzetta*, 1929, 59, 313—319).—The stability of arsenious sulphide sols is greatly enhanced by the addition of 0.6% of gelatin, although the surface tension, determined by the stalagmometric method, is unaltered. On the other hand, the surface tension and stability of ferric hydroxide sols are unaffected by the addition of 0.04% of gelatin.

F. G. TRYHORN.

Oxidation of colloidal arsenic, antimony, and copper sulphides. M. SWIDERSKA, W. KOSTANECKA, and P. WARSZAWSKA (*Rocz. Chem.*, 1929, 9, 411—417).—Colloidal arsenious sulphide undergoes oxidation in the presence of atmospheric oxygen, the products being arsenious oxide, free sulphur, and sulphuric acid. The last-named substance has a precipitative influence on the colloid present, and to this influence may be ascribed many of the apparently anomalous properties of arsenious sulphide sols. Oxygen has a similar effect on antimonious sulphide sols, but free sulphur is not formed in this case. With copper sulphide sols, the sulphuric acid, which is formed initially, disappears to some extent later, probably as a result of the formation of polythionic acids, and copper is not found in the filtrate until the excess of hydrogen sulphide has been expelled; at this point the sulphuric acid content of the suspension becomes constant.

R. TRUSZKOWSKI.

Emulsions: stability, area per molecule in the interfacial film, distribution of sizes, and the oriented wedge theory. W. D. HARKINS and N. BEEMAN (*J. Amer. Chem. Soc.*, 1929, 51, 1674—1694).—The size distribution of the oil droplets in liquid hydrocarbon emulsions produced by oleate soaps is the same for lithium, sodium, and caesium oleates. This result is independent of the viscosity

of the hydrocarbon, but the higher is this viscosity the greater is the diameter of the larger drops. The size distribution in fresh emulsions is independent of the soap concentration, but it varies on ageing. Emulsions made with soap solutions $>0.01M$ are stable over long periods of time; emulsions produced by very dilute soaps are unstable. The method of preparation has no influence on the maximum diameter of the drops. The presence of the corresponding hydroxide at a concentration above $1M$, or of oleic acid at $0.1M$, causes an increase in the number of small drops at the expense of the large drops. Variation in the hydrocarbon chains of the soaps has no effect on the size distribution, except in the case of potassium chaulmoograte, when the number of the smallest drops is greatly increased. The emulsions of water in oil produced by magnesium and aluminium soaps show a size distribution similar to that of the oil-in-water types; benzene-in-water emulsions also show the same size distribution. Calculation of the molar areas at the interfacial film in oil-in-water emulsions indicates that none of the soap films is thicker than unimolecular; it shows, indeed, that concentrated emulsions may be produced by means of an interfacial soap film in which the number of soap molecules is less than corresponds with a closely-packed unimolecular film.

S. K. TWEEDY.

Chemical effects of high-frequency sound waves. II. Emulsifying action. W. T. RICHARDS (J. Amer. Chem. Soc., 1929, 51, 1724—1729).—The emulsification of water and benzene and of water and mercury is due largely to action at the walls of the containing vessel. In the case of mercury the action depends on the amount of this metal present; an excess may arrest the emulsification, which is attributed to the damping action of the metal on the waves in the glass. Water is probably emulsified in the mercury; the action is accelerated by the presence of ammonium chloride. The walls of glass vessels are slightly emulsified in water when subjected to the action of high-frequency sound waves; small, uniform glass particles are not fractured by intense sound waves. A method of roughly estimating relative sound intensities by emulsifying action is described.

S. K. TWEEDY.

Certain phenomena in electric and magnetic fields. T. KUCZYŃSKI (Przemysł Chem., 1929, 13, 137—144, 161—167).—Microscopical examination of emulsions in high-frequency alternating fields shows that the drops of the dispersed phase first undergo deformation and then arrange themselves in chains along the lines of force. In emulsions of water in oil, coagulation then supervenes, the chains conducting the current, whilst in the case of oil in water coagulation does not occur, and the chains distribute themselves over the regions of least current density. In charging a condenser with an emulsion as dielectric, energy is absorbed, not only in polarising the dielectric, but also in the mechanical work associated with the deformation of the drops of dispersed phase, and changes in their distribution throughout the disperse phase. The dielectric constant of emulsions depends on the distribution of the dispersed phase. It is shown mathematically that, where the drops of the latter

are small in comparison with the condenser, the dielectric constant does not depend on their size, but is a function of their aggregate volume, provided that they are uniformly distributed throughout the medium.

R. TRUSZKOWSKI.

Influence of light on some colloids. (MISS) S. ROY (J. Indian Chem. Soc., 1929, 6, 431—440; cf. Ganguly and Dhar, A., 1922, ii, 604).—Observations on the coagulation, electric conductivity, and extinction coefficients of sols of stannic, aluminium, and thorium hydroxides, of antimony, arsenious, and mercuric sulphides, and of uranium and cupric ferrocyanides, when exposed to light, show that all, except the ferrocyanides, acquire increased conducting power after exposure. A short exposure increases the stability of arsenious and antimony sulphides and uranium and cupric ferrocyanides, but on longer exposure all become less stable, and sols of antimony sulphide, mercuric sulphide, and uranium ferrocyanide coagulate completely. F. L. USHER.

Process of coagulation in smokes. H. S. PATTERSON, R. WHYTELAW-GRAY, and W. CAWOOD (Proc. Roy. Soc., 1929, A, 124, 502—522; cf. A., 1927, 9, 17).—Using an improved method of counting, the effect of particle size and the degree of heterogeneity on the rate of coagulation of ammonium chloride and resin smokes has been investigated. The particles are made brighter and more easily observable by introducing moisture into the cell. The series of particulate volume curves representing the results show that the process of coagulation in dilute clouds is not a simple linear function of the time, and that the average value of K in the equation $\sigma = \sigma_0 + Kt$ (cf. A., 1927, 1139) increases definitely with fall of weight concentration. From an estimate of the amount of solid matter present in the dispersed state it appears that the actual weight concentration of the smoke is invariably smaller than the weight volatilised, and that there is no constant proportionality between the two. If counting experiments are made with smokes of different concentrations in which the actual mass present in the particulate state is determined experimentally, then the previous haphazard variations disappear, and in all cases the change in form of the curves runs parallel to the mass of material in the smoke and the results are expressible by a comparatively simple formula. With a view to explore the early stages of coagulation the smoke was diluted immediately after formation by blowing a rapid stream of air over the volatilising material, and in this way evidence was obtained that the true initial number of particles was extremely high—probably of the order of 10^{12} per c.c. It is inferred that the smoke is formed initially by molecular collision, in contradistinction to the idea of condensation around nuclei already present. The results indicate why it is so difficult to obtain smokes of the same behaviour on different occasions, since reproducibility not only depends on following the same procedure for dispersal, but is also conditioned by the time at which the very rapid initial coagulation is slowed down by dilution. The collision theory of coagulation is discussed at length, and the underlying postulates of the Smoluchowski theory for systems originally homogeneous and the

modifications necessary to make it generally valid are considered. The course of coagulation may be expressed by the semi-empirical relation $\sigma = \sigma_0 + 2.20 \times 10^{-8}(1 + 9 \times 10^{-6}r^{-1})t$, where σ is the particulate volume of the smoke at time t , σ_0 the initial particulate volume, and r the average radius of the particles.

L. L. BIRCUMSHAW.

Coagulation of colloidal solutions. G. ROSSI and A. MARESCOTTI (*Gazzetta*, 1929, 59, 319—330).—Determinations have been made of the coagulating power of hydrochloric acid, sodium hydroxide, and magnesium sulphate for arsenious sulphide and ferric hydroxide sols of varying concentrations. By counting the particles at different dilutions it was found that both arsenious sulphide and ferric hydroxide sols increase in dispersion on dilution, but that the increase with the former sol is much greater than with the latter. As a consequence the ratio between the amount of electrolyte necessary for coagulation and the concentration of the sol increases with dilution much more for arsenious sulphide than for ferric hydroxide sol.

F. G. TRYHORN.

Coagulation of colloidal titanic hydroxide. S. K. MAJUMDAR (*J. Indian Chem. Soc.*, 1929, 6, 357—360).—A comparison of the flocculation values of various electrolytes for sols of titanic hydroxide has shown the latter to be a typical positive hydrosol. "Ageing" for three months made the sol considerably more stable to all electrolytes studied, without affecting the order of their coagulating power. The addition of methyl or ethyl alcohol produced sensitisation toward most electrolytes.

F. L. USHER.

Influence of dilution on the coagulation of certain colloids. A. F. GERASIMOV and A. S. URSHUMSKI (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 393—411).—The influence of dilution on the coagulation of certain colloids was determined by observing the direction of the change, if any, of the concentration of the coagulating agent in g. per c.c. on dilution and simultaneous addition of increasing amounts of coagulator. In the case of colloidal gold, using sodium chloride as the coagulator, an increasing stability was found with dilution. Colloidal silver, on the other hand, shows a decreasing stability with dilution independent of whether it has been dialysed or not or whether sodium or potassium nitrate has been used as the coagulator. This disagrees with the results obtained previously by Freundlich and Loening (*A.*, 1922, ii, 696). Adding ammonium sulphate or Paal's albuminous protective mixture to the silver colloid, then diluting, and adding the coagulator has no particular effect on the coagulation, and in the limit the coagulation tends to become equal to that in their absence. Colloidal arsenious sulphide was also investigated; using sodium chloride as coagulator the stability increases, with magnesium chloride the stability is unchanged, whilst with barium chloride it decreases quite rapidly. Also in this case addition of potassium sulphate and agar-agar leads finally to values equal to those for the chlorides alone. Attention is directed to the importance of the physico-chemical individuality of the coagulating cation quite independent of its valency. Thus in the coagulation of silver colloids the coagulation decreases

more rapidly with sodium nitrate as the coagulator than with potassium nitrate, and in the case of arsenious sulphide also the coagulation is quite different for magnesium chloride and barium chloride. Experiments with Prussian-blue in the presence of a constant or varying concentration of oxalic acid confirm the results obtained by Volshin (*A.*, 1910, ii, 1048) except that in the presence of a fixed concentration of oxalic acid the break in the curve is much less pronounced.

A. FREIMAN.

Influence of stirring on rate of coagulation of colloids. K. JABECZYNSKI and (MLLE.) G. SZAMES (*Rocz. Chem.*, 1929, 9, 335—339).—See this vol., 761.

Coagulation of gelatin sols in alcohol-water mixture. S. GHOSH, S. N. BANERJEE, and N. R. DHAR (*J. Indian Chem. Soc.*, 1929, 6, 321—331).—Positively charged sols of gelatin (1%) in aqueous alcohol (about 87 vol.-%) become more stable on dilution when flocculated with hydrochloric acid and chlorides of potassium and magnesium, whereas with potassium sulphate and ferrocyanide the flocculation values decrease on dilution. Ionic antagonism was observed with mixtures of potassium chloride and sulphate, magnesium chloride and potassium sulphate, hydrochloric acid and potassium sulphate, and hydrochloric acid and potassium chloride. Positive acclimatisation was produced in flocculation by hydrochloric acid and potassium and magnesium chlorides. Negatively charged 0.1% gelatin sols show flocculation values which decrease with dilution in the case of hydrochloric acid and chlorides of potassium, magnesium, and barium, and increase in the case of potassium hydroxide, sulphate, and ferrocyanide. No marked ionic antagonism was observed, and there was negative acclimatisation during flocculation by hydrochloric acid, barium and magnesium chlorides, and aluminium nitrate, whereas positive acclimatisation was noticed with potassium hydroxide. The results are theoretically discussed.

F. L. USHER.

Protective action of colloids. S. OGATA (*Hokkaido J. Med.*, 1928, 6, 251—258).—Colloidal gold was precipitated by solutions more concentrated than 0.032*N*-sodium chloride, 0.001*N*-barium chloride, or 0.00124*N*-ferric chloride; protection was observed with glue solutions more concentrated than 0.00004, 0.00004, and 0.00029%, respectively. The larger threshold value with ferric chloride solution is due to hydrolysis, since with buffered solutions the results are identical. Similar results were obtained with colloidal copper ferrocyanide and mastic.

CHEMICAL ABSTRACTS.

Dissolution of albumin coagula by neutral salts. R. WILHEIM (*Kolloid-Z.*, 1929, 48, 217—231).—Serum-albumin which has been coagulated by heat can be brought into solution by treatment with concentrated solutions of certain salts (*e.g.*, thiocyanates, salicylates, and benzoates). After dialysing away the salt, the albumin is again coagulable. The salts concerned hinder the coagulation by heat. Two essential conditions for this dissolution are a minimal concentration of the salt and a sufficient amount of liquid, the latter depending on the amount of albumin coagulum. The dissolution is therefore supposed to occur in two stages: in the first stage the coagulated

albumin swells, this being controlled by the concentration of salt, and in the second stage the swollen albumin is dispersed, according to the amount of liquid available. Many other salts produce this effect when in sufficiently high concentration and the anions increase in effectiveness according to the order of the Hofmeister series. Since the process of dissolution appears to be definitely a swelling phenomenon, it would seem that the coagulation by heat is due to an energetic loss of water, and this view is supported by the fact that lithium halides, which have a strong swelling effect, also dissolve the albumin coagula. The solutions of albumin in alkali thiocyanates and salicylates are salted out with difficulty, even when the electrolyte has been dialysed away; such solutions are precipitated by acids. Measurements of the viscosity of the solutions with different concentrations of thiocyanate or salicylate in the cold show only a slight and variable increase in viscosity, but if the solution be boiled the viscosity-concentration curve rises very steeply, passes through a maximum, and then falls to the value for the unheated solution. This behaviour is probably connected with alterations in the degree of dispersion. The osmotic pressure is reduced after boiling the solutions.

E. S. HEDGES.

Changes in the viscosity and hydrogen-ion concentration of some inorganic substances during the process of jelly formation. S. PRAKASH and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 391—409; cf. Dhar and Chakravarti, A., 1928, 124).—The viscosities of a number of inorganic sols have been measured in a capillary viscosimeter during gelatinisation and found to increase exponentially with time. The behaviour of ferric and aluminium hydroxides is, however, exceptional. The hydrogen-ion concentration decreases during the first half hour, on the average by about 50% of the initial value. The results are discussed theoretically.

F. L. USHER.

Intensity of the Tyndall light in agar gels as a function of the degree of hydration. E. HARTSCHEK (Kolloid-Z., 1929, 48, 246—248).—The curve connecting the intensity of light scattered by agar gels with the concentration of the gel is maximal at about 13% of agar. By comparing the values with those obtained by Krishnamurti (this vol., 260) for the intensity of scattered light in agar sols and gels of the same concentration and at the same temperature, it is concluded that the increase in the Tyndall light on setting to a gel is not caused by hydration alone, but may be caused by the increase in the size of the particles brought about by strong hydration. In the hydration of agar there is a reduction of the total volume of the system agar+water, which will have the effect of raising the refractive index.

E. S. HEDGES.

Reactions between silver nitrate or copper sulphate and potassium ferrocyanide in gelatin. M. S. DUNIN and F. M. SCHEMIKIN (J. Russ. Phys. Chem. Soc., 1929, 61, 575—586).—Periodic precipitation of silver ferrocyanide, with the formation of a rosette-shaped figure, is observed when a drop of silver nitrate solution is placed on gelatin containing 0.01—0.05N-potassium ferrocyanide; this pheno-

menon does not take place if ferrocyanide is added to silver nitrate present in gelatin. At higher concentrations of ferrocyanide periodic precipitation takes place only beneath the drop of silver nitrate. A similar rosette is obtained when copper sulphate is substituted for silver nitrate in the above reaction; in the case of copper, at higher concentrations of ferrocyanide, a series of concentric rings forms around the drop. The actual shape of the figures obtained in the above experiments also depends on the kind of gelatin used.

R. TRUSZKOWSKI.

Influence of amount of surplus liquid on the swelling maximum of rubber jellies. C. M. BLOW and P. STAMBERGER (Rec. trav. chim., 1929, 48, 681—694).—The degree of swelling of a fixed quantity of rubber in varying amounts of benzene, toluene, and light petroleum has been measured and found to depend on the initial ratio of the solid and liquid phases, as shown by other workers with gelatin and water (cf. Ostwald and Kohler, A., 1928, 237). The liquid remaining unabsorbed after the completion of swelling always contained dissolved rubber, and when used to swell fresh rubber caused a lowering of the swelling maximum. The effect is reversible and is due, not to adsorbed impurities, but to the presence of dissolved rubber in the external liquid.

F. L. USHER.

Electrolysis in gels. II. P. HAPPEL, R. E. LIESEGANG, and O. MASTBAUM (Kolloid-Z., 1929, 48, 252—254).—A layer of gelatin containing dilute potassium nitrate is electrolysed between two platinum wires. Before passing the current, a drop of an electrolyte (e.g., calcium chloride) is placed in the field and after electrolysis the plate is placed in some reagent which will react with the electrolyte (e.g., silver nitrate for calcium chloride), so that the alteration in the shape of the drop becomes apparent. In the experiment described the drop spreads towards the anode.

E. S. HEDGES.

Mol. wt. of proteins, especially of the hæmocyannin of the blood of the snail (*Helix pomatia*). C. BAUMELER (Rev. gén. Colloid., 1929, 7, 145—152).—An account is given of Svedberg's work on the determination of the mol. wt. of proteins by sedimentation methods. The hæmocyannin of the snail has a remarkably high mol. wt., surpassing that of other proteins, but it may nevertheless be crystallised easily.

E. S. HEDGES.

Stability of humours, its causes, effects, and remedies. A. LUMIÈRE (Rev. gén. Colloid., 1929, 7, 158—165).—The principles of colloid chemistry are applied to the problem of the preservation of the normal colloidal state of humours.

E. S. HEDGES.

General dilution law and mechanism of electrolytic dissociation. W. TRETJAKOV (Z. Elektrochem., 1929, 35, 440—451).—The fraction, F , of an electrolyte which on dissolution passes into free ions is connected with the degree of ionisation, α , given by conductivity measurements, by $F = \alpha / \sqrt{[1 + nD/V_1 \cdot \alpha^{3m/2n}]}$, D being the dielectric constant of the solvent, n the valency of the ions, m the number of ions into which an electrolyte dissociates, and V_1 the volume of solvent (litres) in which each g.-mol.

of electrolyte is dissolved. This value is substituted for α in the Ostwald dilution expression and numerous tables are given showing its applicability to various salts and acids. The values of K are considered to be more satisfactory than those calculated from the equations of Ostwald and Rudolphi. The deviations corresponding with concentrated solutions are attributed to the ions becoming solvated. A more general expression is developed using the relationship $\alpha = F + eA$ (e =ratio of the velocity of the free ions to that of the solvated ions; A =fraction of solvated ions). The values of e calculated for a series of electrolytes from conductivity data reveal that the expression $e = nKD/2$ is approximately valid. The validity of the above equations is also tested in the cases of a number of electrolytes in non-aqueous solvents.

H. T. S. BRITTON.

Equilibrium law for electrolytes and ionic hydration. K. JABŁCZYŃSKI and C. SEIDENGART (Rocz. Chem., 1929, 9, 418—430).—Cryoscopic measurements of alkali chloride and hydrogen chloride solutions and of their mixtures, as well as of the mol. wt. of carbamide and of mannitol in solutions of these chlorides, give results in complete agreement with those calculated from the equation of Jablczynski and Wisniewski (A., 1922, ii, 190).

R. TRUSZKOWSKI.

Interionic forces and the ionisation of weak electrolytes. H. M. DAWSON (Proc. Leeds Phil. Soc., 1929, 1, 491—496).—A brief outline of the author's work on catalysis in solution in its bearing on the interionic force effects in solutions of weak electrolytes. This work affords new and independent evidence of the electrical field effects indicated by the Debye-Hückel theory, but it shows that the ionic strength hypothesis cannot be reconciled with the behaviour of acids in both salt-free and salt-containing solutions.

L. S. THEOBALD.

B.-p. elevation of acetone solutions as related to the interionic attraction theory. A. L. ROBINSON (J. Physical Chem., 1929, 33, 1193—1199; cf. A., 1928, 944).—The b. p. of 0.001—0.3*M*-acetone solutions of anhydrous and hydrated sodium iodide, cobalt chloride, and lanthanum nitrate have been determined, and are in good agreement with the requirements of the Debye-Hückel theory. The results obtained with the hydrated salts indicate that definite ionic hydrates do not exist.

L. S. THEOBALD.

Mutual salting-out of ions. J. A. V. BUTLER (J. Physical Chem., 1929, 33, 1015—1023).—Theoretical. The effect of the forces exerted by the electric field of an ion on the solvent molecules and on the distribution of the ions in its neighbourhood is discussed. An equation for the salting-out of a substance by an electrolyte is derived in a simple manner and is shown to be equivalent to the expression obtained by Debye and McAulay (A., 1925, ii, 171) using a different principle. The result is applied to the mutual salting-out of ions.

L. S. THEOBALD.

Dissociation constants of organic acids. I. Primary dissociation constants of some alkylmalonic acids. II. Primary dissociation constants of some cyclic 1:1-dicarboxylic acids.

A. I. VOGEL (J.C.S., 1929, 1476—1487, 1487—1494).—I. From measurements of the conductivities of the free acids at concentrations between 0.0001*M* and 0.01*M* and of the disodium salts at concentrations between 0.0002*M* and 0.004*M* the following primary dissociation constants have been calculated: malonic 14.10×10^{-4} , methylmalonic 7.99×10^{-4} , ethylmalonic 10.30×10^{-4} , dimethylmalonic 6.57×10^{-4} , methylethylmalonic 13.94×10^{-4} , diethylmalonic 63.9×10^{-4} , ethyl-*n*-propylmalonic 73.7×10^{-4} , and di-*n*-propylmalonic acid about 90×10^{-4} . The last acid appears to behave as a strong electrolyte, since there is no evidence of a primary dissociation constant over the whole concentration range studied.

II. The following primary dissociation constants have been computed from accurate measurements of the conductivities of the free acids and of their disodium salts in aqueous solution over a fairly wide range of concentration: cyclobutane-1:1-dicarboxylic acid, 6.97×10^{-4} ; cyclopentane-1:1-dicarboxylic acid, 5.47×10^{-4} ; cyclohexane-1:1-dicarboxylic acid, 3.4×10^{-4} . cycloPropane-1:1-dicarboxylic acid is abnormal, inasmuch as it behaves as a strong electrolyte, giving a dissociation constant of about 0.14, which, however, is not constant over the concentration investigated.

F. G. TRYHORN.

Ionisation constant of codeine. H. BAGGESGAARD-RASMUSSEN and I. MARTIN (Dansk Tidskr. Farm., 1929, 3, 197—207).—The acidity constant and the basicity constant for the ionisation of codeine, $R(\text{base}) + H^+ = RH^+(\text{acid})$ are found from electro-metric measurements to be 6.7×10^{-9} and 7.9×10^{-7} , respectively. The partition coefficient of codeine between chloroform and water is $83 \pm 10\%$.

C. W. GIBBY.

Equilibria between hydroxy-acids and their anhydro-derivatives. M. GEHRKE and H. H. WILLRATH (Z. physikal. Chem., 1929, 142, 301—308).—A 0.1*N*-solution of lactic acid containing about 37% of lactide shows practically no change on keeping for 3 days at the ordinary temperature, but after boiling for about 20 hrs. complete conversion of the lactide into free acid takes place. A freshly-prepared glycollic acid solution is entirely free from glycollide. The hydrolysis curves of α - and β -hydroxybutyric acids indicate the existence, at equilibrium, of 4—5% of lactide derivative, assuming the latter to contain one free carboxyl group.

H. F. GILLIE.

Esterification equilibrium and active molecules. S. POZNANSKI (Rocz. Chem., 1929, 9, 354—360).—A verification of Swiętosławski's equation, $K_1 - KZ_3Z_4/Z_1Z_2$, where K is the equilibrium constant of the system ethyl alcohol-acetic acid-ethyl acetate-water, and Z_1, Z_2, Z_3, Z_4 are the deviations of the volatility of each of the components from that of the corresponding pure liquid. The value of K_1 is $14(+10\%)$, and is independent of the proportions of the various components of the mixture.

R. TRUSZKOWSKI.

Influence of salts on the activity of acetic acid molecules in aqueous solution. E. LARSSON (Svensk Kem. Tidskr., 1929, 41, 130—141).—The distribution of acetic acid between solutions of the chlorides of sodium, potassium, calcium, strontium,

and barium, on the one hand, and benzene, ether, or amyl alcohol on the other hand, has been determined. The activity coefficients of acetic acid in salt solutions of concentrations ranging from 0.125 to 3 mols. per litre have been calculated from the results. The values obtained for each salt with the different organic solvents agree satisfactorily, but differ from those derived from the distribution of acetic acid between salt solutions and the gaseous phase (cf. McBain and Kam, J.C.S., 1919, **115**, 1332); this may be due to the higher temperature (100°) employed in the latter case.

H. F. HARWOOD.

Tervalent carbon. VII. Accurate determination of dissociation equilibrium. Determination of heat of dissociation of hexaphenylethane. K. ZIEGLER and L. EWALD. **VIII. Molecular volume of hexaphenylethane and analogues.** K. ZIEGLER and F. DITZEL (Annalen, 1929, **473**, 163—193, 194—210).—VII. An apparatus in which dilution of a solution of hexaphenylethane is possible is described and the extinction coefficients of the solutions so obtained are measured in the visible spectrum. Extrapolation of the extinction coefficient, ϵ_v , to affords a measure of the degree of dissociation (α) which equals $\epsilon_v/\epsilon_\infty$. Application of Ostwald's dilution law gives the expression $K=4\alpha^2/(1-\alpha)v$, where v = volume in which 1 mol. of hexaphenylethane is dissolved. For hexaphenylethane in benzene solution at 20° the value of K is $4.1 \times 10^{-4} \pm 5\%$. The corresponding values for tetraphenyldi-*n*-naphthylethane in cyclohexane at 20° and bis-2:3:4-triphenyl-6-methylchromenyl in benzene at 25° are $3.1-3.36 \times 10^{-1}$ and $1 \times 10^{-3} \pm 4\%$, respectively. Solutions of pentaphenylcyclopentadienyl (conveniently prepared by the action of potassium phenylisopropyl on bromopentaphenylcyclopentadiene) in various solvents show absorption maxima at about 5800—5900 Å. The values of ϵ fall into two groups, (a) light-stable solutions in cyclohexane, benzene, and ether, 6360—6720, (b) light-sensitive solutions in acetone, chloroform, and ethyl acetate, 5680—6000. The various results afford no evidence of the tautomerism of triarylmethyls. The extinction curve for pentaphenylcyclopentadienyl shows a decrease in the maximum value of ϵ for rise in temperature. The heat of dissociation of hexaphenylethane in various solvents is about 11.5 kg.-cals. This is a characteristic constant and is independent of the solvent.

VIII. To determine the mol. vol. of the C_6H_4 group density determinations of 38 solid substances have been carried out at 0°, and the values found vary from 53—54 to 66 (limits). The variations correspond with the differences in the values of the methylene group using Biltz's zero point volumes (A., 1927, 498). The values of $C_{\text{arom.}}$ and H are calculated to be 5.86, 3.69, and 6.28 at 0° (cf. Biltz, *loc. cit.*). Using these values for the calculation of it is found that 76% of the values for 34 substances examined agree within 3% and 94% within 4%. Compounds containing a relatively large number of aliphatic carbon atoms give values for v_m which are too low, but arylated hydrocarbons (not dissociable) give values usually of the order $+1-2\%$. The variation in the mol. vol. of hexaphenylethane,

crystallised from various solvents, is of the same order.

H. BURTON.

Hydrolysis of certain beryllium salts of strong acids. V. ČUPR (Coll. Czech. Chem. Comm., 1929, **1**, 377—386).—The hydrogen-ion concentration in N - to 0.001*N*-solutions of beryllium sulphate, chloride, bromide, chlorate, and perchlorate has been measured electrometrically and colorimetrically. The ratio $[H^+]/C$ varies with concentration in the same manner for all salts studied except beryllium sulphate. It falls on dilution as far as 0.1*N*, and then rises again to a constant value. The exceptional behaviour of beryllium sulphate is probably due to the formation of the ion HSO_4' .

C. W. GIBBY.

Partition of strong bases and strong acids in saturated aqueous solutions. V. I. NIKOLAIIEV (Z. anorg. Chem., 1929, **181**, 249—279).—The equilibria in the following four quaternary systems have been determined and are illustrated by space models based on the regular tetrahedron; (a) $Na_2O-N_2O_5-HCl-H_2O$, (b) $K_2O-N_2O_5-HCl-H_2O$, (c) $Na_2O-K_2O-N_2O_5-H_2O$, and (d) $Na_2O-K_2O-HCl-H_2O$. In system (a) at 15° the neutral saturated solution contains equal molecular proportions of sodium chloride and nitrate; with rising temperature the ratio $NaCl/NaNO_3$ falls rapidly to a minimum of 0.08 at 162°, then rises slightly to 0.13 at 210°. At 25° this ratio falls steadily with increasing concentration of sodium hydroxide to practically zero in a 40% solution of the alkali; at 100° in acid solution the ratio falls from 0.13 to zero with increase in the total acidity from 0 to 12%. In the corresponding potassium system (b) the saturated neutral solution contains an equimolecular mixture of chloride and nitrate at 50°; at 25° the equimolecular mixture is obtained only when 37.27% of free alkali is present or when the total free and combined nitric acid is 20.88%. In the nitrate system (c) addition of nitric acid decreases the combined solubility in such a way that the decrease in mol.-% of total nitrate is equal to the increase in mol.-% of nitric acid up to an addition of 10 mol.-% of acid. The ratio $NaNO_3/KNO_3$, originally 2.51 in neutral solution at 25° decreases with addition of nitric acid to a minimum of 0.51 with 0.62 mol. of acid, then increases again to 3.9 with 0.98 mol. of acid per mol. of salt. This behaviour is due to the formation of the additive compound $KNO_3 \cdot 2HNO_3$. Addition of sodium hydroxide increases the $NaNO_3/KNO_3$ ratio to a maximum of 4.41 with 0.369 mol. of alkali per mol. of salt; further addition of alkali decreases this ratio to 0.72 with 1 mol. of alkali per mol. of salt. Potassium hydroxide, on the other hand, decreases the solubility of potassium nitrate almost to zero with 0.19 mol. of alkali per mol. of salt without appreciably varying the solubility of the sodium salt. In the corresponding chloride system (d) the molecular solubilities are equal at 90°; below this temperature the ratio $KCl/NaCl$ is less than, and above 90° is greater than, unity. It is suggested that the influences controlling the partition of an acid between two bases or of a base between two acids are the heat of neutralisation, the heat of dissolution, and the heat of hydration.

A. R. POWELL.

Soluble lakes of aurintricarboxylic acid. W. E. THURUN (J. Physical Chem., 1929, **33**, 977—983).—The equilibrium existing between alumina, aurintricarboxylic acid, and the resulting lake has been investigated colorimetrically. Values for the ratio (free alumina)/(total alumina)/(lake) are fairly constant and give a mean of 1.41. With other oxides replacing alumina, the corresponding values are for ferric iron 0.15, chromium 1.41, ferrous iron 1.61, and beryllium 2.22. The existence of two kinds of lake is indicated, and the results show that lake formation depends on the insolubility of the hydrous oxide and that an excess of dye can counteract the solubility of the oxide. With alumina, the intensity of colour of the lake is the same when formed at the ordinary temperature during 24 hrs., at the b. p. during 1 min. followed by rapid cooling, or at 60° during 10 min. followed by rapid cooling. The addition of gum arabic prevents the flocculation of excess of alumina but does not alter the colour intensity of the lake. The volume and p_H value of acid solutions have no effect on the colour intensity provided that sufficient time is allowed or that lake formation is accelerated by rise of temperature.

L. S. THEOBALD.

Effect of neutral salts on p_H of phosphate buffer mixtures. H. W. ROBINSON (J. Biol. Chem., 1929, **82**, 775—802).—The effect of the presence of various neutral salts on the p_H of phosphate buffer solutions of different concentrations has been observed and the results are treated mathematically. The effects of potassium, sodium, and lithium salts are predominantly those of the cations and increase in the order mentioned; the effect depends on the total ionic strength of the buffer, which is not proportional to the total phosphate ion concentration owing to variations in the proportion of primary and secondary phosphate. From the results it is possible to calculate the p_H of a phosphate buffer containing known amounts of neutral salts, and also to deduce the amount of salt solution with which a phosphate buffer must be diluted in order that its p_H may remain unchanged.

C. R. HARRINGTON.

Oxidation-reduction systems of biological importance. IV. Cysteine complexes with metals of the iron group. L. MICHAELIS and E. S. G. BARRON (J. Biol. Chem., 1929, **83**, 191—210).—Cysteine gives a Bordeaux-red complex with nickel, the formation of which is independent of the presence of oxygen. With cobalt in the absence of oxygen a complex is formed which is green when viewed in bulk unless the cysteine be in large excess, when it is pink. This complex is a powerful reducing agent, its potential at p_H 7.5 matching that of the hydrogen electrode, and is converted in presence of an oxidant (ferricyanide, a dye, or even cystine) or by contact with atmospheric oxygen into a stable brown compound. The oxygen consumption increases with the amount of cobalt until the solution contains 1 atom of cobalt per 3 mols. of cysteine, such a solution absorbing 0.5 mol. of oxygen or reducing an equivalent amount of oxidant. The course of the reaction is not always the same, however, the oxidation by ferricyanide proceeding in two stages, and that by phenolindophenol following a smooth course.

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The violet complex of cysteine with iron is analogous to the stable brown complex with cobalt, and it is the instability of the former complex which renders iron a catalyst for the oxidation of cysteine, whilst cobalt has no such catalytic action.

C. R. HARRINGTON.

Chemical antagonism of ions. IV. Effect of salt mixtures on glycine activity. H. S. SIMMS (J. Gen. Physiol., 1929, **12**, 783—792).—The changes in p_H on adding sodium chloride, potassium chloride, magnesium chloride, and calcium chloride either singly or in pairs to a 0.01M-solution of glycine containing 0.5 equivalent of sodium hydroxide are shown to be analogous to the changes produced in a gelatin solution (cf. this vol., 140, 647).

P. G. MARSHALL.

Influence of ethyl ether and of dimethylpyrone on the availability of hydrogen chloride in alcoholic solution. V. E. S. MITCHELL and J. R. PARTINGTON (J.C.S., 1929, 1562—1568).—The rate of esterification of phenylacetic acid in dry alcoholic solution under the influence of hydrogen chloride is accelerated in the presence of small amounts of ethyl ether, and is retarded by the addition of small amounts of water or of dimethylpyrone. The effect of dimethylpyrone becomes analogous to that of water if the former is regarded as dibasic, and therefore capable of uniting with 2 mols. of hydrogen ion, reducing thereby any catalytic action due to hydrogen ion. The slight accelerating effect of dry ether is due possibly to a solvent effect, or to the predominance of the solvent effect over retardation due to union with hydrogen ion. It is probable, however, that ethyl ether does not behave as a base under these conditions.

F. G. TRYHORN.

Hydrazine: solubility relations of hydrazine picrate, and the equilibrium $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$. E. C. GILBERT (J. Physical Chem., 1929, **33**, 1235—1246).—The solubility of hydrazine picrate in solutions of ammonium chloride and of ammonium chloride and ammonium picrate has been determined at 20°. The solubilities of the hydrazine and other picrates in salt solutions show a considerable deviation from the law of constancy of the ionic product where the solvents have a common ion. This effect is not noticeable except in homoionic solvents, and is specific, apparently, for the picrate ion. The solubility of hydrazine picrate in ammonium chloride solutions at 20° can be represented by the equation $\log s/s_0 = 0.004\mu - 0.25\mu$ for values of μ , the ionic strength, up to 0.12. The coefficient at 20° of the equilibrium $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$ has been determined from the solubility data of hydrazine picrate in ammonium chloride-ammonia solutions and leads to a value of $5.3 - 6.5 \times 10^{-9}$ for the dissociation constant of the $N_2H_5^+$ ion.

L. S. THEOBALD.

Existence of monocalcium aluminate in solution. A. TRAVERS and SCHNOUTKA (Compt. rend., 1929, **189**, 182—183).—Addition of lime water (or baryta) to a solution of an aluminium salt precipitates gelatinous hydrated alumina quantitatively when the ratio of CaO to Al_2O_3 reaches 3. When the ratio is increased to 4, the precipitate is dissolved. Hydrated monocalcium aluminate, however, cannot be crystallised from such solutions, as decomposition

occurs on evaporation, but after addition of an excess of lime water, crystals are obtained the form of which depends on the p_H of the solution. These phenomena are due to the low solubility product of the poly-calcium aluminates compared with the mono-compound.

J. GRANT.

Equilibrium between alcohols and salts. III. G. C. GIBSON, J. O. DRISCOLL, and W. J. JONES (J.C.S., 1929, 1440—1443).—The solubilities of the sulphates of magnesium, zinc, cadmium, manganese, cobalt, and zinc in methyl and ethyl alcohols have been measured at temperatures between 15° and 55°. The following alcoholates have been prepared by dissolving the metal in methyl alcohol containing 100% sulphuric acid: $MgSO_4 \cdot 3.5MeOH$; $ZnSO_4 \cdot 2.5MeOH$; $ZnSO_4 \cdot MeOH$; $FeSO_4 \cdot 1.5MeOH$. Between 15° and 55° cadmium, thorium, manganous, cobalt, and nickel sulphates exist in equilibrium with their respective saturated solutions as the non-alcoholated salts. The stabilities of the above methyl alcoholates, and the extent of the basic decomposition of copper and zinc sulphates by methyl alcohol, have been studied. In the case of copper basic decomposition is complete. F. G. TRYHORN.

System gold-mercury. I. I. PLAKSIN (J. Russ. Phys. Chem. Soc., 1929, 61, 521—534).—Thermal and micrographic methods indicate the formation of the compounds $AuHg_2$ and Au_2Hg . The former is stable below 310°; at higher temperatures it is converted into Au_2Hg with the liberation of mercury. At 420° the second compound forms a liquid alloy and a solid solution of mercury in gold. The maximum concentration of mercury in gold solid solutions is 16 at.-%. The compound $AuHg_2$ undergoes polymorphic changes at 122° and at -36°. A similar change occurs in the compound Au_2Hg at 402°. The liquidus curve thus consists of six sections, the transition points being at -36°, at 122° (1.3 at.-% Au), at 310° (13.5%), at 402° (50.3%), and at 420° (55.6%). The eutectic lies very close to the ordinate for pure mercury, and the eutectic temperature is practically the same as for mercury alone.

R. TRUSZKOWSKI.

Equilibrium diagram of the iron-vanadium system. S. OYA (J. Study Met., 1928, 5, 349—356).—By suitable adjustment of the proportion of aluminium and sodium carbonate employed, vanadium of 98.5% purity has been obtained from ammonium vanadate. The iron-vanadium alloys form solid solutions in all ranges of composition. The A4 point for iron is rapidly lowered by the addition of vanadium, whilst the A3 point is rapidly raised. The A2 point rises to 15% V, is slowly lowered at 20% V, and is rapidly lowered to the ordinary temperature at 35% V.

CHEMICAL ABSTRACTS.

System water-hexamethylenetetramine. V. EVRARD (Natuurwetensch. Tijds., 1929, 11, 99—107).—The solubility diagram has been mapped from -10° to 165°. The curve consists of three parts: the first, the ice line, starts at 0° for pure water and ends at -10.3° and 29.8% of the solute; the second, corresponding with solubility of the hydrate (6 mols. H_2O), extends from the end of the first to the point 13°, 46.8% solute, and the third rises from this point

very steeply, almost parallel with the temperature axis. The solutions in pure water are very stable.

S. I. LEVY.

Effect of high temperatures on some metallic sulphides. PICON (Compt. rend., 1929, 189, 96—98; cf. A., 1927, 328).—The sulphides of chromium, molybdenum, tungsten, uranium, aluminium, and magnesium are volatilised or dissociated at 1200—1300° in a carbon resistance furnace. Dissociation occurs in all cases in a vacuum, although it is small for aluminium and magnesium sulphides.

J. GRANT.

Reduction equilibrium of lead sulphide and the chemical constants of sulphur and hydrogen sulphide. K. JELLINEK and A. DEUBEL (Z. Elektrochem., 1929, 35, 451—457).—The equilibrium $PbS + H_2 \rightleftharpoons Pb + H_2S$ was investigated at various temperatures between 655° and 1000° by passing hydrogen over the heated sulphide at definite rates and measuring the ratio of hydrogen to hydrogen sulphide in the issuing gases. From experiments at a fixed temperature and varying rates, it was possible to derive the equilibrium ratio (cf. Jellinek and Zakowski, A., 1925, ii, 401). From the published specific heats calculations have been made of the pressures of sulphur vapour existing in equilibrium at the different temperatures, of the heat of formation of crystalline lead sulphide (40.8 kg.-cal.), and the heat of transition from the form in which it is precipitated to the crystalline state (5.5 kg.-cal.). The chemical constants of sulphur vapour and hydrogen sulphide have also been derived.

H. T. S. BRITTON.

Equilibrium between molten metals and salts. XVII. Calcium and sodium and their chlorides. R. LORENZ and R. WINZER (Z. anorg. Chem., 1929, 181, 193—201).—The equilibria in the system $CaCl_2 + 2Na \rightleftharpoons 2NaCl + Ca$ have been investigated at 600—800°. When the salt phase contains 16—98.5 mol.-% of calcium chloride the metal phase has a constant composition, namely, 0.95 at.-% Ca and 99.05 at.-% Na. With lower concentrations of calcium chloride in the salt phase the calcium in the metal phase is a function of the composition of the salt phase, the equilibrium curve agreeing with that deduced from the phase rule in cases where there is only a limited solubility of the metals in one another. The equilibria in the system are independent of the temperature within the above limits and of the relative proportions of the salt and metal phases.

A. R. POWELL.

Double decomposition in the absence of a solvent. IX. System $AgCl + KI \rightarrow AgI + KCl$. A. P. ROSTKOWSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 595—605).—The existence of the compound $4AgI \cdot KI$ is indicated by the equilibrium data.

R. TRUSZKOWSKI.

Systems: borates and halides of sodium in the fused state. B. STALHANE (Z. Elektrochem., 1929, 35, 486—492).—Almost complete isotherms of the ternary systems $Na_2O - B_2O_3 - NaCl$ at 850° and $Na_2O - B_2O_3 - NaBr$ at 830° have been worked out. In each isotherm, two liquid phases coexist, the lighter one being rich in borate and the heavier rich in halide.

H. T. S. BRITTON.

Saturated solutions of salts having one common ion. E. V. KUKLIN (J. Russ. Phys. Chem. Soc., 1929, **61**, 667—680).—The composition of the saturated solution is affected by double salt formation and by the relative solubilities of the simple and double salts. A. FREIMAN.

Equilibrium between two solids in a common solvent. V. K. PERSCHKE (J. Russ. Phys. Chem. Soc., 1929, **61**, 441—444).—From the point of view of free-energy changes the author discusses the question of the solubilities of two solids which do not react with each other or with the common solvent. At a given temperature the simultaneous solubilities should be the same as when each dissolves separately. This is confirmed by investigations of the system azobenzene-carbamide-ethyl alcohol.

A. FREIMAN.
System $\text{NaNO}_3\text{--Na}_2\text{SO}_4\text{--MgCl}_2\text{--H}_2\text{O}$ at 0° , 10° , 25° , 50° , 75° , and 100° . G. LEIMBACH and A. PFEIFFENBERGER (Caliche, 1929, **11**, 61—85).—Details are given of the phase relations at 0° , 10° , and 25° , and the results obtained are compared with those of other observers. H. F. GILLBE.

Mesophases. IV. Further examples of aqueous mesophases. V. Influence of electric and magnetic fields. H. ZOCHER and V. BIRSTEIN (Z. physikal. Chem., 1929, **142**, 177—185, 186—194; cf. this vol., 876).—IV. Sodium and potassium palmitates, stearates, and oleates have been studied. Only sodium and potassium oleates form mesophases. Ammonium oleate solutions prepared by the action of concentrated ammonia on oleic acid gave no evidence of an aqueous mesophase. Sodium naphthenate forms a smectic mesophase in aqueous solution. Cetyl xanthate similarly forms a smectic phase in hot concentrated aqueous solution. The dispersion of the double refraction of this solution is anomalous. Sols of cetyl xanthate have been prepared in benzene, toluene, and xylene which show moderately strong negative stream double refraction. Friedel's observations (A., 1923, ii, 223) on the mesophase formed by bromophenanthrenesulphonic acid have been confirmed. It is further shown that the nematic phase formed at moderate concentrations, in contrast to the nematic phases already known, shows a negative stream double refraction and forms drops with optically positive radii. Commercial lecithin forms a mesophase; pure synthetic lecithin does not.

The structure of a smectic phase does not always make itself evident, since the diffuse double refraction obtained is also given by many gels and sols. In the latter cases the double refraction is to be ascribed to the anisotropic colloidal particles.

V. The dielectric and magnetic anisotropy of nematic phases is negative in the case of compounds such as *p*-azoxyanisole, for which the molecular structure is symmetrical. For nematic phases of substances of asymmetrical molecular structure, the magnetic and dielectric anisotropy is positive. By the use of strong fields (about 10,000 volts/cm.), it is shown that, contrary to Friedel's statement (A., 1923, ii, 223), nematic phases of the cholesterol type, such as that of optically active amyl ethoxybenzylidene-amino- α -methylcinnamate, are oriented and become

doubly refracting. The optical activity is decreased considerably by the field; removal of the field is accompanied by the disappearance of the double refraction and the restoration of the normal optical activity.

Smectic phases are also influenced by electric fields of suitable strength. In all the cases studied, the dielectric anisotropy is negative even when that of the corresponding nematic phase is positive. The magnetic anisotropy is positive. F. J. WILKINS.

Free energy charts for predicting equilibrium pressures and concentrations. R. F. NIELSEN (Ind. Eng. Chem., 1929, **21**, 568—571).—A form of chart is suggested which admits the direct reading of physical and chemical equilibrium concentrations if a single chart be prepared for each pure substance concerned. The charts employ lines of constant pressure or concentration with temperatures as abscissæ and some function of free energy as ordinate. The methods of preparation are explained and an example of the use of the graphs is given. Problems involving electrolytes can be solved by the use of this type of graph. H. INGLESON.

Charts for predicting equilibria. M. RANDALL (Ind. Eng. Chem., 1929, **21**, 571—572).—A method of preparing the charts which is a modification of that suggested by Nielsen (preceding abstract) is explained and examples of the use of the charts are given. H. INGLESON.

Extension of the Clausius-Maxwell criterion. L. SCHAMES (Helv. phys. Acta, 1928, **1**, 417—420; Chem Zentr., 1929, i, 978).

Partial molal heat capacities and relative partial molal heat functions in solutions of molten metals. A. N. GUTHRIE and E. E. LIBMAN (J. Amer. Chem. Soc., 1929, **51**, 1711—1715).—Calculations are made for solutions of lead and antimony and of bismuth and cadmium from previously published thermal data. The relative partial molal heat functions are zero for all temperatures and at all concentrations of these binary solutions. The partial molal heat capacities are constant, independent of concentration, and are equal to the molal heat capacities of the pure components in the liquid state. S. K. TWEEDY.

Heat of mixing of molten metals. IV. M. KAWAKAMI (J. Study Met., 1928, **5**, 346—348).—It is deduced that $\Delta H = \Delta H' + RT\{y \log_e (x/y) + (1-y) \log_e (1-x)/(1-y) + yQ_A(T_{0A} - T)/T_{0A} + (1-y) \times Q_B(T_{0B} - T)/T_{0B}\}$, where $\Delta H' = yH'_A + (1-y)H'_B$ and ΔH is the heat of mixing A and B in the mol. proportion $y/(1-y)$ in the solid states to form a solid solution; y and x are the mol. fractions of A in equilibrium at T° Abs., Q_A and Q_B the heats of fusion, T_{0A} and T_{0B} the m. p., H'_A the heat evolved when 1 mol. of the liquid A is mixed with an infinitely large quantity of the liquid mixture composed of x and $(1-x)$ mol. fraction of A and B, and H'_B the heat evolved when B is mixed with an infinitely large quantity of that mixture. Values are recorded for bismuth-zinc, lead-cadmium, lead-tin, and tin-cadmium mixtures. When $y=1$, $RT \log_e x + Q_A(T_{0A} - T)/T_{0A} + \Delta H'_A = 0$, where x is the solubility of A in B, applying to the binary system having no solid solubility. CHEMICAL ABSTRACTS.

Determination of the limiting heat of dissolution of some hydrated salts (direct method). J. PERREU (Compt. rend., 1929, 189, 167—169).—The limiting heats of dissolution for various salts have been determined by extrapolation of the heat of dissolution-concentration curves to the saturation point. The data recorded are: $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (—13.54), $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (—21.845), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (—16.83), $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (—4.73), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (—2.44).

J. GRANT.

Measurement of the limiting heat of dissolution of hydrated salts (method of heats of dilution). J. PERREU (Compt. rend., 1929, 189, 285—287).—The heats of dilution of sodium carbonate and sulphate, barium chloride, copper sulphate, and disodium hydrogen phosphate (L) were measured at 11—12° by diluting in a calorimeter a known weight of standard solution with the amount of water necessary to lower the concentration to the same value as in the measurement of the initial molecular heat of dissolution (X_N) of the salt in a large volume of water. If Δ is the heat of molecular dilution and A the heat of addition, the modified Matignon formula $L = X_N - (\Delta + A)$ gives values of L in close agreement with those obtained by the direct method. A was determined directly by adding a small amount of water to a large excess of saturated solution (cf. preceding abstract).

J. GRANT.

Heat of solidification and heat of dissolution of sucrose. A. TIAN (Compt. rend., 1929, 189, 164—167).—A zero or compensation method is described for the determination of the heat of solidification of sucrose (X). This is based on the fact that the heat of dissolution of pure supercooled sucrose is positive (this vol., 1045), whilst that of crystalline sucrose is negative. If Q_s and Q_l are the molecular heats of dissolution of sucrose in the solid and liquid states, respectively, and α is the weight of crystalline sucrose which when mixed with unit weight of supercooled substance gives no thermal effect, $X - Q_l - Q_s = -(\alpha + 1)Q_s = 4595$ at 15.93°. The solubility curves of solid and liquid sucrose meet at the m. p.

J. GRANT.

Modification of the moving-boundary method for the determination of transference numbers. H. P. CADY and L. G. LONGSWORTH (J. Amer. Chem. Soc., 1929, 51, 1656—1664).—A metal anode soluble under the action of the current is used as the source of indicator ions, and a single ascending boundary only is observed, viz., that between the solution of electrolyte originally placed in the cell and the heavier electrolyte having a common anion and an unlike cation formed from the metal anode. This boundary starts at the anode. The transport numbers determined by this method are independent of the potential gradient over a wide range of the latter. Automatic adjustment of the concentration of the indicator ion occurs in accordance with Kohlrausch's relationship (Ann. Physik, 1897, 62, 209). The range of application of the method is briefly discussed.

S. K. TWEEDY.

Hittorf's explanation of electrolytic conduction. S. RAY (Z. Elektrochem., 1929, 35, 469—470).—It is suggested that the ionic velocity ordinarily measured

refers only to the final velocity of an ion, viz., in the vicinity of an electrode. Elsewhere, the velocity varies with the time the ion has been moving and its distance from the electrodes. The average velocities of anions and cations are stated to be equal, which therefore accounts for the amounts of ions discharged at the electrodes being proportional to the atomic or mol. wt.—a fact which cannot be explained on the Hittorf view.

H. T. S. BRITTON.

Inapplicability of Ohm's law to alternating-current circuits containing capacity and resistance. M. H. AHMADI and H. L. TANDON (Z. Elektrochem., 1929, 35, 471—473).—Theoretical; cf. Ray, this vol., 228.

H. T. S. BRITTON.

Frequency dependence of the electrical conductance of solutions of strong electrolytes. H. FALKENHAGEN and J. W. WILLIAMS (J. Physical Chem., 1929, 33, 1121—1134; cf. A., 1928, 596, 957, 1330).—Theoretical. The dispersion of electrical conductance consequent on the existence of a finite time of relaxation is further discussed together with the influence of concentration, ionic mobility, dielectric constant, temperature, and valency on this effect.

L. S. THEOBALD.

Dielectric loss in electrolyte solutions in high-frequency fields. W. T. RICHARDS and A. L. LOOMIS (Proc. Nat. Acad. Sci., 1929, 15, 587—593).—An expression is given connecting power loss in a liquid dielectric with its conductivity, dielectric constant, and the frequency of the field to which it is subjected. This is tested and verified over a considerable range of frequencies and conductivities for sodium chloride, lead acetate, mercuric chloride, and for some disperse and heterogeneous systems. Its application to physiological behaviour in high-frequency fields is discussed.

N. M. BLIGH.

Determination of conductivity of electrolytes with alternating current of low frequency. A. H. W. ATEN and (MISS) L. M. BOERLAGE (Rec. trav. chim., 1929, 48, 698—710; cf. A., 1921, ii, 159).—Comparative measurements of the resistance of electrolytes, using a galvanometer with alternating current of 50 cycles, and a telephone with frequencies of 1100 and 2300, have shown that the former arrangement can be used for resistances above 200 ohms with an accuracy of 0.01% if the liquid is contained in a cell of the Washburn type with well-platinised electrodes. For resistances above 10,000 ohms the galvanometer is always preferable to the telephone. Methods of dealing with capacity effects due to the cell and to the water in the thermostat are discussed.

F. L. USHER.

"Water correction" in the measurement of electrical conductivity of very dilute aqueous solutions of electrolytes. I. M. KOLTHOFF (Rec. trav. chim., 1929, 48, 664—680).—The conductivity of very dilute aqueous solutions of salts, acids, and bases has been studied in order to ascertain the best method of eliminating the uncertainty due to the conductivity of the water used in their preparation. A summary of previous work is given. In using "equilibrium water" (i.e., water saturated with and left exposed to the laboratory air) emphasis is laid on the importance of securing equilibrium with the air

at the temperature at which the measurements are made. Such water is suitable for neutral salts and strong acids down to a concentration $5 \times 10^{-5}N$. In the former case the results obtained by subtracting the total conductivity of the water from that of the solutions agreed within 0.5% with those obtained by using "ultra-pure" water (prepared by removing dissolved carbon dioxide from "equilibrium water" with purified air). The resistance of solutions of strong acids at concentrations $>10^{-4}N$ is the same whether they are made with "equilibrium water" or with "ultra-pure" water, and no correction for the conductivity of dissolved carbonic acid must be applied. At lower concentrations irregularities are encountered due to traces of alkaline impurities. Platinised electrodes give rise to slight adsorption effects with both salts and acids. In determining the conductivity of very dilute ($<10^{-4}N$) solutions of bases "ultra-pure" water must be substituted for "equilibrium water," the glass vessels must be paraffined, and blank platinum electrodes used in order to secure reproducible results. Equations have been derived for calculating the correction to be applied if "equilibrium water" is used for determining conductivities of slightly soluble hydroxides. The work of Remy and Kuhlmann (cf. A., 1925, ii, 30, 119, 299) is considered untrustworthy.

F. L. USHER.

Viscosity and conductance of mixed solutions of lead nitrate and ammonium nitrate. G. MALQUORI (Gazzetta, 1929, 59, 355—362).—The conductance and viscosity of solutions of lead nitrate, of ammonium nitrate, and of mixtures of these two salts have been measured between 15° and 60° . From the divergences shown by the conductances, corrected for viscosity, of the mixed solutions from those calculated from the mixture law, evidence is adduced for the existence of a complex of the type $Pb(NO_3)_2 \cdot 2NH_4NO_3$, giving rise probably to complex ions $Pb(NO_3)_4^{2-}$.

F. G. TRYHORN.

Great mobility of hydrogen and hydroxyl ions in aqueous solutions. M. SCANAVY-GRIGORIEVA (Z. anorg. Chem., 1929, 181, 337—346).—Conductivity measurements of aqueous solutions of potassium chloride, potassium hydroxide, and hydrochloric acid, ranging from $0.001M$ to M , and of similar solutions containing 50% of glycerol, show that the proportional decrease in conductivity due to the increased viscosity is no greater for the neutral salt than for the acid and alkali. The results consequently do not support the Danneel-Grotthus theory of conductivity.

H. F. HARWOOD.

Lead dioxide-lead sulphate electrode. W. C. VOSBURGH and D. N. CRAIG (J. Amer. Chem. Soc., 1929, 51, 2009—2019).—The *E.M.F.* of the cell $Hg|Hg_2SO_4, PbSO_4, H_2SO_4(c), [H_2SO_4(c)PbO_2, PbSO_4]|Pt$ was measured at $20^\circ, 25^\circ, 30^\circ, 35^\circ$, and 40° , c varying between $1M$ and $3.5M$. The temperature coefficient varies with c . The effect of dissolved oxygen and of the method of preparation of the lead dioxide was also studied. The *E.M.F.* of the cell $H_2(Pt)|H_2SO_4(\text{unit activity})|H_2SO_4(\text{unit activity}), PbO_2, PbSO_4|(Pt)$ was calculated to be 1.681 volts at 25° . From this the *E.M.F.* of the lead accumulator, assuming the double sulphate theory, is calculated as 2.03 volts, which result

is regarded as supporting this theory. Revised values for the activity coefficients of sulphuric acid are calculated from *E.M.F.* results here recorded. For the reaction $PbO_2 + 2Hg + 2H_2SO_4(1.036M) = Hg_2SO_4 + PbSO_4 + 2H_2O$, at 25° , the free energy change is $-43,960$ g.-cal., the entropy change -2.58 g.-cal./ 1° , and the heat of reaction $-44,730$ g.-cal. The last figure agrees with the value calculated from thermochemical data.

S. K. TWEEDY.

Polarographic studies with the dropping mercury cathode. III. Deposition of cadmium from cyanide solutions. I. PINES (Coll. Czech. Chem. Comm., 1929, 4, 387—391; cf. Nejedly, this vol., 885).—The deposition potentials of cadmium in solutions containing cadmium salts only and in solutions containing potassium cyanide have been determined. The deposition potential in cyanide solutions agrees with the calculated reversible electrode potential. Cadmium can be deposited completely and reversibly at the dropping mercury cathode in any concentration of cyanide. In fairly dilute solutions, $Cd(CN)_3^-$ ions are formed; $[Cd(CN)_3^-]/[Cd^{2+}][CN^-]^3 = 8 \times 10^{18}$.

C. W. GIBBY.

Potential of an inert electrode in a solution of acetaldehyde. L. RAPKINE (Compt. rend., 1929, 189, 171—173).—The electrode potential of buffered 2% solutions of acetaldehyde at 40° varies linearly with the p_H up to p_H 10, at which point there is an inflexion towards the electronegative region, whilst at p_H 12 it cuts the co-ordinate of the limiting potential of dextrose. The potential is established more rapidly and becomes more negative in value as the alkalinity increases, and aldehyde-sugar condensation in alkaline media is therefore indicated. The irreversible nature of the potential was demonstrated by the addition of milk dehydrase and an acceptor (methylene-blue), and by titration with potassium ferricyanide.

J. GRANT.

Potential differences across the boundaries between solutions of mixed univalent chlorides. E. R. SMITH (Bur. Stand. J. Res., 1929, 2, 1137—1143).—Potential differences across the boundaries between solutions of mixed univalent chlorides (hydrogen chloride and sodium chloride) have been measured using a flowing junction and silver-silver chloride electrodes. There is no evidence of complex formation and potentials can be accurately computed from the formula $E = (RT/F) \log_e [(1 - N_{Na}) - x_2(N_H - N_{Na})] / [(1 - N_{Na}) - x_1(N_H - N_{Na})]$, where x_1 and x_2 represent molal proportions of sodium chloride to the total electrolyte concentration, and N_{Na} and N_H are the cation transference numbers in solutions of the pure electrolytes at the same concentration as the total concentration of the mixture.

C. J. SMITHells.

Ammonia-oxygen gas cell. C. MARIE and C. HAENNY (Compt. rend., 1929, 189, 149—150).—The system $air|Pt|pyrex\ glass|Pt|NH_3$ becomes a conductor above 480° , and the *E.M.F.* falls from 1.090 volts at 570° to 0.951 volt at 790° . The observed values correspond with those calculated from thermochemical data for the equation $4NH_3 + 3O_2 = 2N_2 + 6H_2O$.

J. GRANT.

Variation in the concentration of dilute amalgams of alkali and alkaline-earth metals caused by passing an electric current through them. M. LE BLANC and R. JACKH (Z. Elektrochem., 1929, 35, 395—409).—Dilute amalgams were electrolysed in glass tubes, straight and bent, for various periods of time with different current densities and the changes in concentration of alkali or alkaline-earth metal which occurred in the cathode, middle, and anode compartments were measured. With sodium amalgam the sodium travels to the anode, and the quotient of the difference in concentration of the sodium in the anode and cathode compartments and the current density gradually decreases as the temperature is raised from 25° to 75°, the maximum value of the quotient at any given temperature being attained after about 2000 hrs. The quotient is proportional to the original concentration of the amalgam, and when the electrolysis is carried out in a bent tube, instead of in a straight one, it is quadrupled. Similar increases in the difference between the concentration of the sodium in the amalgam at the two electrodes with increasing current density were found at other temperatures. In the case of barium amalgams the barium travels towards the anode, whereas the reverse is true of lithium and calcium amalgams. The cause of these changes in concentration cannot be traced back to thermoelectric effects. H. T. S. BRITTON.

Theory of passivity. R. MULLER (Z. Elektrochem., 1929, 35, 459—460).—The activation of iron is stated to be due to the equilibrium $\text{Fe} \rightleftharpoons \text{Fe}^{++} + 2e$, and passivation to $\text{Fe} \rightleftharpoons \text{Fe}^{+++} + 3e$, so that the change from the active to the passive state may be represented by $\text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++} + e$. The activating effect of hydrogen and the passivating effect of oxygen are considered to be due to displacements of this equilibrium to the left and right respectively as the result of electron interchanges. H. T. S. BRITTON.

Passivity of metals. I. N. STRANSKI and Z. C. MUTAFTSCHIEV (Z. Elektrochem., 1929, 35, 393—395).—The passivation of metals is discussed in relation to their crystal structure. The mode of dissolution of individual crystals is supposed to be due to the attack of the solvent being restricted to the corners and ultimately to the edges which happen to be exposed in the surfaces of the metals. If a relatively smaller network produced by the corners and edges should become exposed after the dissolution of a metal has been proceeding for some time, then anodic activity will become diminished, eventually giving rise to passivity. The superposition of oxide layers on metal surfaces and their effects are also discussed. H. T. S. BRITTON.

Unimolecular reactions. L. S. KASSEL (Proc. Nat. Acad. Sci., 1929, 15, 601—603).—Bourgin's application of quantum mechanics to unimolecular reaction rates (cf. this vol., 771) is discussed critically. N. M. BLIGH.

Types of unimolecular reactions. O. K. RICE (Proc. Nat. Acad. Sci., 1929, 15, 459—462).—Since there is evidence that chemical reactions are to be explained on the basis of the quantum mechanical resonance phenomenon, relations between types of reactions which have been treated by quantum

methods are pointed out. The types considered are: predissociation, in which a molecule is excited by absorption of radiation of a given frequency in two different ways, unimolecular decompositions of complex organic compounds, in which activation must be assumed, and the more complicated case of photochemical decomposition. N. M. BLIGH.

Rate of recombination of atomic hydrogen. H. M. SMALLWOOD (J. Amer. Chem. Soc., 1929, 51, 1985—1999).—The rate of the reaction $2\text{H} = \text{H}_2$ was determined calorimetrically between 0.5 and 0.9 mm. The results show that the reaction proceeds according to the "three-body" mechanism. The reaction is catalysed by nitric oxide, perhaps owing to the formation of an intermediate molecule $\text{H}-\text{NO}$. One fifth to one sixth of the atomic hydrogen present will react with solid sulphur to form hydrogen sulphide. S. K. TWEEDY.

Ignition temperature of some gases. H. K. SEN and H. N. CHATTERJEE (J. Indian Chem. Soc., 1929, 6, 441—450; cf. McDavid, A., 1918, ii, 10).—The ignition temperature of mixtures of hydrogen and oxygen of varying composition has been determined in soap bubbles, ignition being produced by contact with an electrically heated platinum wire. The ignition temperature decreases with decreasing length of the wire, becoming lowest for a point source. It is lower for large than for small bubbles. When the wire is wound on different insulating materials the ignition temperature rises in the order mica, silica, porcelain, glass. F. L. USHER.

Formation and decomposition of ozone. E. H. RIESENFELD (Z. angew. Chem., 1929, 42, 729—734).—The decomposition of ozone at low concentrations is unimolecular, and at high concentrations bimolecular. The rate of the unimolecular reaction is depressed and the rate of the bimolecular decomposition accelerated in presence of inert gases. The decomposition apparently involves a series of chain reactions and the influence of the added gases is such that they break the chain by actual participation in one of the reactions involved. J. S. CARTER.

Rate of decomposition of nitrogen pentoxide at moderately low pressures. H. C. RAMSPERGER, M. E. NORDBERG, and R. C. TOLMAN (Proc. Nat. Acad. Sci., 1929, 15, 453—459).—In view of divergent results (cf. Hibben, A., 1928, 601; Loomis, *ibid.*, 961; Sprenger, *ibid.*, 1099; Rice, *ibid.*, 1193) experiments were made with special attention to the elimination of errors due to occlusion and adsorption. A reaction vessel of very large volume was used to minimise surface errors, and the reaction was followed by periodically freezing out the oxides of nitrogen and measuring the pressure of the residual oxygen. Data for a large number of experiments are tabulated; the pressure rates of decomposition are calculated and are found to agree within the limits of experimental error with those available for high pressures. It is concluded that, down to the pressures investigated, nitrogen pentoxide shows no change in its specific first-order rate of decomposition. N. M. BLIGH.

Velocity of reaction between iodide and persulphate ions. W. OOSTVEEN (Rec. trav. chim.,

1929, 48, 697).—A note on papers by King and Jette (this vol., 771), re-affirming the part played by the tri-iodide ion in the reaction between the iodide and persulphate ion. F. L. USHER.

Kinetics of the oxidation of iodide ion by acid dichromate solutions in presence of a neutral salt. R. F. BEARD and N. W. TAYLOR (J. Amer. Chem. Soc., 1929, 51, 1973—1985).—The above reaction was investigated at 25° in presence of sodium chloride and perchloric acid over a wide range of hydrogen-ion concentration. The reaction is of the first order with respect to potassium dichromate (DeLury, A., 1903, ii, 471), having a constant k . The graph of k against μ , μ being the ionic strength of the solution, is very similar to the activity curves of strong acids when plotted as a function of μ . A minimum occurs at $\mu=0.7$. Some theoretical justification for the shape of this curve in the region of dilute sodium chloride solutions is obtained on the ground of Bronsted's reaction-rate theory and Debye and Huckel's interionic attraction theory, provided the total reaction is regarded as being quinquemolecular. The reaction is not wholly bimolecular with respect to iodine; two simultaneous reactions occur, which the experiments in presence of 1.5*M*-sodium chloride indicate to be: $H^+ + I^- + Cr_2O_7^{2-} = HI + Cr_2O_7^{2-}$ and $2H^+ + 2I^- + Cr_2O_7^{2-} = (HI)_2 + Cr_2O_7^{2-}$, the latter reaction accounting for the oxidation of about 65% of the iodine.

S. K. TWEEDY.

Rate of oxidation of hydrazine by ferricyanide. E. C. GILBERT (Z. physikal. Chem., 1929, 142, 139—150).—The rate of oxidation of hydrazine by ferricyanide in a buffer solution of p_H about 6 has been measured at 20°. The reaction is of the third order, being unimolecular in respect of the hydroxyl ion, ferricyanide ion, and $N_2H_5^+$ ion, i.e., is equivalent to a reaction of the second order, unimolecular in respect of the hydrazine molecule and ferricyanide ion, so that under the experimental conditions the hydrazine molecule is more reactive than the $N_2H_5^+$ ion. This is interpreted as indicating the formation of an unstable complex of ferricyanide ion and hydrazine, $N_2H_4 + Fe(CN)_6^{3-} \rightarrow [N_2H_4 \cdot Fe(CN)_6]^{3-} \rightarrow N_2H_3 + H^+ + Fe(CN)_6^{4-}$. The N_2H_3 then either decomposes quantitatively, or is oxidised to nitrogen and water, almost instantaneously, no ammonia being formed.

R. CUTHILL.

Thermodynamic relations in the hydrolysis of esters by alkali hydroxide and sodium carbonate. A. MUSIL (Monatsh., 1929, 52, 192—219).—Skrabal's thermodynamic considerations (cf. A., 1924, ii, 666, 667, 842) in statical systems have been extended to the effect of temperature on velocity coefficients in kinetic systems. Expressions are obtained for the velocity of hydrolysis of esters by alkali hydroxide and by sodium carbonate, for the heats of hydrolysis and dissociation, and for the temperature coefficients. The rate of hydrolysis of ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate (at 0.2°, 10°, 20°, and 30°) of *i*-amyl acetate (at 10°, 20°, and 30°) and of *n*-propyl acetate at 30° in the presence of sodium carbonate and 0.01*N*-potassium ferricyanide has been determined. An improved technique is described. These and related results together with those obtained by H.

Olsson ("Die Abhängigkeit der Hydrolysegeschwindigkeit der Ester von der Konstitution," Lund, 1927) on the hydrolysis by alkali hydroxide of these esters are in fair agreement with the calculated values.

A. I. VOGEL.

Kinetic salt effect. III. Influence of non-electrolytes on salt effect in ionic reactions. A. N. KAPPANNA (J. Indian Chem. Soc., 1929, 6, 419—430; cf. this vol., 516).—The reaction between monobromoacetate and thiosulphate ions has been further studied in order to determine the effect of altering the dielectric constant of the solvent, since this has a marked influence on the activity coefficients of the ions. The velocity coefficients were determined at ionic strengths varying from 0.0025 μ to 0.305 μ , in 20, 40, 60, and 80% solutions of alcohol and in 30% and 50% solutions of sucrose. The slopes $d \log k/d\sqrt{\mu}$ differ considerably from those required by the Debye-Hückel limiting equation in 20, 40, and 60% alcoholic solutions, but in the 30 and 50% sucrose solutions up to ionic strengths 0.015 and 0.010, respectively, the Debye-Hückel expression predicts the course of the reaction with fair accuracy. The temperature coefficients of the velocities have also been measured and found to remain constant for a given solvent over the entire range of ionic concentration. No general relationship could be traced between the percentage of alcohol and the velocity coefficient.

F. L. USHER.

Action of hydrochloric acid on alcohol. VI. Velocity coefficients. S. KILPI (Z. physikal. Chem., 1929, 142, 195—210).—Velocity measurements have been made of the reaction between hydrochloric acid and alcohol in various alcohol-water mixtures at 96.5° and 110°. A strict integration of the differential equation of reaction velocity has been carried out. The values of the velocity coefficients have been calculated from this equation and also from an approximate integrated form which assumes that the velocity coefficient of the reaction between alcohol and hydrogen chloride is constant during the course of the reaction. For alcohol-water mixtures containing less than 0.5*M*-alcohol the approximate equation is satisfactory. At higher concentrations the more accurate form has to be used.

F. J. WILKINS.

Velocity of saponification of methyl acetate by sodium hydroxide at 25°. W. T. GOOCH and (Miss) E. M. TERRY (J. Amer. Chem. Soc., 1929, 51, 1959—1965).—An exact measurement at 25° of the velocity coefficient of the hydrolysis of methyl acetate of 0.008*M* and 0.016*M* concentration in 0.01*M*- and 0.02*M*-aqueous sodium hydroxide solution gives 11.67 moles per min., independent of exposure to diffused daylight (cf. Walker, A., 1906, ii, 732). An apparatus for taking samples of the reaction mixture for analysis at noted times is described. A mechanical shaker in which the liquid is whirled within, but independent of, an open container is also described.

S. K. TWEEDY.

Stability of *tert*-amyl trichloroacetate in different solvents. L. M. ANDREASOV (Ukraine Chem. J., 1928, 3, 467—470).—The decomposition of *tert*-amyl trichloroacetate at 25° and 50° in chloroform, carbon tetrachloride, benzene, acetone, nitro-

benzene, ether, ethyl acetate, and carbon disulphide solution and in presence of 1 c.c. of a 0.5% solution of trichloroacetic acid has been determined. The extreme slowness of the reaction rendered it impossible to calculate a reaction constant, but even after 200 hrs. equilibrium was not reached. The percentage decomposition is smallest at 25° in benzene solution and at 50° in nitrobenzene, whilst both at 25° and 50° it is highest in carbon disulphide. The percentage decomposition of the ester in ethyl benzoate solution at 50° is very high and is explained as being due to the decomposition of the complex formed between the ester and ethyl benzoate (cf. Konovalov, A., 1907, ii, 854).

A. FREIMAN.

Kinetics of the interaction of esters with potassium alkoxides. I. Reaction between potassium ethoxide and ethyl acetate in ethyl alcohol-water mixtures. R. F. W. SELMAN and P. B. FLETCHER (Trans. Faraday Soc., 1929, 25, 423—435).—The velocity of the reaction between potassium ethoxide and ethyl acetate depends on the amount of water present. Fractionation of the reaction products on a large scale by Cox's method (A., 1919, ii, 83) shows that no ether is produced. The solid residue consists mainly of potassium acetate. The reaction comprises: (i) the hydrolytic action of water on the potassium ethoxide, and (ii) the hydrolysis of the ester by the potassium hydroxide so formed. An expression corresponding with the dual reaction is derived; it involves the equilibrium relations of the first stage and the velocity equation of the second, assuming it to be bimolecular. The experimental values of the velocity coefficient thus found are composed of the equilibrium constant of the first reaction and the theoretical velocity coefficient of the hydrolysis. They, however, justify the assumption that the latter reaction is bimolecular.

H. T. S. BARRON.

Thermal decomposition of methylisopropyl-di-imide, a homogeneous unimolecular reaction. Thermal decomposition of azoimide and methyl azide. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1929, 51, 2134—2143).—The thermal decomposition of methylisopropyl-di-imide is homogeneous and unimolecular over the range 250—332°, but the velocity coefficient falls at pressures below a few cm. (cf. A., 1927, 737). Analogous results were obtained with methyl azide. In the former case the reaction is explained by Rice and Ramsperger's second theory (*ibid.*, 833), the molecule being assumed to have 33 degrees of freedom. The reactions which occur are: $3\text{NMe}\cdot\text{NPr}^\beta \rightarrow 3\text{N}_2 + \text{C}_3\text{H}_6 + \text{C}_4\text{H}_{10} + \text{C}_6\text{H}_{14}$ and $\text{NMe}\cdot\text{NPr}^\beta \rightarrow \text{N}_2 + \text{CH}_4 + \text{C}_3\text{H}_6$. The two radicals in the compound are probably not combined at the instant of reaction, but are separately dislodged and combine at random later. The thermal decomposition of azoimide is not homogeneous.

S. K. TWEEDY.

Ketonic decomposition of β -ketocarboxylic acids. K. J. PEDERSEN (J. Amer. Chem. Soc., 1929, 51, 2098—2107).—The kinetics of the decomposition of $\alpha\alpha$ -dimethylacetoacetic acid were investigated at 18° in hydrochloric acid solution, in which the reaction is unimolecular, and in buffer solutions: $\text{CAcMe}_2\cdot\text{CO}_2\text{H} = \text{CHAcMe}_2 + \text{CO}_2$. The dissociation

constant of the acid is 3.14×10^{-4} . The reaction is accelerated by aniline. The acid is relatively unstable, whence it follows that the keto-form of the β -ketocarboxylic acids is unstable. It is suggested that only the keto-form undergoes ketonic decomposition, amines catalysing the reaction by producing an intermediate compound with this form, which compound yields carbon dioxide more rapidly than the free keto-form.

S. K. TWEEDY.

Velocity of oxidation of amines by potassium permanganate. B. V. TRONOV and L. S. NIKONOVA (J. Russ. Phys. Chem. Soc., 1929, 61, 541—549).—The relative velocities of oxidation of triethylamine by potassium permanganate in alkaline and in acid solutions are as $10^6 : 3.3$, of piperidine as $2.8 \times 10^5 : 92$, of quinoline as $5.2 \times 10^3 : 1.4 \times 10^5$, of isoquinoline as $9.5 \times 10^3 : 3.8 \times 10^4$, of pyridine as $1 : 74$, and of 2-methylpyridine as $21 : 126$. The values obtained for oxidation of these substances in neutral solution differ little from those in alkaline solution. It is concluded that pyridine is less resistant towards oxidation when present in the form of a salt.

R. TRUSZKOWSKI.

Velocity of oxidation of benzoic [and other] acids by potassium permanganate in alkaline solution. B. V. TRONOV and A. A. GRIGORIEVA (J. Russ. Phys. Chem. Soc., 1929, 61, 653—665).—The following acids were investigated in the form of their sodium salts: benzoic, *o*-chlorobenzoic, *p*-bromobenzoic, *o*-, *m*-, and *p*-nitrobenzoic, *o*-, *m*-, and *p*-toluic, salicylic, *m*- and *p*-hydroxybenzoic, anthranilic, *m*- and *p*-aminobenzoic, *o*-, *m*-, and *p*-phthalic, anisic, gallic, α - and β -naphthoic, phenylacetic, phenylpropionic, mandelic, benzilic, cinnamic, *o*-, *m*-, and *p*-nitrocinnamic, pyromucic, benzene-sulphonic, α - and β -naphthonic, and sulphanilic. The salts were treated with an equimolecular amount of sodium hydroxide (0.1N or N). The potassium permanganate was used in 5.5% solution, the temperature being kept at 18—20°. Except in the case of *o*-chlorobenzoic acid all substituents accelerate the reaction. Chlorine, bromine, a nitro-group, a carboxyl group, and a methoxy-group increase the rate of reaction from 2 to 100 times; the increase for a sulphonic group is of the order 10^4 times and for a hydroxyl or an amino-group of the order 10^5 times. The effect of position is not yet clear, although the position of the carboxyl group has some slight effect. The stability of the furan ring is much less than that of the benzene ring.

A. FREIMAN.

Velocity of dissolution of copper. R. GLAUNER (Z. physikal. Chem., 1929, 142, 67—91).—The velocity of dissolution of copper foil in various reagents was determined, the foils having different crystal layers exposed. The liquids used were hydrochloric, hydrobromic, nitric, sulphuric, perchloric, and acetic acids, ammonium persulphate, and ammonia, and mixtures of hydrochloric acid, sulphuric acid, acetic acid, and oxalic acid, respectively, with hydrogen peroxide. A mathematical expression for the velocity of dissolution is derived. It is a differential equation of one or two terms. The first term is dependent on the initial velocity of the reaction as conditioned by the nature and concentration of the

solvent. The second term accounts for the auto-catalytic effect of copper in the solution. The equation is tested for a series of solvents, and the agreement, in the majority of cases, is good. There are a few cases where the equation satisfies only the initial conditions, and others where the agreement is good only in the later stages of the reaction. The applicability of the Nernst-Brunner diffusion theory is discussed, and it is shown that the constants of the differential equation are proportional to the diffusion coefficients of the solvent and the copper salt formed. Opposed to this are the observed differences in dissolution velocity with different crystalline structure which cannot be accounted for by the original theory.

A. J. MEE.

Kinetics of dissolution of cadmium in hydrochloric acid. K. JABŁCZYŃSKI and H. WAJCHSEL-FISZ (Rocz. Chem., 1929, 9, 340—347).—The velocity of dissolution of cadmium in 5*N*-hydrochloric acid at 25° diminishes to zero within about 40 min., after which *K* rises gradually to a constant value 20 hrs. later. Subsequently a further slight progressive increase in velocity is found. The temperature coefficient of the reaction is 2.02, and it is concluded that the process of dissolution of cadmium in hydrochloric acid is one of a purely chemical nature, independent of diffusion.

R. TRUSZKOWSKI.

Oxidation of copper at high temperatures. F. J. WILKINS (Z. Elektrochem., 1929, 35, 500—501).—The data obtained by Feitknecht (this vol., 517) relating to the oxidation of copper between 600° and 1020° are shown to satisfy the equation $x^2 = kt + c$, *x* being the oxygen combined in time *t*, and *k* and *c* being constants. The diffusion occurring at the boundaries of crystals is held to be less than that at their lattices.

H. T. S. BRITTON.

Rate of dissolution of alloys in hydrochloric acid. P. FISCHER (Z. Elektrochem., 1929, 35, 502—505).—The rate of dissolution in 0.5*N*- and *N*-hydrochloric acid solution of zinc and of its alloys containing 2.5, 5, and 10% Pt; 10% Sb; 2.5, 5, and 10% Ag; arsenic; 5, 10, and 20% Pb; and 20% Hg was measured by revolving pieces of metal having the same surface area in the acid and measuring the volumes of hydrogen evolved after equal periods of time had elapsed. Pure zinc showed no signs of dissolving in 0.5*N*-hydrochloric acid after 2 days. The effects of the various metals in the alloys in accelerating dissolution showed no parallelism with their order in the electro-potential series, but seemed to be related with the hydrogen over-voltage; thus platinum with the lowest hydrogen over-voltage had the greatest influence, and mercury with the highest hydrogen over-voltage had an extremely small effect. Respecting the "theory of local action," it is emphasised that it is not only the magnitude of *E.M.F.* set up between the two metals, but it is essentially the magnitude of the current available, and this is determined also by the number of local elements actually present.

H. T. S. BRITTON.

Induced reactions. W. D. BANCROFT (J. Physical Chem., 1929, 33, 1184—1192).—Previous classifications of induced reactions are discussed and

a new one based on the induction factor, *i.e.*, the ratio of the amount of the actor reacting with the acceptor to the amount reacting with the inductor, is advanced. This eliminates the difficulty of interpreting reaction velocity experiments, but is liable to serious error if the actor reacts at an appreciable rate with the acceptor. All induced reactions can be arranged in three groups or combinations of these; the acceptor may react with a lower stage of the actor, or with a reaction product of the inductor, or the actor may react with a reaction product of the inductor and acceptor. Consecutive reactions are those in which the acceptor reacts with a stable oxidation or reduction product of the inductor and should be classed as induced reactions.

L. S. THEOBALD.

Homogeneous catalysis. N. A. MILAS (Proc. Nat. Acad. Sci., 1929, 15, 596—601; cf. this vol., 149).—To test the view that a negative catalyst for auto-oxidation should be a good reducing agent or easily oxidisable, quantitative experiments were made which showed that anthraquinone acts as a truly negative catalyst in the oxidation of anethole, but can be recovered quantitatively at the end of the reaction. The effect of anthraquinone and benzoquinone, which was the stronger inhibitor, on the maximum oxygen absorption rate of anethole was measured for several concentrations. This absorption rate is emphasised as a most characteristic property in all auto-oxidation reactions, and an equation is derived, and verified experimentally, connecting the maximum oxygen absorption rate, the concentration of the catalyst, and the time necessary for the oxidation rate to reach a maximum value.

N. M. BLIGH.

Auto-oxidations. N. A. MILAS (J. Physical Chem., 1929, 33, 1204—1216).—The view is advanced that in all auto-oxidations the atoms to which the oxygen molecule is initially added make definite contributions of two electrons to it; metastable or dative peroxides (Menzies, A., 1928, 349), characterised by high instability and energy content, are formed and may either revert instantaneously to ordinary peroxides by transferring their excess energy to other molecules, or initiate the oxidation of other molecules. Various auto-oxidations, together with the inhibition and acceleration of such reactions, are discussed in the light of the above views.

L. S. THEOBALD.

Autocatalytic decomposition of thiosulphuric acid. K. JABŁCZYŃSKI and S. FRENKENBERG (Rocz. Chem., 1929, 9, 327—334).—See this vol., 772.

"Oxygen activation" or "induced oxidation." XIV. W. P. JORISSEN and A. H. BELINFANTE (Rec. trav. chim., 1929, 48, 711—725; cf. A., 1927, 326).—A summary of work on induced oxidation done since 1851 is given. Measurements of the absorption of oxygen by various mixtures containing sodium sulphite show that the following substances can act as "acceptors": indole, mannitol, *n*-propyl alcohol, glycol, *cis*- and *trans*-cyclohexane-1:2-diol, inositol, sodium potassium tartrate, glycerol, erythritol, laevulose, sucrose. In some instances the extent of the induced oxidation depends on the hydrogen-ion concentration in the solution.

F. L. USHER.

Rapid absorption of hydrogen by solutions of permanganate containing silver. F. HEIN and W. DANIEL (*Z. anorg. Chem.*, 1929, **181**, 78—82).—Absorption of hydrogen by aqueous solutions of permanganate is considerably accelerated in presence of silver salts, especially silver nitrate. There is apparently for each concentration of permanganate an optimum concentration of silver at which the rate of absorption is maximal. Under favourable conditions the whole of the hydrogen in appropriate gaseous mixtures can be absorbed. J. S. CARTER.

Oxidation of sodium sulphite by air in the presence of ferrous hydroxide and a theory of negative induced reaction. S. MIYAMOTO (*Bull. Chem. Soc. Japan*, 1929, **4**, 132—142, and *Sci. Papers Inst. Phys. Chem. Res.*, 1929, **11**, 81—92; cf. A., 1926, 915).—The inhibiting effect of a primary on a secondary reaction is termed a negative induced reaction in which the activated molecules of the reactants of the secondary reaction lose their activity, before they can react, through the presence of the primary reaction. Three kinds of negative induced reactions can occur in which the active states of the molecules of the reactants of the secondary reaction can be transferred to the molecules of (i) the reactants, (ii) the reaction products, and (iii) to both reactants and reaction products of the primary reaction. The oxidation of sodium sulphite and stannous hydroxide in sodium hydroxide or carbonate solution (A., 1928, 598) by air is an example of the first kind, whilst that of sodium sulphite and ferrous hydroxide in sodium hydroxide is now shown to be of the second kind. The velocity of oxidation of sodium sulphite in the presence of ferrous hydroxide by means of air decreases rapidly with time, a direct transference of activation taking place from sodium sulphite molecules to those of ferric hydroxide, the reaction product of the primary reaction. In confirmation, the velocity of oxidation of sodium sulphite in the presence of ferric hydroxide is shown to be small, and sodium sulphate is also without effect. L. S. THEOBALD.

Effect of neutral salts on the velocity of oxidation of organic compounds by potassium permanganate. B. V. TRONOV and A. A. LUKANIN (*J. Russ. Phys. Chem. Soc.*, 1929, **61**, 727—734).—The effect of sodium and potassium chloride and nitrate, potassium perchlorate, potassium sulphate, and of sodium carbonate on the oxidation of ethyl alcohol in an alkaline medium at temperatures of 16.8—26.8° was investigated. The addition of neutral salts increases the rate of reaction almost proportionally to the amount used. The nature of the cation or anion and variation of the concentration of the potassium permanganate used (0.0001—0.0004*M*) have no marked effect. The temperature coefficient calculated in terms of the percentage of active oxygen lost increases on addition of potassium chloride and still more on addition of potassium sulphate. The authors finally conclude that neutral potassium permanganate is a more effective oxidising agent than the permanganate ion. A. FREEMAN.

Catalysis by silver of the union of hydrogen and oxygen. D. L. CHAPMAN and W. K. HALL (*Proc. Roy. Soc.*, 1929, A, **124**, 478—493).—The method

adopted by Hughes and Bevan for testing whether a nickel surface was covered with a layer of oxide (A., 1928, 27) has been used in an investigation of the catalysis by silver of the reaction between hydrogen and oxygen. Determinations of the accommodation coefficients of hydrogen at silver surfaces support the assumption of Chapman, Ramsbottom, and Trotman (A., 1925, ii, 310) that silver which has been heated to redness in oxygen and allowed to cool in the gas is covered with a film of oxide. At the same temperature and pressure hydrogen molecules remove less heat from a hot metallic surface than from one which has been subjected to the action of oxygen at a high temperature. A series of experiments is described which shows that when a surface of metallic silver is brought into contact with gaseous oxygen in sufficient quantity to form more than a complete unimolecular layer of oxide, it becomes coated almost immediately with a film of oxide, and that this oxide, formed at a low temperature, is a much more effective catalyst than that formed at a high temperature and is also more easily reduced by hydrogen. There appear therefore to be two forms of silver oxide, and it is assumed that in the active film, formed at a low temperature, some of the silver oxide molecules are in relatively unstable positions, but that on raising the temperature the arrangement becomes more stable and the film in consequence less active chemically. The mechanism of the catalysis is in both cases one of alternate oxidation and reduction. The accommodation coefficient of hydrogen (at 16° and 48810×10^{-6} mm.) at a silver surface heated at 100° is calculated to be 0.25; the corresponding value for an oxidised surface is 0.28. L. L. BIRCUMSHAW.

Influence of various salts on the dissolution of pure aluminium in hydrochloric acid. J. CALVERT (*Compt. rend.*, 1929, **189**, 183—186; cf. B., 1929, 438).—Platinic chloride (4×10^{-5} to 0.21 mg. per litre) hastens the action of 0.5*N*-hydrochloric acid on pure aluminium to an extent which increases with the amount present; the effect is greater than that produced by an equivalent amount of gold. Nickel and relatively large amounts of mercury have similar but less marked effects, whilst other metals have little or no influence. In 2.5*N*-acid, copper (5 mg. per litre) diminishes the period of induction, whilst mercuric chloride (20 mg. per 800 c.c.) produces a period of induction followed by attack more rapid than in the pure acid. Smaller quantities of mercury (1 mg. per 800 c.c.) give rise to irregularly alternating phases of activity and passivity. J. GRANT.

Catalysis of solids by solids. II. Catalytic decomposition of mercuric oxide. S. Z. ROGINSKI, L. M. SAPOSCHNIKOV, and N. A. KUTSCHERENKO (*Ukraine Chem. J.*, 1929, **4**, 99—119).—To discover the actual mechanism of the thermal decomposition of mercuric oxide crystals of the substance were placed in a tube which was heated electrically at 360—380° and was evacuated to 10^{-4} — 10^{-5} mm. after being closed by another tube, containing liquid air, which reached almost to the bottom of the first tube. After several hours' heating nothing but pure mercury was found to be condensed on the outside of the second tube. The authors therefore conclude

that the mercuric oxide decomposes directly into mercury and oxygen and that it does not vaporise and then decompose. They observed neither a period of induction nor an initial acceleration of the process of decomposition, but they found that the velocities of decomposition are different for the red and the yellow oxide. The yellow oxide decomposes about six times as fast as the red oxide, but by powdering the red oxide its rate of decomposition increases until, when the powder is very fine, the rate becomes almost equal to the rate for the yellow oxide. The catalytic effect of the following oxides on the rate of decomposition of mercuric oxide was also studied: nickel, ferric, manganese, manganese dioxide, cobaltocobaltic, cupric, stannic, lead, chromium, cadmium, zinc, magnesium, titanium, uranium, aluminium, and silica; also barium sulphate and barium carbonate. Silica and chromium oxide which react with mercuric oxide retard the decomposition; the others, particularly nickel oxide, accelerate it. It was also found that the catalytic effect for the same catalyst varies according to its mode of preparation. The theory of intermediate compound formation is criticised and is shown to be untenable in this case. The catalytic activity of a solid is assumed to be due to a large number of small electric fields covering the surface of the catalyst and the difference in the activity of different oxides to be due to differences in intensity, distribution, and distances apart of these fields.

A. FREIMAN.

Catalytic activity of molten tin. Relative efficiencies of tin and its oxides as catalysts for the reduction of nitrobenzene vapour. G. WILLIAMS (Trans. Faraday Soc., 1929, 25, 446—451).—Unlike Brown and Henke (A., 1924, ii, 31), the author observed that the reduction of stannic oxide by hydrogen is extremely slow at 300°, and that a temperature of about 500° is required for reduction to be complete within 1—2 hrs. (cf. Fink and Mantell, B., 1927, 369; A., 1928, 257). The author has obtained high yields of aniline by the reduction of nitrobenzene vapour with hydrogen at 310° with tin oxide catalysts. No evidence was obtained of the reduction of the oxide to the metal in the experiments, and it was, moreover, found that normal specimens of tin (contrary to Brown and Henke) do not catalyse this reaction at this temperature, which happens to be above the m. p. of tin.

H. T. S. BRITTON.

Electrolysis with diaphragm. (Formulae of Foerster and of Guye.) O. ESSIN (Z. Elektrochem., 1929, 35, 492—500).—From a consideration of the concentrations and conductivities of the electrolyte used (an alkali metal salt) and the alkali formed and the mobilities of the various ions involved, the author has derived an expression which is shown to lead to the theoretical formula of Foerster and Jorre (A., 1900, ii, 343) and to the empirical formula of Guye (A., 1903, ii, 586; 1904, ii, 29), relating to the current efficiency of the electrolytic production of alkali in a cell in which a diaphragm is interposed between the electrodes. Two series of experiments are described in which a perforated nickel anode, an iron net cathode, and potassium carbonate solutions of different concentrations as anolytes and catholytes were used.

The current efficiencies actually obtained are compared with the corresponding values calculated with the author's formula and those of Foerster and of Guye.

H. T. S. BRITTON.

Formation and properties of very thin electrolytic nickel films. K. M. OESTERLE (Z. Elektrochem., 1929, 35, 505—519).—The nickel deposits obtained from *N*-nickel chloride solution, buffered to various p_H -values with "acetate mixture," "acetate mixture" and gelatin, ammonium chloride, or boric acid, on platinum or silver cathodes, using a nickel anode and a cathodic current density of 2.5 amp./dm.², have been investigated by means of measurements (a) with the contractometer (Kohlschütter and Jakober, A., 1927, 1016), (b) with the Pendel magnetometer, (c) of the normal electrode potentials, and (d) with Debye and Scherrer's X-ray apparatus. The crystal structure, and consequently the physical properties, of the deposits depend on the p_H value of the electrolyte and also on the presence of gelatin, which in serving as a protective colloid of the dispersed nickel hydroxide, caused a bright smooth layer to be formed. The data corresponding with those deposits obtained from solutions of p_H 4.5—6.0 illustrate how great an effect a small change in may have on the quality of the layer. It is within this range that the electrolyte becomes contaminated with small amounts of nickel hydroxide.

H. T. S. BRITTON.

Electrolytic zinc refining. II. Influence of foreign elements on the hydrogen overvoltage. H. SETO.—See B., 1929, 648.

Cataphoresis of lead sulphate. E. L. JEWETT (J. Physical Chem., 1929, 33, 1024—1026).—The part played by cataphoresis in a lead accumulator in the Luckow process for the electrolytic preparation of insoluble lead salts and in the electrolytic determination of lead is discussed.

L. S. THEOBALD.

Electrolytic preparation of iodoform without the use of platinum. A. VYSKOCIL (Chem. Listy, 1929, 23, 212—215, 249—251).—In the electrolytic preparation of iodoform from ethyl alcohol the platinum anode may be replaced by one of coinage nickel (25% Ni, 75% Cu) or of carbon, but not of chromium, nichrome, nickel, copper, or brass. The copper-nickel anode does not undergo corrosion in the presence of sodium carbonate.

R. TRUSZKOWSKI.

Connexion between absorbed energy and velocity in photochemical reactions of the $I^{0.5}$ type. A. J. ALLMAND (J.C.S., 1929, 1557—1560).—When the velocity of a photochemical reaction is proportional to the first power of the intensity, if reaction chains are not set up, the quantum efficiency γ is a characteristic for the reaction. For the $I^{0.5}$ type of reaction γ is not characteristic and is a function of intensity, thickness of the reaction vessel, and concentration of reactant. An attempt is made to derive a quantity which shall be as characteristic of the $I^{0.5}$ reactions as γ is of the $I^{1.0}$ reactions. It is suggested that the photochemical susceptibility σ (Henri and Wurmser, J. Physique, 1913, 3, 305) or the coefficient of utilisation Γ (Tian, Ann. Physique, 1916, 5, 248) fulfils this function. F. J. WILKINS.

Primary process of light absorption and activation in photochemical reactions. K. P. BASU (J. Physical Chem., 1929, 33, 1200—1203).—In photochemical reactions the abnormal yield per quantum of radiation absorbed is due partly to the activation of more than one molecule of the absorbing substance by one quantum of incident radiation. The increase in photochemical efficiency with an increase in frequency of the incident radiation is explained by the increase in scattering and the number of activated molecules which accompanies the greater frequency. L. S. THEOBALD.

Chemical reactions in infra-red radiations (7304 Å.). A. K. BHATTACHARYA and N. R. DEAR (J. Indian Chem. Soc., 1929, 6, 451—464; cf. this vol., 516).—Work previously described has been extended to 30 reactions which have been found to be accelerated by radiation of wave-length 7304 Å., and the general conclusions with regard to quantum efficiency and temperature coefficients previously arrived at are confirmed. F. L. USHER.

Extinction coefficient of Br_3' ions and its function in photochemical reactions. R. M. PURAKAYASTHA (J. Indian Chem. Soc., 1929, 6, 361—373).—In order to ascertain the function of tribromide ions in the photochemical oxidation of organic acids by bromine in the presence of potassium bromide, the extinction coefficient of this ion has been determined for 5360, 5460, and 5790 Å. The oxidation of mandelic and lactic acids by bromine, which has no appreciable velocity in darkness, is unimolecular in the absence of bromide, but when a bromide is added, or when the hydrobromic acid formed in the reaction is allowed to accumulate, it becomes zeromolecular, the velocity coefficient increasing with the ratio of free bromine to tribromide ion. The results are satisfactorily accounted for by assuming that only that fraction of the incident light which is absorbed by the bromine molecules is photochemically active. F. L. USHER.

Photochemical equilibrium in nitrogen peroxide. III. Comparison of the thermal, photochemical, and electrical decompositions, and a general theory of the change. IV. Relation between fluorescence and photochemical action. R. G. W. NORRISH (J.C.S., 1929, 1604—1611, 1611—1621).—III. The thermal decomposition of nitrogen peroxide possesses a heat of activation of 32,000 g.-cal. (this vol., 33). For the photochemical reaction, however, a minimum excitation to about 80,000 g.-cal. is required in order that reaction may follow at the next collision. It is thus necessary to distinguish between the two molecular conditions of excitation and activation. The former involves a partition of the absorbed energy between electronic, vibrational, and rotational degrees of freedom, whilst the latter occurs only when the vibrational and rotational energy is raised to a critical value. The earlier work (this vol., 893) on the relation between quantum efficiency and wave-length demonstrated that blue light of wave-length 4360 Å. is without photochemical activity, although it causes molecular excitation to the extent of 64,000 g.-cal. Such absorbed energy cannot be degraded to heat, for in that case sufficient

energy would be provided to cause decomposition. It must therefore be re-radiated, the de-excitation of the electronic degree of freedom being followed by fluorescence. Further, in light which is incompletely active photochemically the fluorescence will be restricted. For wave-lengths giving a quantum efficiency of two (complete photochemical activity) there will be no fluorescence.

It is suggested that the fluorescence observed by Zenneck and Strasser (A., 1912, ii, 127) when nitrogen peroxide is decomposed in an alternating discharge is capable of an analogous interpretation. The fluorescence is due to radiation from excited molecules which do not decompose, formed by collisions of the first kind with electrons.

IV. The relationship predicted between fluorescence and photochemical action in nitrogen peroxide has been verified experimentally. Light of wave-length 4360 Å. (photochemically inactive) produces an orange fluorescence and violet light (4050 Å., photochemically incompletely active) a greenish-yellow fluorescence. The spectra of the fluorescent radiations are identical, possessing two wide maxima at about 6400 and 5900 Å., different intensity distributions accounting for the colour difference. Addition of oxygen destroys the fluorescence. From the concentration required, it is estimated that the mean life of the excited molecule is 5×10^{-8} sec., a result which is supported by the observation that the fluorescence is unpolarised. In view of the comparatively long life of the excited molecule, it is possible that even for wave-lengths which are almost completely photochemically active a small fraction of excited molecules will fluoresce before reaction occurs. A very faint fluorescence of this nature has been observed at λ 3650 Å. It is shown that reaction follows when one of the reactant molecules possesses among its vibrational and rotational degrees of freedom 26,000 g.-cal. It is suggested that the energy of activation, 32,000 g.-cal., is just sufficient to stimulate the vibrational and rotational degrees of freedom to this extent. This conclusion is probably of general significance. F. J. WILKINS.

Photosensitised and photochemical decomposition of hydrazine. J. C. ELGIN and H. S. TAYLOR (J. Amer. Chem. Soc., 1929, 51, 2059—2082).—Gaseous hydrazine is completely decomposed by ultra-violet radiation at a rate which is independent of temperature (15—45°): (i) $2\text{N}_2\text{H}_4 = 2\text{NH}_3 + \text{N}_2 + \text{H}_2$; (ii) $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$. Reaction (i) has ten times the rate of (ii). As a whole, the reaction is unimolecular in character; this, however, is here meaningless. The rate is uninfluenced by addition of nitrogen, hydrogen, or ammonia.

The thermal decomposition of hydrazine in a quartz vessel commences at about 250°: (in) $3\text{N}_2\text{H}_4 = 4\text{NH}_3 + \text{N}_2$; a small quantity of hydrogen is also liberated, but not from the ammonia, which is stable even at 500°. The reaction is heterogeneous and of unimolecular character. On the surface of heated platinum or tungsten wire reaction (i) occurs.

The photochemical decomposition of hydrazine sensitised by mercury vapour to light of 2537 Å. was also investigated. Reaction (i) occurs with forty

times the speed of reaction (ii), so that the latter becomes negligible. The reaction, which proceeds chainwise, has a rate which is at least twice that of the sensitised reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ (which reaction was briefly examined) and is independent of the presence of nitrogen, ammonia, and hydrogen, but is proportional to the incident radiation intensity. The quantum efficiency of the sensitised hydrazine decomposition is about 13, which indicates an efficiency of 0.3 for the sensitised ammonia decomposition. The spectrum of gaseous hydrazine indicates that this substance offers another example of "pre-dissociation." The results as a whole are satisfactorily explained by a reaction mechanism based on a dissociation of primarily excited molecules into either $\text{N}_2\text{H}_3 + \text{H}$ or 2NH_2 as a primary process. The results show that hydrazine cannot form an intermediate product in ammonia decomposition, but the mechanism type proposed for the latter by Bates and Taylor (A., 1927, 1153) is favoured.

S. K. TWEEDY.

Photochemical oxidation with potassium dichromate. D. S. MORTON (J. Physical Chem., 1929, 33, 1135—1141).—Experiments on the light and dark reactions between ethyl alcohol and potassium dichromate in the presence of varying concentrations of sulphuric acid show that (i) under suitable conditions, dichromate solutions are photochemically active for light absorbed by dichromate, (ii) with increasing acidity the oxidising power of the dichromate solution increases and the apparent action of light decreases, and (iii) the light reaction can be varied from approximately zero to totality by varying the concentration of sulphuric acid. The general insensitivity of chromic acid to light implied by Luther and Forbes (A., 1909, ii, 632), although correct for the high acidity used in their experiments, is misleading.

L. S. THEOBALD.

Photolysis of potassium ferrioxalate solutions.

I. Experimental. **II. Discussion.** A. J. ALLMAND and W. W. WEBB (J.C.S., 1929, 1518—1531, 1531—1537).—I. The influence of concentration of photolyte, wave-length, added neutral salts, intensity, intermittent illumination, and inhomogeneous light have been studied on the quantum efficiency (γ) of the photolysis of potassium ferrioxalate solutions. Between the limits studied, 0.02*M* and 0.06*M*, γ is independent of the concentration of the photolyte. Increase of wave-length from 313 to 436 μ causes a decrease in γ from 1.6 to 0.9. Addition of strong electrolytes increases γ . Potassium oxalate forms an exception in that it causes a slight decrease in γ . For the light used (wave-length 365 μ together with some of 405 μ), γ is independent of the intensity and of whether the illumination is constant or intermittent. The use of light forming a continuous band between 390 and 460 μ causes a degree of decomposition which is about 20% lower than that calculated on the assumption that the action of the rays is additive. Although these results agree with the work of Padoa and Vita (A., 1924, ii, 322) they cannot be regarded as definitive owing to the possibility of certain errors. Results not liable to these errors were obtained with light containing two or more of

the three mercury lines 365, 405, and 436 μ . They show that the degree of decomposition is 25—30% greater than that corresponding with an additive effect of the different wave-lengths.

II. It is suggested that the primary result of the absorption of a light quantum is the activation of the ferrioxalate ion, a process which is regarded as involving the partial dislocation of the union between the ferric ion and one of the attached oxalate ions. Reaction occurs following on the collision of a ferrioxalate ion so activated with a normal ion. On the basis of this theory it is possible to explain the influence of concentration of photolyte, wave-length, intensity, and intermittent illumination on the quantum efficiency γ of the photolysis. The influence of neutral salts is not understood. An explanation of the increase of γ obtained with inhomogeneous light which was suggested by the existence of the Raman effect is put forward.

F. J. WILKINS.

Physical development and nature of the latent image. R. E. OWEN.—See B., 1929, 623.

Technique of photographic measurement of absorption in the ultra-violet. V. HARDNUNG (Helv. phys. Acta, 1928, 1, 472—507; Chem. Zentr., 1929, i, 1130—1131).—Two methods are described and applied to the examination of glass. Experiments performed with betaine, glycine, and sarcosine, with a view to test Pfeiffer's theory of the structure of betaine, were inconclusive.

A. A. ELDRIDGE.

Decomposition of ethylene by ultra-violet light. R. B. MOONEY and E. B. LUDLAM (Trans. Faraday Soc., 1929, 25, 442—445).—The ultra-violet absorption spectrum of very pure ethylene has been investigated. Absorption is practically complete from 1850 to 1990 Å., about 75% at 2020 Å., and slight absorption at 2060—2110 Å. The long wave-length limit of absorption, viz., 2110—2130 Å., coincides with that calculated from the heat of dissociation of ethylene into acetylene and atomic hydrogen. Light radiations of wave-length shorter than 2110 Å. cause ethylene to decompose giving acetylene as one of the decomposition products. Contrary to the view of Bates and Taylor (A., 1927, 1153), the presence of mercury vapour is not essential for the decomposition.

H. T. S. BRITTON.

Photochemical reaction between cinnamic acid and chlorine in carbon tetrachloride solution. K. P. BASU (J. Indian Chem. Soc., 1929, 6, 341—352).—In the photochemical reaction between chlorine and cinnamic acid in carbon tetrachloride solution the quantum efficiency is 2 at 4360 Å., 4 at 4040 Å., and 7 at 3665 Å. A "chain" mechanism is therefore indicated, and the following scheme is suggested: (1) $\text{Cl}_2 + h\nu = \text{Cl}^* + \text{Cl}$, (2) $\text{R} + \text{Cl}^* = \text{RCl}^*$, (3) $\text{RCl}^* + \text{Cl}_2 = \text{RCl}_2 + \text{Cl}^*$. The increase of quantum efficiency with increase of frequency of the incident light is explained by assuming that the activated monochloride carries with it in the form of kinetic energy part of the higher energy content of the activated chlorine atom associated with light of higher frequency, and that the length of the "chain" is proportional to the energy associated with the monochloride formed. The temperature coefficient of the

reaction varies from 1.1 at 3665 Å. to 1.38 at 4360 Å. No fluorescence could be detected in a solution of chlorine in carbon tetrachloride. F. L. USHER.

Oxidation of some hydroxy-acids by bromine.

I. The light reaction. II. The dark reaction. R. M. PURAKAYASTHA (J. Indian Chem. Soc., 1929, 6, 375—383, 385—390; cf. Ghosh and Basu, A., 1928, 970).—I. The photochemical oxidation of lactic, phenyl-lactic, mandelic, and citric acids by bromine has been studied with the object of elucidating the large increase in the unimolecular velocity coefficient with diminution of the concentration of bromine. The velocity coefficients are nearly proportional to the concentration of the organic acid, and inversely proportional to that of the bromine. There is an induction period which vanishes in the presence of potassium bromide. The quantum efficiency for light about 4700 Å. is 15, 13, 13, and 3 in the order in which the acids are named above. The experimental results, whilst supporting the view previously put forward, that the bromine atoms which are the primary products of the photochemical action become deactivated by collision with oxygen molecules, indicate that this view is incomplete, since the reaction velocity is determined solely by the ratio of bromine to tribromide ion, irrespective of the concentration of total bromine or free bromine. The induction period is probably due to the formation of complexes between bromine and the reacting acid.

II. The influence of various electrolytes on the rate of oxidation of phenyl-lactic acid and mandelic acid in the dark has been studied. Unimolecular velocity coefficients are obtained in the presence of potassium bromide and of hydrobromic acid. The velocity coefficient is lowered more by hydrobromic acid than by potassium bromide. The reaction is accelerated by hydrochloric acid and still more by potassium chloride, and is also catalysed by the sulphate ion. Addition of sodium hydroxide to the system containing potassium bromide increases the velocity coefficient regularly, whence it is inferred that the organic acid anion is alone reactive. When the hydrogen-ion concentration is maintained constant the reaction is due to free bromine molecules only.

F. L. USHER.

Effect of ultra-violet light on proteins. M. ARTHUS [with G. BOSHELL] (Arch. Int. Physiol., 1928, 30, 244—249; Chem. Zentr., 1929, i, 1083).—Fibrinogen of the citrate-plasma of rabbits and horses loses its coagulability at 56°; it is no longer precipitated by sodium chloride, nor does it afford fibrin with thrombin or calcium chloride. Fibrinogen solutions (Hammarsten) on irradiation deposit a precipitate and are no longer coagulated by the toxin of *Crotalus terrificus*. Caseinogen is converted into a substance which is not precipitated by acetic acid; gelatin in sodium fluoride solution exhibited a diminished solidifying power. A. A. ELDRIDGE.

Oxidising action of solar light on a solution of zymosterol in oil. E. ROUSSEAU (Compt. rend., 1929, 189, 173—174).—Solutions of zymosterol (m. p. 92.1°) in olive oil are slowly and progressively oxidised under the influence of solar radiation at 25°, although to a smaller extent than ergosterol or

cholesterol (this vol., 895). Strict comparison is not possible, as the cholesterol used (m. p. 146.3°) probably contained traces of ergosterol. J. GRANT.

Effect of ultra-violet light on some toxins and antitoxins. M. ARTHUS [with H. N. W. COLLINS] (Arch. Int. Physiol., 1928, 30, 250—266; Chem. Zentr., 1929, i, 1084).—The toxins of *Crotalus terrificus*, *Lachesis lanceolatus*, *Vipera Russellii*, and *Naja tripudians* are decomposed by irradiation with ultra-violet light. With cobra venom the coagulation-inhibiting action was sometimes replaced by a slightly accelerating action. Presence of horse-serum, egg-white, or Witte peptone protected the snake venoms from decomposition on irradiation. Anti-cobra, -dabaia, and -bothrops sera were little affected by irradiation unless diluted. A. A. ELDRIDGE.

Reduction of cuprous chloride. S. SEN (Z. anorg. Chem., 1929, 181, 427—428).—Cuprous chloride is readily reduced to metallic copper by warming its saturated ammoniacal solution with a little sodium potassium tartrate and 40% formaldehyde, care being taken to avoid excess of the latter, since otherwise cuprous oxide is precipitated.

H. F. HARWOOD.

Physical and chemical properties of beryllium. K. ILLIG (Wiss. Veröff. Siemens-Konz., 1929, 8, [1], 74—82).—A review of the literature dealing with the physical properties of beryllium and its behaviour towards acids, bases, gases, and various oxides.

A. R. POWELL.

Preparation of beryllium by thermal methods. K. ILLIG and M. HOSENFELD (Wiss. Veröff. Siemens-Konz., 1929, 8, [1], 26—29).—An historical survey of methods of producing beryllium by heating the oxide, chloride, fluoride, and various double salts with alkali or alkaline-earth metals.

A. R. POWELL.

Preparation of beryllium chloride from beryl. R. W. WINTERS and L. F. YNTEMA.—See B., 1929, 641.

Beryllium and its chloride. J. M. SCHMIDT (Ann. Chim., 1929, [x], 11, 351—446).—Beryllium chloride is obtained by heating a mixture of the oxide and sugar charcoal (the latter in 25% excess) in a current of chlorine at 900°, but is best prepared by heating the oxide (from the pure sulphate) contained in a silica tube, part of which is maintained electrically at 900°, in a current of dry carbonyl chloride, the beryllium chloride formed condensing in the cold posterior end of the tube. Beryllium chloride combines with dry ammonia to form the compound $\text{BeCl}_2 \cdot 2\text{NH}_3$; if the action of ammonia is prolonged the product contains other complexes. Similar results are obtained with sodamide. Dry ammonia and beryllium chloride dissolved in a mixture of anhydrous benzene and acetone give a complex containing some of the solvent. Attempts to prepare the bromide by heating the chloride in a mixture of hydrogen bromide and hydrogen were partly successful; the amounts of conversion into the bromide at 325° and 400° were 12% and 16%, respectively.

Thermal analyses of mixtures of anhydrous beryllium chloride and various metallic chlorides were made. It combines with the chlorides of lithium,

sodium, barium, and univalent thallium to give chloroberyllates of the type M_2BeCl_4 , and only the thallium salt is fusible without decomposition. Thermal analysis also indicated the existence of another compound, $TlBe_2Cl_5$. The presence of compounds $MBeCl_3$ was not detected. Very fusible mixtures are formed with some chlorides; e.g., a mixture of 41.3 parts of sodium chloride and 58.7 parts of beryllium chloride has m. p. 215°.

The conductivity of beryllium chloride in methyl, ethyl, or amyl alcohol, pyridine, and in ethyl bromide over a wide range of concentration has been measured. The conductivity-concentration curves are abnormal and do not obey Kohlrausch's square-root law in dilute solutions. This is probably due to complex formation with the solvent.

Attempts to prepare pure beryllium by reduction of the chloride with sodium, lithium, calcium, magnesium, or cerium gave a product containing at most 70–80% Be. Electrolysis of the chloride was abandoned owing to the difficulty of finding a sufficiently resistant anode. Reduction of the oxide with carbon gave only the carbide below 2000°; above this temperature beryllium is obtained, but volatilises as formed. If the reduction is carried out above 2000° in a high-frequency electrical induction furnace in the presence of copper or iron, an alloy of beryllium and the metal from which beryllium cannot be easily separated is obtained. Electrolysis of a mixture of 2 parts of barium fluoride and 1 part of beryllium chloride placed in the cavity of a cylindrical block of graphite, the base of which contains a layer of the barium fluoride-iodide or calcium fluoride-chloride eutectics or of an equimolecular mixture of beryllium fluoride and sodium fluoride, the graphite serving as anode and the cathode consisting of a water-cooled iron cylinder, the latter being gradually raised as the electrolysis proceeds as in the preparation of calcium, gave beryllium in the form of rods weighing about 6 g. and of 99.5–99.8% purity.

The following m. p. of salts mixed with 5% of beryllium were obtained: sodium chloride, 822°; potassium chloride, 800°; calcium chloride, 788°; barium chloride, 970°; sodium fluoride, 1045°; barium fluoride, 1050°; beryllium fluoride (1 part) and barium fluoride (2 parts), 1075°. The result for calcium chloride is not in accord with that of Engle and Hopkins (B., 1924, 473), who found that the m. p. could be lowered to 650°.

Attempts to measure the electrolytic potential of beryllium in ethyl and amyl alcohols and in pyridine and also the decomposition potential of the chloride in these solvents are described. The anomalous results are due to interactions between the metal and solutions of its chloride in the organic solvents. Beryllium reacts with ethyl alcohol to form the ethoxide, a decomposition which is greatly accelerated by the presence of the chloride. Solutions of beryllium chloride in pyridine dissolve silver chloride very readily, the solubility of silver chloride in pyridine saturated with beryllium chloride being 22.5 times that in pure pyridine.

A. I. VOGEL.

Action of magnesium amalgam on nitrates, and its action on nitrous acid, and salts of the

oxy-acids of sulphur and the halogens. P. NEOGI and R. C. BHATTACHARYYA (J. Indian Chem. Soc., 1929, 6, 333–340; cf. A., 1928, 855).—The nitrates of beryllium, cerium, and uranium, on reduction with 5% magnesium amalgam, give hyponitrites, the solutions of which are decomposed during concentration. Aluminium, thallium, and thorium nitrates give the hydroxides only. Ammonia is formed in all cases, hydroxylamine only in the case of cerium nitrate. Free nitrous acid yields no hydroxylamine and very little ammonia, the main product being magnesium nitrite, which is not further reduced. Sulphates, sulphites, and dithionates are unaffected, whilst thiosulphates are reduced to a mixture of sulphite and sulphide with evolution of hydrogen sulphide. Persulphates are reduced to sulphates, bromates, iodates, and periodates to the corresponding halides, whilst chlorates and perchlorates are not reduced even at 50°.

F. L. USHER.

Preparation of fluorescent substances. I. Sulphides of calcium, strontium, and barium. N. F. SHIROV (Ukraine Chem. J., 1928, 3, 209–227).—The choice and preparation of the starting materials, the selection of apparatus and conditions to be observed, and the method of preparation of the above luminophores are discussed. The pure carbonates are mixed with sulphur, sugar (to reduce any sulphate formed to sulphide), a flux (which is usually a salt of sodium, potassium, or lithium, e.g., sodium borate, lithium phosphate), and with an activator (which is a nitrate of any metal, e.g., copper, caesium, lead, etc.). For the preparation of complex luminophores either magnesium oxide or calcium tungstate is also added. Lenard and Vanino's results were partly repeated. Barium sulphide with rubidium and calcium sulphide and strontium sulphide with manganese give very poor luminophores. The best red luminophores are those of barium sulphide with copper and rubidium, the best yellow luminophores are those of strontium and barium sulphides with lead, copper, antimony, and thallium. Indium and calcium sulphide give a bluish-green luminophore, whilst indium or zirconium in strontium sulphide gives yellowish-green luminophores and thorium in calcium sulphide a bluish-violet luminophore. Complex luminophores of composition strontium sulphide-copper, strontium sulphide-uranium, bismuth-strontium-barium sulphide-thorium, lead, copper, calcium sulphide-thallium, uranium, bismuth, and rubidium were prepared.

A. FREIMAN.

Hydrated polycalcium aluminates. A. TRAVERS and SCHNOUTKA (Compt. rend., 1929, 188, 1677–1679).—If the authors' method (A., 1928, 1104) for the preparation of hydrated tricalcium aluminate from solutions of calcium nitrate and potassium aluminate is carried out other than at p_H 11.57–11.62 the resulting crystals contain 3–4 parts of CaO to 1 part of Al_2O_3 . These have now been shown by selective dissolution of the free lime in hydrochloric acid to be solid solutions of calcium hydroxide and hydrated tricalcium aluminate, the actual composition being dependent on the p_H of the medium.

J. GRANT.

Use of barium perchlorate as a drying agent and ammonia absorbent. G. F. SMITH (Chemist-Analyst, 1929, 18, 18—24).—Directions for the preparation, and data concerning the use, of barium perchlorate are given. CHEMICAL ABSTRACTS.

Pure aluminium orthohydroxide. P. A. THIESSEN and K. L. THATER (Z. anorg. Chem., 1929, 181, 417—424).—Aluminium orthohydroxide, $\text{Al}(\text{OH})_3$, has been prepared by the careful decomposition of aluminium triethyl with water. By the action of water on a solution of aluminium triethyl in absolute alcohol the hydroxide is obtained as a gelatinous precipitate, whilst the passage of a stream of nitrogen charged with the vapour of aluminium triethyl through water yields a fine granular precipitate; both correspond with the formula $\text{Al}(\text{OH})_3$. The substance in suspension in water shows a weak positive charge, and must consequently be regarded as a base. H. F. HARWOOD.

Basic gallium acetate and [ammonium] sulphate and gallium oxalate. A. TCHAKIRIAN (Compt. rend., 1929, 189, 251—252).—*Basic gallium acetate*, $4\text{Ga}(\text{OAc})_3 \cdot 2\text{Ga}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, is deposited slowly at the ordinary temperature as white, hygroscopic micro-crystals from a mixture of a solution of a gallium salt, neutralised with ammonium carbonate, with a 30% excess of acetic acid. *Basic gallium ammonium sulphate*,

$3(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{Ga}_2(\text{SO}_4)_3 \cdot 5\text{Ga}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$, is precipitated from a warm mixture of solutions of gallium and ammonium alums in the presence of less than 10% of sulphuric acid. *Gallium oxalate*, $\text{Ga}_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$, a hygroscopic, micro-crystalline powder which is easily hydrolysed, is prepared by boiling a solution of gallium nitrate with oxalic acid in the presence of sufficient concentrated nitric acid to destroy the excess of oxalic acid, which otherwise dissolves the oxalate. J. GRANT.

New type of rare-earth salts. G. A. BARBIERI (Atti R. Accad. Lincei, 1929, [vi], 9, 906—909).—Tervalent rare-earth metals of the cerium group form argentocyanides and aurocyanides, but it has not been found possible to obtain analogous salts of other trivalent metals. The following argentocyanides are described: *cerium*, $\text{Ce}[\text{Ag}(\text{CN})_2]_3 \cdot 3\text{H}_2\text{O}$; *lanthanum*, $(+ 3\text{H}_2\text{O})$; *neodymium*, $(+ 3\text{H}_2\text{O})$; *lutecobalt*, $[\text{Co}(\text{NH}_3)_6][\text{Ag}(\text{CN})_2]_3$; the three *aurocyanides* have analogous formulæ. T. H. POPE.

Extraction of commercial rare-earth residues with a view to the concentration of illinium. R. W. BALL [with J. A. HARRIS] (J. Amer. Chem. Soc., 1929, 51, 2107—2112).—Efficient methods of extracting rare earths from double sulphate residues are described; they involve either fusion with sodium carbonate followed by evaporation with sulphuric acid and subsequent extraction with water, or digestion with hot, saturated sodium hydroxide solution and subsequent extraction of the residue with nitric acid. Commercial hydrated oxides of the rare earths are preferably extracted with nitric acid and hydrogen peroxide. S. K. TWEEDY.

Addition of ammonia to lead nitrate and lead sulphate. W. KRINGS (Z. anorg. Chem., 1929, 181, 309—336).—Lead nitrate forms three additive compounds with ammonia, the *hexammine*, *triammine* (m. p. 115°), and the *monoammine*. The hexammine is stable only below 0°, whereas the triammine not only has a more or less definite m. p., but also appears to form a eutectic with the monoammine, a preparation containing 2 mols. of ammonia to 1 mol. of nitrate becoming a viscous liquid at 99—100°. The vapour tension of the monoammine reaches 760 mm. at about 160°. At -70° lead nitrate absorbs more ammonia than corresponds with the hexammine, but the excess of ammonia appears to be retained in solid solution. Lead sulphate forms a diammine and a tetrammine, both of which are much less stable than the nitrate amines. The heat of formation of the nitrate hexammine is approximately the same as those of the halide hexammines, and that of the sulphate tetrammine approximately the same as those of the halide tetrammines. The densities and vapour pressures of the amines at various temperatures are tabulated. A. R. POWELL.

Dichloroamine. R. M. CHAPIN (J. Amer. Chem. Soc., 1929, 51, 2112—2117).—Chlorination of excess of ammonium ions at the ordinary temperature yields solely monochloroamine when the p_H of the solution exceeds 8.5, and nitrogen trichloride when the p_H is below 4.4. Dichloroamine is practically the sole product between p_H 4.5 and 5.0. It may also be produced by suitably acidifying a monochloroamine solution. S. K. TWEEDY.

Action of hydrazine on quinquevalent arsenic in weakly acid solution. II. H. KUBINA (Z. anal. Chem., 1929, 78, 1—36; cf. A., 1928, 972).—In the reduction of quinquevalent arsenic to the trivalent state by means of hydrazine salts in acid solution some elementary arsenic is always formed; the amount depends on the concentration of the acid, being a maximum when 1.5*N*-hydrochloric acid is used. With 5.5*N*-acid only minimal amounts of arsenic are produced, arsenic trichloride being practically the sole product. The arsenic results in consequence of the secondary reaction $\text{AsH}_3 + \text{AsCl}_3 = 2\text{As} + 3\text{HCl}$, which has been proved to be quantitative. It is suggested that its formation is due to the production of quadrivalent arsenic and di-imide as unstable intermediate compounds, and experiments showed that the addition of an arsenite to the original reaction mixture of arsenate, hydrazine salt, potassium bromide, and hydrochloric acid greatly increased the production of elementary arsenic, presumably by favouring the formation of the quadrivalent form. Napoli's statement that hydrogen arsenide in contact with boiling hydrochloric acid yields arsenic trichloride could not be confirmed. Further experiments on the decomposition of hydrogen arsenide which results when a mixture of the gas with hydrogen and a little air is heated in presence of hydrochloric acid showed that the formation of arsenic does not take place according to the equation $4\text{AsH}_3 = 4\text{As} + 6\text{H}_2$, but is due to the acceleration of the reaction $4\text{AsH}_3 + 3\text{O}_2 = 4\text{As} + 6\text{H}_2\text{O}$ by hydrochloric acid. H. F. HARWOOD.

Reduction of dichromates to basic chromium salts. G. GRATHER and T. NAGAHAMA (Hokkaido J. Agric., 1928, 24, 25—38).—Acid solutions of potassium dichromate are reduced, in order of decreasing effect, by lactic acid, tartaric acid, dextrose, tannin, glycerol, formaldehyde, sodium thiosulphate, sodium sulphite, sodium sulphide.

CHEMICAL ABSTRACTS.

Chromium ethoxides: preparation and properties. P. A. THIESSEN and B. KANDELAKY (Z. anorg. Chem., 1929, 181, 285—294).—Passage of dry hydrogen chloride into absolute alcohol containing small pieces of chromium results in the formation of a dark red solution which, after distilling off part of the alcohol and keeping for some weeks over sulphuric acid in a vacuum, deposits dark green, tetragonal crystals of the compound $\text{CrCl}_3 \cdot 4\text{EtOH}$, which loses 1 mol. of alcohol at 50° in a vacuum. When a 10% solution of either compound in absolute alcohol is treated with an equivalent quantity of sodium the chlorine is removed and the solution, after filtration and cooling, deposits short, green prisms of *chromium ethoxide monoalcoholate*, $\text{Cr}(\text{OEt})_3 \cdot \text{EtOH}$. Evaporation of the filtrate from the above compound affords an amorphous residue of *chromium ethoxide*, $\text{Cr}(\text{OEt})_3$.

A. R. POWELL.

Reduction of alkali tungstates by hydrogen. J. A. M. VAN LIEMPT (Z. anorg. Chem., 1929, 181, 425—426).—Polemical against Spitzin (cf. A., 1925, ii, 1191; this vol., 165). The reduction of sodium tungstate by hydrogen at 1100° is represented by the equation $\text{Na}_2\text{WO}_4 + 3\text{H}_2 = \text{W} + 2\text{NaOH} + 2\text{H}_2\text{O}$. Potassium tungstate is not reduced under these conditions, but volatilises unchanged.

H. F. HARWOOD.

Uranium tetroxide dihydrate. A. ROSENHEIM and H. DAHR (Z. anorg. Chem., 1929, 181, 177—182).—Contrary to the statements of Hüttig and Schroeder (A., 1922, ii, 510) uranium tetroxide dihydrate exists and has been prepared in amorphous and crystalline forms.

J. S. CARTER.

Reactivity of iodine cyanide in different organic solvents. E. CHARGAFF (J. Amer. Chem. Soc., 1929, 51, 1999—2002).—The reactivity of iodine cyanide towards silver benzoisulphinide is independent of the solvent (ether, alcohol, carbon disulphide, etc.), contrary to the behaviour of iodine (A., 1928, 1131). Iodine cyanide, therefore, probably functions not as a mixed halogen but as a salt of hydrocyanic acid and iodine hydroxide. The results confirm the hypothesis that the iodine cyanide molecule differs in structure from the iodine molecule.

S. K. TWEEDY.

Oxygen compounds of rhenium. I. NODDACK and W. NODDACK (Z. anorg. Chem., 1929, 181, 1—37).—Mainly an amplification of work previously published (this vol., 411). The *potassium*, *silver*, and *neodymium* salts of per-rhenic acid are described.

J. S. CARTER.

Composition of iron fluoride. E. DEUSSEN (Monatsh., 1929, 52, 107—116).—Ferric hydroxide is dissolved in an excess of 40% hydrofluoric acid, evaporated, and allowed to crystallise in presence of nitric acid (cf. Peters, A., 1898, ii, 419). The salt obtained is stable in dry air, alters gradually when

exposed to the atmosphere, and has the composition $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (cf. Peters, *loc. cit.*). There are two hydrated ferric fluorides, the second crystallising with $4.5\text{H}_2\text{O}$ (cf. Weinland, Lang, and Fikentscher, A., 1926, 136).

Krupp's steel V2A (Fe 70%; Cr 23%; Ni 7%) is acted on by aqueous hydrofluoric acid, rapidly with 20%, but less rapidly with 5%. Iron is the chief substance dissolved.

H. BURTON.

Iron tetranitrosyl. W. MANCHOT and E. ENK (Annalen, 1929, 470, 275—283).—When iron carbonyl is treated with nitric oxide under pressure, best at $44\text{--}45^\circ$, a violently exothermic reaction occurs, giving black crystals of *iron tetranitrosyl*, an unstable substance of which the dissociation pressure is variable. This when treated with dilute sulphuric acid gives the compound $\text{Fe}(\text{NO})\text{SO}_4$; with liquid ammonia a brown product is formed, for which the formula $\text{Fe}(\text{NO})_3 \cdot \text{NH}_3$ is tentatively suggested. The substance reacts with pyridine, aniline, pyrrole, and (violently) with hydrazine, and with the appropriate reagents gives rise to the compounds $\text{Fe}(\text{NO})_2\text{S}_2\text{O}_3\text{K}$, $\text{Fe}_4(\text{NO})_7\text{S}_3\text{K}$, $\text{Fe}(\text{NO})_2\text{SEt}$, and $\text{Fe}(\text{NO})_2(\text{S} \cdot \text{CS} \cdot \text{OEt})_2$.

E. W. WIGNALL.

Methyl alcohol compound of iron nitrosyl. W. MANCHOT and H. GALL (Annalen, 1929, 470, 271—274).—In attempts to obtain from the compound $\text{Fe}(\text{NO})_3\text{Fe}(\text{CO})_5$ a compound free from carbon monoxide, it was found that the replacement of carbon dioxide by nitric oxide was facilitated by the presence of methyl alcohol. When iron pentacarbonyl in methyl-alcoholic solution was treated with nitric oxide at the ordinary temperature, a black product was obtained, which was found to contain carbon, but did not give carbon monoxide when treated with acid; it actually contained methyl alcohol, retained up to 200° . The formula of the compound is probably $\text{Fe}(\text{NO})_2\text{MeOH}$. No similar product was obtained when acetone, acetic acid, or chloroform was used as solvent.

E. W. WIGNALL.

Characterisation of sulphur-nitric oxide compounds of univalent iron, cobalt, and nickel. W. MANCHOT and G. LEHMANN (Annalen, 1929, 470, 255—261).—The sulphur-nitric oxide compounds of the above metals (this vol., 526) are compared with the hyponitrites. When the former are treated with dilute acid, they give rise to nitric oxide, and to nitrous oxide and nitrogen; these are presumably formed by the reduction of the nitric oxide by the univalent metal, which becomes oxidised to the bivalent, and, in the case of iron, to the trivalent state. Since the reducing action of hydrogen sulphide vitiates results, measurements of the amounts of the different gases produced were made after decomposing the compounds by silver sulphate, with or without added acid; it has not been found possible to relate the proportions of the gases to the extent of oxidation of the metal. When the decomposition was carried out in presence of ferric sulphate, the yield of nitric oxide was increased, owing to the hindering of the reduction process.

In contrast with the above results, the hyponitrites were found not to give nitric oxide, whether or not ferric sulphate was present. It is therefore concluded

that the sulphur-nitric oxide compounds do not contain a hyponitrite grouping, and that the nitric oxide is attached (co-ordinately) as a neutral molecule.

E. W. WIGNALL.

Constitution of sulphur-nitric oxide compounds of univalent iron, cobalt, and nickel. W. MANCHOT (Annalen, 1929, 470, 261—270).—A theoretical discussion of the structure of these compounds on the basis of Sidgwick's co-ordination theory. A compound such as $\text{Fe}(\text{NO})_2\text{SEt}$, which is soluble in benzene and other organic solvents, and is thus homopolar, is considered to have the nitric oxide groupings attached to the iron atom by co-ordinated covalencies (donated by nitrogen), and the $\cdot\text{SEt}$ grouping attached by a normal (shared) covalency, which may also become an electrovalency, as is shown by the small but actual conductivity of the substances. The following new compounds are mentioned: $\text{Co}(\text{NO})_2\text{SEt}$; $\text{Co}(\text{NO})_2\text{SPh}$; $\text{Ni}(\text{NO})\text{SPh}$; $\text{Ni}(\text{NO})\text{SPh}, \text{C}_5\text{H}_5\text{N}$.

E. W. WIGNALL.

Cobalt oxides and systems with oxygen. M. LE BLANC and E. MOBRUS (Z. physikal. Chem., 1929, 142, 151—176).—Cobaltous oxide prepared by igniting the carbonate in a vacuum absorbs oxygen, the absorbent power being the greater the lower is the temperature of ignition; also the higher is the temperature at which the solid is brought in contact with the gas, the more is taken up. The oxygen absorbed is activated, reacting immediately with hydrogen iodide. Below about 100° , the absorption causes no change in the lattice, but the system $\text{CoO}, n\text{O}_2$ is unstable, and at higher temperatures is transformed into the system $\text{Co}_3\text{O}_4, m\text{O}_2$, the lattice being converted into that of cobaltocobaltic oxide. On thermal decomposition, this system proves to be bivariant, consisting of a single solid phase of variable composition. When treated with oxalic acid, the cobaltous salt is formed, and the excess of oxygen corresponding with the cobaltocobaltic oxide rapidly oxidises the acid, whilst the free oxygen reacts only slowly, thus proving that the solid is actually cobaltocobaltic oxide with absorbed oxygen, and not cobaltic oxide; the system $\text{CoO}, n\text{O}_2$ behaves similarly. Thermal decomposition of pure cobaltocobaltic oxide shows the existence of an equilibrium $\text{Co}_3\text{O}_4 \rightleftharpoons 3\text{CoO} + 0.5\text{O}_2$, whereas with pure cobaltous oxide the decomposition pressure is less than 0.1 mm., even at 1250° . None of the experiments gives indication of the existence of any oxides other than cobaltous and cobaltocobaltic; the dry methods for the preparation of cobaltic oxide to be found in the literature actually give the system $\text{Co}_3\text{O}_4, m\text{O}_2$. Hydrated cobaltic oxide may, however, be prepared by precipitating an aqueous solution of cobaltic sulphate with alkali. Oxalic acid in aqueous solution is slowly oxidised at 100° by air, the reaction being catalytically accelerated by cobaltous ions.

R. CUTHILL.

Cobalt with a covalency of four: new series of complex compounds. E. G. V. PERCIVAL and W. WARDLAW (J.C.S., 1929, 1505—1512).—A new series of compounds of the formula $\text{R}_2[\text{CoX}_4]$, where $\text{R} = \text{C}_5\text{H}_5\text{N}$, $\text{C}_6\text{H}_5\text{N}$, or $\text{C}_{10}\text{H}_{10}\text{N}$ and X is a halogen, has been isolated by the addition of the appropriate base to a solution of the cobalt halide in solution in

the corresponding concentrated halogen acid. The complex chlorides were also prepared by the addition of the organic hydrochloride to an alcoholic solution of cobaltous chloride. Determinations of the mol. wt. and conductivities of these compounds indicate that they are not double salts of the type $2\text{RX}, \text{CoX}_2$, but complex salts of the formula $\text{R}_2[\text{CoX}_4]$. Definite evidence is therefore provided of the existence of the CoX_4^{2-} ions postulated by Donnan and Bassett (J.C.S., 1902, 81, 939) to account for the blue colour of solutions of cobalt halides in alcohol or concentrated halogen acids.

Cobaltous diquinolinium chloride has m. p. $170-171^\circ$; its *monohydrate* has also been isolated. The corresponding *dipyridinium* and *di-2-methylquinolinium* compounds have m. p. $169-170^\circ$ and $239-240^\circ$, respectively. *Cobaltous diquinolinium bromide* has m. p. $164-165^\circ$; the corresponding *dipyridinium* and *di-2-methylquinolinium* compounds, m. p. $165-166^\circ$ and $231-232^\circ$, respectively. *Cobaltous diquinolinium iodide* has m. p. $156-157^\circ$; the compound $\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$ has m. p. $196-197^\circ$. F. J. WILKINS.

Colours of cobaltous hydroxide. C. W. STILLWELL (J. Physical Chem., 1929, 33, 1247—1271).—The colours obtained by the interaction between cobalt chloride and potassium hydroxide under various conditions have been investigated microscopically and also by means of X-ray analysis. Freshly-precipitated cobaltous hydroxide is green to yellowish-green by transmitted light, and is gelatinous, laminar, amorphous, and metastable. The blue colour is essentially a reflected colour; it is probably a Tyndall blue scattered by small crystal nuclei which form within the amorphous matrix as the gelatinous precipitate ages to the crystalline form. The freshly precipitated hydroxide tends to change to the rose-coloured hydroxide which is granular in appearance and is the stable, crystalline form. No other crystalline forms were produced; the light blue, aged precipitate is crystalline, but it has the same structure as the rose-coloured hydroxide. The blue of the aged precipitate is also structural. Adsorbed cobaltous chloride inhibits crystal growth, favours the formation of the green precipitate, and hinders that of the rose. Freshly-precipitated nickelous hydroxide is laminar and amorphous, and tends to stabilise the corresponding amorphous cobalt hydroxide. The change from green to blue of freshly-precipitated cobaltous hydroxide is not due to oxidation.

When cobaltous chloride solution is added to potassium hydroxide solution in amounts greater than the molecular ratio 1:1.5 and the precipitate is allowed to remain in contact with the mother-liquor, ageing occurs and the colour of the precipitate changes from green to blue to rose; the final rose-coloured precipitate is a basic salt of cobalt and is the only crystalline product formed under the experimental conditions; the blue is a mixture of the rose and the green; and the green is amorphous, containing small amounts of crystalline hydroxide and basic salt.

L. S. THEOBALD.

"Tartratecobaltinitrite" [existence of the cobaltyl group]. M. WIKUL (Z. anorg. Chem.,

1929, 181, 121—130).—The suggested formula of a complex salt used for the determination of potassium (A., 1928, 264) contains a cobaltyl (CoO) group. The plausibility of this assumption has been investigated and although no complete confirmation has resulted, a salt of composition corresponding approximately with the formula $(\text{CoO})_2\text{SO}_4 \cdot \text{NaHSO}_4$ has been isolated. J. S. CARTER.

Action of hydrogen at high pressures and at high temperatures on solutions of ruthenium salts. V. N. IPATIEV and O. E. ZVAGINCEV (J. Russ. Phys. Chem. Soc., 1929, 61, 823—825).—The reducing action of hydrogen at pressures of 60—150 atm. and from the ordinary temperature up to 350° has been studied for slightly acidified aqueous solutions of ammonium, potassium, and sodium pentachlororuthenates. With rising temperature and increasing pressure the product isolated varied from the hydrated oxides of ruthenium, $\text{Ru}(\text{OH})_3 \cdot \text{aq.}$ and $\text{Ru}(\text{OH})_3$, to Ru_2O_3 and metallic ruthenium. No intermediate oxides were formed, nor was a blue solution formed as by the reduction of ruthenium salts with zinc and hydrochloric acid. A. FREIMAN.

Indicators. N. A. ZAITZEV (J. Chem. Ind. Moscow, 1928, 5, 722—723).—Ammonium 5:5'-*p*-diphenylenebisazobis-8-anilino-1-naphthalenesulphonate (from tetrazotised benzidine and phenyl-peri-acid) is pink; with acids it becomes blue. 5-*p*-Acetamidophenylazo-8-anilino-1-naphthalenesulphonic acid (from diazotised acetyl-*p*-phenylenediamine and phenyl-peri-acid) is less sensitive to acids. Since it is insensitive to aniline hydrochloride it is suitable for the titration of aniline. 5-(4-Sulpho-1-naphthaleneazo)-8-anilino-1-naphthalenesulphonic acid and 4-(4-anilino-5-sulpho-1-naphthaleneazo)-5-hydroxynaphthalene-2:7-disulphonic acid are suitable for the titration of alkali hydroxides.

CHEMICAL ABSTRACTS.

Possible, ready replacement of the Zerewitinov method. K. ZIEGLER and F. DERSCH (Ber., 1929, 62, [B], 1833—1834).—Intensely coloured organic compounds of the alkali metals (sodium triphenylmethyl; potassium phenylisopropyl) are suitable for titrimetric determination of active hydrogen. The substance is preferably weighed, without solvent, in a nitrogen-filled tube and titrated with the alkali compound until the colour persists. The titer of the solution is determined previously by addition of a dry aliphatic bromide (*n*-butyl bromide) and determination of bromine by Volhard's method after treatment with water. Alternatively, an excess of metallic derivative is used followed by addition of alkyl bromide until the colour is discharged and titration of bromine. H. WREN.

Determination of water in micas. K. I. VISKONT and I. P. ALIMARIN (Trans. Inst. Econ. Min. Met., Moscow, 1928, No. 40, 18 pp.).—To avoid evolution of hydrogen by interaction of water and ferrous oxide, the substance is heated with platinum-black, lead oxide, and sodium tungstate.

CHEMICAL ABSTRACTS.

Apparatus for the determination of water by the distillation method. J. PRITZKER and R. JUNGKUNZ (Chem.-Ztg., 1929, 53, 603).—A new

form of apparatus which permits of the employment of liquids of any sp. gr. for treating the substance under examination is described; the expelled water is collected in a graduated tube and measured directly. If the water content of the material does not exceed 25% the determination can be completed in 5 min., and the results compare satisfactorily with those obtained by other methods. H. F. HARWOOD.

Determination of chloride ion in reagents. A. FROST (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 6, 35—37).—Addition of nitric acid first increases and then decreases the turbidity, the maximum effect being obtained with 13% acid; sulphuric acid behaves similarly. Ammonium or potassium nitrate, potassium or sodium sulphate, potassium chlorate, cadmium sulphate, and zinc acetate (1 g. per 20 c.c.) increase the turbidity by 20% and 40% when the chloride-ion concentration is 0.44—0.11 and 0.55—0.20 mg. per 20 c.c. respectively.

CHEMICAL ABSTRACTS.

Gravimetric titration and micro-determination of hydrochloric and arsenic acids. B. ORMONT (J. Russ. Phys. Chem. Soc., 1929, 61, 355—362).—See this vol., 41.

Determination of bromine in sea-water and estuary waters. A. I. KOGAN (Ukraine Chem. J., 1928, 3, 131—137).—Methods of determination of small quantities of bromine in the presence of large quantities of chlorine are reviewed and the applicability to the determination of bromine in sea-water and estuary waters is considered. Vescelski's method (Z. anal. Chem., 1899, 39, 81) is inapplicable, whilst Berg's method (A., 1926, 1017) gives good results. Bromine is determined colorimetrically by adding 3 drops of 20% sulphuric acid to 10 c.c. of sea-water and then chlorine water until the maximum depth of colour is attained. The solution is then shaken with 5 c.c. of chloroform and the extract compared with a solution of a known weight of potassium bromide in estuary water from which the bromine has been previously entirely removed. With ordinary water as solvent for the potassium bromide the results are too low as compared with those found by Berg's method. A. FREIMAN.

Potentiometric determination of bromine, octovalent and quadrivalent osmium in hydrobromic acid solutions. W. R. CROWELL and H. D. KIRSCHMAN (J. Amer. Chem. Soc., 1929, 51, 1695—1702).—The above titration may be effected by means of tervalent titanium. Three inflexions in the titration curve correspond respectively with the reduction of bromine to bromide ion, the reduction of octovalent osmium to quadrivalent osmium, and the reduction of quadrivalent osmium to the tervalent state. This last inflexion is unsuitable for quantitative work. Some results of Hendrixson (A., 1923, ii, 781) are confirmed. S. K. TWEEDY.

Determination of sulphur in steels etc. K. SWOBODA.—See B., 1929, 601.

Determination of sulphur in antimony. C. G. SNYDER.—See B., 1929, 603.

Determination of sulphuric acid in presence of chromic acid. D. TARASENKOV (Trans. Inst.

Pure Chem. Reagents, Moscow, 1927, No. 6, 31—34).—Excess of sodium hydroxide is added and titrated back with sulphuric acid to sodium dichromate and sulphate, using Congo-red as indicator. The chromic acid is determined iodometrically in a strongly acid solution. **CHEMICAL ABSTRACTS.**

Iodometric determination of a mixture of sulphide, sulphite, and thiosulphate. R. WOLLAKE (Z. anal. Chem., 1929, 77, 401—406).—The procedure is identical with that of Kurtenacker and Bittner (A., 1925, ii, 239) save for the determination of thiosulphate. This constituent is determined by addition of an excess of iodine to an acidified aliquot portion and titration back with sodium sulphite, the resulting tetrathionate being determined by the cyanide method of Kurtenacker and Fritsch (A., 1921, ii, 502). **J. S. CARTER.**

Volumetric determination of polysulphides. P. SZEKERÉNYI (Z. anal. Chem., 1929, 78, 36—40).—A portion of the polysulphide solution is boiled for 2—3 min. with an excess of a standardised solution of sodium sulphite, whereby all polysulphide is converted into thiosulphate. The cooled solution is titrated with 0.1*N*-iodine after addition of sodium hydrogen carbonate. Another portion of the original solution is titrated in the cold with 0.1*N*-iodine, and this figure, together with the iodine value corresponding with the sodium sulphite added, subtracted from the first. The difference corresponds with the sulphur present as polysulphides, each c.c. of 0.1*N*-iodine representing 0.0032 g. of sulphur. An alternative method is based on the change in alkalinity when a polysulphide is oxidised with an alkaline solution of hydrogen peroxide. A portion of the solution is titrated with *N*-acid, using methyl-orange as indicator. A second portion is treated with zinc sulphate to remove sulphides, filtered, and the thiosulphate in the filtrate titrated with iodine solution. A third portion is treated with a known volume of *N*-sodium hydroxide and 10—20 c.c. of 30% hydrogen peroxide until oxidation is complete, and the residual alkalinity found by titration. The decrease in total alkalinity, less twice the titration corresponding with the thiosulphate present in the oxidised portion, gives the amount of polysulphide present, each c.c. of *N*-acid corresponding with 0.016 g. of sulphur.

H. F. HARWOOD.

Analytical applications of sodium hyposulphite. B. S. EVANS (Analyst, 1929, 54, 395—405).—Sodium hyposulphite reduces salts of copper, silver, mercury, bismuth, selenium, lead, arsenic, and antimony to the elementary state in alkaline solutions and the reduction is not obstructed by many oxidising agents which would react in an acid medium. Potassium cyanide prevents the precipitation of copper but favours that of antimony, and the separation, at least in the case of lead, antimony, and bismuth, is rapid and complete. The following processes have been worked out in detail: determination of antimony in high-antimony copper alloys; small amounts of bismuth in tin-zinc alloys; small amounts (0.01—0.2%) of antimony in lead and lead alloys; separation of cadmium from bismuth; and lead from antimony.

D. G. HEWER.

Determination of selenium dioxide in sulphuric acid. T. RAIKHINSTEIN (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 6, 27—30).—For 0.01—0.00005% SeO_2 , 0.1 c.c. of a 4% aqueous solution of codeine phosphate is added to 10 c.c. of the solution in concentrated sulphuric acid, and the selenium is determined colorimetrically. Arsenic acid, if below 1%, gives no coloration; ferric iron, if present in excess of 0.0015% (or, if phosphoric acid is also present, 0.0074%), also gives a blue coloration.

CHEMICAL ABSTRACTS.

Rapid determination of nitrogen by Kjeldahl's method. H. LUNDIN and J. ELLBURG.—See B., 1929, 596.

Determination of nitric nitrogen by alkaline reduction with powdered aluminium. A. SEYEWETZ (Bull. Soc. chim., 1929, [iv], 45, 463—465).—Sodium hydroxide solution is added at the rate of 2—3 drops per sec. to 150 c.c. of water, 10 g. of powdered aluminium, and an amount of nitrate equivalent to about 1 g. of potassium nitrate, at 50°. When the reaction has ceased, the liquid is distilled into *N*-sulphuric acid.

C. W. GIBBY.

Jena glass filtering crucibles. [Determination of phosphorus and potassium.] R. H. SIMON.—See B., 1929, 625.

Electrometric titration of boric acid. I. V. GREBENSCHTSCHIKOV and T. A. FAVORSKAIA (J. Russ. Phys. Chem. Soc., 1929, 61, 561—574).—The titration curves of boric acid solutions exhibit a series of breaks, the number and position of which depend on the previous history of the solution. Further, cryoscopic measurements show that the mol. wt. of boric acid in aqueous solution falls on keeping from 72 in a fresh solution to a limiting value of 59. This transformation is accelerated by heat, the equilibrium mixture probably containing a series of variously hydrated and associated acids. In titrating boric acid solutions in the presence of indicators the result will depend on the method of preparation of the solution and on its age.

R. TRUSZKOWSKI.

Oxidisability of silicon and of Moissan and Siemens' allotropic modification. A. SANFOURCHE (Compt. rend., 1929, 188, 1672—1675; cf. Bedel, this vol., 756, 997).—Silicon may be gradually but completely converted into silica by successive treatments with hydrofluoric acid followed by ignition at 150°, the silica produced at each stage being determined from the percentage loss in weight. The rate of conversion depends on the method of production and state of division of the silicon, and it is concluded that an allotropic modification of silicon partly soluble in hydrofluoric acid (Moissan and Siemens) does not exist. There is also evidence of lower oxides (Si_3O_2 and Si_3O_4) which impart a brown colour to the supposed allotropic form and liberate hydrogen on addition of the acid.

J. GRANT.

Determination of small amounts of potassium in presence of much sodium by a direct, gasometric method. G. JANDER and H. FABER (Z. anorg. Chem., 1929, 181, 189—192).—A micro-

modification of the method previously described (A., 1928, 980). J. S. CARTER.

Qualitative reagent for sodium. E. R. CALEY (J. Amer. Chem. Soc., 1929, 51, 1965—1969).—A saturated solution of uranyl acetate and cobalt acetate in 6% acetic acid, when added in large volume, favours the precipitation from solution of sodium uranyl cobalt acetate in preference to the corresponding potassium compound. The precipitate approximates to the composition $3\text{UO}_2(\text{OAc})_2 \cdot \text{Co}(\text{OAc})_2 \cdot \text{NaOAc} \cdot 6\text{H}_2\text{O}$. The presence of potassium does not appreciably influence the detection of sodium by means of the reagent. The reagent is only moderately sensitive to lithium, and is unaffected by heavy metals. However, phosphates must always be absent. The use of the reagent in Noyes' scheme of qualitative analysis is described.

S. K. TWEEDY.

Determination of hardness in water by means of soap solution. G. BRUHNS.—See B., 1929, 662.

Analytical chemistry of beryllium. H. FISCHER (Wiss. Veroff. Siemens-Konz., 1929, 8, [1], 9—20).—Iron in quantity exceeding that of the beryllium interferes with the quinalizarin colorimetric titration of beryllium (A., 1928, 385). To separate beryllium from large quantities of iron both metals are precipitated with ammonia from a cold solution, the precipitate is collected, washed, dried, and ignited over a blast, the mixed oxides are reduced in hydrogen, and the metallic iron is extracted with hydrochloric acid. Strongly ignited beryllia is insoluble in all acids except hydrofluoric; the residue is therefore dissolved in warm hydrofluoric acid, the solution treated with sodium hydroxide to 0.25*N*, and titrated colorimetrically with quinalizarin. To determine beryllium in copper, nickel, or zinc alloys, 0.5 g. is dissolved in concentrated hydrochloric acid and a little hydrogen peroxide, the solution evaporated to dryness on the water-bath, the residue dissolved in water, and 10% potassium cyanide solution added until the precipitate ceases to dissolve; after addition of 50 c.c. of *N*-sodium hydroxide the solution is diluted to 200 c.c. and the beryllium titrated. For the determination of beryllium in beryl and similar minerals 1 g. of the finely-ground substance is intimately mixed with 1 g. of sodium fluosilicate and the mixture heated at 680—710° in a porcelain crucible. The aqueous extract of the product is treated with sodium hydroxide etc., as described above. Ammonia does not precipitate beryllia completely from fluoride solutions; they must therefore be evaporated with sulphuric acid before addition of ammonia for the gravimetric determination of beryllia.

A. R. POWELL.

Simple qualitative analysis of alloys. D. SCRUTO (Notiz. chim.-ind., 1928, 3, 698—701; Chem. Zentr., 1929, i, 1029—1030).—Methods suitable for instructional purposes are described.

A. A. ELDRIDGE.

Solubility influences and quantitative analysis. L. DEDE (Z. angew. Chem., 1929, 42, 723).—Polemical against Wendehorst (A., 1928, 726). Cadmium is not completely precipitated as carbonate by an excess of ammonium carbonate, but good results

are obtained by precipitation with potassium carbonate, even in presence of potassium chloride, and ignition to oxide at 900°; ignition at 1000° results in loss by volatilisation.

A. R. POWELL.

[Solubility influences and quantitative analysis.] E. WENDEHORST (Z. angew. Chem., 1929, 42, 723—724).—The author reaffirms the interference of potassium chloride in the carbonate precipitation of cadmium and considers that Dedehorst's precipitate contained sulphate or alkali salt (cf. preceding abstract).

A. R. POWELL.

Spectroscopic detection of lead in gold-copper-silver alloys. W. GERLACH and E. SCHWEITZER (Z. anorg. Chem., 1929, 181, 101—102).—The method previously described (A., 1928, 859) is applicable only to specimens of gold of low silver content. For the detection and approximate determination of small quantities of lead in gold alloys containing appreciable amounts of copper and silver the lead line 4057.8 appears to be suitable.

J. S. CARTER.

Spacu's sensitive reaction for copper and thiocyanate. Reagent for polysulphides. A. J. FOLCINI (Rev. Centro Estud. Farm. Bioquim., 1928, 17, 305—309; Chem. Zentr., 1929, i, 562).—Spacu's and Fleming's reactions are not specific for thiocyanate. Spacu's reaction for copper is improved by the substitution of polysulphide for thiocyanate. Dianisidine and diaminofluorene behave similarly to toluidine and benzidine (cf. A., 1924, ii, 502; 1925, ii, 1003).

A. A. ELDRIDGE.

Action of complex halides and cyanides on certain aromatic diamines. A. J. FOLCINI (Rev. Centr. Estud. Farm. Bioquim., 1928, 17, 413—417; Chem. Zentr., 1929, i, 1132).—The blue precipitate produced in presence of copper by iodides with diamines of the diphenyl series is not produced by other halides, but the reaction is given by cyanides as well as by thiocyanates (cf. preceding abstract).

A. A. ELDRIDGE.

Volumetric determination of mercury. H. B. DUNNICLIFF and H. D. SURI (Analyst, 1929, 54, 405—410).—The mercury is first converted into chloride. Equal volumes of a 25% sodium tartrate solution and stannous chloride solution are mixed in the presence of a constant current of carbon dioxide, the hydrochloric acid is neutralised with sodium hydrogen carbonate, the solution diluted to 80—90 c.c., stirred (still in presence of carbon dioxide), and standardised by the ferric alum and titanous chloride method. The above process is repeated, but before dilution 10 c.c. of the mercuric chloride solution are added; after quickly filtering through a Gooch crucible with a double layer of barium sulphate filter-paper and asbestos into a burette in an atmosphere of carbon dioxide, 10 c.c. of the filtrate are added to an excess of a hot solution of standard ferric alum, acidified with hydrochloric acid, and the excess is titrated against titanous chloride. The percentage error in 15 determinations varied from +0.55 to -0.22. In an alternative method, the stannous chloride solution is neutralised as before, mercuric chloride solution added, and after complete reduction diluted to known volume and filtered. A

known volume of filtrate is added to standard iodine solution more than sufficient for oxidation of the stannous chloride in the filtrate, and the excess titrated against 0.05*N*-sodium thiosulphate. The degree of accuracy is much the same as in the first method, and the method should not be relied on for concentrations below 0.025*N*. D. G. HEWER.

Volumetric determination of mercury. M. L. COLOMBIER (J. Pharm. Chim., 1929, [viii], 10, 15—24).—Methods described in the literature are examined experimentally; the method of Denigès (Bull. Soc. chim., 1895, 15, 862) receives special attention and slight improvements of it are suggested.

R. J. W. LE FÈVRE.

Determination of minute quantities of mercury. J. BODNÁR (Z. angew. Chem., 1929, 42, 826; cf. Thilenius and Winzer, this vol., 531; Stock and Zimmerman, *ibid.*, 784).—Attention is directed to a previous publication (*ibid.*, 614). J. S. CARTER.

Potentiometric standardisation of ceric sulphate [solutions]. K. SOMEYA (Z. anorg. Chem., 1929, 181, 183—188).—In presence of sulphuric acid solutions of ceric sulphate may be titrated potentiometrically using potassium ferrocyanide and *vice versa*. In presence of hydrochloric acid, solutions of alkali iodides may be similarly titrated with ceric sulphate solutions. The end-point in the latter case is more marked in presence of potassium cyanide.

J. S. CARTER.

Separation of aluminium as hydroxide from steels. W. J. SHANEMAN and J. J. GALLAGHER.—See B., 1929, 601.

Volumetric determination of manganese as manganic salt. R. LANG and F. KURTZ (Z. anorg. Chem., 1929, 181, 111—120).—The method is based on the induced oxidation of manganous to manganic salts in presence of dichromate and arsenite (A., 1928, 600). The neutral or slightly acid solution of manganous salt, which should contain not more than 0.2 g. of manganese, is acidified with 25 c.c. of 5*N*-sulphuric acid; 5 g. of sodium fluoride and 5—10 c.c. of syrupy phosphoric acid are then added and the whole is treated with 45 c.c. of a solution of potassium dichromate containing 15 g. per litre and 50 c.c. of a solution containing 15 g. of arsenious oxide and 10 g. of sodium carbonate per litre. After addition of 3 drops of a solution of 1 g. of diphenylamine in 100 c.c. of phosphoric acid the manganic salt is titrated with a solution of ferrous sulphate until the colour changes from blue to green. Mercuric, aluminium, calcium, and (when present in appreciable amounts) ammonium salts interfere. If it is desired to determine iron in presence of manganese, the former may be determined by Knop's method (A., 1924, ii, 351) and the latter, after addition of sodium fluoride etc., by the present method.

J. S. CARTER.

Decomposition of potassium permanganate to solid manganese oxides in oxidation reactions. [Determination of manganese and arsenic.] B. REINITZER and F. HOFFMANN (Z. anal. Chem., 1929, 77, 407—441).—An examination of the constitution of the precipitates obtained at various stages in titrations with permanganate involving

complete eventual precipitation of manganese as dioxide shows that only in the Volhard process for the determination of manganese is the precipitate always free from lower oxides. In all other cases the initial precipitates contain lower oxides which are finally converted into the dioxide. Conversion into dioxide is complete only when the titrated solution is maintained at 95—100° and when the acidity is low. Manganese may be titrated in a manner similar to that previously described (A., 1926, 705) in media made alkaline with sodium phosphate and containing potassium chloride. Flocculation of manganese dioxide is assisted by addition of barium chloride towards the end of the titration. In boiling solutions containing acetic acid and sodium acetate arsenites are quantitatively oxidised to arsenates according to the equation $3\text{As}_2\text{O}_3 + 2\text{Mn}_2\text{O}_7 = 3\text{As}_2\text{O}_5 + 4\text{MnO}_2$. Analysis of a precipitate which had deposited in a stock solution of potassium permanganate showed the presence of both manganese dioxide and manganic oxide.

J. S. CARTER.

Determination of ferrous iron in silicate rocks. II. Electrometric. B. A. SOULE (J. Amer. Chem. Soc., 1929, 51, 2117—2120).—A warm solution of the ore in mixed hydrochloric and hydrofluoric acids, prepared and maintained in an atmosphere of carbon dioxide, is titrated electrometrically with ceric sulphate. The titration is rapid and accurate, arsenic from the glass vessels having no disturbing effect (A., 1928, 725, 861).

S. K. TWEEDY.

Determination of bi- and ter-valent cobalt. V. CUVELLIER (Natuurwetensch. Tijds., 1929, 11, 123—130).—Cobalt in the bi- and ter-valent states may be differentiated and determined by titrations based on successive oxidations and reductions. Hydrogen peroxide or sodium perborate in sodium hydroxide solution oxidises both cobalt and iron; the excess of oxidising agent is removed by boiling, and the solution reduced by means of a known excess of stannous chloride. The excess and the ferrous salt are then oxidised by means of a known excess of potassium dichromate, and this excess is in turn reduced by titration with a standardised ferrous sulphate solution. By this method of analysis, the formula determined for the black colloidal mineral from the Star of the Congo mine at Katanga, which contains finely disseminated malachite and chrysocolla, was $3\text{Co}_2\text{O}_3 \cdot 2\text{CuO} \cdot 10\text{H}_2\text{O}$; this mineral has recently been described as heterogenite, for which the formula $\text{CoO} \cdot 2\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ was originally put forward.

S. I. LEVY.

Drop method of detecting molybdenum. N. A. TANANAIEV and G. A. PANTSCHENKO (Ukraine Chem. J., 1929, 4, 121—122).—A method is described which allows of the detection of 0.001 mg. of molybdenum in a drop of solution (0.02 c.c.). A drop each of hydrochloric acid, of the solution to be tested, again of hydrochloric acid, and finally of a potassium thiocyanate solution are placed in turn on a filter-paper. A drop of a stannous chloride solution is then added, when any red colour due to iron disappears and the crimson colour due to the presence of molybdenum appears. The test can be employed in the presence

of titanium, uranium, tungsten, or vanadium, and is applicable in the analysis of steel and minerals.

A. FREEMAN.

Determination of molybdenum in steel. W. F. MURRAY.—See B., 1929, 601.

Rapid detection of tungsten in ores. A. PETROVSKY.—See B., 1929, 603.

Rapid determination of tin in lead-base alloys containing antimony. T. B. DIANA.—See B., 1929, 647.

Rapid determination of vanadium in ferro-vanadium. J. SILBERSTEIN.—See B., 1929, 647.

Determination of vanadium in steel. J. KASSLER.—See B., 1929, 601.

Colorimetric determination of bismuth. FRICK and ENGEMANN (Chem.-Ztg., 1929, 53, 505—507).—A review of the various modifications of the iodide method for the colorimetric determination of bismuth.

A. R. POWELL.

Separation of bismuth from lead. I. FRICK and ENGEMANN (Chem.-Ztg., 1929, 53, 601—602).—The usual methods for the separation of small amounts of bismuth from lead are too tedious for technical purposes, and a new method has been devised, which is both rapid and exact. The nitric acid solution of the two metals, containing up to 0.2% of bismuth, is diluted to 300 c.c., and a few drops of Congo-red are added. Sodium hydroxide is added until the p_H value of the solution is between 3 and 5.2, as shown by the bluish-red colour of the indicator, whereupon 20 c.c. of a 0.7% solution of cinchonine hydrochloride are introduced, and the liquid is set aside for 30 min. The precipitate is collected, washed with a cold, very dilute solution of the precipitant until free from lead, redissolved in nitric acid, and the bismuth in solution determined colorimetrically.

H. F. HARWOOD.

Separation of bismuth by rapid electrolysis in acid solution. A. JILEK and J. LUKAS (Coll. Czech. Chem. Comm., 1929, 1, 369—376).—Satisfactory deposits of bismuth can be obtained by electrolysis after the following treatment: after slight acidification with nitric acid, sucrose and a considerable excess of hydrofluoboric acid are added, giving rise to a complex salt. To obviate the disturbing action of the nitric acid, the acidity is first reduced by adding potassium hydroxide, and the resultant precipitate redissolved by sucrose and hydrofluoboric acid. Electrolysis is carried out in hot solution with a small current. A similar procedure can be used for sulphate solutions. For bismuth chloride solutions containing hydrochloric acid, potassium citrate is used for neutralising the acid instead of potassium hydroxide.

C. W. GIBBY.

Micro-determination of bismuth. P. DUMONT and M. BOUILLENNE (Compt. rend. Soc. Biol., 1928, 99, 1247—1248; Chem. Zentr., 1929, i, 562).—The colour reaction with an excess of potassium iodide is employed (cf. A., 1928, 1348).

A. A. ELDRIDGE.

Spectro-analytical method for the rapid determination of iridium, rhodium, and palladium in platinum. W. GERLACH and E. SCHWEITZER (Z. anorg. Chem., 1929, 181, 103—110; cf. A., 1927,

845).—Observation lines are tabulated for the determination of quantities of rhodium and iridium in platinum of the order 10—0.1% with an accuracy of $\pm 10\%$. No such data are given for palladium, but suitable lines are indicated.

J. S. CARTER.

Benzidine reaction in mineralogical analysis. M. DOMINIKIEWICZ (Przemysł Chem., 1929, 13, 233—236).—The benzidine reaction is not given by ozone. The reaction is positive for pyrolusite, manganite, hausmannite, psilomelane, and ilmenite, and is negative for chromite and cassiterite.

R. TRUSZKOWSKI.

Apparatus for strong ultra-violet and infra-red light and photography with heat rays. J. PLOTNIKOV (Z. Elektrochem., 1929, 35, 434—438).

—Three types of apparatus, involving a carbon arc, strong sunlight, or magnesium light, for the production of strong ultra-violet or strong infra-red radiations are described.

H. T. S. BRITTON.

Small gas muffle oven. F. W. HORST (Chem. Fabr., 1929, 280—281).—A small muffle oven with diatomite insulation is described.

J. S. CARTER.

Apparatus for determination of m. p. W. FRIEDEL (Biochem. Z., 1929, 209, 65—73).—The apparatus consists of a suitably bored copper cylinder in which are placed a thermometer and a capillary tube containing the substance under examination. A highly-magnified image of the tube can be thrown on an attached screen so that the behaviour of small amounts of substance when heated can be watched with ease.

W. MCCARTNEY.

Apparatus for demonstration [by projection on a screen] of m.-p. and f.-p. determinations. W. SCHMIDT (Chem. Fabr., 1929, 279).

Influence of time of outflow and subsequent drainage on burette measurements. J. LINDNER and F. HASLWANTER (Z. angew. Chem., 1929, 42, 821—825).—Burettes were emptied at various rates and the subsequent drainage was measured after various time intervals. The data are discussed in their bearing on errors introduced into volumetric determinations.

J. S. CARTER.

Rapid calibration of pipettes and burettes. A. T. SHOHL (Ind. Eng. Chem. [Anal.], 1929, 1, 152—153).—The required weights and one of a pair of tared flasks are placed on the pan of a rough balance. The other tared flask is placed on the other pan. Mercury, covered by a layer of water to obtain a suitable meniscus, is run from the apparatus to be calibrated into the second flask until the balance just turns.

J. S. CARTER.

Volumeter using water as the measuring medium. J. A. FRIES (Ind. Eng. Chem. [Anal.], 1929, 1, 123—125).—The volume of flasks etc. is determined by connecting them to a burette filled with water and observing the change in the water level when the stop-cock is opened. The procedure and the method of calculation are described.

J. S. CARTER.

Nitrometer without rubber connexions for semi-micro-chemical work. E. BERL, K. HOFMANN, and R. BEMMANN (Chem. Fabr., 1929, 359—360).—The apparatus described presents certain new

features in control by manipulation of suitably pierced stop-cocks. The customary arrangement of nitrometer and levelling tube is replaced by a gas burette sealed within a glass jacket; the burette and jacket may be connected by manipulation of a stop-cock at the base. J. S. CARTER.

Stopcock [for vacuum work] in which contamination by grease is prevented, and its application to a problem in gas technique. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1929, 51, 2132—2134).—The lowest edge only of the cock is lubricated; an annular "washer" of mercury prevents access of gas to the grease. The use of such a tap constructed to work also as a McLeod gauge in measuring velocities of gaseous reactions is indicated. S. K. TWEEDY.

Vacuum contraction of density bulbs. M. BECKERS (J. Amer. Chem. Soc., 1929, 51, 2042—2051).—An investigation of the contraction of density globes on evacuation by the hydrostatic and by Travers' method confirms the validity of Moles and Miravalles' empirical formula for the contraction of such globes (A., 1924, ii, 451). The contraction appears to be a linear function of the pressure difference to which the bulb is submitted. S. K. TWEEDY.

Pyrex glass as a radium container. S. C. LIND (Science, 1928, 68, 643—644).—Longitudinal and transverse cracks developed in 1 year in a 250-c.c. pyrex flask half-filled with 265 mg. of radium chloride solution (cf. Curtis, Nature, 1927, 120, 406). Incipient scaling accompanied by interference colours was also noted. L. S. THEOBALD.

Simple apparatus for direct reading of corrosion of metals, formation of incrustations, and the oxidising power of solutions (Todt oxidimeter). L. KOHLER (Chem.-Ztg., 1929, 53, 567; cf. Todt, this vol., 145, 270).—The apparatus consists of electrodes of a noble metal and the metal under examination immersed in the corrosive liquid and connected to a recording instrument. J. S. CARTER.

Portable apparatus for p_H determination. A. ITANO (Ber. Ohara Inst. landw. Forsch., 1929, 4, 19—26).—A simple and inexpensive type of portable potentiometer which has been designed for p_H determinations with quinhydrone and calomel electrodes, together with a form of quinhydrone electrode suitable for p_H determinations with volumes of solution of the order of 0.02 c.c., are described. Data which are thought to establish that the error of the instrument is of the order of 1% are given. E. A. LUNT.

Apparatus for hydrogen-ion determinations. H. K. MULFORD and F. R. GREENBAUM (J. Amer. Pharm. Assoc., 1929, 18, 564—568).—An apparatus based on the Hildebrand arrangement, and reading to an accuracy of 0.01 is described. The p_H values of 49 medicinal solutions are recorded. The apparatus is unsuitable for the determination of the hydrogen-ion concentration of solutions containing copper, arsenic, bismuth, antimony, and mercury when a quinhydrone electrode is employed. C. C. N. VASS.

Bimetallic electrodes for titrations involving a change of hydrogen-ion concentration. R. M. FUOSS (Ind. Eng. Chem. [Anal.], 1929, 1, 125—128; cf. Furman and Wilson, A., 1928, 382).—The electrode pairs, antimony-lead, antimony-amalgamated copper, bismuth-silver, and copper-copper oxide, have all given satisfactory results when used for potentiometric titrations involving changes in hydrogen-ion concentration. For general acidimetric work the antimony-amalgamated copper pair is preferred. J. S. CARTER.

Flexible seal for electrodes. M. C. MARSH (J. Sci. Instr., 1929, 6, 234—235).—A flexible seal for electrodes through metal or thick glass walls is described. A short length of tightly-fitting rubber tubing is placed on the rod forming the lead, and is splayed out on each side of the wall by tightening two nuts threaded on to the rod. C. W. GIBBY.

Electrolytic conductivity bridge. D. C. GALL (J. Sci. Instr., 1929, 6, 231—233).—A substitution method of measuring electrolytic conductivities, involving only the accuracy of the resistance box, is described. C. W. GIBBY.

Electrically-heated thermostats. L. HOCK and C. L. NOTTEBOHM (Z. Elektrochem., 1929, 35, 458; cf. van Campen, this vol., 786).—The ordinary electrical control of a thermostat can be greatly improved by placing a 4-microfarad condenser in parallel with the mercury contact which is connected to a 2-volt accumulator (cf. Nottebohm, Diss., Giessen, 1929). H. T. S. BRITTON.

Thermostat constant to 0.001°. F. R. WINTON (J. Sci. Instr., 1929, 6, 214—217).—A sensitive toluene-mercury thermoregulator has as contact at the open end a wire having the tip covered with burnt sealing wax. The variations in this resistance control the grid bias of a thermionic valve, the anode current of which passes through the heating resistance. Numerous essential precautions are described. C. W. GIBBY.

Pyknometer for viscous substances. E. H. RIESENFELD and T. HAMBURGER (Chem.-Ztg., 1929, 53, 547).—The apparatus comprises a thick-walled cylindrical vessel 10 mm. high and 16 mm. internal diameter covered with a cover-glass 2 mm. thick. The cylinder is filled with the oil or other viscous liquid to be examined, so that the surface of the liquid is just above the upper edges and the cover is then pressed down without including any air bubbles, after which the determination is made as with the ordinary pyknometer. A. R. POWELL.

Large-capacity laboratory condensers. D. F. OTHMER (Ind. Eng. Chem. [Anal.], 1929, 1, 153).—Two double-coil jacketed condensers are described. In one water flows inside the coils and in the other water flows outside the coils. J. S. CARTER.

Modification of the Kjeldahl trap. G. H. W. LUCAS (Ind. Eng. Chem. [Anal.], 1929, 1, 140).—The usual bulb trap is replaced by an arrangement in which vapours leave the Kjeldahl flask through a 1-cm. tube fused into a distillation flask. Spray etc. is returned to the Kjeldahl flask by means of a

3-mm. tube sealed to the bottom of the distillation flask. As an extra precaution a small funnel packed with glass wool is suspended in the neck of the distillation flask just below the side arm.

J. S. CARTER.

Simple extraction apparatus for liquids. H. BACH (Chem.-Ztg., 1929, 53, 517).—The apparatus of Baas and Bosmann (Pharm. Weekblad, 1893, No. 9) for the extraction of liquids with ether has been modified by providing a separate overflow tube from the extraction vessel back to the ether distillation flask and sealing the delivery tube for the ether vapour into the upper part of the extraction flask well above the surface of the liquid being extracted. The extraction flask is also provided with a stopcock at its lower end for withdrawing the spent liquid.

A. R. POWELL.

Colour measurement by means of Moll's extinctions. M. J. VAN TUSSENBOECK (Chem. Weekblad, 1929, 26, 374—381; cf. A., 1927, 537).—The radiant energy transmitted by standard baths of oil coloured by addition of selected yellow and red dyes is balanced against that transmitted by selected filters of which the permeability for given wave-lengths is known. In order to make the

apparatus sensitive to rays in the visible spectrum, infra-red rays are suppressed by means of copper sulphate solution. The effect of bleaching oils by various refining methods is determined by measuring the amounts of energy transmitted for the range of visible light, the results being mapped on a curve relating wave-length to transmitted energy.

S. I. LEVY.

Spinning target X-ray generator. A. MULLER (Nature, 1929, 124, 128).

Production of high Lo Surdo fields. Y. ISHIDA and S. HIYAMA (Nature, 1929, 124, 129).

Alcoholometric tables. A. V. RAKOVSKI (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 5, 5—112).—New tables have been prepared by critical use of published data.

CHEMICAL ABSTRACTS.

Nomography. XV. Electrometric determination of p_H . O. LIESCHE (Chem. Fabr., 1929, 279—280).—A nomogram for the derivation of p_H values from the observed *E.M.F.* is given.

J. S. CARTER.

Nomography. O. LIESCHE (Chem. Fabr., 1929, 373—374).—Charts for converting pycnometer weighings (water and liquid both at 20°) into d_4^{20} are given.

Geochemistry.

Atmospheric precipitations. II. III. W. LIESGANG (K. Mitt. Ver. Wasserversorg., 1928, 4, 178—182, 261—265; Chem. Zentr., 1929, i, 1208).—A discussion of the composition of rain and snow.

A. A. ELDRIDGE.

Differences in the condition of sea-water at the margins of two opposing tidal currents. T. G. THOMPSON and R. C. MILLER (Science, 1928, 68, 517—518).—Analysis of two samples of water taken from opposing currents in the channel north of San Juan island and within a few feet of each other show differences of 2.4° in temperature, 0.22 in and of 2.8 parts Cl per 1000 parts of water. Colour, sp. gr., and carbon dioxide content also differed considerably. Such changes are suggested to be of marked biological importance.

L. S. THEOBALD.

Alkaline reserve of sea-water. R. MARGARIA (Atti R. Accad. Lincei, 1929, [vi], 9, 816—820).—The absorption of carbon dioxide by sea-water is approximately proportional to the pressure of the gas up to 51.6 mm., at which pressure 13.3 c.c. of carbon dioxide (at 0° and 760 mm.) are absorbed per 100 c.c. of sea-water. From these data, and from the known solubility of carbon dioxide in a prepared water of salinity equal to that of sea-water, the amounts of carbon dioxide simply dissolved and combined as hydrogen carbonate in the latter are computed, and hence by Hasselbach's modification of Henderson's formula the p_H value of the sea-water is derived. The bearing of these data on the dependence of the p_H value of sea-water on the tension of carbon dioxide in contact with it is discussed and its physiological importance indicated.

F. G. TRYHORN.

Meteorite from Ballinger, Texas. H. H. NININGER (J. Geol., 1929, 37, 88—90).—The meteorite contained Fe 91.48, Ni 6.54, Co 0.48, Cu 0.07, P 0.26, S 0.01, SiO₂ 0.12, C 0.09, O 1.03%, with traces of chromium and magnesium. Platinum (0.19 oz. per ton) was also present.

CHEMICAL ABSTRACTS.

Origin of moldavite. J. CHLOUPEK (Naturwiss., 1929, 17, 598—600).—A summary of a paper by F. Hanus (Abh. Prag. Akad. Wiss., 1928, 37, [24]). Moldavites are aluminium silicates (90%) occurring as greenish glassy solids with a rounded appearance. The material is not readily fusible (m. p. 1300—1400°). The evidence points to a meteoritic origin.

R. A. MORTON.

Synthesis of kaolin. R. SCHWARZ (Rec. trav. chim., 1929, 48, 695—696).—Explanatory. The author regards the synthesis of kaolin by van Nieuwenburg and Pieters (cf. this vol., 280) as a further proof of the correctness of his theory of the formation of kaolin in nature.

F. L. USHER.

Blue rock salt. C. DOELTER (Monatsh., 1929, 52, 241—252).—A discussion of the distribution and of the origin of the colour in blue rock salt. Siedentopf's hypothesis that the colour is due to the presence of sodium of ultramicroscopic dimensions, the view that the colour is induced by exposure to radium, and also other theories are considered to be improbable. The author's view is that a pigment containing iron and manganese, and possibly organic substances or sulphur, is responsible for the blue colour.

A. I. VOGEL.

Radium in rocks. I. Radium content of some representative granites of the eastern

seaboard of the United States. C. S. PIGGOT (*Amor. J. Sci.*, 1929, [v], 17, 13—34).—A detailed account is given of the experimental procedure to be used in the determination of the radium content of rocks. The main results obtained have been described already (this vol., 163). It is further stated that part of the radioactive material may be leached out of a granite by hot water. Apparently some of this material is associated with the interstices between the grains and with the surfaces of the grains rather than with their interiors. F. J. WILKINS.

Formation of cupriferous "black earths" in Niari (French Congo). R. BURKHARDT (*Arch. Sci. Phys. Nat.*, 1929, [v], 11, 163—183; cf. this vol., 788).—Analyses of "black earths" and limestones from various parts of Niari are given.

C. W. GIBBY.

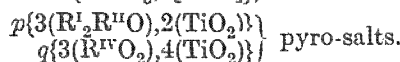
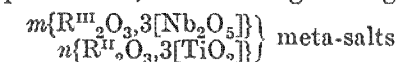
Niobium : tantalum ratios of titanium minerals. G. VON HEVESY, E. ALEXANDER, and K. WÜRSTLIN (*Z. anorg. Chem.*, 1929, 181, 95—100).—The niobium and tantalum contents of a number of titanium minerals have been determined by a combination of chemical and X-ray spectroscopic methods. The average atomic ratio of titanium to niobium for rutile, titanite, and perovskite is about 3000 and the titanium : tantalum ratio is about 7000. The corresponding values for ilmenite are about 100 times as great. J. S. CARTER.

Composition of apophyllite. B. GOSSNER and O. KRAUS (*Z. Krist.*, 1928, 68, 595—615; *Chem. Zentr.*, 1929, i, 496—497).—The fluorine content of apophyllite varies between 1.2 and 1.5%; the formula $4[\text{H}_2\text{Si}_2\text{O}_5, \text{Ca}(\text{OH})_2] \cdot \text{KF}$ is proposed. Analysis shows that 28—44 mol.-% of the potassium fluoride has been replaced by hydroxide without marked disturbance of the atomic lattice. X-Ray investigation gave: a 12.73, c 15.84 Å.; $a:c=1:1.244$; the unit cell contains 4 mols.; space-group

A. A. ELDRIDGE.

Analyses of echenite. Echenite-blomstrandite-priorite series. G. P. TSCHERNIK (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 735—770).—The results obtained by previous workers from the analyses of echenite and blomstrandite are discussed and the methods used by the author described. Typical Ural echenite had d 5.00—5.36; that of blomstrandite was 4.97, and of priorite 4.67. Uranium is absent from typical Ural echenites, but is an essential constituent of both blomstrandite and priorite, although echenites having an abnormally high radioactivity were assumed to contain uranium. Lead is always found in blomstrandite but not in echenite, whilst thorium is

found in all minerals of the echenite-blomstrandite-priorite series. In echenites of maximal d 11—12% Th, in blomstrandite 8.5% Th, and in priorite 0.5—0.75% Th is present. With respect to their rare-earth content the minerals of the echenite series can be divided into two groups. In the typical echenites the cerites exceed the yttrites, whilst in blomstrandite the relation is reversed. The author assumes that the actual proportions in which the separate component elements of the cerite group are found is the same as found in monazite, i.e., Ce_2O_3 20, La_2O_3 15, Nd_2O_3 3, and Pr_2O_3 1. Zirconium dioxide is not a component of the Ural echenites, but is found to an extent of about 0.5—1.5% in some blomstrandites, whilst it is absent from others. Tin is always found in the minerals of this family and so is silicon, which replaces titanium. There are also present small quantities of alkaline earths, lime, of bivalent iron, and magnesium. Iron is found to the extent of 2.3% in echenites, 1.5—2% in blomstrandite, and 5% in priorite. 1—2% of lime are found in blomstrandite and 4% in priorite. Traces of fluorine are also found and so are traces (1%) of water and gases which escape on heating. Although the composition is not fixed and cannot be expressed by a simple formula, the following are suggested:



A. FREIMAN.

Theory of the formation of fusain. R. LIESKE (*Brennstoff-Chem.*, 1929, 10, 185—191).—Study of the mode of occurrence of fusain has established the following facts: (1) the deposits are usually lenticular in shape, (2) the fusain has been formed in hollow spaces containing a greater or smaller amount of gas, (3) the fusain has not been subjected to direct earth pressure in the same way as has the surrounding bright or dull coal, (4) the fusain has not been subjected to the infiltration of finely-divided or colloidal humin substances. These observations, for which previous theories fail to account, lead to the assumption that fusain has been formed by the coalification of coarser particles of plant material which have collected in the lenticular spaces filled with gas produced by the decomposition of the surrounding material. The differences in the conditions to which the plant material within these hollow spaces and that in the surrounding mass are subjected account fully for the observed differences in the final products. A. B. MANNING.

Organic Chemistry.

Isomerism and configuration. A. C. LUNN and J. K. SENIOR (*J. Physical Chem.*, 1929, 33, 1027—1079).—A theoretical paper in which a mathematical treatment is developed. L. S. THEOBALD.

Vapour-phase oxidation of isomeric octanes. II. Octanes with branched chains. III. Effect

of lead tetraethyl; relation of oxidation to engine detonation. J. C. POPE, F. J. DYKSTRA, and G. EDGAR (*J. Amer. Chem. Soc.*, 1929, 51, 2203—2213, 2213—2220).—The oxidation of γ -methylheptane, γ -ethylhexane, β -methyl- γ -ethylpentane, β -dimethylhexane, and $\beta\beta$ -trimethylpentane has been studied by the methods previously described for

n-octane (this vol., 906). The effect of temperature on the oxygen consumed, and on the amounts of carbon monoxide and dioxide produced from mixtures of hydrocarbon with oxygen sufficient for complete combustion, is shown graphically for each isomeride. The onset of the "low-temperature disturbance" (the "aldehyde oxidation"), involving a large increase in the production of carbon monoxide, is observed only with γ -methylheptane (280—305°) and γ -ethylhexane (285—302°). The "high-temperature disturbance," accompanied by complete combustion, begins in the three cases examined, namely, γ -ethylhexane, β -methyl- γ -ethylpentane, and $\beta\beta\delta$ -trimethylpentane, at 560°, 520°, and 515°, respectively. The curves for the low-temperature oxidation of all the isomerides except $\beta\beta\delta$ -trimethylpentane are similar in general nature. When allowance is made for the formation of small amounts of unsaturated hydrocarbons, the oxygen consumption agrees closely with that calculated from the amounts of oxides of carbon formed, by means of the equations used in the case of *n*-octane. The results are in accordance with the view that oxidation begins at the methyl group at the end of the longest unbranched chain in the molecule and continues along the chain, giving aldehydes of successively lower mol. wt., until a branch is reached. The resulting ketone is more resistant, and little further oxidation takes place until the temperature of complete combustion is reached. This temperature becomes higher as the amount of oxygen consumed in the low-temperature oxidation increases, being highest with *n*-octane. The oxidation of $\beta\beta\delta$ -trimethylpentane begins at 515° and goes directly to completion. In general, the temperature of initial attack rises with the degree of branching of the molecule. The probable behaviour of other hydrocarbons is discussed.

Curves are given for the consumption of oxygen by, and production of oxides of carbon from, *n*-octane, alone and with 0.3 vol. and 1.07 vol.-% of lead tetraethyl, and from heptaldehyde, alone and with 1% of lead tetraethyl, under the conditions described above. With *n*-heptaldehyde the presence of lead tetraethyl greatly retards the aldehyde oxidation and raises its temperature of onset from 235° to 270°. The production of carbon dioxide remains unaffected. With *n*-octane the initial oxidation to octaldehyde and, in consequence, the subsequent formation of carbon dioxide is slightly retarded, and the aldehyde oxidation much retarded. The tendencies of 10% solutions of each of the above isomeric octanes in a "standard gasoline" to produce engine detonation have been compared. The order of decreasing ease of detonation is *n*-octane, γ -methylheptane, γ -ethylhexane, β -methyl- γ -ethylpentane, $\beta\epsilon$ -dimethylhexane, and $\beta\beta\delta$ -trimethylpentane. This is also the order of the extents to which these hydrocarbons undergo low-temperature oxidation, as found experimentally, and as given by the length of the longest unbranched carbon chain. Thus a repression of the aldehyde oxidation, whether by the presence of lead tetraethyl or by a change in structure, is accompanied by a decreasing tendency to detonate. The behaviour of other paraffins and the mechanism of detonation are discussed in view of this generalis-

ation. Much detailed matter is presented for which the original papers must be consulted.

H. E. F. NOTTON.

Polymerisation of ethylene by the electric discharge. Synthesis of butene and hexene. G. MIGNONAC and R. V. DE SAINT-AUNAY (Compt. rend., 1929, 189, 106—108; cf. this vol., 537).—Ethylene was submitted to an electric discharge, using a current of high frequency (d'Arsonval apparatus) in a closed circuit containing a circulating pump, and condensers at -60°; 80—90% of the ethylene was transformed into Δ^a -butene and Δ^a -hexene, identified by their ozonides. The authors' theory that, under the influence of the discharge, certain ethylene molecules are activated and link with unactivated molecules to form butene, which can then link with further activated ethylene to form hexene, is supported by the fact that, when the circulation of the gas is accelerated and the temperature of the condensers lowered to -80°, butene is the main product, whereas with less vigorous condensation mostly hexene is produced.

B. W. ANDERSON.

Aliphatic diolefines. II. Preparation and physical constants of Δ^a -hexadiene. F. CORTESE (J. Amer. Chem. Soc., 1929, 51, 2266—2269).—Pure diallyl, obtained in good yield from allyl bromide, or chloride, and magnesium in ether (cf. Lespieau, A., 1912, i, 934), has b. p. 59.57°/760.0 mm., f. p. -140.9°, d_4^{25} 0.6863, 1.4012.

H. E. F. NOTTON.

Contact isomerisation of an aliphatic tetrahydroterpene. N. D. ZELINSKI and R. J. LEVINA (Ber., 1929, 62, [B], 1861—1863).— $\gamma\gamma$ -Dimethyl- Δ^a -octene, b. p. 154°/753 mm., d_4^{25} 0.7396, 1.4212, is isomerised by passage in a current of carbon dioxide over palladised asbestos at 200°/1 atm. to $\gamma\gamma$ -dimethyl- Δ^b -octene, b. p. 161°/744 mm., d_4^{25} 0.7458, n_D^{25} 1.4259. The intermediate production of $\gamma\gamma$ -dimethyl- $\Delta^a\Delta^b$ -octadiene is postulated.

H. WREN.

Thermochemical investigation of petroleum. Thermochemical change in squalene. R. ABE and G. SHOBAYASHI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 496—501).—On heating squalene, exothermic reaction sets in at 300°. Probably, preliminary polymerisation is followed by the formation of volatile hydrocarbons from the unstable polymerisation products. The favourable action of aluminium chloride on cracking is thus explained.

B. W. ANDERSON.

Ozonisation of unsaturated gaseous hydrocarbons. IV. Ozonisation of acetylene. E. BRINER and R. WUNENBURGER (Helv. Chim. Acta, 1929, 12, 786—790).—When acetylene and ozonised oxygen (7% O₃) were passed alternately through liquid methyl chloride and the apparatus was swept out by a stream of dry air after each saturation the residue after removing the solvent contained glyoxal (81%), formic acid (5.6%), and traces of formaldehyde.

R. J. W. LE FEVRE.

Trichloronitrosomethane, dichloroformoxime (phosgene oxime), and their derivatives. W. PRANDTL and K. SENNEWALD (Ber., 1929, 62, [B], 1754—1768).—Carbon disulphide is converted by

potassium dichromate and hydrochloric acid into trichloromethylsulphonyl chloride, transformed by hydrogen sulphide and anhydrous sodium carbonate in presence of absolute alcohol into sodium trichloromethylsulphinate. The last-named substance is converted into *trichloronitrosomethane*, b. p. 5.0° to 5.5°/70 mm., d_4^{20} 1.50, either by cautious warming with 10% nitric acid or by regulated addition of 68% nitric acid to its aqueous solution. The compound decomposes slowly when preserved, rapidly when heated, into nitrosyl chloride, nitric oxide, trichloronitromethane, and *trichloromethyldichloromethyleneamine*, $\text{CCl}_3\cdot\text{N}\cdot\text{CCl}_2$. It is slowly hydrolysed by water or aqueous alkalis, of which 3 mols. are required for complete decomposition, dichloronitromethane being apparently produced. It reacts slowly with oxygen at the ordinary temperature or its b. p., but is converted at 120° into nitrogen peroxide, trichloronitromethane, and hexachloroethane. Chromic acid oxidises it to trichloronitromethane. It appears to be reduced quantitatively to methylamine by iron filings and acetic acid, whereas hydrogen sulphide or aluminium amalgam in alcohol converts it into *dichloro-oximinomethane* (phosgene oxide). *Trichloromethyldichloromethyleneamine*, b. p. 170°/1 atm., 77°/30 mm., d_4^{20} 1.698, is a colourless, stable liquid reduced by iron filings in acetic acid to ammonia. *Dichloro-oximinomethane* has m. p. 39—40° after softening at 38—39°, b. p. 129°/1 atm., 53—54°/28 mm. It is stable at the atmospheric temperature, slowly hydrolysed by cold water to carbon dioxide, hydrogen chloride, and hydroxylamine. It is vigorously decomposed by aqueous alkalis without yielding well-defined products. Under definite conditions, trichloronitrosomethane and aniline afford *chloroanilobenzeneazomethane*, $\text{NPh}\cdot\text{CCl}\cdot\text{N}\cdot\text{NPh}$, m. p. 208° (decomp.). H. WREN.

[Preparation of] *methylene bromide*. W. W. HARTMAN and E. E. DREGER (*Organic Syntheses*, 1929, 9, 56—57).

[Preparation of] *pentamethylene bromide*. J. VON BRAUN (*Organic Synthesis*, 1929, 9, 70—71).

Reaction between nitrobenzene and secondary alcohols. R. E. LYONS and M. E. PLEASANT (*Ber.*, 1929, 62, [B], 1723—1727; cf. A., 1927, 234).—The action of nitrobenzene on isopropyl alcohol in the presence of sodium hydroxide follows the course: $3\text{CHMe}\cdot\text{OH} + \text{SNO}_2\text{Ph} \longrightarrow 6\text{NH}_2\text{Ph} + \frac{\text{NPh}}{\text{NPh}}\text{O} + 3(\text{CO}_2\text{H})_2 + 3\text{H}\cdot\text{CO}_2\text{H}$. Under similar conditions, acetone is readily oxidised to the same products. Azoxybenzene is not reduced by isopropyl alcohol or acetone under these conditions. Benzoin is transformed into benzoic acid and azoxybenzene with a little azobenzene; benzil and aniline do not appear to be formed. H. WREN.

Configurative relationship of ζ -methylheptan- β -ol with lactic acid. Effect of unsaturation on optical activity. P. A. LEVENE and H. L. HALLER (*J. Biol. Chem.*, 1929, 83, 177—183).— ζ -Methyl- Δ^6 -hepten- β -ol was resolved by the phthalate method; the insoluble *brucine* salt had $[\alpha]_D^{24} -4.2^\circ$, and gave a *hydrogen phthalate*, $[\alpha]_D^{25} +60.3^\circ$, which yielded the *d*-carbinol, b. p. 60—61°/4 mm., $[\alpha]_D +19.0^\circ$ in ether

(α -*naphthylcarbamate*, m. p. 64—66°, $[\alpha]^{22} +32.8^\circ$); the mother-liquors yielded a carbinol, b. p. 87°/22 mm., $[\alpha]_D^{25} -16.2^\circ$ in ether. The *d*-carbinol, with ozone, gave *l*- γ -hydroxyvaleraldehyde, b. p. 43—46°/1—2 mm., $[\alpha]_D -7.8^\circ$ in ether; this, when oxidised with silver oxide, yielded *d*- γ -hydroxyvaleric acid, $[\alpha]_D^{25} +18.8^\circ$ (silver salt, $[\alpha]^{25} +5.4^\circ$). The *d*-methylheptenol, when reduced with hydrogen and palladium, gave *d*- ζ -methylheptan- β -ol, b. p. 61—63°/4 mm., $[\alpha]_D^{25} +13.0^\circ$ in ether (α -*naphthylcarbamate*, m. p. 75—77°, $[\alpha]^{25} +16.4^\circ$ in alcohol); the latter carbinol is therefore configuratively related to *d*-lactic acid. The statement of Pickard and Kenyon (*J.C.S.*, 1911, 99, 47) that unsaturation increases the magnitude of rotation does not hold universally; such increase is, however, constantly observed when the double linking is situated in the γ -position to the asymmetric carbon atom. C. R. HARRINGTON.

***r*-Citronellol.** J. DŒUVRE (*Bull. Soc. chim.*, 1929, [iv], 45, 403—412).—Magnesium methylheptenylbromide with magnesium β -chloroethoxybromide yields β -methyl- Δ^6 -heptene, b. p. 115—120° (*dibromo*-derivative, b. p. 108—110°/15 mm.), and *r*-citronellol, b. p. 115—117°/15 mm., d_4^{20} 0.863, n_D^{20} 1.4588 [allophanate, m. p. 105—106° (cf. A., 1928, 1113)]. On ozonisation *r*-citronellol yields 8% of formaldehyde, 17% of formic acid, and 76% of acetone, indicating 22% of α - and 76% of β -form, and hence the condensation has produced no appreciable isomerisation. With ethylene oxide, magnesium methylheptenyl bromide yields a little β -methyl- Δ^6 -heptene, ethylene bromohydrin, and a small amount of *r*-citronellol and polymerisation products. Repetition of the process of G.P. 423,544 (B., 1926, 771) afforded 60% of β -methyl- Δ^6 -heptene, b. p. 120—121°, d_4^{25} 0.728, and ethylene bromohydrin, b. p. 61—62°/23 mm., with only a very small amount of citronellol. With trioxymethylene in a hydrogen atmosphere, magnesium methylheptenyl bromide affords in 3 days 15% of a mixture, b. p. 121°, of β -methyl- Δ^6 -heptene and β -methyl- Δ^6 -heptadiene and 45% of $\beta\zeta$ -dimethyl- Δ^6 -hepten- α -ol, b. p. 105—106°/18 mm., d_4^{25} 0.859, n_D^{25} 1.4547. $\beta\zeta$ -Dimethyl- Δ^6 -heptenyl bromide, b. p. 99—100°/18 mm., d_4^{25} 1.123, n_D^{25} 1.4749 (yield 45%), gives a magnesium derivative which with trioxymethylene similarly affords about 40% of a mixture of 28% of the α - and 72% of the β -forms of *r*-citronellol, together with $\beta\zeta$ -dimethyl- Δ^6 -heptene, b. p. 142—143°, d_4^{25} 0.768, n_D^{25} 1.4321. This preparation of *r*-citronellol confirms the constitution of *d*-citronellol and *l*-rhodinol, the difference between the latter consisting in the different proportions of the α - and β -forms present (cf. this vol., 907).

R. BRIGHTMAN.

Partial esterification of polyhydric alcohols. VIII. Proposed standards in work on configuration of glycerol derivatives. A. FAIRBOURNE (*J.C.S.*, 1929, 1151—1153; cf. A., 1927, 131; this vol., 292).—The " $\alpha\beta$ " and " $\alpha\gamma$ "-dimethyl ethers of glycerol prepared as described by Gilchrist and Purves (A., 1926, 153) and Zunino (A., 1899, i, 410), which were proposed as reference compounds by Hibbert, Whelen, and Carter (this vol., 292), have been shown to be identical. The products show the

same characteristic properties and yield the same *p*-nitrobenzoyloxydimethoxypropane, m. p. 43°.

R. K. CALLOW.

[Preparation of] chloromethyl ether. C. S. MARVEL and P. K. PORTER (Organic Syntheses, 1929, 9, 58—59).

Preparation of boric esters. E. KHOTINSKY and S. POUPKO (Ukraine Chem. J., 1929, 4, 13—18).—In the preparation of the esters of boric acid by the action of fused borax on primary alcohols in the presence of gaseous hydrogen chloride, in equivalent amounts, the reaction appears to stop half-way, since the yield of ester never exceeds 48% and only half of the hydrogen chloride is used. The methyl, b. p. 63—65°, ethyl, b. p. 120°, propyl, b. p. 175—177°, isobutyl, b. p. 210—211°, and isopentyl, b. p. 254—255°, esters were obtained.

M. ZVEGINTZOV.

Diethyl pentasulphides. I. and II. G. R. LEVI and A. BARONI (Atti R. Accad. Lincei, 1929, [vi], 9, 772—778, 903—906).—Treatment of ethyl mercaptan with sulphur chloride and sulphur yields ethyl tri- and tetra-sulphides, together with an ethyl pentasulphide, probably

b. p. 119°/26 mm., d^{20}_4

1.1687, n_D^{20} 1.60269, and an isomeric pentasulphide, b. p. 130°/26 mm., d^{20}_4 1.1620, n_D^{20} 1.59517. The latter is transformed into the former when heated above 200°.

T. H. POPE.

Action of niobium and tantalum pentachloride on organic compounds. III. H. FUNK and K. NIEDERLÄNDER (Ber., 1929, 62, [B], 1688—1691; cf. A., 1928, 876).—The action of cold glacial acetic acid on tantalum pentachloride affords the tetra-acetate, $TaCl(OAc)_4$, occasionally as the additive compound, $TaCl(OAc)_4 \cdot 4CH_3 \cdot CO_2H$. At a higher temperature the substance $Ta_2O_5Cl(OAc)_3$ is produced. The various acetates are hydrolysed by water to the compound $TaO_5(OAc)$. Niobium pentachloride yields the substance $Nb_2O_5Cl(OAc)_3$. With methyl and ethyl alcohol, tantalum pentachloride affords the compounds $TaCl_2(OMe)_3$ and $TaCl_2(OEt)_3$. Niobium pentachloride yields ill-defined products with these alcohols.

H. WREN.

Titration of acetic anhydride in mixtures of ethyl or methyl alcohol and water. J. F. M. CAUDRI (Rec. trav. chim., 1929, 48, 778—792).—The anomalous results of Lumière and Barbier (A., 1906, i, 791) for the titration of acetic anhydride with sodium hydroxide in dilute aqueous-alcoholic solution are explained by the partial esterification of the anhydride. The amount of ester formed is considerable even in very dilute solutions and is greater in dilute methyl alcohol than in dilute ethyl alcohol. In agreement with deductions made from Wegscheider's theory (A., 1918, ii, 394), it is found that the amount of acetic anhydride converted into the ester during titration with sodium hydroxide in aqueous-alcoholic solution depends chiefly on the temperature (the higher the temperature the lower is the yield of ester) and on the alcohol concentration, but is independent of the initial concentrations of the anhydride and alkali except when these are very small. This type of reaction is shown to be general for the interaction of esters of organic and inorganic

acids, acid anhydrides, and chlorides with organic compounds containing the $\cdot ONa$ group. Thus by the interaction of sodium hydroxide and benzoyl chloride or benzoic anhydride in aqueous acetone solution, ester formation is shown to occur, although the isolation of the ester-like compound was not possible in this case. On the basis of these results it was found that acetic anhydride may be accurately determined in dilute aqueous-alcoholic solution by the potentiometric method, using a standard solution of ammonia in the burette.

J. W. BAKER.

Interaction of bromine with acetic anhydride. V. Bromination and chlorination compared. Some properties of acetic chloroacetic anhydride. H. B. WATSON and C. E. GREGORY (J.C.S., 1929, 1373—1375).—Acetic chloroacetic anhydride (Anthoine, Jahresber., 1883, 1032) decomposes when heated into acetic anhydride and chloroacetic anhydride. When refluxed with chloroacetic acid (1 mol.), acetic acid and chloroacetic anhydride are formed. It reacts with hydrogen chloride at the ordinary temperature to give acetyl chloride and chloroacetic acid. When acetic acid and chloroacetyl chloride are heated together, hydrogen chloride is evolved, and from the product are separated acetyl chloride, acetic acid, and chloroacetic anhydride, with relatively small amounts of chloroacetic acid and acetic anhydride. One stage of the scheme proposed for the halogenation of acetic acid (A., 1925, i, 1232; 1928, 716), which is further discussed, therefore occurs as (a) $CH_3X \cdot COX + AcOH = CH_2X \cdot CO \cdot OAc + HX$, and (b) $CH_2X \cdot CO \cdot OAc + HX = CH_2X \cdot CO_2H + AcX$.

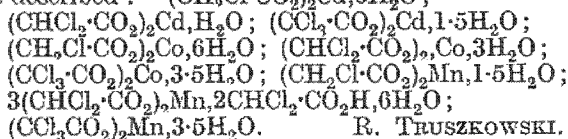
R. K. CALLOW.

Activity of the halogens in halogen-substituted esters. B. V. TRONOV, A. I. AKIVIS, and V. N. ORLOV (J. Russ. Phys. Chem. Soc., 1929, 61, 345—353).—The activity of the halogens in the ethyl esters of a number of aliphatic halogeno-acids was investigated. The degree of activity of the halogen in a particular ester was found by measuring its velocity of reaction with pyridine, piperidine, quinoline, and metallic sodium. Experiments with the amines were carried out without a solvent, those with sodium methoxide in a methyl-alcoholic solution. The reagents were mixed in equimolecular proportions, the temperature being kept at 18—20°. The amount of halogen which had reacted in a given time was determined either gravimetrically or by Volhard's method. The degree of activity was determined by calculating the times necessary for an equal percentage of halogen to react in the different compounds. It was found that bromine reacts with the amines several hundred times as fast as chlorine, that the activity of the halogens decreases with an increase in the number of halogens in the chain, that bromine shows an activity with quinoline and pyridine about 3 times as high when in the α -position as when in the β -position and about 10—12 times as high as when in the γ -position. Also that the substitution of a hydrogen atom in a halogen-substituted acetate or propionate by a carbethoxy-group decreases the activity of both chlorine and bromine, whilst a substitution of an acetyl group increases the activity quite considerably, and finally that pyridines acts about 2.7—4.3 times as rapidly as

quinoline. The results with sodium methoxide are less trustworthy, since it can react, not only with the halogen, but also with the carbonyl group.

A. FREIMAN.

Cadmium, manganous, and cobaltous chloroacetates. L. FOGEL, T. RUBINSZTEIN, and A. TAUMAN (Rocz. Chem., 1929, 9, 348—353).—The preparation and crystalline form of the following salts are described: $(\text{CH}_3\text{Cl}\cdot\text{CO}_2)_2\text{Cd}\cdot 6\text{H}_2\text{O}$;



R. TRUSZEWSKI.

Reaction between amylene and dichloroacetic acid. L. M. ANDREASOV (Ukraine Chem. J., 1929, 4, 93—94).—The rate of reaction between amylene and dichloroacetic acid was investigated in benzene, chloroform, carbon disulphide, ethyl alcohol, and ether, in order to compare the reactivities of dichloroacetic and trichloroacetic acids. It is very slow, and in the order benzene > chloroform > carbon disulphide. In the so-called "active" solvents (ethyl alcohol and ether) the reaction does not take place at all, due, probably, to the formation of inert solvation complexes by the two reacting substances.

M. ZVEGINTZOV.

Reaction limits in the formation of amyl trichloroacetate in mixtures of solvents. L. M. ANDREASOV (Ukraine Chem. J., 1929, 4, 89—92).—The reaction limits between amylene and trichloroacetic acid were investigated in the mixtures of inert solvents: benzene-carbon tetrachloride and carbon tetrachloride-carbon disulphide. Although the limits in the pure solvents were similar, a simple straight-line relation could be expected in mixtures, but the graphs were very complex, being, in the case of the system carbon tetrachloride-benzene, convex and showing pronounced maxima, the position of which depended in the concentration of the reacting substances, whilst on the system carbon tetrachloride-carbon disulphide they were convex for a concentration of 0.75 mol./litre and concave for 0.375 mol.

M. ZVEGINTZOV.

[Preparation of] *n*-butyryl chloride. B. HELFERICH and W. SCHAEFER (Organic Syntheses, 1929, 9, 32—33).—Butyric acid is treated with thionyl chloride.

A. A. ELDRIDGE.

Oxidation of simple and complex unsaturated fatty acids and hydrocarbons with perbenzoic acid. K. H. BAUER and O. BAHR (J. pr. Chem., 1929, [ii], 122, 201—213).—Unsaturated acids are primarily oxidised by perbenzoic acid to oxido-acids, $\text{CH}_3\cdot[\text{CH}_2]_x\cdot\text{CH}=\text{CH}\cdot[\text{CH}_2]_y\cdot\text{CO}_2\text{H}$, which by hydro-

lysis with aqueous potassium hydroxide form the corresponding polyhydroxy-fatty acid. The following examples are given: oleic acid, oxido-oleic acid, m. p. 52°, dihydroxystearic acid, m. p. 96°; elaidic acid, *oxidoelaidic acid*, m. p. 57.5—58.5° (*methyl ester*, m. p. 32—33.5°), dihydroxystearic acid, m. p. 132°; erucic acid, *oxidoerucic acid*, m. p. 67.5° (from which, by treatment with hydrazine hydrate, *hydrazinoerucic acid*, m. p. 94.5°, is obtained), dihydroxy-behenic acid, m. p. 133°; ricinoleic acid, *hydroxy-*

oxidoricinoleic acid, an oil, trihydroxystearic acid, m. p. 110°; ricinelaiddic acid, *hydroxyoxidoricinelaiddic acid*, trihydroxystearic acid, m. p. 110°; linoleic acid, *dioxidolinoleic acid*, an oil, tetrahydroxystearic acid, m. p. 175°.

Dicyclopentadiene yields mono- and di-oxido-derivatives. The last gives a *mercurichloride*, m. p. 154°. Indene with perbenzoic acid gives an oily oxidation product, from which β -hydrindone is isolated.

R. J. W. LE FÈVRE.

Fatty acids associated with rice starch. L. LEHRMANN (J. Amer. Chem. Soc., 1929, 51, 2185—2188).—Hydrolysis of rice starch with dilute hydrochloric acid gives about 0.6% by weight of a mixture of palmitic (36%), oleic (35%), and linoleic (29%) acids, approximately in the proportions named. The mixture does not contain compounds of nitrogen, sulphur, phosphorus, and halogens and no glycerol or phytosterol is liberated during the hydrolysis. The acyl residues must be combined with the carbohydrate molecule (cf. B., 1926, 686).

H. E. F. NOTTON.

Composition of α -elæostearic acid, the most important component of Chinese wood (tung) oil. J. BOESEKEN.—See B., 1929, 607.

Oleosylvic acid. F. BALAS and R. HAZUKOVÁ (Coll. Czech. Chem. Comm., 1929, 4, 401—410).—Oleosylvic acid can be separated by fractional crystallisation of its di-*d*-amylamine salt into abietic acid and *d*-pimaric acid, m. p. 212—213°, $[\alpha]_D + 78.4^\circ$ in alcohol. The following salts of *d*-pimaric acid are also described: *propylamine*, m. p. 158°, $[\alpha]_D + 79.7^\circ$ in chloroform; *dipropylamine*, m. p. 112°, $[\alpha]_D + 72.2^\circ$ in alcohol; *tetramethylammonium*, m. p. 230° (decomp.); *di- α -amylamine*, m. p. 113°, $[\alpha]_D + 42.5^\circ$ in alcohol; *piperidine*, m. p. 133°, $+ 61.6^\circ$ in alcohol; *quinine*, m. p. 195°, $[\alpha]_D + 57.8^\circ$ in alcohol; *quinidine*, m. p. 90°, *cinchonidine*, m. p. 175°, $[\alpha]_D - 30.5^\circ$ in chloroform. Abietic acid forms the following salts: *dipropylamine*, m. p. 160°, *di- d -amylamine*, m. p. 133°, $[\alpha]_D - 17.1^\circ$ in alcohol; *piperidine*, m. p. 114°, *quinine*, m. p. 180°; *quinidine*, m. p. 198°, *cinchonidine*, m. p. 178°. *Di- d -amylammonium dihydro- d -pimarate* has m. p. 120° and $[\alpha]_D + 16.2^\circ$ in chloroform.

R. J. W. LE FÈVRE.

Constitution of linoleic acid. R. D. HAWORTH (J.C.S., 1929, 1456—1461).—Contrary to the statement of Takahashi (cf. A., 1919, i, 468; 1921, i, 303) it has been found that linoleic acid isolated from soya bean is identical with that obtained from poppy-seed oil. Goldsobel's conclusions (J. Russ. Phys. Chem. Soc., 1906, 38, 904) that linoleic acid is octadeca- Δ^8 -dienoic acid have been confirmed by oxidation experiments. Oxidation with potassium permanganate in alkaline solution gave *n*-hexoic, azelaic, and oxalic acids in 80% of the theoretical yield, whilst traces of malonic acid were detected by the formation of hydrogen formazyl. Satiivic acid yielded mainly *n*-valeric, suberic, and oxalic acids when oxidised with potassium permanganate in cold alkaline solution, but in warm solution increasing amounts of azelaic and *n*-hexoic acids were obtained. The existence of various tetrabromo- and tetrahydroxy-additive products of linoleic acid is explained on steric grounds.

A. A. GOLDBERG.

Syntheses of ethyl acetoacetate and malonate. H. LUX (Ber., 1929, 62, [B], 1824—1827).—Powdered sodium is covered with a boiling mixture of ether and ethyl carbonate to which acetone is gradually added. After treatment with acetic acid, ethyl acetoacetate is obtained in 38—41% yield (calculated on sodium or acetone). Ether may be replaced by benzene. Ethyl malonate is prepared in 18% yield by the addition of ethyl acetate to sodium and boiling ethyl carbonate and benzene; ethyl acetoacetate is obtained simultaneously.

H. WREN.

[Preparation of] **lævulic acid.** B. F. MCKENZIE (Organic Syntheses, 1929, 9, 50—51).

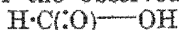
Preparation of tertiary α -hydroxy-acids. R. HELLMANN (Bull. Soc. chim., 1929, [iv], 45, 412—414).—Methyl α -hydroxy-ketones, $\text{OH}\cdot\text{CRR}'\cdot\text{COMe}$, obtained by hydration of dialkylethinylcarbinols (Locquin and Wouseng, A., 1923, i, 302; 1924, i, 822) in presence of acid mercuric sulphate, are oxidised by alkaline hypochlorite or hypobromite. α -Hydroxy- α -propylvaleric acid, m. p. 80° (methyl ester, b. p. 83 — $84^\circ/10$ mm.), α -hydroxy- $\alpha\beta$ -trimethylbutyric acid, m. p. 141° , and α -hydroxy- α -methylvaleric acid (yield 70%), b. p. 127 — $128^\circ/10$ mm. (methyl ester, b. p. 65 — $66^\circ/15$ mm., ethyl ester, b. p. $68^\circ/9$ mm.), have been thus prepared.

R. BRIGHTMAN.

Existence of an isomeride of oxalic acid. A. E. TSCHITSCHIBABIN (J. Russ. Phys. Chem. Soc., 1929, 61, 607—612).—The theoretical possibility of the existence of *cis-trans*-isomerism of oxalic acid is considered and certain results obtained by earlier workers are reviewed in the light of this possibility.

R. TRUSZKOWSKI.

Constitution of maleic acid. K. VON AUWERS and L. HARRES (Ber., 1929, 62, [B], 1678—1688).—Spectroscopic examination of a series of compounds of the fumaric acid group in many of which the methyl group or halogen atom is present as substituent shows certain peculiarities as a consequence of the individual nature of its conjugated system which do not fall outside the limits of the usual spectrochemical laws. In the case of the corresponding derivatives of maleic acid the exaltations in refractive power and index of dispersion caused by the introduction of a methyl group or halogen atom into the parent molecule are inexplicable if the open-chain structure is assumed, but are expected if Anschütz' cyclic structure is adopted. The latter conception is supported by the optical behaviour of anhydrides of the maleic acid group. The spectrochemical properties of the maleic series show that some type of equilibration of valency exists between the neighbouring carboxyl groups. The Anschütz formulation represents the extreme expression of the observed



facts for which possibly the scheme

$$\begin{array}{ccc} & \cdots & \text{::} \\ & \text{H}\cdot\text{C}(\text{OH})\text{=O} & \end{array}$$

(I.)

The following data, amongst others, are recorded. Ethyl fumarate, d_4^{25} 1.0522, n_D^{25} 1.43957; propyl fumarate, d_4^{25} 1.0120, n_D^{25} 1.44278; methyl mesaconate, d_4^{25} 1.1266, n_D^{25} 1.45789; ethyl mesaconate, d_4^{25} 1.0516, 1.45130; α -methyl β -ethyl mesaconate, d_4^{25} 1.0821, n_D^{25} 1.45345; β -methyl α -ethyl mesa-

conate, d_4^{25} 1.0851, n_D^{25} 1.45470; β -methyl ester α -chloride, d_4^{25} 1.2368, n_D^{25} 1.47775, β -ethyl ester α -chloride, d_4^{25} 1.1823, n_D^{25} 1.47521, and α -ethyl ester β -chloride of mesaconic acid, d_4^{25} 1.1777, n_D^{25} 1.47325; methyl dimethylfumarate, m. p. 41° , d_4^{25} 1.0494, n_D^{25} 1.43688; ethyl dimethylfumarate, d_4^{25} 1.0244, n_D^{25} 1.44570; methyl chlorofumarate, b. p. $108^\circ/15$ mm., d_4^{25} 1.3028, 1.44570; ethyl chlorofumarate, b. p. $119^\circ/12$ mm., d_4^{25} 1.1822, n_D^{25} 1.45979; methyl bromofumarate, m. p. 27.5 — 28.5° , b. p. $115^\circ/9$ mm., d_4^{25} 1.5381, n_D^{25} 1.47935; ethyl bromofumarate, b. p. 135 — $136^\circ/12$ mm., d_4^{25} 1.4174, n_D^{25} 1.48194; propyl maleate, d_4^{25} 1.0271, n_D^{25} 1.44329; methyl citraconate, d_4^{25} 1.1097, n_D^{25} 1.44710; ethyl citraconate, d_4^{25} 1.0420, n_D^{25} 1.44269; methyl chloromaleate, b. p. $100^\circ/17$ mm., d_4^{25} 1.2775, n_D^{25} 1.46170; ethyl chloromaleate, b. p. $105^\circ/10$ mm., d_4^{25} 1.5497, n_D^{25} 1.48756; methyl pyrocinchonate, d_4^{25} 1.0997, 1.45552; ethyl pyrocinchonate, d_4^{25} 1.0434, n_D^{25} 1.45262; maleic anhydride, d_4^{25} 1.3001, n_D^{25} 1.45135; citraconic anhydride, d_4^{25} 1.2469, n_D^{25} 1.47070; chloromaleic anhydride, d_4^{25} 1.5455, n_D^{25} 1.50933; bromomaleic anhydride, d_4^{25} 1.9642, n_D^{25} 1.54236; pyrocinchonic anhydride, d_4^{25} 1.1070, n_D^{25} 1.43842. H. WREN.

Configurative relationship of chlorosuccinic acid to chloropropionic and lactic acids. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, 83, 185—190).— $\Delta^{\alpha\alpha}$ -Hexadien- γ -ol, b. p. 133 — 134° , d_4^{25} 0.8596, n_D^{25} 1.4464, obtained from acraldehyde and allyl bromide with zinc, was converted into the hydrogen phthalate. From the insoluble brucine salt was obtained a product with $[\alpha]_D^{25} +18.0$, which yielded a carbinol, b. p. 133 — 134° , $[\alpha]_D^{25} +12.9^\circ$ in ether; this, with phosphorus trichloride, gave 1- γ -chloro- $\Delta^{\alpha\alpha}$ -hexadiene, $[\alpha]_D^{25} -13.2^\circ$ in ether, which, with ozone, yielded *d*-chlorosuccinic acid, m. p. 168 — 171° , $[\alpha]_D^{25} +18.9^\circ$ in water. 1- $\Delta^{\alpha\alpha}$ -Hexadien- γ -ol, $[\alpha]_D^{25} -6.2^\circ$ in ether, was reduced with hydrogen and palladium to *d*-hexan- γ -ol. *l*-Chlorosuccinic acid is therefore configuratively related to *d*-malic, *l*-lactic, and *l*- α -chloropropionic acids.

C. R. HARRINGTON.

Walden inversion. II. H. N. K. RORDAM (J.C.S., 1929, 1282—1290; cf. A., 1928, 1215).—Two types of Walden inversion are distinguished, viz., (a) reactions in which the fission of the active molecule is spontaneous or caused by some molecule which is neither identical with nor contains the entering radical, including replacement of halogen by hydroxyl ions or of hydroxyl by halogen ions, and (b) reactions in which the course of inversion is the result of propinquity of radicals in an additive phase, and to which the author's theory does not apply. Further data on a reaction of type (a), between sodium *l*-bromosuccinate and potassium xanthate in presence of sodium nitrate, have now been obtained. The simplified expression $n - kc_x F$ deduced from the theory (*loc. cit.*) indicates a linear relation between n , the fraction of the product with the original configuration, and c_x , the mean concentration of the entering radical. Such a relation is actually found within limits where the simplified equation may be expected to apply, and the derived values of F are in fair agreement with values from other sources. R. K. CALLOW.

Action of piperidine on ethyl $\alpha\alpha'$ -dibromoadipate. J. VON BRAUN (Ber., 1929, 62, [B], 1694).—If piperidine is allowed to act on the ester without initial cooling so that a sudden, very marked heating of the reactants occurs, ethyl β -piperidinopropionate is formed in amount not exceeding 40% (cf. Fuson and Bradley, this vol., 425); if reaction occurs slowly, the amount of piperidinopropionic ester is very small in comparison with that of ethyl dipiperidinoadipate (cf. von Braun, A., 1926, 1128).

H. WREN.

Production of kojic acid from pentoses by *Aspergillus oryzae*. F. CHALLENGER, L. KLEIN, and T. K. WALKER (J.C.S., 1929, 1498—1505).—The investigation of the growth of *Aspergillus oryzae* diastase on arabinose and xylose showed that kojic acid is formed and not pyromeconic acid as would be expected from analogy with the behaviour of dextrose. The formation of kojic acid involves the breakdown of the pentose molecule and the synthesis of a six-carbon compound. This is similar to the formation of citric acid by the growth of *A. niger* on arabinose and xylose. The mould grows well on glycuronic acid, but neither comenic acid nor kojic acid nor any hydroxypyrrone derivative could be detected. Both pyromeconic and comenic acids were found to be toxic to *A. oryzae*.

A. A. GOLDBERG.

Polygalacturonic acid. W. WŁOSTOWSKA (Rocz. Chem., 1929, 9, 371—389).—Polygalacturonic acid, $[\alpha]_D^{20} + 279.5^\circ$, prepared from beet pectic acid, contains 94.2% of hexuronide groups and 93.2% of galacturonide groups. The product examined contains 7% of araban; 100 g. of polygalacturonic acid neutralise 543.1 c.c. of *N*-sodium hydroxide. Its empirical formula is $[C_6H_8O_8]_n$, and it appears to be a condensation product of galacturonic acid. It has no action on Fehling's solution. On the addition of sodium hydroxide to polygalacturonic acid solution a transient green coloration appears at p_H 9; sodium polygalacturonate is precipitated when the concentration of alkali attains 10%. Vitreous or gelatinous precipitates are formed on addition of alkaline-earth salts to solutions of the sodium salt. The p_H of 0.1% solutions of polygalacturonic acid is 3.1. The electro-titration curve of this acid shows that it behaves as a monobasic acid, i.e., the carboxyl groups are all dissociated to the same extent, the dissociation constant being 0.8×10^{-4} . The viscosity of polygalacturonic acid solution is highest at p_H 1.5, least at p_H 2.1, and rises to a second maximum at p_H 6.3. The surface tension of 0.1% solutions varies from 80 to 90, according to the age of the solution and its previous treatment. The particles of the acid are charged negatively, the isoelectric point being at p_H 2.2. More than 80% of the particles have a magnitude less than $5\mu\mu$. Sodium polygalacturonate may be obtained in 3—5% solutions; at higher concentrations, the solutions gelatinise. Cryoscopic measurements of the sodium salt solution show that the mol. wt. of polygalacturonic acid is not less than 594.

R. TRUSZKOWSKI.

Preparation of allomucic acid and derivatives. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1929, 51, 2167—2170).—Mucic acid is epimerised

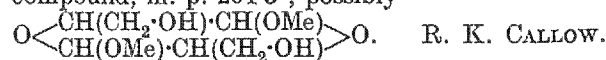
by prolonged heating with 10% aqueous pyridine (cf. A., 1927, 340; Fischer, A., 1891, 1193) to allomucic acid (33% yield). This is converted through the syrupy monolactone into the *monoamide*, m. p. 175—176°, and esterified by a large excess of alcohol and sulphuric acid to *ethyl allomucate*, m. p. 138°, converted by ammonia into *allomucodiamide*, m. p. 209° (decomp.), darkening from 185°. Although allomucic acid resembles mannosecaric acid (A., 1928, 741) in having two *cis*-hydroxyl groups adjacent to each carboxyl, it does not (a) reduce Fehling's solution, (b) form a dilactone, or (c) give coloured products when boiled with 10% sodium hydroxide.

H. E. F. NOTTON.

Precipitant for aldehydes. H. LEEFMANN and C. C. PINES (Bull. Wagner Free Inst., 1929, 4, 15—16).—Photomicrographs are given of the distinctive precipitates produced by dimethyldihydroresorcinol with formaldehyde and acetaldehyde (cf. Stepp, A., 1922, i, 300; Vorländer, this vol., 949).

R. K. CALLOW.

Methylation of *dl*-glyceraldehyde. H. G. REEVES (J.C.S., 1929, 1327—1329).—An attempt has been made to methylate *dl*-glyceraldehyde in the hope of determining its structure by conversion into a methylglycerol. The action of methyl sulphate and alkali, or of methyl alcohol at 100° yielded non-reducing oils. Treatment with methyl-alcoholic hydrogen chloride at the ordinary temperature gave a 5% yield of a non-reducing bimolecular *monomethyl* compound, m. p. 204.5°, possibly



Isomeric trithioacetaldehydes. E. V. BELL, G. M. BENNETT, and F. G. MANN (J.C.S., 1929, 1462—1465).—The supposed γ -isomeride of the α - and β -trithioacetaldehydes (Mann and Pope, *ibid.*, 1923, 123, 1178) is shown by m. p. evidence to be identical with the eutectic mixture of these two isomerides (60% α and 40% β). The explanation of its formation and of other peculiarities of the case is discussed. A crystallographic examination of the two isomerides is recorded.

A. A. GOLDBERG.

Cyclic acetals. II. R. DWORZAK and K. HERRMANN (Monatsh., 1929, 52, 83—106; cf. this vol., 421).—Cyclic acetals have been prepared from glycols and various aliphatic ketones or aromatic aldehydes by (a) condensation of equimolecular quantities of the reactants at 0° with hydrogen chloride (Franke and Gigerl, A., 1928, 759), (b) using excess of ketone containing 1% of hydrogen chloride in presence of anhydrous sodium sulphate at the ordinary temperature (Fischer and Pfahler, A., 1920, i, 807), (c) as b but in presence of 0.25—0.5% of sulphuric acid (Boeseke, A., 1923, i, 86), and (d) as a but with 40% sulphuric acid as condensing agent (Hibbert and Timm, A., 1924, i, 710). The yields are essentially the same by any of the methods. Acetone does not condense with trimethylene glycol, but with ethylene glycol and glycerol there are obtained 7.6—8.0 and 74—77% of the corresponding isopropylidene derivatives, respectively. Methyl ethyl ketone does not condense with trimethylene glycol; with ethylene glycol and glycerol the cyclic *methylethylmethylethylene* derivatives, b. p. 113.5°

and 150°, respectively, are obtained in yields of 11—15 and 60%. The following cyclic acetals are obtained using the requisite aldehyde or ketone: *dipropyl-methylene* derivatives of ethylene glycol (28—30%), b. p. 172.5—174°/760 mm., trimethylene glycol (0—2.7%), b. p. 187°, and glycerol (10%), b. p. 160°; *benzylidene* derivatives of ethylene glycol (28%), b. p. 223—225° (cf. Hibbert and Timm, *loc. cit.*), trimethylene glycol (32—38.5%), m. p. 41—41.5°, and glycerol (50—52%); *m-toluylidene* derivatives of trimethylene glycol (23—24.7%), b. p. 140°/12 mm. (ethylene glycol does not react), and glycerol (5—6%), b. p. 158°/11 mm., and *anisylidene* derivatives of trimethylene glycol (30%), b. p. 164—165°/11 mm. (ethylene glycol does not react), and glycerol (13%), b. p. 163.5—165°/10 mm., m. p. 20°. The above glycerol ethers are formulated as $\alpha\beta$ - or $\alpha\gamma$ -derivatives. In general, ketones give rise to five-membered ring acetals, whilst aldehydes favour the formation of six-ring compounds; this is explained by the Ingold-Thorpe strain theory. The presence of methyl groups in the aldehyde or ketone results in a distinct lowering of the amount of acetal produced. The factors governing the formation of acetals are "tendency of formation" and the overcoming of ring tension; these are approximately equal.

H. BURTON.

Rate of ring-closure of the $\alpha\delta$ -diketones. I. A. TREFILIEV and RAZUMOV (Ukraine Chem. J., 1929, 4, 19—35, and J. Russ. Phys. Chem. Soc., 1929, 61, 699—712).—The mechanism of the formation of the monoethyl ester of carbopyrotritaric acid by the action of hydrogen halides on ethyl diacetylsuccinate was investigated, with a view to elucidate whether a rapid ring closure of the $\alpha\delta$ -diketone, with the formation of a furan derivative, occurs first, followed by a partial hydrolysis of the di-ester to the mono-ester. Since the bromo-derivatives of ethyl carbopyrotritarate are insoluble in hydrobromic acid, the reaction mixture of ethyl diacetylsuccinate and hydrobromic acid was treated with bromine, to remove the furan derivative as soon as it was formed. A canary-yellow solid was obtained, which was very unstable, hydrolysing in air with loss of bromine, first with the formation of a ruby-red solid and then with separation of ethyl carbopyrotritarate, b. p. 275—278°. The yellow and red solids were found by analysis to be the *hexa*- and *tetra*-bromo-derivatives of the ethyl ester. Treatment of ethyl acetylsuccinate under the same conditions with iodine in concentrated hydriodic acid yielded a green *tetra*- and brown *di-iodide*. All these halogen derivatives were very unstable, and decomposed completely into the halogen and original ester in moist air, so that they were considered to be oxonium compounds of the furan ring. Attempts to prepare similar products from ethyl metronate proved unsuccessful, whilst with furan itself a complex mixture of condensation products was obtained, which could not be analysed. M. ZVEGINTZOV.

Rotatory power and structure in the sugar group. XIX. Preparation of aldonic acids. C. S. HUDSON and H. S. ISBELL (J. Amer. Chem. Soc., 1929, 51, 2225—2229, and Bur. Stand. J. Res., 1929,

3, 57—62).—Aldoses are oxidised almost quantitatively by bromine water in presence of calcium or barium benzoate to the corresponding aldonic acids. The removal by the benzoate of the hydrogen bromide formed accelerates the reaction and prevents the hydrolysis of compound sugars, such as lactose and maltose (cf. Fischer and Meyer, A., 1889, 485, 1132). The preparation of calcium gluconate, of the double cadmium xylonate and bromide, +8.8°, and of calcium lactobionate, and the hydrolysis of the last to galactose and gluconic acid, are described in detail.

H. E. F. NOTTON.

Decomposition of sugars by alkalis. F. FISCHLER (Z. angew. Chem., 1929, 42, 682—684).—Dilute solutions of most sugars, admixed with 50% potassium hydroxide solution, give definite rings of iodoform crystals when a dilute solution of iodine in potassium iodide is poured carefully on the surface and the whole cooled; with *laevulose*, very little iodoform only is obtained, even with concentrated solutions. Sucrose gives a positive result, although on distillation no methylglyoxal is obtained. The behaviour of dihydroxyacetone and methylglyoxal towards Ost's solution in presence of sulphites is compared with that of sucrose, to show that the latter is in fact decomposed by alkalis with formation of trioses.

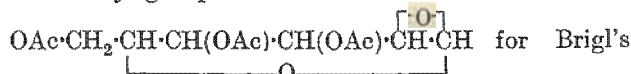
S. I. LEVY.

Acetate of free aldehydic form of dextrose. M. L. WOLFROM (J. Amer. Chem. Soc., 1929, 51, 2188—2193).—Careful treatment of the penta-acetate, m. p. 45—47°, of glucose ethyl mercaptal (cf. Schneider and Sepp, A., 1918, i, 252), prepared by an improved method, with cadmium carbonate and mercuric chloride in aqueous acetone gives *glucose $\beta\gamma\delta\epsilon\zeta$ -penta-acetate*, m. p. 116—118°, $[\alpha]_D^{25} +2.7^\circ$ in *s*-tetrachloroethane (optical and crystallographic properties; *semicarbazone*, m. p. 150—151°), which gives a positive Schiff's reaction. H. E. F. NOTTON.

Reactivity of dextrose in presence of hydrochloric acid. II. E. A. MOELWYN-HUGHES (Trans. Faraday Soc., 1929, 25, 435—442).—Polarimetric evidence of the formation of diglucose shows that dextrose and glucoside-glucose kept in *N*-hydrochloric acid solutions at the same temperature reach the same equilibrium, which is dependent on the total dextrose content of the solution and not on its origin. Nascent dextrose, *i.e.*, immediately after its liberation from a glucoside, is considered to be straight-chained and does not accelerate diglucose formation. The rate of transformation of reactive dextrose in *N*-hydrochloric acid solutions containing salicin indicates that the change is unimolecular. The author (A., 1928, 374) has shown that the nascent dextrose molecule is energised, and the inference now made is that it is not sufficiently activated for condensation purposes. In view of the large value of the energy of activation of the condensation process and the fact that normal tetramethylglucose condenses to octamethyldiglucose, it is considered that diglucose formation is brought about by thermal activation, and not by the interposition of a structurally active form of dextrose having a definite chemical existence. H. T. S. BRITTON.

Carbohydrates. VIII. $\alpha\beta$ -Derivatives of dextrose. P. BRIGL and R. SCHINLE (Ber., 1929,

62, [B], 1716—1723).— α -Chloro- $\gamma\delta\zeta$ -triacylglucose is converted by silver carbonate in aqueous acetone into $\gamma\delta\zeta$ -triacylglucose, m. p. 110—112°, $[\alpha]_D^{25} +139.1^\circ$ in ethyl acetate, transformed by silver oxide and methyl iodide into $\gamma\delta\zeta$ -triacyl- $\alpha\beta$ -dimethylglucose, m. p. 74—75°, $[\alpha]_D^{25} +6.28^\circ$ in chloroform, $[\alpha]_D^{25} 88^\circ$ in alcohol. The last-named compound is hydrolysed by methyl-alcoholic ammonia to $\alpha\beta$ -dimethylglucose, m. p. 95—97°, $[\alpha]_D^{25} -23.90^\circ$ in alcohol, and by 0.2*N*-sulphuric acid into β -methylglucose, characterised as the phenylhydrazone, m. p. 178°, $[\alpha]_D^{25} -12.31^\circ$ in pyridine. Treatment of the methylglucose with an excess of phenylhydrazine affords solely glucosazone, thus establishing the β -position of the methyl group and the constitution

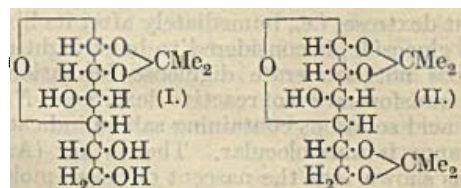


glucose anhydride triacetate (cf. Hickinbottom, this vol., 174). The structure of Pictet's glucosan therefore becomes uncertain.

Tribenzoylglucose is converted by thionyl chloride in carbon tetrachloride into the cyclic *sulphite*, $\text{C}_{27}\text{H}_{22}\text{O}_{10}\text{S}$, m. p. 139—140°, $[\alpha]_D^{25} -136.7^\circ$ in chloroform. H. WREN.

Derivatives of isopropylideneglucose. Rearrangement reactions in carbohydrate group. I. K. JOSEPHSON (Annalen, 1929, 472, 217—229).—Mainly an account of work already reviewed (this vol., 912). The following is new. γ -Acetyl- $\alpha\beta$ -isopropylideneglucose reacts with triphenylmethyl chloride in presence of pyridine at the ordinary temperature, yielding γ -acetyl- ζ -triphenylmethyl- $\alpha\beta$ -isopropylideneglucose, sinters at 55°, $[\alpha]_{\text{H}_2\text{O}}^{25} -16^\circ$ in chloroform, acetylated by acetic anhydride in pyridine solution to $\gamma\epsilon$ -diacetyl- ζ -triphenylmethyl- $\alpha\beta$ -isopropylideneglucose, sinters at 64°, $[\alpha]_{\text{H}_2\text{O}}^{25}$ yellow about $+5^\circ$ in chloroform. H. BURTON.

Constitution of glucose-monoacetone and -diacetone, and of the derived $\gamma\epsilon\zeta$ -trimethylglucose and γ -monomethylglucose. C. G. ANDERSON, W. CHARLTON, and W. N. HAWORTH (J.C.S., 1929, 1329—1337).—Direct evidence has now been obtained in favour of the butylene-oxide ring structure for diisopropylideneglucoses (I and II) and against the



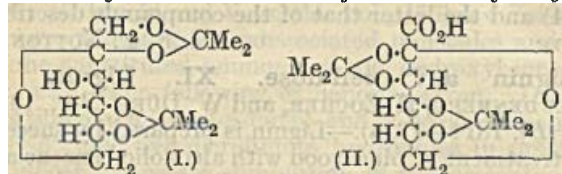
propylene- or ethylene-oxide structures proposed by Irvine and others (J.C.S., 1913, 103, 573; 1915, 107, 1710; 1922, 121, 2146). Consideration of the space formulæ of the glucofuranose and glucopyranose forms of dextrose shows that the former alone provides favourable *cis*-positions for condensation with acetone groups. Moreover, the former, with substitution in the $\alpha\beta$ - or $\alpha\zeta$ -positions, respectively, is alone consistent with recent work and with the isolation of γ -methylglucose from diisopropylideneglucose and of $\gamma\epsilon\zeta$ -trimethylglucose of glucofuranose structure from

isopropylideneglucose by methylation, followed by hydrolysis. The preparation and determination of the constitution of these products are now described.

γ -Methylglucose, m. p. 160—161°, prepared from diisopropylideneglucose, is converted into the methylglucoside, and this is methylated with methyl iodide and silver oxide. The oil obtained is hydrolysed with 5% hydrochloric acid and yields $\beta\gamma\delta\zeta$ -tetramethylglucose. γ -Methylglucosephenylosazone has m. p. 178—179° (Irvine and Scott, J.C.S., 1913, 103, 575, give 164—165°) and is shown to be identical with γ -methylfructosephenylosazone (cf. following abstract) both by mixed m. p. determinations and by the identity of the rate of mutarotation and the initial and final values of $[\alpha]_D^{25}$ ($-109^\circ \rightarrow -9^\circ$) in alcohol. *iso*Propylideneglucose is best methylated by treatment with methyl sulphate and alkali. Conversion of the product into the trimethyl methylglucoside and hydrolysis by dilute hydrochloric acid yields $\gamma\epsilon\zeta$ -trimethylglucose (phenylosazone, m. p. 70—72°), which is converted into tetramethyl-methylglucoside by methyl sulphate and alkali. Hydrolysis yields $\beta\gamma\epsilon\zeta$ -tetramethylglucose and a *by-product*, m. p. 97—98°. Oxidation of the former with bromine water yields a product identical with $\beta\gamma\epsilon\zeta$ -tetramethyl- γ -gluconolactone from other sources and yielding an identical phenylhydrazide. R. K. CALLOW.

Constitution of α - and β -fructosediacetones. Alleged oxidative degradation of the derived monomethyl- and tetramethyl-fructoses. C. G. ANDERSON, W. CHARLTON, W. N. HAWORTH, and V. S. NICHOLSON (J.C.S., 1929, 1337—1346).—3-Methylfructose, obtained from diisopropylidenefructose by methylation and removal of the acetone residues, has, when adequately purified, m. p. 128—130°, $[\alpha]_D^{25} -84.1^\circ \rightarrow -53.5^\circ$, and yields a phenylosazone, m. p. 177—179° (cf. Irvine and Hynd, J.C.S., 1909, 95, 1220; Irvine and Scott, *ibid.*, 1913, 103, 573). The reported oxidation to $\alpha\beta$ -dihydroxy- γ -methoxybutyric acid (Irvine and Hynd, *loc. cit.*) is erroneous. The sugar is recovered unchanged after treatment with bromine water, and itself has the properties, such as formation of a compound with barium hydroxide, attributed to the acid. The "diethyl dimethoxyhydroxyglutarate" obtained by Irvine and Patterson (J.C.S., 1922, 121, 2146) from α -diisopropylidenefructose by alternate hydrolysis and methylation and subsequent oxidation of the tetramethylfructose with nitric acid has previously (Haworth, Hirst, and Learner, A., 1927, 649) been assigned the constitution of ethyl trimethylfructuronate, and this is now confirmed by its oxidation with permanganate to yield d-2 : 3 : 4-trimethyl- δ -arabonolactone, m. p. 44°, $[\alpha]_D^{25} -177.3^\circ \rightarrow -10.2^\circ$, which has properties similar to those of the *l*-lactone (Drew, Goodyear, and Haworth, A., 1927, 750). The conclusions that the tetramethyl fructose is 1 : 3 : 4 : 5-tetramethylfructopyranose and that the monomethylfructose is γ -methylfructose (cf. preceding abstract) are thus confirmed, and the formula I for α -diisopropylidenefructose is supported. Another example of this attack by oxidising agents on the $\text{CH}_2\cdot\text{OMe}$ group in position 1 is provided by the oxidation of β -diisopropylidenefructose to a diisopropylidene-

fructuronic acid (II) (Ohle, A., 1926, 150). This is converted by simultaneous methylation and hydrolysis



with methyl sulphate and sodium hydroxide, and final methylation with Purdie's reagents, into methyl tetramethylfructuronate (Haworth, Hirst, and Learner, *loc. cit.*) which yields the amide, m. p. 118—119°. Hydrolysis of the fructuronic acid with dilute sulphuric acid and subsequent methylation gives an isomeric product which yields an amide, m. p. 100—101°, identical with that from the oxidation of tetramethyl- γ -fructose (Haworth, Hirst, and Nicholson, A., 1927, 859). The formula II for Ohle's acid is thus confirmed, and it is demonstrated that its ring structure is displaced in contact with sulphuric acid to give a five-membered ring acid.

R. K. CALLOW.

Volumetric determination of invert sugar by reduction in solutions containing sucrose. IV. Influence of calcium salts on the reduction. A. A. GABREELS and A. L. VAN SCHERPENBERG (Chem. Weekblad, 1929, 26, 394—398).—At low sucrose concentrations calcium salts exert considerable inhibitory influence on the reduction of copper in alkaline solution. The determination of invert-sugar in alkaline tartrate solutions containing sucrose may be effected normally if the tartrate concentration is about 69.2 g. per litre. The phenomenon of acid adsorption on the walls of glass apparatus has been shown to be due principally to a permutit type of reaction.

H. F. GILLBE.

Solidification of sucrose. Catalysis by water. A. TIAN (Compt. rend., 1929, 188, 1675—1677).—Sucrose, fused rapidly at about 100° to avoid decomposition, remains in the colourless, vitreous, super-cooled state indefinitely in the absence of moisture, or for 5 months in an atmosphere having a water-vapour pressure less than 5 mm. of mercury at 16°. With vapour pressures of 5—11 mm. it absorbs water until a maximum is reached, when the sugar crystallises, after which water is slowly lost. Micro-calorimetric measurements show the catalytic effect of water as a function of time, viz., heat absorption for 1 hr. due to dissociation, followed by liberation of heat of crystallisation which rises to a maximum and slowly falls to zero after a few days.

J. GRANT.

Crystalline turanose. C. S. HUDSON and E. PACSU (Science, 1929, 69, 278).—Crystals of turanose formed from a syrup of hydrolysed melezitose after keeping for several years have been successfully used to seed fresh syrups and obtain rapid crystallisation. The crystals are moderately soluble in methyl alcohol, from which they can be easily recrystallised in prisms, m. p. 157°, $[\alpha]_D^{20} + 43.5$ to 75.6° (const.) in 3—20 min. in water.

L. S. THEOBALD.

Triphenylmethyl ethers of di- and tri-saccharides. Constitution of maltose, sucrose, and raffinose. K. JOSEPHSON (Annalen, 1929, 472,

230—240).—Treatment of di- and tri-saccharides with triphenylmethyl chloride in pyridine solution at the ordinary temperature gives ethers in which primary alcoholic hydrogen atoms are replaced by the triphenylmethyl group. Thus, maltose yields a *di(triphenylmethyl)* derivative [6-*triphenylmethylglucosido*-

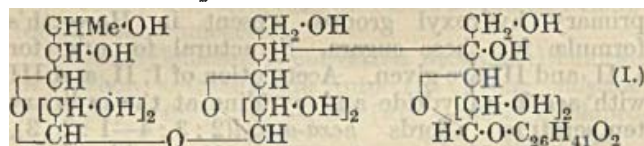
(1 : 5)-6-*triphenylmethylglucose*(1 : 5)] (for nomenclature see Bergmann, A., 1926, 152) (I), m. p. 137—139° (corr.), $[\alpha]_D^{25} + 78^\circ$ in alcohol; sucrose furnishes a *tri(triphenylmethyl)* derivative [6-*triphenylmethylglucosido*(1 : 5)-1 : 6-*di(triphenylmethyl)fructoside*(2 : 5)] (II), m. p. 127—129° (corr.), $[\alpha]_D^{25} + 44.3^\circ$ in alcohol, and raffinose gives a *tri(triphenylmethyl)* derivative

[6-*triphenylmethylgalactosido*(1 : 5)-*glucosido*(1 : 5)-1 : 6-*di(triphenylmethyl)fructoside*(2 : 5)] (III), m. p. about 130°, $[\alpha]_D^{25} + 79^\circ$ in alcohol. The number of triphenylmethyl groups introduced agrees with the number of primary hydroxyl groups present in Haworth's formulae for these sugars. Structural formulae for I, II, and III are given. Acetylation of I, II, and III with acetic anhydride and pyridine at the ordinary temperature affords *hexa-acetyl*(2 : 3 : 4—1 : 2 : 3), m. p. 116—119° (corr.), $[\alpha]_D^{25} + 91^\circ$ in chloroform, *penta-acetyl*(2 : 3 : 4—3 : 4), sinters at 125—126°, $[\alpha]_D^{25} + 57^\circ$ in chloroform, and *octa-acetyl* derivatives (2 : 3 : 4—2 : 3 : 4—3 : 4), m. p. 123—125° after sintering at 118—120°, $[\alpha]_D^{20} + 66^\circ$ in chloroform, respectively. The sets of numbers in parentheses indicate the positions of the acetyl groups in the sugar units. Treatment of these acetyl derivatives with hydrogen bromide in acetic acid solution effects almost quantitative fission into triphenylmethyl bromide.

H. BURTON.

Saponins and related compounds. A. W. VAN DER HAAR (Rec. trav. chim., 1929, 48, 726—742).—Exhaustive extraction of the powdered root of Honduras sarsaparilla with light petroleum yields sitosterol, subsequent extraction with ether yielding the sitosterol glucoside, m. p. 290—295°, isolated by Power and Salway (J.C.S., 1914, 105, 201), which is not identical with the parillin obtained by Schulz (Arb. pharmakol. Inst. Dorpat, 1896, xiv., since it gives a positive Liebermann cholesterol test and yields sitosterol on hydrolysis. Renewed extraction of the residue with 99% methyl alcohol and precipitation of the extract with ether yields a mixture of sarsaponin and parillin, which is thus separated from the calcium and magnesium derivatives of the polysaccharides. This mixture dissolved in water and precipitated with 30% alcohol yields pure crystalline parillin (+4H₂O and anhydrous), m. p. 238—240°, $[\alpha]_D^{20} - 63.7^\circ$, although a large quantity of this product remains in pseudo-solution with the soluble amorphous sarsaponin. The latter cannot be separated from the residual parillin and thus cannot be isolated as a chemical individual. Hydrolysis of this mixture (containing 9.6% of water) with 5% sulphuric acid followed by aqueous-alcoholic sulphuric and hydrochloric acid hydrolysis yields dextrose (30.85%), rhamnose (8.8%), and sapogenin (41%). The final residue insoluble in light petroleum, ether, and methyl alcohol, when heated with 45% alcohol and dialysed

yields the calcium and magnesium compounds of polysaccharides which are precipitated with alcohol and ether. On hydrolysis these yield 7.4% of insoluble matter but no sapogenin, their composition being: water 8.2%, ash 1%, pentoses 5.1%, methylpentoses 2.95%, aldehydic acids 3%, and fermentable hexoses 42.5%. Hydrolysis of pure parillin also yields parigenin, m. p. 203°, $[\alpha]_D - 69.6^\circ$ (48.56%) (acetyl derivative, m. p. 130°), dextrose (41.84%), and rhamnose (15.8%), these results corresponding almost exactly with the decomposition $C_{44}H_{72}O_{17} + 3H_2O = C_{26}H_{42}O_3 + 2C_6H_{12}O_6 + C_6H_{12}O_5$. The composition thus assigned to parillin and parigenin agrees with the analysis and mol. wt. determinations of these compounds. By distillation with zinc dust in a current of hydrogen parigenin yields a sesquiterpene (probably a mixture) and not a monoterpene as stated by Kaufmann and Fuchs (A., 1924, i, 196). On the basis of these results coupled with the observation that whilst



parigenin contains only one hydroxyl group, parillin possesses no reducing properties, the structure I is assigned to the latter compound. By the interaction of tetra-acetylglucosidyl bromide and parigenin in the presence of quinoline in boiling toluene, and deacetylation of the product, a small yield of an artificial saponin, m. p. 225—230°, is obtained.

J. W. BAKER.

Diffusion of high-molecular substances into very thin layers on a water surface and its use as a method of determining the form and size of the molecule and micelle. I. Application to polysaccharides. J. R. KATZ and P. J. P. SAMWELL (Annalen, 1929, 472, 241—267).—A more detailed account of work previously reviewed (A., 1928, 937).

H. BURTON.

Molecular structure of inulin; new anhydrofructose. J. C. IRVINE and J. W. STEVENSON (J. Amer. Chem. Soc., 1929, 51, 2197—2203).—Inulin triacetate is converted by nitric acid in chloroform into a mixture of fructose triacetate dinitrate with 20% of anhydrofructose triacetate ($+0.5C_2H_4O_2$), m. p. 123°, $[\alpha]_D +1.5^\circ$ in chloroform (cf. this vol., 683), which is separated by means of boiling alcohol. This is obtained in approximately the same yield by hydrolysing inulin triacetate with acetic acid containing 0.03% of sulphuric acid, and from the insoluble residue left when inulin is subjected to graded acetolysis (Barnett, A., 1921, i, 164). It is converted by dimethylamine in methyl alcohol into an anhydrofructose, m. p. 143—145°, $[\alpha]_D +30.17^\circ$ in water, which does not reduce Fehling's solution and is quantitatively hydrolysed to levulose by dilute acids. Methylation with methyl sulphate and alkali, and finally with silver oxide and methyl iodide, gives a dimeride of trimethylanhydrofructose, b. p. 166°/0.1 mm., $n_D 1.4730$, $[\alpha]_D +23.8^\circ$, which is partly depolymerised by hydrogen chloride in methyl alcohol to the monomeric form, $n_D 1.4610$. These results indicate that inulin contains anhydrofructose residues of two different types in the ratio of

4:1, the former being the source of the γ -fructose derivatives previously isolated (cf. J.C.S., 1920, 117, 1474) and the latter that of the compounds described above.

H. E. F. NOTTON.

Lignin and cellulose. XI. Lignin. K. FREUDENBERG, H. ZOCHER, and W. DURR (Ber., 1929, 62, [B], 1814—1823).—Lignin is prepared by successive treatment of pine wood with alcoholic benzene and cold 5% sodium hydroxide. Pentosans and hemicelluloses are removed by boiling 1% sulphuric acid and the residue is treated with Schweizer's solution. The product has a pale yellowish-brown colour and contains 16% of methoxyl and 1.1—1.4% of formaldehyde. After treatment with syrupy phosphoric acid and hydrochloric acid ($d 1.19$) the methoxyl content has increased to 17%. Treatment with alkali increases the resistance of lignin to attack by calcium hydrogen sulphite and the effect is enhanced by the following boiling with dilute acid. There does not appear to be any chemical difference between lignin from spring and autumn wood, although the morphological distinction is very marked. Histological investigation suggests that the lignin permeates the membrane like a network which remains intact after removal of nearly three fourths of the tissue substance. The surface is very markedly developed. Methylene-blue is adsorbed in large amount and water and alcohols are tenaciously retained. The behaviour towards benzyl alcohol and aniline indicates the saturation of a network which resists extension. Lignin appears to be wetted by all types of liquid and to retain its form when dried.

Treatment of lignin, obtained from wood by alcoholic benzene followed by hydrochloric and phosphoric acids, with *p*-toluenesulphonyl chloride followed by hydrazine indicates the presence of 5—6 secondary alcoholic hydroxyl groups and 1 phenolic hydroxyl group. If a treatment with alkali hydroxide is interspersed, the action of *p*-toluenesulphonyl chloride remains unchanged, but sulphinic acid is not produced by hydrazine, so that phenolic hydroxyl groups do not appear present. Possible structures of the lignin molecule are discussed in detail.

H. WREN.

Genuine lignin. III. Action of diazomethane on pine wood. W. FUCHS and O. HORN (Ber., 1929, 62, [B], 1691—1693).—Treatment of pine wood with diazomethane ultimately yields a product containing about 16% of methoxyl, from which a lignin with 19.7% of methoxyl can be isolated. Since the original lignin, isolated by treatment with hydrochloric acid, contains 15.4% of methoxyl, it follows that one hydroxyl group susceptible to diazomethane is present in a molecule of mol. wt. about 800. The methylated lignin exhibits double refraction. Willstätter lignin resembles lignin in wood, since it gives a methylated product with 20.8% of methoxyl. Cotton-wool and filter-paper are methylated with greater difficulty than the cellulose in wood by ethereal diazomethane; under similar conditions, dextrose is unaffected.

H. WREN.

Decomposition of quaternary ammonium and sulphonium hydroxides. IV. J. VON BRAUN, W. TEUFFERT, and K. WEISSBACH (Annalen, 1929, 472, 121—142).—The decomposition of quaternary

ammonium hydroxides into an alcohol and tertiary amine (reaction *B* of Hanhart and Ingold, A., 1927, 650; cf. Ingold and Vass, this vol., 175) is considered to be a function of undissociated molecules and not of the substituted ammonium and hydroxyl ions (cf. *loc. cit.*). The following evidence is given. Decomposition of trimethyl-*n*-butyl- and -*n*-decyl-ammonium and *N*-dimethylpiperidinium hydroxides in presence of glycerol causes a diminution in the percentage of olefine formed (Hanhart and Ingold's reaction *A*), with a corresponding increase in the amount of tertiary amine produced by reaction *B* (the possible intermediate formation of glycerolates is noted). In presence of potassium hydroxide an increase in the amount of olefine is obtained. Decomposition of trimethyl-*n*-decylammonium hydroxide in aqueous solution (2–16%) at 200° also results in a preponderance of dimethyldecylamine; the ratio of this and decylene produced is essentially the same at all the concentrations studied.

With sulphonium hydroxides the percentage of olefine produced is diminished in presence of glycerol and increased in presence of potassium hydroxide. Decomposition of dimethyl- β -phenylethylsulphonium hydroxide results essentially in the production of styrene (cf. A., 1924, i, 632). The yields of olefines previously reported (A., 1911, i, 610; 1912, i, 165) are too low. The error is due to contamination of the quaternary ammonium hydroxides by carbonates (produced during evaporation of the hydroxide solutions in the atmosphere). The following compounds were prepared during the investigation: *docosyl bromide*, b. p. 225°/0.6 mm., m. p. 44°; *trimethyldocosylammonium bromide*, decomp. about 240°; *dimethyldocosylamine*, b. p. about 190°/0.6 mm. (*hydrochloride*, m. p. 180°; *picrate*, m. p. 84°); Δ -*docosylene*, b. p. 174–178°/0.6 mm., m. p. 41°. *n*-Hexyl bromide and ammonium dithiocarbamate react in warm alcoholic solution yielding *hexyl dithiocarbamate*, m. p. 50°, converted by potassium hydroxide solution into *hexyl mercaptan*. Treatment of this with methyl iodide and methyl-alcoholic sodium methoxide gives *methyl n-hexyl sulphide*, b. p. 61–62°/15 mm. (*methiodide*, m. p. 68°). *n*-Decyl dithiocarbamate, m. p. 76°; *n*-decyl mercaptan, b. p. 114–115°/13 mm.; *methyl n-decyl sulphide*, b. p. 125°/13 mm. (*methiodide*), and *methyl β -phenylethyl sulphide*, b. p. 111°/12 mm. [*methiodide*, m. p. 130° (decomp.)], are obtained similarly. A small amount of decyl alcohol is produced together with decylene and dimethyldecylamine during the decomposition of trimethyldecylammonium hydroxide.

Treatment of an aqueous-alcoholic solution of sodium hydrogen selenide with decyl bromide in an atmosphere of hydrogen affords *decyl hydrogen selenide*, b. p. 128–129°/13 mm., methylated in the usual way to *methyl decyl selenide*, b. p. 137–138°/14 mm. When this is treated with methyl iodide *trimethylselenonium iodide*, decomp. 173°, results.

H. BURTON.

Poly-acid amines and diamines containing sulphur. Z. FÖLDI (Ber., 1929, 62, [B], 1700–1709).—Pentamethylenediamine is converted by phenyl ϵ -bromoamyl ether in boiling alcohol into NN'-*di- ϵ -phenoxyamylpentamethylenediamine hydro-*

bromide, m. p. 275–276° (corresponding *picrate*, m. p. 162–163°), converted by hydrobromic acid (*d* 1.72) into NN'-*di- ϵ -bromoamylpentamethylenediamine hydrobromide*, m. p. 260–263° (decomp.) (corresponding *picrate*, m. p. 162–163°). The di-bromo-compound is transformed by alcoholic ammonia into *pentamethylenedipiperidine* [CH₂]₅(NC₅H₁₀)₂, m. p. 237° (*picrate*, m. p. 193–195°), whereas its *dibenzene-sulphonyl* derivative is converted by successive treatment with alcoholic ammonia and fuming hydrobromic acid into NN'-*di- ϵ -aminoamylpentamethylenediamine hydrobromide* (corresponding *picrate*, m. p. 195–196°). ϵ -Chloroamylbenzamide and pentamethylenediamine in boiling alcohol give NN'-*di- ϵ -benzamidoamylpentamethylenediamine hydrochloride*, m. p. 252–254° (corresponding *picrate*, m. p. about 110°), which is hydrolysed to NN'-*di- ϵ -aminoamylpentamethylenediamine hydrochloride*, not molten below 300°. The *monoguanidine* derivative of the free base, its *picrate*, m. p. 170°, non-crystalline *hydrochloride*, and *tetra-nitrate*, m. p. 150°, are described.

ϵ -Chloroamylbenzamide is converted by alcoholic ammonia into *di- ϵ -benzamidoamylamine*, m. p. 68–72°, rising to 93–96° after preservation over sodium hydroxide; the non-crystalline *picrate* and *tribenzoyl* derivative and the *hydrochloride*, C₂₃H₃₃O₂N₃·HCl, m. p. 200°, are described. Hydrolysis of the dibenzoyl derivative affords *di- ϵ -aminoamylamine*, b. p. 129°/0.1 mm. [*hydrochloride*, m. p. about 285° (decomp.); *picrate*, m. p. 200°; *picrate*, m. p. 156–158°, and *nitrate*, m. p. 162°, of the diguanidine derivative]. ϵ -Iodoamylbenzamide and alcoholic ammonia afford *monobenzoylcadaverine hydriodide*, m. p. 175°. Di- ϵ -amyltrimethylenediamine and thiocarbamide *S*-ethyl ether hydrobromide afford the monoguanidine derivative of the diamine, isolated as the *dihydrobromide*, not molten below 300°, and *sulphate*, m. p. about 255°.

ϵ -Chloroamylbenzamide and sodium sulphide in boiling alcohol afford *di- ϵ -benzamidoamyl sulphide*, m. p. 96°, whereas with sodium disulphide the product is *di- ϵ -benzamidoamyl disulphide*, m. p. 132–133°. *Di- ϵ -aminoamyl sulphide*, b. p. 141–143°/1 mm., its *hydrochloride*, m. p. about 240–245° (decomp.), *picrate*, m. p. 179°, *diguanidine* derivative (*hydrobromide*, m. p. 123–125°; *picrate*, m. p. 148–150°) are described. *Di- ϵ -aminoamyl disulphide*, b. p. 135–140°/1 mm. (decomp.), yields a *diguanidine* derivative (*dipicrate*, m. p. about 162–165°). H. WREN.

Decomposition of α -amino-alcohols and their salts on heating. K. A. KRASUSKI (Ukraine Chem. J., 1929, 4, 61–74; cf. this vol., 1078).—The behaviour of α -amino-alcohols on heating and the formation of halogen derivatives from them, were investigated. Dimethylaminoethylcarbinol when heated for 3 hrs. in a sealed tube at 100° with excess of fuming hydrobromic acid charred, with the separation of ammonium bromide. A similar result was obtained with aminotrimethylcarbinol, although traces of isobutaldehyde were also detected. The hydrochloride of dimethylaminoethylcarbinol when heated gave methyl isopropyl ketone, b. p. 94–96°, together with condensation products. With the hydrochloride of dimethylethylaminoethylcarbinol the products were the same, together with traces of tri-

methylethylene oxide, which may be regarded as the first stage of the reaction. Aminotrimethylcarbinol hydrochloride gave isobutaldehyde and its polymeride, m. p. 60—61°.

The same products were obtained if the phosphate of the aminocarbonol was employed. The hydrochlorides of the primary hydroxy-amine of hexylene oxide and dimethylaminoisopropylcarbinol yielded the corresponding ketones, a ketone, b. p. 121—128°, and pinacolin. The hydrochlorides of these two aminocarbonols decomposed so readily that on diazotisation and hydrolysis only small quantities of the glycols were obtained, the main products being the ketones. Only those aminocarbonols decomposed easily of which the corresponding glycols readily formed aldehydes and ketones, since aminodimethylcarbinol hydrochloride on heating gave only traces of the aldehyde.

The decomposition of the aminocarbonols was found to take place, under certain conditions, in alkaline solution, and to be favoured by the introduction of alkyl groups into the amino-group. The formation of the α -oxide was an intermediate stage. The mechanism of the decomposition of choline and its derivatives, and the reaction between piperazine and trimethylethylene oxide, are discussed.

M. ZVEGINTZOV.

Action of ammonia on isopropylethylene oxide. K. A. KRASUSKI and F. F. KRIVONOS (Ukraine Chem. J., 1929, 4, 79—84).—*iso*Propylethylene oxide was obtained by treating *isopropylethylene* with hypochlorous acid or perbenzoic acid, the yields in either case not exceeding 30%. With excess of ammonia the oxide yielded α -amino- γ -methylbutan- β -ol, b. p. 174°/754 mm., whilst with smaller quantities of ammonia the corresponding secondary amine, $[\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2]\text{NH}_2$, b. p. 265—268°, was obtained. The rate of the reaction is in accordance with the authors' rule, that the rate of the action of ammonia on the α -oxides decreases with increase of mol. wt., and is greater for oxides containing a primary carbon atom than for those containing a secondary one, since ammonia reacts with *isopropylethylene* oxide more slowly than with *isobutylene* oxide, but faster than with trimethylethylene oxide.

M. ZVEGINTZOV.

Action of ethylamine on isobutylene oxide and isobutylene chlorohydrin. K. A. KRASUSKI and V. D. KUCENOS (Ukraine Chem. J., 1929, 4, 75—77).—Equimolecular amounts of ethylamine and *isobutylene* oxide in aqueous solution when heated in a sealed tube for 8 hrs. at 100° furnished almost pure ethylaminotrimethylcarbinol, b. p. 156°, which yielded with dry gaseous hydrogen chloride a hydrochloride, m. p. 153°. The aminocarbonol can likewise be obtained by treating *isobutylene* chlorohydrin with ethylamine under the same conditions. With ammonia instead of ethylamine, the primary, secondary, and tertiary aminocarbonols resulted, the proportion depending on the concentration of ammonia. With diethylamine, the corresponding diethylaminotrimethylcarbinol was obtained. M. ZVEGINTZOV.

Reaction between nitrous acid and certain amino-acids at 45°. C. L. A. SCHMIDT (J. Biol.

Chem., 1929, 82, 587—594).—Prolonged action of nitrous acid at 45° yielded more nitrogen than corresponded with the free amino-groups in arginine, cysteine, cystine, glycine, tryptophan, and glycyglycine; β -(α -oxindole)propionic acid yielded the whole of its nitrogen, whilst the corresponding tetrahydro-compound failed to react; other amino-acids tested reacted normally. The excess liberation of nitrogen in the anomalous cases is apparently due to secondary oxidative reactions. C. R. HARRINGTON.

Preparation of the glyceryl esters of the aliphatic amino-acids. WEIZMANN and L. HASKELBERG (Compt. rend., 1929, 189, 104—108; cf. A., 1926, 716).—*Glycine* glyceryl ester, m. p. 160—170°, and *dl-alanine* glyceryl ester, m. p. 219°, were obtained by heating the sodium salts of the respective acids with glycerol α -monochlorohydrin. They are hygroscopic compounds, almost insoluble in the usual organic solvents except methyl alcohol. Similarly, by the use of $\alpha\beta$ -distearyl α -iodohydrin, m. p. 52·5°, and $\alpha\beta$ -dipalmityl α -iodohydrin, m. p. 43·6°, prepared by Fischer's method (A., 1920, i, 807), the following were obtained: α -glycyl- $\alpha'\beta$ -dipalmitylglyceride, m. p. 215°; α -glycyl- $\alpha'\beta$ -distearylglyceride, m. p. 170°; α -*dl-alanyl*- $\alpha'\beta$ -dipalmitylglyceride, m. p. 216°; α -*dl-alanyl*- $\alpha'\beta$ -distearylglyceride, m. p. 233°; α -*dl-leucyl*- $\alpha'\beta$ -dipalmitylglyceride, m. p. 219°, and α -*dl-leucyl*- $\alpha'\beta$ -distearylglyceride, m. p. 150°. These compounds are soluble in hot water (cloudy solution) and in hot methyl and ethyl alcohols, but insoluble in most of the usual solvents. B. W. ANDERSON.

Use of aniline in preparing amino-acids. H. C. BENEDICT (J. Amer. Chem. Soc., 1929, 51, 2277).—Glycine, alanine, α -aminoisobutyric acid, and α -amino-*n*-valeric acid are conveniently isolated by adding aniline to alcoholic solutions of their hydrochlorides (cf. Cox, A., 1928, 993). H. E. F. NOTTON.

Influence of glycine on f.-p. depression. K. OGURA, T. SHITO, and S. YAMANO (Hokkaido J. Med., 1928, 6, 421—424).—F.-p. determinations indicate combination between potassium chloride and boric acid or glycine in aqueous solution.

CHEMICAL ABSTRACTS.

[Preparation of] *dl-alanine*. E. C. KENDALL and B. F. MCKENZIE (Organic Syntheses, 1929, 9, 4—7).

Specific rotatory power of *d*-arginine. A. HUNTER (J. Biol. Chem., 1929, 82, 731—736).—*d*-Arginine has $[\alpha]_D^{20} +21\cdot94^\circ$ in presence of 1 mol. and $[\alpha]_D^{20} +26\cdot54^\circ$ in presence of 8 mols. of hydrochloric acid. Treatment of arginine in the Van Slyke apparatus with nitrous acid liberates one fourth of the total nitrogen in 5 min. C. R. HARRINGTON.

Synthesis of optically active, substituted asparagines. I. O. LUTZ (Ber., 1929, 62, [B], 1879—1884).—*l*-Bromosuccinmonoamide dissolved in water is converted by a methyl-alcoholic solution of *o*-toluidine at the atmospheric temperature into *d-o-toluidinosuccinmonoamide*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 164—166°, $[\alpha]_D^{20} -70\cdot7^\circ$ in *N*-hydrochloric acid. The following substituted *succinmonoamides* have been prepared: *d-p-toluidino*-, m. p. 100—101°, $[\alpha]_D^{20}$

—55.8° in *N*-hydrochloric acid; *d*-*o*-anisidino-, m. p. 153—154°, $[\alpha]_D^{25}$ —72.2° in 0.5*N*-hydrochloric acid; *d*-*m*-phenetidino-, $[\alpha]_D^{25}$ —71.3° in *N*-hydrochloric acid; *d*-*p*-phenetidino-, m. p. 139—140°, $[\alpha]_D^{25}$ —43.6° in 0.2*N*-hydrochloric acid; *d*-xytidino-(1:2:4-), m. p. 145—146°, $[\alpha]_D^{25}$ —67.8° in 0.2*N*-hydrochloric acid; *d*-*p*-xytidino-(1:2:5-), m. p. (indef.) 138—139°, $[\alpha]_D^{25}$ —48.2° in 3*N*-hydrochloric acid. H. WREN.

[Preparation of] cyanoacetamide. B. B. CORSON, R. W. SCOTT, and C. E. VOSE (Organic Syntheses, 1929, 9, 36—37).

[Preparation of] *n*-butyl carbamate. T. L. DAVIS and S. C. LANE (Organic Syntheses, 1929, 9, 24—26).

Ureides of brominated valeric acids. S. WEIL, J. LANGIERT, and A. KASSUR (Rocz. Chem., 1929, 9, 464—470).—The following substances have been prepared: methylisopropylbromoacetyl bromide, b. p. 130°/15 mm., ethylisopropylbromoacetyl bromide, b. p. 145°/20 mm., menthyl methyl- and ethyl-isopropylbromoacetates, b. p. 173—175°/20 mm., and 161°/11 mm., respectively, bornyl methyl- and ethyl-isopropylbromoacetates, b. p. 170°/11 mm., and 178°/10 mm., respectively, and methyl- and ethyl-isopropylbromoacetylcarbamides, m. p. 177—179° and 197°, respectively. The narcotic action of these ureides is no greater than that of α -bromoisovalerylcarbamide.

R. TRUSZKOWSKI.

Methylcrotononitriles. F. DE LAET (Bull. Soc. chim. Belg., 1929, 38, 163—167).— β -Methylcrotononitrile, prepared by dehydration of the cyanohydrin of isobutaldehyde, has d_4^{20} 0.83136, n_D^{20} 1.43720. This nitrile was also prepared in a less pure state by dehydration of γ -hydroxyisovaleronitrile. By the action of sulphuric acid on the nitrile the corresponding amide, m. p. 107—108°, was obtained. Dehydration of the cyanohydrin of methyl isopropyl ketone yielded $\alpha\beta$ -dimethylcrotononitrile, d_4^{20} 0.84321, n_D^{20} 1.44554, from which the corresponding amide, m. p. 130.5°, was prepared.

B. W. ANDERSON.

Tertiary phosphines containing higher alkyl radicals. W. C. DAVIES, P. L. PEARSE, and W. J. JONES (J.C.S., 1929, 1262—1268).—Tertiary phosphines have been prepared by the interaction of Grignard reagents with phosphorus trichloride (cf. Davies and Jones, this vol., 303) and with aryl-dichlorophosphines. The method is restricted by the yield of Grignard reagent and by side reactions in the case of magnesium *sec.*- and *tert.*-alkyl halides. Tri-*iso*alkylphosphines are more readily converted into the oxides in air than the *n*-compounds, whilst aryl derivatives are unaffected. The following are described: *Tri-n-propylphosphine*, b. p. 103.5°/50 mm., 187.5°/760 mm., d_4^{25} 0.807 (carbon disulphide compound, m. p. 108°; mercurichloride, m. p. 137°); *methyltri-n-propylphosphonium iodide*, m. p. 212.5°; *tetra-n-propylphosphonium bromide*, decomp. 200°; *phenyltri-n-propylphosphine*, b. p. 159°/50 mm., d_4^{25} 0.925 (mercurichloride, m. p. 192.5°); *phenylmethyltri-n-propylphosphonium iodide*, m. p. 137°; *phenyltri-n-propylphosphonium bromide*, m. p. 131.5°; *p-tolyltri-n-propylphosphine*, b. p. 174°/50 mm., d_4^{25} 0.921 (mercurichloride, m. p. 129.5°); *p-tolylmethyltri-n-propylphosphonium iodide*, m. p. 81.5°; *p-tolyltri-n-propyl*

phosphonium bromide, m. p. 125.5°; *triisobutylphosphine*, b. p. 126°/50 mm. (carbon disulphide compound; mercurichloride, m. p. 191.5°; methyltriisobutylphosphonium iodide, m. p. 287°); *phenyltriisobutylphosphine*, b. p. 168°/50 mm., d_4^{25} 0.910 (mercurichloride, m. p. 158.5°); *phenylmethyltriisobutylphosphonium iodide*, m. p. 166.5°; *p-tolyltriisobutylphosphine*, b. p. 182.5—184.5°/50 mm., d_4^{25} 0.915 (mercurichloride; methiodide); *tri-n-amylyphosphine*, b. p. 185.5°/50 mm., d_4^{25} 0.820 (carbon disulphide compound, m. p. 55°); *phenyltri-n-amylyphosphine*, b. p. 210°/50 mm., d_4^{25} 0.902 (mercurichloride, m. p. 108°; methiodide, m. p. 90.5°); *p-tolyltri-n-amylyphosphine*, b. p. 220°/50 mm., d_4^{25} 0.898 (mercurichloride, m. p. 112°; methiodide); *tri-(di- β -methylbutyl)phosphine*, b. p. 113—117°/10 mm.; *phenyltri-(di- β -methylbutyl)phosphine*, b. p. 198°/50 mm., d_4^{25} 0.906 (mercurichloride, m. p. 120°; methiodide, m. p. 150°); *p-tolyltri-(di- β -methylbutyl)phosphine*, b. p. 210—211°/50 mm., d_4^{25} 0.902 (mercurichloride, m. p. 99°; methiodide, m. p. 131°); *tri-(γ -methylbutyl)phosphine*, b. p. 131°/11 mm. (carbon disulphide compound, m. p. 79.5°; methiodide); *phenyltri-(γ -methylbutyl)phosphine*, b. p. 198.5°/50 mm., d_4^{25} 0.900 (mercurichloride, m. p. 152°; methiodide, m. p. 181.5°); *p-tolyltriisooamylyphosphine*, b. p. 210°/50 mm., d_4^{25} 0.894 (mercurichloride, m. p. 107°; methiodide, m. p. 150°); *phenyltri-(δ -methylamyl)phosphine*, b. p. 219°/50 mm. (methiodide, m. p. 146°; ethiodide, m. p. 115.5°); *p-tolyltri-(δ -methylamyl)phosphine*, b. p. 234—235°/50 mm., d_4^{25} 0.888 (mercurichloride, m. p. 110.5°; methiodide). Where attempts were made to use magnesium isopropyl and *sec.*-butyl bromides no tertiary phosphine could be obtained. R. K. CALLOW.

Conductivity of magnesium ethyl iodide in ethereal solution. N. V. KONDYREV and A. K. SUST (Ber., 1929, 62, [B], 1856—1861).—The proportion of magnesium iodide formed during the preparation of magnesium ethyl iodide increases with diminution of the amount of ether. The equivalent conductivity of magnesium ethyl iodide in ether has been determined at 0°, 5°, 10°, 15°, and 20°. The maximal conductivity is observed at different temperatures for different concentrations; every concentration of magnesium ethyl iodide in ether corresponds with a definite degree of association of the complex. Magnesium iodide is not a component of the organometallic complex; its presence increases the conductivity additively. H. WREN.

True mixed organomagnesium carbonates. D. IVANOV (Compt. rend., 1929, 189, 51—53).—The following true mixed organomagnesium carbonates, $RO\cdot CO\cdot OMgBr$ (as distinct from mixed magnesium carboxylates, $R\cdot CO\cdot OMgBr$), have been prepared from the appropriate mixed organomagnesium alcoholate shaken with carbon dioxide in a closed flask: *ethyl*, *propyl*, *isopropyl*, *butyl*, *isobutyl*, *isoamyl*, and *cyclohexyl bromomagnesium carbonates*, also *butyl* and *benzyl chloromagnesium carbonates*. These mixed carbonates are sparingly soluble in ether, but soluble in alcohols, pyridine, etc.; when treated with water they give the corresponding alcohol and a basic of magnesium carbonate, whilst with acid they form the alcohol with evolution of carbon dioxide.

B. W. ANDERSON.

Lead tetramethyl and the application of magnesium alkyl chlorides in the preparation of organometallic compounds. E. KRAUSE (Ber., 1929, 62, [B], 1877—1878).—Apart from the question of economy, magnesium alkyl iodides are unsuitable for the preparation of organometallic compounds on account of the pronounced side reactions, the higher b. p. of the alkyl iodide residues, and the specific affinity of iodine for the metallic atom. There is no general objection to the use of bromides; with the chlorides the yields are particularly good. Lack of activity towards magnesium is overcome by the use of finely-divided metal. Lead tetramethyl is readily prepared by use of magnesium methyl chloride (the initial lead trimethyl decomposing during distillation of the ether into lead and lead tetramethyl) or from lead trimethyl bromide. During the sealing of lead tetramethyl in glass tubes, violent explosions may occur.

H. WREN.

Photochemical and oxidative degradation of carbonyls. H. REHLEN, A. GRUHL, and G. VON HESSLING (Annalen, 1929, 472, 268—287).—There is practically no reaction between ethyl mercaptan and iron penta- or nona-carbonyl in the dark at the ordinary temperature, but with an excess of the pentacarbonyl at 60° slow formation of carbon monoxide, hydrogen, and bisironmercaptotricarbonyl (I), $[\text{Fe}_2(\text{SEt})_2(\text{C}_3\text{O}_3)_2]$, m. p. 75.5° (cf. A., 1928, 1114), occurs. Irradiation of the mixture with light from a mercury vapour lamp causes the reaction to proceed 30—50 times as fast. A mixture of the pentacarbonyl (1 vol.) and mercaptan (5 vols.) reacts at 38° according to the scheme: $2\text{Fe}(\text{CO})_5 + 2\text{EtSH} = (\text{I}) + 4\text{CO} + \text{H}_2$; a secondary reaction also occurs, probably the slow decomposition of I to iron mercaptide. With a mixture of equal vols. of the reactants at 3—5° the ratio hydrogen : carbon monoxide evolved is 1 : 9.2. This is due to the reaction $2\text{Fe}(\text{CO})_5 + 2\text{EtSH} = (\text{I}) + 3\text{CO} + \text{H} \cdot \text{CHO}$; the formaldehyde liberated is polymerised during irradiation. In both the above cases the reactions taking place are: (a) $2\text{Fe}(\text{CO})_5 \rightarrow \text{Fe}_2(\text{CO})_9 + \text{CO}$; (b) $\text{Fe}_2(\text{CO})_9 + 2\text{EtSH} \rightarrow (\text{I}) + \text{H}_2\text{C}_3\text{O}_3$; (c) $n\text{H}_2\text{C}_3\text{O}_3 \rightarrow 3n\text{CO} + n\text{H}_2$ at the higher temperature and $\rightarrow 2n\text{CO} + n(\text{H}_2\text{CO})_n$ at the lower temperature. When a mixture of iron pentacarbonyl (1 vol.) and acetylacetone (5 mols.) is irradiated at about 130° until evolution of gas ceases, the products formed are hydrogen, carbon monoxide, ferric acetylacetone, m. p. 180°, and a substance (probably an impure peroxide of ferrous acetylacetone); 20—25% of the carbonyl is unchanged. Nickel carbonyl and acetyl chloride react at 50—55° thus: $\text{Ni}(\text{CO})_4 + 2\text{AcCl} = 4\text{CO} + \text{NiCl}_2 + \text{Ac} \cdot \text{Ac}$. The additive compound, $\text{NiCl}_2 \cdot \text{C}_4\text{H}_6\text{O}_2$, is isolated; decomposition of this with water gives diacetyl. Irradiation has no influence on the reaction. In presence of oxygen about 25% of the carbon monoxide is oxidised to carbon dioxide, and acetic acid and anhydride are also produced.

H. BURTON.

Spatial models of aromatic compounds and the interpretation of isomerism. S. HAECKEL (J. pr. Chem., 1929, [ii], 122, 182—200).—With the usual model of the carbon atom consisting of a ball with four stiff wires representing valencies, a model of

benzene is constructed in which the valencies form the edges of a thin hexagonal prism with carbon atoms at alternate corners; this resembles Sachse's model. The sides represent six similar parallelograms of forces. This model accounts for various properties of benzene, its hydro-derivatives, and of benzoquinone. In polycyclic compounds the analogous models, by consideration of the parallelograms of force involved, enable the positions of reactivity to be deduced in a manner resembling that of Thiele's theory. The configurations are in agreement with the results of X-ray analysis. An explanation is afforded of the existence of stereoisomeric forms of 2 : 3-diphenylindone and of 9 : 10-dihydroanthracene derivatives (Schlenk, A., 1928, 1031).

R. K. CALLOW.

Atom models of aromatic compounds. H. MARK (J. pr. Chem., 1929, [ii], 122, 349).—An acknowledgment to Haackel (preceding abstract) in connexion with the work of Bergmann and Mark (this vol., 689), with whose views the latter authors are in agreement.

J. W. BAKER.

Action of cyclohexene and its derivatives on organic compounds in the presence of aluminium chloride. M. D. BODROUX (Ann. Chim., 1929, [x], 11, 511—582).—Interaction of cyclohexene, b. p. 83—84°, d^{20}_4 0.809, n^{20}_D 1.445, with benzene and aluminium chloride gave chiefly phenylcyclohexane, b. p. 240°/743 mm., d^{20}_4 0.947, n^{20}_D 1.528, and a small quantity of 1 : 2-diphenylcyclohexane, m. p. 169—170°; naphthalene furnished two cyclohexylnaphthalenes, a liquid, b. p. 341—347°/747 mm., d^{20}_4 1.021, n^{20}_D 1.597, and a solid, m. p. 31° (picrate, m. p. 100—101°), which was the 2-compound, since dehydrogenation with sulphur gave 2-phenylnaphthalene, m. p. 101—102°, together with a dicyclohexylnaphthalene, m. p. 151—152°; tetrahydronaphthalene yielded a mixture of cyclohexyltetrahydronaphthalenes, b. p. 329—335°/768 mm., d^{20}_4 0.9855, n^{20}_D 1.5498, containing some of the 2-compound, since a poor yield of 2-phenylnaphthalene was obtained by dehydrogenation with sulphur at 230—250°. The following condensations were carried out in the presence of carbon disulphide and aluminium chloride: cyclohexene and diphenyl gave a mixture of two cyclohexyldiphenyls, a solid, m. p. 75—76°, and a liquid, b. p. 238—240°/30 mm., d^{20}_4 1.028, n^{20}_D 1.598, together with a little dicyclohexyldiphenyl, m. p. 205—206°; cyclohexene and diphenylmethane yielded diphenylcyclohexylmethane, b. p. 252—257°/35 mm., d^{20}_4 1.005, n^{20}_D 1.571, and *p*-benzyl-diphenyl, m. p. 85°; cyclohexene and dibenzyl furnished two cyclohexyldibenzyls, a solid, m. p. 68—69°, and a liquid, b. p. 240—244°/25 mm., d^{20}_4 0.994, n^{20}_D 1.564.

The interaction between bromine and the following hydroaromatic hydrocarbons in the presence of a small quantity of aluminium bromide has been studied: cyclohexylbenzene gave hexabromobenzene, m. p. 315—316°; cyclohexyltoluene and cyclohexylcymene gave pentabromotoluene, m. p. 231—232°; cyclohexylmesitylene yielded tribromomesitylene, m. p. 223—224°; 2-cyclohexylnaphthalene and also its liquid isomeride gave a hexabromonaphthalene, m. p. 250—252°.

cycloHexene condenses with the following phenols

in the presence of aluminium chloride and usually in carbon disulphide solution: phenol gave chlorocyclohexane, *phenyl cyclohexyl ether*, b. p. 247—249°/756 mm., d^{25}_D 0.999, n^{25}_D 1.527, *p*-cyclohexylphenol, m. p. 130—131° (*methyl ether*, b. p. 275.5—276.5°/748 mm., m. p. 57—58°; *ethyl ether*, m. p. 41—42°; *n*-propyl ether, m. p. 36°; *n*-butyl ether, m. p. 29°), and *o*-cyclohexylphenol, m. p. 56—57° (*methyl ether*, b. p. 267—268°/749 mm., d^{25}_D 1.007, n^{25}_D 1.5365; *ethyl ether*, b. p. 276—278°/750 mm., d^{25}_D 0.976, n^{25}_D 1.5223; *n*-propyl ether, b. p. 292—294.5°/758 mm., d^{25}_D 0.966, n^{25}_D 1.5198; *n*-butyl ether, b. p. 305—307°/756 mm., d^{25}_D 0.955, n^{25}_D 1.5137); anisole yielded cyclohexylanisole (mixture of 2- and 4-compounds, since demethylation with hydrobromic acid yielded 2- and 4-cyclohexylphenols); carvacrol gave *carvacryl cyclohexyl ether*, b. p. 305—310°, d^{25}_D 0.966, n^{25}_D 1.5215, and a cyclohexylcarvacrol, b. p. 315—325° (mixture of two isomerides).

1-Methyl- Δ^4 -cyclohexene, b. p. 104—105°/762 mm., d^{17}_D 0.804, n^{25}_D 1.442 (prepared by dehydration of 1-methyl-4-cyclohexanol with orthophosphoric acid), condenses in the presence of aluminium chloride with benzene to form dimethyldicyclohexylbenzene, b. p. 230—235°, d^{20}_D 0.962, n^{25}_D 1.533, and a methylcyclohexylbenzene, b. p. 247—251°/759 mm., d^{20}_D 0.918, n^{25}_D 1.512 (treatment of the latter with bromine and aluminium bromide afforded penta- and hexa-bromobenzene); *p*-xylene yielded methylcyclohexyl-*p*-xylene, b. p. 275—285°, d^{24}_D 0.927, n^{25}_D 1.522, whilst diphenylmethane furnished methylcyclohexyldiphenylmethane, b. p. 238—248°, d^{25}_D 1.01, n^{25}_D 1.574 (slightly impure). In the presence of aluminium chloride menthene, b. p. 165—167°/763 mm., d^{20}_D 0.807, n^{25}_D 1.451 (prepared in 92% yield from menthol and orthophosphoric acid), condenses with benzene with the formation of menthylbenzene, b. p. 194—210°, d^{24}_D 0.9145, n^{25}_D 1.5068 (mixture of isomerides), whilst Δ^1 phenylcyclohexene condenses similarly with benzene to give a product, b. p. 267—300°, the exact nature of which was not ascertained.

A. I. VOGEL.

[Preparation of] iodobenzene. F. B. DAINS and R. Q. BREWSTER (Organic Syntheses, 1929, 9, 46—48).

I. Nitro- and halogenonitro-benzenesulphonic acids. II. Preparation and solubility in water of some salts of nitro- and halogenonitro-benzenesulphonic acids. III. Nitro- and halogenonitro-benzenesulphonic acids. J. N. ELGERSMA (Rec. trav. chim., 1929, 48, 752—764, 765—769, 770—777).—I. The following have been prepared by Blanksma's method (A., 1901, i, 460) by oxidation of the corresponding disulphides and their properties investigated: *o*- and *p*-nitro-, 2:4-dinitro-, 4- and 5-chloro-2-nitro-, 6-chloro-3-nitro-, and 4-bromo-2-nitro-benzenesulphonic acids, all of which are found to contain varying amounts of water of crystallisation. In agreement with Hodgson and Wilson (A., 1925, i, 532), 4:4-dinitrodiphenyl disulphide can be separated by boiling alcohol into two forms, m. p. 170° (most soluble) and 181°, respectively, a small quantity of a substance, m. p. 139°, also being obtained. When equivalent quantities of 4-chloro-2-nitrobenzenesulphonic acid and aniline are heated at 185° the aniline salt, m. p. 207°, is obtained, whilst reduction

of its sodium salt with zinc dust in boiling aqueous solution yields the corresponding 2-amino-acid, converted by bromine water into 3-chloro-2:4:6-tribromoaniline with elimination of the sulphonic group. Fischer's proof (A., 1892, 182) of the structure of 6-chloro-3-nitrobenzenesulphonic acid is invalid, since the same *p*-phenylenediaminesulphonic acid would be obtained by treatment with alcoholic ammonia and reduction if the sulphonic group were in position 2 instead of 1. Rigid proof of the correctness of the structure assigned is, however, furnished by the following reactions. By boiling with aqueous sodium hydroxide the corresponding nitrophenolsulphonic acid, which is converted by bromine water into 2:6-dibromo-*p*-nitrophenol, is obtained, whilst by heating in a sealed tube with alcoholic ammonia the original sulphonic acid yields 3-nitro-6-aminobenzenesulphonic acid, similarly converted into 2:6-dibromo-*p*-nitroaniline, or, by elimination of the amino-group by diazotisation, into pure *m*-nitrobenzenesulphonic acid.

II. The solubilities of the alkali salts of various nitro- and halogenonitro-benzenesulphonic acids in water at 25° have been determined. The solubility of the potassium salts of *o*-, *m*-, and *p*-nitro-, 2:4-dinitro-, 4-chloro-2-nitro-, 5-chloro-2-nitro-, 6-chloro-3-nitro-, and the 4-bromo-2-nitro-acids are, respectively, 9.63, 3.04, 5.95, 4.70, 0.87, 1.59, 2.83, and 1.68 g. of anhydrous salt/100 g. of water; those of the corresponding rubidium salts are, respectively, 16.08, 6.09, 5.80, 3.90, 1.93, 1.07, 1.32, and 1.80, and of the caesium salts 20.74, >37, 5.46, 2.50, 6.98, 1.51, and 6.09 g. of anhydrous salt/100 g. of water, respectively. Although no general rule can be formulated, the introduction of a nitro-group into benzenesulphonic acid decreases the solubility of the salts investigated, a further decrease being caused by the introduction of a halogen atom or a second nitro-group independently of the positions of these groups in the benzene ring. The very sparing solubility of the potassium salt of 4-chloro-2-nitrobenzenesulphonic acid renders this acid a suitable reagent for the detection of potassium even in the presence of other metallic ions except caesium and rubidium, a concentration of 1 in 360 yielding a crystalline precipitate within 4 min. Most of the salts are anhydrous, but a few contain water of crystallisation the amount of which was determined.

III. The equivalent conductivity of the various nitro- and halogenonitro-benzenesulphonic acids and some of their salts has been determined in aqueous solution at various dilutions at 25° by the usual method. The value of Λ is almost constant for the whole series (376—378) and agrees well with the value of Rimbach or Walden for an acid composed of 18 atoms, but is in disagreement with the value of Wightman and Jones (A., 1911, ii, 689) for *m*-nitrobenzenesulphonic acid. All are strong acids and are almost completely ionised at $v=64$.

J. W. BAKER.

[Preparation of] *o*-bromotoluene. L. A. BIGELOW (Organic Syntheses, 1929, 9, 22—23).

Aromatic compounds of fluorine. III. Nitration of fluorotoluenes. G. SCHIEMANN (Ber., 1929, 62, [B], 1794—1805; cf. A., 1927, 654).—*o*-Fluoro-

toluene, b. p. 30°/26 mm., loses hydrogen fluoride with somewhat greater readiness than its isomerides. Diazotisation of *m*-toluidine and treatment of the product with hydrofluoboric acid affords *m*-tolylidiazonium fluoborate, $C_7H_7N_2BF_4$, decomp. 108°, converted when heated into *m*-fluorotoluene, b. p. 114—115°/758 mm., in 87% yield. Nitric acid (d 1.51) is added gradually to *m*-fluorotoluene at -15° to $+20^\circ$ and the mixture is ultimately heated to 55°. Fractional distillation of the product combined with suitable cooling of the individual fractions gives 3-fluoro-4-nitrotoluene, m. p. 53.2° (corr.) [crystallographical data] (identified by conversion into 4-nitro-3-methoxytoluene, m. p. 60—61°), 3-fluoro-2-nitrotoluene, b. p. 92.2—92.6° (corr.)/11 mm., m. p. 17.5—18°, and, mainly, 3-fluoro-6-nitrotoluene, b. p. 97—98°/10 mm., m. p. 27—28° [oriented by transformation into 6-nitro-3-methoxytoluene, m. p. 52° (corr.)]. Reduction of 3-fluoro-6-nitrotoluene with tin and hydrochloric acid affords 5-fluoro-*o*-toluidine, b. p. 92—94°/15 mm., [picrate, m. p. 199° (decomp.) after softening and darkening at 192°; benzoyl derivative, m. p. 166°; *p*-nitrobenzoyl compound, m. p. 168°]. The amine is converted through the diazonium fluoborate, decomp. 114—115°, into 2:5-difluorotoluene, b. p. 117°/775 mm. *o*-Fluorotoluene when treated similarly to the *m*-compound (see above) yields unchanged material, 2-fluoro-5-nitrotoluene, b. p. 99.4—99.6° (corr.)/13 mm., m. p. 41.5° (oriented by conversion into 5-nitro-2-methoxytoluene, m. p. 62—63°, and 5-nitro-2-methoxybenzoic acid, m. p. 150°), and 2-fluoro-6-nitrotoluene, b. p. 97—97.2° (corr.)/11 mm., m. p. -2° . Partial nitration of *p*-fluorotoluene with nitric acid (d 1.51) at -10° to -15° affords 4-fluoro-3-nitrotoluene, b. p. 104.2° (corr.)/9 mm., m. p. $+1^\circ$ to $+2^\circ$, and 2:6-dinitro-*p*-cresol, m. p. 81°.

H. WREN.

Chromic *p*-toluenesulphonates. G. JANTSCH and K. MECKENSTOCK (Monatsh., 1929, 52, 169—184).—Treatment of green chromic chloride with silver *p*-toluenesulphonate followed by concentration of the aqueous solution gave hydrated chromic *p*-toluenesulphonate. Crystallisation below 12° afforded a bluish-violet hydrate containing $16H_2O$; vapour-pressure measurements showed that this hydrate is stable between -0.5° and $+12^\circ$. The hydrate content could not be determined directly, owing to hydrolysis at about 50°; mixtures of hydrates with 8 to $12H_2O$ were obtained by crystallisation at ordinary temperatures. Isothermal decomposition of the bluish-violet salt at 10° and of the greyish-green mixed hydrate at 30°, over sulphuric acid established the existence of a hydrate, $[Cr(OH_2)_6][SO_3 \cdot C_6H_4Me \cdot H_2O]_3$; tensimetric measurements indicated that this hydrate is stable at 61°/10 mm. Further dehydration over sulphuric acid gave a green tetrahydrate, sparingly soluble in water. Attempts to isolate the lower hydrates by crystallisation at 76° were unsuccessful, mixtures being obtained. Transport number experiments for these complexes at temperatures from 0° to 95° are described.

A. I. VOGEL.

[Preparation of] *n*-butyl *p*-toluenesulphonate.

A. T. ROOS, H. GILMAN, and N. J. BEABER (Organic Syntheses, 1929, 9, 28—30).

[Preparation of] ω -nitrostyrene. D. E. WORRALL (Organic Syntheses, 1929, 9, 66—68).

Electrochemical oxidation of *m*-xylene-4-sulphonic acid. M. YOKOYAMA (Helv. Chim. Acta, 1929, 12, 756—785).—Oxidation of the above acid at a lead dioxide anode (*M*-solution, 0.04 amp./cm.² at 75—80°, 10 farad./mol.) gave as principal products: dimethylmaleic anhydride, 6-sulpho-4:5-dihydroxy-*m*-toluic acid (I), and 6-sulpho-*m*-toluic acid. By electrolysis at a lower temperature (40—50°), another product, probably sulphoisophthalic acid, was formed, and possibly fumaric acid. Using a platinum anode (*M*-solution, 0.03 amp./cm.², 50 farad./mol. at 25—35°) there were obtained (traces of) a quinone, m. p. 143—160°, the sulphonic acid I, and *m*-tolualdehyde-6-sulphonic acid (phenylhydrazone). Electrolytic oxidation of *o*-xyloquinone dissolved and suspended in sulphuric acid afforded dimethylmaleic anhydride and maleic acid, whilst that of *m*-6-xylenol-4-sulphonic acid gave the sulphonic acid I accompanied by dimethylmaleic anhydride. These observations accord with the author's interpretation of the mechanism of the electrolytic oxidation of *m*-xylene-4-sulphonic acid.

R. J. W. LE FEVRE.

Aromatic compounds of fluorine. IV.

Fluorine derivatives of diphenyl. G. SCHIEMANN and W. ROSELIUS (Ber., 1929, 62, [B], 1805—1814; cf. this vol., 1051).—2-Aminodiphenyl is converted into the corresponding diazonium fluoborate, decomp. 80.5—81°, and thence into 2-fluorodiphenyl, m. p. 71—72°, d_4^{25} 1.2452. Diphenyl-4-diazonium fluoborate, decomp. 115.5—116°, d_4^{25} 1.430, 4-fluorodiphenyl, m. p. 74—75°, d_4^{25} 1.247, diphenyl-3-diazonium fluoborate, decomp. 90.5—91°, and 3-fluorodiphenyl, m. p. 26—27° (corr.), d_4^{25} 1.2874, are described. Treatment of 4:4'-difluorodiphenyl with nitric acid affords 4:4'-difluoro-3-nitrodiphenyl, m. p. 94.5—95°. 3:4:4'-Trifluorodiphenyl, m. p. 83°, d_4^{25} 1.481, when slowly warmed with nitric acid (d 1.40) to 100—105° gives 3:4:4'-trifluoro-5-nitrodiphenyl, m. p. 103.8° (corr.), in 88.5% yield. 3:4:4'-Trifluoro-5-aminodiphenyl, m. p. 71.5° (corr.), from the nitro-compound, tin, and hydrochloric acid, is transformed through the diazonium fluoborate, decomp. 102—102.5°, into 3:4:4':5-tetrafluorodiphenyl, m. p. 138.5—139° (corr.), d_4^{25} 1.708. 4:4'-Difluorodiphenyl is oxidised by chromic acid in presence of glacial acetic acid and vanadium pentoxide to 4-fluorobenzoic acid. This acid is also obtained when 3:4:4'-trifluoro- or 3:4:4':5-tetrafluoro-diphenyl is treated similarly.

H. WREN.

Existence and stability of free radicals. H. BURTON and C. K. INGOLD (Proc. Leeds Phil. Soc., 1929, 1, 421—431).—Theoretical. The application by Flürscheim (A., 1905, i, 614; cf. Ziegler, A., 1924, i, 308, 850) of his theory of the alternately large and small affinity-content of a consecutive series of linkings, to explain the tendency of dissociation of hexa-arylethanes, is held to be invalid, since it does not explain the dissociation of tetra-arylhydrazines, decaphenyl-*n*-butane, and hexa-*p*-nitrophenylethane. An alternative explanation is advanced, based on the observations that aryl groups are able to activate both anionotropic and prototropic systems (Burton and

Ingold, A., 1928, 634; Burton, *ibid.*, 880; this vol., 554; Ingold and Shoppee, this vol., 556, 927), and hence confer on an attached atom the power of tolerating an electric charge of either sign. The occurrence of three distinct forms of triphenylmethyl, namely, the neutral radical (electron septet), the anion, and the cation, is thus readily explained. The hypothesis predicts or interprets (where known) that (a) the dissociation of hexa-arylethanes is promoted to a greater extent by polynuclear aromatic systems than by phenyl, (b) introduction of substituents to increase the stability of the anion should also increase the stability of the free radical, (c) a similar increase in the stability of the cation should inhibit radical formation. The addition of alkali metals to olefinic hydrocarbons (Schlenk and Bergmann, A., 1928, 1031) is known to proceed only when at least one aryl group is attached to the carbon atom at which the addition of the metal occurs. A free radical is then produced (electron septet on the adjacent carbon atom) and its ultimate behaviour depends on the presence (further addition, cf. triphenylmethyl) or absence (polymerisation) of aryl groups. The production of a similar additive compound by the attachment of a conjugated, unsaturated aliphatic group indicates the possibility of existence of aliphatic free radicals. The stability of the free radicals from tetra-aryldiazines and diaryl peroxides should increase with the stability of the cation, whilst a similar condition for free hydrazyls is obtained by introducing both electron-releasing and -restraining groups.

H. BURTON.

Preparation of free radicals of the triaryl-methyl series. A. E. ARBUSOV and B. A. ARBUSOV (Ber., 1929, 62, [B], 1871—1877).—Diethyl hydrogen phosphite, b. p. 72°/11 mm., prepared from phosphorus trichloride and ethyl alcohol, is converted by sodium in ether into sodium diethyl phosphite, which with triphenylmethyl chloride in benzene and ether affords diethyl triphenylmethylphosphinate, m. p. 119.5—120.5°. Triphenylmethyl bromide and sodium diethyl phosphite, in presence and absence of air, respectively, afford triphenylmethyl peroxide and triphenylmethyl; the fate of the phosphorus residue is obscure. In the presence of anhydrous alcohol the reactants give triphenylmethyl ethyl ether. In air and nitrogen, respectively, diphenyl- α -naphthylmethyl bromide and sodium diethyl phosphite in ether give diphenyl- α -naphthylmethyl peroxide and diphenyl- α -naphthylmethyl, respectively.

H. WREN.

Triphenylmethane derivatives. H. WIELAND and H. KLOSS (Annalen, 1929, 470, 201—223).—When dimagnesium acetylene bromide is treated with triphenylmethyl chloride in ether, an intensely violet product is obtained, decomposed by water to the colourless, stable *hexaphenylbutinene*, $\text{CPh}_3\text{:C:C:CPh}_3$ (I), m. p. 260°. With fuming nitric acid this gives a *hexanitro-derivative*, m. p. above 300°. The formation of the last, and the stability of the hydrocarbon towards oxidising agents, support the formula I. The formula I is also confirmed by the preparation of a tri-*p*-tolyl compound (see below). Dimagnesium phenylacetylene bromide similarly gives rise to stable *hexa- α -xy-tetraphenylpropinene*, CPh:C:CPh_3 (II), m. p.

139°, which gives a *tetranitro-derivative*, m. p. 182° (decomp.), and can be reduced in presence of platinic oxide (although not of palladium-black) to *hexa- α -xy-tetraphenylpropane*, m. p. 126°; using tri-*p*-tolylmethyl chloride as reagent, the product is *hexa- α -phenyl- γ -tri-*p*-tolylpropinene* (III), m. p. 141°, which is reduced catalytically to *hexa- α -cyclohexyl- γ -tri-*p*-tolylpropane*, m. p. 126°. During the preparation of II an intense greenish-blue halochromic effect is observed; no such effect occurs in the preparation of III.

Unsuccessful attempts were made to bring triphenyl-ethyl chloride into reaction with a magnesium derivative. The action of diphenylmethyl chloride, however, on the derivative from acetylene gives *hexa- α -xy-tetraphenyl- Δ^2 -butinene* (cf. Brand, A., 1921, i, 784), a reactive substance catalytically reduced, in presence of palladium-black, to the saturated compound. From phenylacetylene, *hexa- α -xy-triphenyl- Δ^2 -propinene* (IV), m. p. 79°, is formed, catalytically hydrogenated, in presence of palladium-black, to *hexa- α -xy-triphenylpropane*, (V), m. p. 46°, and in presence of platinic oxide to *hexa- α -cyclohexyl- γ -diphenylpropane* (VI), b. p. 160—170°/1 mm. The compound V is also prepared by reducing *hexa- α -xy-triphenylpropyl alcohol* (VII) (cf. Ziegler, A., 1925, i, 131) by phosphorus and hydriodic acid. Attempted oxidation of VII to a bimolecular product, using potassium permanganate in acetone, gave instead *hexa- α -xy-hexaphenyl- Δ^2 -hexadiene* (VIII) (cf. Moureu, A., 1927, 355), which is also formed by reduction of VII, using titanium chloride. The compound VIII is analogous in structure to hexaphenylethane, and it is found that solutions of the compound, colourless below 100°, become orange-red at high temperatures, and that the mass (above 174°) is intensely red; the compound is stable towards oxygen, and a further difference from hexaphenylethane is that coloured solutions which have been cooled revert very slowly to the colourless state at 20°, although more rapidly at 80°. It is considered that the phenylacetylene group has a smaller valency requirement than phenyl.

Treatment of *hexa- α -xy-tetraphenyl- Δ^2 -butinene- α -diol* with phosphorus pentachloride in ethereal solution gave *2-chloro-3-phenyl-1-diphenylmethyleineinden*, m. p. 158°, a red compound, of which the structure was determined by oxidation to benzophenone and *o*-benzoylbenzoic acid, and by reduction. Gentle reduction by hydriodic acid leads to *3-phenyl-1-diphenylmethyleineinden* (cf. Brand, A., 1924, i, 720); more energetic reduction, or catalytic hydrogenation, leads to *1-phenyl-3-diphenylmethyldihydroindene*, m. p. 133° (cf. Salkind, this vol., 56); moderate reduction by hydriodic acid gives *3-phenyl-1-diphenylmethylenedihydroindene*, m. p. 115°, which can be catalytically reduced to the preceding compound.

In addition to the above, the question of hexaphenylacetone is also investigated. The interaction of sodium triphenylmethyl (Schlenk, A., 1916, i, 380) and triphenylacetyl chloride gives a *sodium ketyl* which is decomposed by water to a *ketone*, $\text{C}_{39}\text{H}_{30}\text{O}$ (IX), m. p. 183—184° (without decomp.); since this is hydrolysed to triphenylmethane and triphenylmethane-*p*-carboxylic acid, and reduced by zinc and hydrochloric acid to the *hydrocarbon*,

$\text{CHPh}_2 \cdot \text{C}_6\text{H}_4(p) \cdot \text{CH}_2 \cdot \text{CPh}_3$, m. p. 177° (different from Schlenk's hexaphenylpropane, A., 1913, i, 34), it is considered to have the structure $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4(p) \cdot \text{CO} \cdot \text{CPh}_3$. During the formation of the original ketyl, carbon monoxide was evolved, and a considerable quantity of triphenylmethyl was formed. The hexaphenylacetone of Schlenk and Bergmann (A., 1928, 1040), m. p. $80-81^\circ$, is not obtained.

Sodium triphenylmethyl and diphenylacetyl chloride give pentaphenylacetone. E. W. WIGNALL.

Bromination of α s-diphenyldimethylethylene. K. ZIEGLER and K. BAHR (Ber., 1929, 62, [B], 1695—1697).— α s-Diphenyldimethylethylene is converted by cautious treatment with bromine in carbon disulphide into the very unstable dibromide, m. p. 57° (decomp.), transformed when heated on the water-bath into γ -phenyl- β -methylallyl bromide, m. p. $57-58^\circ$, identical with the product derived from γ -phenyl- β -methylcinnamyl alcohol and hydrogen bromide in glacial acetic acid. The bromination of $\alpha\alpha\beta$ -triphenyl- β -methylethylene therefore follows the course $\text{CPh}_2 \cdot \text{CMePh} \rightarrow \text{CPh}_2 \cdot \text{Br} \cdot \text{CBrPhMe} \rightarrow \text{CPh}_2 \cdot \text{Br} \cdot \text{CPh} \cdot \text{CH}_2 \rightarrow \text{CPh}_2 \cdot \text{CPh} \cdot \text{CH}_2 \cdot \text{Br}$. H. WREN.

Supposed "ring-inclination isomerism" with derivatives of indene. K. ZIEGLER and F. GROSSMANN (Ber., 1929, 62, [B], 1768—1770).—The action of sodium on 1:1:3-triphenylindene is accompanied by wandering of a phenyl group and leads to a derivative of 1:2:3-triphenylindene. The "dihydro-1:1:3-triphenylindene" of Schlenk and Bergmann (A., 1928, 1031) is 1:2:3-triphenylindene, reduced by sodium and amyl alcohol to dihydro-1:2:3-triphenylidene, m. p. 153° . H. WREN.

1-Chloronaphthalene. Chlorination of naphthalene in solution. P. FERRERO and M. FEHLMANN (Helv. Chim. Acta, 1929, 12, 583—603, and J. pr. Chem., 1929, [ii], 122, 340—343; cf. A., 1928, 627; Traubenberg and Wassermann, A., 1928, 1365).—Chlorination of naphthalene dissolved in solvents which are themselves inert to chlorine (e.g., carbon tetrachloride or 1-chloronaphthalene) gives results inferior to those obtained by direct chlorination of molten naphthalene. The reverse is true of benzene and particularly of chlorobenzene. These solvents are protected from chlorination by the naphthalene even in the presence of iodine; the solvents selected must always possess considerable stability to chlorine, otherwise they protect the naphthalene. Iodine, as a catalyst, favours monohalogenation, ferric chloride promotes polyhalogenation.

Under the optimum conditions (2 mols. of naphthalene, 0.5% of iodine, 450 g. of chlorobenzene, temp. $126-128^\circ$, increase in weight 66—68 g.), the yield of 1-chloronaphthalene on the naphthalene taken is 81% and on the naphthalene consumed 92%; 6—7% of polychloronaphthalenes are also produced. R. J. W. LE FEVRE.

peri-Dibenzyl-naphthalene and two other isomeric hydrocarbons. K. DZIEWONSKI and J. MOSZEW (Rocz. Chem., 1929, 9, 361—370).—The main

products of the reaction between benzyl chloride and naphthalene in the presence of aluminium chloride are 1- and 2-benzyl-naphthalenes. In addition, in the presence of excess of naphthalene, α - and β -dibenzyl-naphthalenes, m. p. 146.5° and 88° , are formed (yield 3—5%), whilst in the presence of excess of benzyl chloride γ -dibenzyl-naphthalene, m. p. 132° (yield 1%), is obtained. The α - and γ -isomerides do not yield picrates; that of the β -compound melts at 107° . The α -isomeride yields 1:8-dibenzoylnaphthalene (diphenylhydrazone; m. p. $270-271^\circ$) on oxidation with nitric acid. The following derivatives of 1:8-dibenzyl-naphthalene are prepared: 4-nitro-derivative, m. p. 141° , 1:8-dibenzyl-naphthalenesulphonic acid (aniline salt, m. p. $252-253^\circ$; chloride, m. p. 151° ; amide, m. p. 167°), and 1-benzoyl-8-benzyl-naphthalene, m. p. 113° . R. TRUSZKOWSKI.

Question of isomerism in the case of 9-phenyl-9-benzylfluorene. R. E. SCHMIDT, B. STEIN, and C. BAMBERGER (Ber., 1929, 62, [B], 1890—1891).—Attempts to repeat the preparation of the isomeric 9-phenyl-9-benzylfluorene, m. p. $125-126^\circ$, from sodium 9-phenylfluorene and benzyl chloride according to Schlenk and Bergmann (this vol., 688) gave only the previously described compound, m. p. $136-136.5^\circ$.

H. WREN.

Question of instances of "non-classical" isomerism among derivatives of anthracene. E. HAACK (Ber., 1929, 62, [B], 1771—1783).—According to Schlenk and Bergmann (A., 1928, 1031), successive treatment of 9-hydroxy-9:10-diphenyl-9:10-dihydroanthracene with potassium and an alkyl halide results in the formation of a colourless, "isomeric diphenylantracene," m. p. 214° . This product is readily obtained when the hydroxy-compound is boiled with xylene containing a little potassium or solid potassium hydroxide or by gradual addition of ethyl alcohol to a boiling solution of diphenylantracene in xylene in presence of potassium. When heated with sulphur at 180° it evolves hydrogen sulphide and yields diphenylantracene, m. p. 247° . Reduction of diphenylantracene with sodium and amyl alcohol gives a dihydrodiphenylantracene, m. p. $227-228^\circ$ (corr.), in addition to the previously isolated dihydro-compound, m. p. $198.5-199.5^\circ$ (corr.); either compound depresses the m. p. of the product, m. p. 214° . Schlenk's product is an additive compound of molar proportions of diphenylantracene, m. p. 247° , and dihydrodiphenylantracene, m. p. $227-228^\circ$ (corr.), since (1) it crystallises from arbitrary mixtures of its two components in addition to one component, (2) its spectrochemical behaviour is in harmony with this conception, (3) it is unchanged by crystallisation from ethyl acetate, acetic acid, carbon tetrachloride, toluene, and alcohol or xylene and alcohol, and (4) the f.-p. diagram indicates very clearly the existence of such a compound.

10-Hydroxy-9-phenyl-10-*o*-tolyl-9:10-dihydroanthracene is converted by potassium hydroxide and boiling xylene into 9-phenyl-10-*o*-tolylantracene, m. p. 257° , which, with potassium and ethyl alcohol in presence of xylene, affords unchanged material and a product, m. p. $170-173^\circ$ after crystallisation from amyl alcohol. Further purification of this product

from acetic anhydride and xylene results in the isolation of 9-phenyl-10-o-tolyl-9:10-dihydroanthracene, m. p. 186—187°. Reduction of phenyltolylanthracene with sodium and amyl alcohol gives a somewhat ill-defined product from which the dihydro-product is separated by means of acetic anhydride and xylene but not of amyl alcohol. An additive compound of phenyltolylanthracene and its dihydro-derivative does not appear to exist. Schlenk's "isomeric phenyltolylanthracene, m. p. 172—173°," is regarded as non-homogeneous phenyltolyl-dihydroanthracene, probably mixed with phenyltolylanthracene, m. p. 257°, and possibly with the isomeric dihydro-derivative.

Complete reduction of 9-phenylanthracene with sodium and amyl alcohol invariably yields a product, m. p. 87°, which evolves 1 mol. of hydrogen sulphide and yields 9-phenylanthracene when heated with sulphur, and hence is regarded as 9-phenyl-9:10-dihydroanthracene. Incomplete reduction affords mixtures, m. p. 87—151° of the two compounds. This behaviour is readily explained from the m.-p. diagram, which also discloses the existence of an additive compound (1:1), m. p. 119—120°. The corresponding synthetic mixture is non-separable when crystallised from a small quantity of methyl or ethyl alcohol, but separable from larger volumes of these solvents. Baeyer's phenyldihydroanthracene, m. p. 120—120.5°, and the analogous product, m. p. 123°, of Schlenk and Bergmann are regarded as equimolecular mixtures of phenylanthracene and 9-phenyl-9:10-dihydroanthracene, m. p. 87°.

H. WREN.

Syntheses of polynuclear anthracenes. L. F. FIESER and E. M. DIETZ (Ber., 1929, 62, [B], 1827—1833; cf. Clar, this vol., 689).—2-Methyl-1:1-dinaphthyl ketone and 2-methyl-1:2'-dinaphthyl ketone have m. p. 171° and 142—143°, respectively. A methyl-1:2-dinaphthyl ketone, m. p. 154.5°, is described. Benzoyl chloride and 2-methylnaphthalene afford phenyl 2-methylnaphthyl ketone, m. p. 71°. Phenanthrene-9-carboxyl chloride and 2-methylnaphthalene give 2-methylnaphthyl 9-phenanthryl ketone, m. p. 170°, passing when heated into 1:2:3:4:5:6-tribenzanthracene, m. p. 224°; 1:2:3:4:5:6-tribenzanthraquinone has m. p. 244°. 2-Naphthoyl chloride and 2:6-dimethylnaphthalene afford 2:6-dimethyl-1:2'-dinaphthyl ketone, m. p. 111°, yielding 3'-methyl-1:2:5:6-dibenzanthracene, m. p. 244—245°, and thence 3'-methyl-1:2:5:6-dibenzanthraquinone, m. p. 223°. 1:5-Di-2'-naphthoyl-2:6-dimethylnaphthalene, m. p. 278°, from 2-naphthoyl chloride and 2:6-dimethylnaphthalene, affords 2:3:8:9-dinaphtho-1:2'-chrysene, m. p. 500°.

H. WREN.

Reduction of aromatic nitro-compounds by hydrogen in presence of platinum-black. V. VESELY and E. REIN (Coll. Czech. Chem. Comm., 1929, 1, 360—367).—See A., 1927, 757.

Aniline-o-sulphonic acid (orthanilic acid). H. E. FIERZ, E. SCHLITTLER, and H. WALDMANN (Helv. Chim. Acta, 1929, 12, 663—668).—A mixture of 2:2'-dinitrodiphenyl sulphide with hydrochloric and nitric acids, at 70°, is treated with chlorine. The

resulting o-nitrobenzenesulphonyl chloride may be hydrolysed and reduced to aniline-o-sulphonic acid (yield 92%) or treated with aqueous ammonia to produce o-aminobenzenesulphonamide, m. p. 150° (crystallographic properties described). With amyl nitrite and hydrochloric acid in ethyl alcohol it yields the diazo-anhydride, $C_6H_4 \begin{smallmatrix} N(N) \\ SO_2 \end{smallmatrix} NH$, which is intensely sweet.

The nitrobenzenesulphonic acids obtained by nitration of benzenesulphonic acid can be separated through their ferrous salts, that of the m-compound being very sparingly soluble, that of the o-compound the most soluble.

R. J. W. LE FÈVRE.

Action of phosphoric oxide on β-anilino-butyral. F. A. MASON (J.C.S., 1929, 1560—1562; cf. A., 1925, i, 834; *ibid.*, 1926, 735).—The action of phosphoric oxide on β-anilino-butyral, in benzene at 15—100°, affords 2-methylquinoline, b. p. 244—247° (picrate, m. p. 196—197°), accompanied by aniline formed as a by-product of hydrolysis; neither di- nor tetra-hydro-2-methylquinoline is produced. An improved preparation of β-anilino-butyral is described. Attempts to condense β-chlorobutyral with toluene-p-sulphonanilide in the presence of sodium ethoxide or amyloxide were unsuccessful.

C. W. SHOPPEE.

[Preparation of] o-nitroaniline. L. EHRENFELD and M. PUTERBAUGH (Organic Syntheses, 1929, 9, 64—65).

New class of organic sulphur bases. T. G. LEVI (Atti R. Accad. Lincei, 1929, [vi], 9, 790—796).—The interaction of an aromatic amine, formaldehyde, and hydrogen sulphide proceeds differently from that occurring with aliphatic amines (this vol., 707), bases containing two aromatic amine residues to one sulphur atom being obtained: $2NH_2Ph + 3CH_2O + H_2S = C_{15}H_{16}N_2S + 3H_2O$, although possibly the arylthioformaldines are formed simultaneously. These new basic compounds apparently contain no tertiary nitrogen, as they give no methiodides, but they react with nitrous acid to form dinitroso-derivatives; their structure is to be discussed later.

Aniline yields the base $C_{15}H_{16}N_2S$, m. p. 107°; p-toluidine, the base, $C_{17}H_{20}N_2S$, m. p. 103°; benzylamine, the base, $C_{17}H_{20}N_2S$, m. p. 93° [hydrochloride (+2HCl), m. p. 144°; nitroso-derivative, $C_{17}H_{18}O_2N_2S$, m. p. 75°]. From the xylydines, no such bases were obtainable, but p-xylylidine gives p-xylylformothialdine, $C_6H_3Me_2 \cdot N \begin{smallmatrix} CH_2 \cdot S \\ CH_2 \cdot S \end{smallmatrix} CH_2$, m. p. 89—90°.

Corresponding selenium bases are obtained in a similar manner, aniline giving a base, $C_{15}H_{16}N_2Se$, b. p. 116°; p-toluidine, a base, m. p. 114°; benzylamine, a base, m. p. 123°; p-xylylidine, a base, $C_{19}H_{24}N_2Se$, m. p. 100°.

T. H. POPE.

Action of phenylcarbimide on urethanes, carbamides, and thiocarbamides. H. LAKRA and F. B. DAINS (J. Amer. Chem. Soc., 1929, 51, 2220—2225).—The following reaction products are mentioned and the mechanism of their formation is discussed: from urethane at 140—160°, ethyl phenyl-allophanate, phenylurethane, phenylisocyanuric acid

(I), and ethyl α -phenylbiuret- ϵ -carboxylate; from phenylurethane at 200—250°, and from ethylurethane at 175°, *s*-diphenylcarbamide (II); from ethyl allophanate at 160°, II and isocyanuric acid (III), and at 170—178°, also I; from carbamide at 100°, mainly α -phenylbiuret; at 120°, also ammonia, biuret, I, II, and III, and at 140°, mainly II; from acetylcarbamide at 130—160°, α -acetyl- γ -phenylcarbamide and III, from benzoylcarbamide at 150°, α -benzoyl- γ -phenylcarbamide; from phenylcarbamide (cf. Kuhn and Henschel, A., 1888, 474) at 100°, II, α -phenylbiuret and $\alpha\epsilon$ -diphenylbiuret; from carbanilide at 150°, $\alpha\gamma\epsilon$ -triphenylbiuret; from phenylmethylcarbamide at 135—140°, and from acetylphenylcarbamide at 200°, only II; from thiocarbamide at 100°, α -phenyl- δ -thiobiuret, m. p. 186°, which is converted by methyl iodide at 100° into the *hydriodide* of α -phenyl- δ -methylisothiobiuret (IV), $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{SMe}$, m. p. 147—148°. Mono- and di-substituted thiocarbamides give no additive products, but only II, and the corresponding alkylthiocarbimide. Methylisothiocarbamide gives at the ordinary temperature the triuret derivative, $\text{NHPh}\cdot\text{CO}\cdot\text{N}\cdot\text{C}(\text{SMe})\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ (V), m. p. 142°, which is also formed from IV and phenylcarbimide, and is hydrolysed by potassium hydrogen sulphide to $\alpha\eta$ -diphenyl- δ -thiotriuret. Ethylisothiocarbamide and phenylcarbimide give an *ethyl thioether*, m. p. 145°, analogous to V. α -Phenyl- β -methylisothiocarbamide gives $\alpha\epsilon$ -diphenyl- δ -methylisothiobiuret, m. p. 108°, but $\alpha\gamma$ -diphenyl- β -methylisothiocarbamide gives at 160—170° only II, phenylthiocarbimide, and triphenylcyanuric acid, and at 200°, methyl mercaptan, II, and carbodiphenylimide. Alkylisothiocarbamides and guanidine (cf. Michael, A., 1905, i, 195) combine with 2 mols. of phenylcarbimide, but with only 1 mol. of phenylthiocarbimide (cf. Johnson, A., 1903, i, 751).

H. E. F. NOTTON.

Forced reaction of phenylcarbimide, phenylthiocarbimide, and benzophenoneanil with magnesium phenyl bromide: unusual type of $\alpha\delta$ -addition. H. GILMAN, J. E. KIRBY, and C. R. KINNEY (J. Amer. Chem. Soc., 1929, 51, 2252—2261).—Prolonged refluxing of phenylcarbimide, phenylthiocarbimide, or the intermediately formed benzophenoneanil with excess of magnesium phenyl bromide in ether and toluene gives, instead of the expected triphenylmethylaniline, mainly *o*-phenylbenzhydrylaniline (I), $\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{NHPh}$, m. p. 144° [*hydrochloride*, m. p. 182.5°; (?)*benzoyl derivative*, m. p. 155—156°]. Triphenylmethylaniline does not react with the Grignard reagent under these conditions. The amine, I, is identified by its synthesis from magnesium *o*-diphenyl iodide and benzylidencaniline. *o*-Iododiphenyl, b. p. 158°/6 mm., 1.6038, is prepared from *o*-aminodiphenyl (Scarborough and Waters, A., 1927, 236). The benzhydrylamine is converted by aqueous or alcoholic hydrochloric acid into 9-phenylfluorene. Attempts to prepare *o*-phenylaminotriphenylmethane by reducing *o*-phenylaminotriphenylcarbinol were unsuccessful. The action of magnesium phenyl bromide on benzophenoneanil involves a new type of $\alpha\delta$ -addition in which the reacting conjugated system is partly in the aromatic nucleus and partly in the side-chain.

H. E. F. NOTTON.

Rubrene. Nitrogenous substances from α -chloro- $\alpha\gamma$ -triphenylallylene. J. ROBIN (Compt. rend., 1929, 189, 252—254).—By the action of aniline on α -chloro- $\alpha\gamma$ -triphenylallylene a 95—100% yield of a *substance*, m. p. 199—200°, is obtained, which cannot be converted into rubrene by heating either alone or with hydrogen chloride. Since this compound is yellow (which eliminates the possible allene structure) and is not an acetylene derivative, since it is also obtained by the action of aniline and zinc chloride on phenyl β -phenylstyryl ketone (I) (into which it is converted by acid hydrolysis), it is probably γ -phenylimino- $\alpha\gamma$ -triphenyl- Δ^2 -propylene, $\text{CPh}_2\cdot\text{CH}\cdot\text{CPh}\cdot\text{NPh}$. Similar action of ammonia yields a series of derivatives, depending mainly on temperature conditions, from which was isolated a 45—50% yield of a colourless *substance*, $\text{C}_{21}\text{H}_{17}\text{N}$, m. p. 95—96° (*hydrochloride*, m. p. 166—167°, converted into rubrene by heating), which also hydrolyses to I and is probably $\alpha\gamma$ -amino- $\alpha\gamma$ -triphenylallylene.

J. W. BAKER.

Influence of the acylating component on chlorination of the basic residue of arylsulphonylarylates. R. SCHULOFF, R. POLLAK, and E. RIESZ [with I. EISNER, G. HITSCHMANN, and M. HOPMEIER] (Ber., 1929, 62, [B], 1846—1855).—Substitution in aromatic amines generally becomes more difficult with increasing strength of the acid used in acylation of the amino-group. The preparation of homogeneous, monochlorinated amines is frequently facilitated by replacement of acetyl by aromatic sulphonyl, particularly nitrosulphonyl groups. Ease of hydrolysis of the arylsulphonylarylates is increased by diminution of the acidity of the sulphonyl component or of the basicity of the amino-component. In the case of the nitrotoluenesulphonyl derivatives it is therefore advantageous to reduce the nitro- to the amino-group previously to hydrolysis.

Chlorination of *p*-toluenesulphon-*p'*-toluidide in ethereal suspension affords *p*-toluenesulphon-2'-chloro-*p'*-toluidide, m. p. 103°, in 60—65% yield, hydrolysed to 3-chloro-*p*-toluidine. A by-product, m. p. 176°, is hydrolysed to a *trichloro-p-toluidine*, m. p. 59—60°. *o*-Nitro-*p*-toluenesulphon-*p*-toluidide, m. p. 130°, is transformed by chlorine in tetrachloroethane at 50° into the corresponding 2'-chloro-compound, m. p. 152°, in 80% yield. *o*-Amino-*p*-toluenesulphon-2'-chloro-4'-methylaniline, m. p. 123°, is described. *p*-Nitro-*o*-toluenesulphon-*p*-toluidide, m. p. 127°, gives the corresponding *monochloro*-derivative, m. p. 154°; homogeneous chlorinated products could not be obtained from β -naphthalenesulphon-*p*-toluidide, m. p. 123°. *p*-Toluenesulphon-*o*-toluidide yields *p*-toluenesulphon-4'-chloro-2'-methylaniline, m. p. 143°, whence 5-chloro-*o*-toluidine, m. p. 29—30°. *o*-Nitro-*p*-toluenesulphon-*o*-toluidide, m. p. 128°, its *monochloro*-derivative, m. p. 139°, and the corresponding *amino*-compound, m. p. 167°, are described. *o*-Toluenesulphon-*o'*-toluidide gives the corresponding *monochloro*-toluidide, m. p. 154°, whereas chlorine could not be introduced into *p*-nitro-*o*-toluenesulphon-*o*-toluidide, m. p. 177°. β -Naphthalenesulphon-*o*-toluidide, m. p. 136°, and its *monochloro*-derivative, m. p. 179°, are described. *p*-Toluenesulphon-, *o*-nitro-*p*-toluenesulphon-, *p*-nitro-*o*-toluenesulphon-, and β -naph-

thalenesulphon-anilides gave, respectively, *p*-toluenesulphon-2':4'-dichloroanilide, a non-homogeneous product, *p*-nitro-*o*-toluenesulphon-*p*'-chloroanilide, m. p. 176°, and β -naphthalenesulphon-*p*'-chloroanilide, m. p. 94°. *p*-Toluenesulphon-2':4'-dichloro-1'-naphthalide, m. p. 188°, is prepared by chlorination of *p*-toluenesulphon- α -naphthalide or *p*-toluenesulphon-4'-chloro-1'-naphthalide, m. p. 161°. *p*-Nitro-*o*-toluenesulphon- α -naphthalide, m. p. 151°, and *p*-nitro-*o*-toluenesulphon-4'-chloro-1'-naphthalide, m. p. 177°, are described. β -Naphthalenesulphon-4'-chloro-1'-naphthalide and *p*-toluenesulphon-1'-chloro-2'-naphthalide have m. p. 160° and 112–114°, respectively. Homogeneous chlorinated compounds could not be prepared from the *p*-toluenesulphon-, *o*-nitro-*p*-toluenesulphon-, *p*-nitro-*o*-toluenesulphon-, and β -naphthalenesulphon-*p*-phenetidides, m. p. 106–107°, 128°, 127°, and 97°, respectively. Di-*p*-toluenesulphonylbenzidine yields successively 3:3'-dichloro-NN'-di-*p*-toluenesulphonylbenzidine, m. p. 194°, and 3:3'-dichlorobenzidine. Di- β -naphthalenesulphonylbenzidine, m. p. 257°, and 3:3'-dichloro-NN'-di- β -naphthalenesulphonylbenzidine, m. p. 237°, are described. *p*-Toluenesulphon-2'-chloro-4'-methylanilide gives a nitro-derivative, $C_{14}H_{13}O_4N_2ClS$, m. p. 197°. *p*-Toluenesulphon-4'-chloro-6'-nitro-2'-methylanilide, m. p. 145°, and *p*-nitro-*o*-toluenesulphon-2'-nitro-4'-methylanilide, m. p. 189°, have been prepared. *p*-Toluenesulphon-*p*'-toluidide is converted by chlorosulphonic acid at the atmospheric temperature into *p*-toluenesulphonyl chloride and a toluidinesulphonic acid.

H. WREN.

3:5:6-Trichloro-2-amino-*p*-xylene and some derivatives. E. BURES and T. RUBES (Časopis Českoslov. Lék., 1928, 8, 225–231; Chem. Zentr., 1929, i, 506–507).—Acet-*p*-xylylide on chlorination, e.g., with dry chlorine in acetic acid, affords as the most highly chlorinated product 3:5:6-trichloro-2-acetamido-*p*-xylene, m. p. 222°, from which 3:5:6-trichloro-2-amino-*p*-xylene, m. p. 206° [picrate, bluish-red, m. p. 100° (decomp.); benzoyl derivative, pink, m. p. 223°], is obtained after boiling for several days with alcoholic potash. The *N*-methyl compound has m. p. 62°. Diazotisation of the amino-compound is effected with difficulty; the diazo-group is most readily replaced by chlorine and least readily by cyano- or hydroxyl groups. 3:5:6-Trichloro-2-hydroxy-*p*-xylene, m. p. 175°, is obtained by adding the corresponding diazonium sulphate to a mixture of sodium sulphate, sulphuric acid, and water at 140° (basic mercury and bismuth salts); 3:5:6-trichloro-2-methoxy-*p*-xylene has m. p. 91°, the corresponding ethoxy-compound m. p. 79°, phenoxy-compound, m. p. 101°, and acetoxy-compound, m. p. 103°. 3:5:6-Trichloro-*p*-xylene has m. p. 96°, 2:3:5:6-tetrachloro-*p*-xylene, m. p. 223°, and 3:4:6-trichloro-2:5-dimethylbenzonitrile, m. p. 213°.

A. A. ELDRIDGE.

[Preparation of] **ac-tetrahydro-8-naphthylamine.** E. B. H. WASER and H. MOLLERING (Organic Syntheses, 1929, 9, 84–89).

Influence of various alcohols in the preparation of cyclic thiocarbamides. E. MARANGONI and M. J. LAMORT (Rev. Centr. Estud. Farm. Bioquim., 1928, 17, 21–26, 64–70; Chem. Zentr., 1929,

i, 503–504).—Of the alcohols used as solvents (methyl, ethyl, propyl, isobutyl, isoamyl, allyl, benzyl, and cyclohexanol; phenol was also employed) for the interaction of α -naphthylamine and carbon disulphide, ethyl and allyl alcohols gave the best yields; the presence of sulphur or xanthate is necessary, except with technical methyl alcohol, which contains acetone. Reaction did not take place when phenol, cyclohexanol, or benzyl alcohol was used.

A. A. ELDRIDGE.

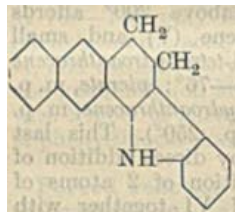
Catalytic hydrogenation under pressure in presence of nickel salts. XIII. α - and β -Hydroxy- and -amino-anthracenes. J. VON BRAUN and O. BAYER (Annalen, 1929, 472, 90–121; cf. A., 1926, 172).—When 1-hydroxyanthracene (I) is reduced with 2 atoms of hydrogen the products formed are 1-hydroxy-9:10-dihydroanthracene (II) (improved method of preparation given), 1-keto-1:2:3:4-tetrahydroanthracene (III) (semicarbazone, m. p. 250°), and an amorphous condensation product of I. Further reduction of II in decahydronaphthalene solution at 210° affords impure 1-hydroxy-1:2:3:4-tetrahydroanthracene, m. p. 109–110° (phenylcarbamide derivative, m. p. 153–154°) (readily converted by atmospheric oxygen into III), tetrahydroanthracene, and 1-keto-1:2:3:4:5:6:7:8-octahydroanthracene. The last two compounds are also obtained during the reduction of I and III. Complete reduction of I gives octahydroanthracene. Reduction of 2-hydroxyanthracene (IV), m. p. 255° (lit. 200°), with 2 atoms of hydrogen above 200° affords 2-hydroxy-9:10-dihydroanthracene (V) and small amounts of 2-hydroxy-1:2:3:4-tetrahydroanthracene (VI), m. p. 148° (acetate, m. p. 75–76°; picrate, m. p. 142°), and 2-keto-1:2:3:4-tetrahydroanthracene, m. p. 148–150° (semicarbazone, m. p. 250°). This last compound is probably formed by direct addition of hydrogen to IV. Further addition of 2 atoms of hydrogen to V yields 40% of VI together with 2-hydroxy-1:2:3:4:5:6:7:8-octahydroanthracene (VII), m. p. 122°, also formed by the addition of 4 atoms of hydrogen to VI. There is a marked tendency in these series of reductions for the replacement of hydroxyl by hydrogen.

Reduction of 1-aminoanthraquinone with zinc dust and ammonia in presence of small amounts of copper powder and potassium hydroxide gives 1-amino-9:10-dihydroanthracene (VIII), m. p. 85° (lit. 60–70°), which when heated at about 240° yields 1-aminoanthracene (IX), m. p. 127°. Treatment of this with boiling acetic acid furnishes the acetyl derivative, m. p. 212° (lit. 198°), of IX and di- α -anthrylamine, m. p. 252°. Catalytic reduction of IX in decahydronaphthalene solution at 200° results in the addition of 8 atoms of hydrogen, and the products formed are octahydroanthracene, 1-amino-1:2:3:4:5:6:7:8-octahydroanthracene, b. p. 188–193°/15 mm. (picrate, decomp. 255° after sintering at 220°; acetyl derivative, m. p. 185°), and 1-amino-5:6:7:8-tetrahydroanthracene (X), m. p. 97° (picrate, decomp. 180°; acetyl derivative, m. p. 190°). Benzenediazonium chloride converts X into the corresponding aminoazo-compound, $C_{20}H_{19}N_3$, m. p. 170°. When reduction of IX is effected with 4 atoms of hydrogen a mixture of VIII and X results; small amounts of tetrahydro-

anthracene and III are also produced. The formation of III is presumably due to the action of water (from nickel oxide and hydrogen) on IX, whereby I and ammonia are obtained. 2-Aminoanthracene (XI) is converted by reduction with 2 atoms of hydrogen chiefly into its 9:10-dihydro-derivative (XII). With 4 atoms of hydrogen the basic products are 2-amino-5:6:7:8-tetrahydroanthracene, m. p. 154° (picrate, decomp. 215° after darkening at 200°; acetyl derivative, m. p. 159—160°; phenylthiocarbimide derivative, m. p. 127°; aminoazobenzene derivative, m. p. 174°) (also obtained by reduction of XII with 2 atoms of hydrogen), and 2-amino-1:2:3:4:5:6:7:8-octahydroanthracene, m. p. 69—70° (picrate, m. p. 245° after darkening at 230°; acetyl derivative, m. p. 165°), formed also during the complete reduction of XI.

Thermal decomposition of the phenylcarbimide derivatives of VI and VII, m. p. 150° and 183°, respectively (cf. Straus and Rohrbacher, A., 1921, i, 172), affords 1:2-dihydroanthracene [1:2-diacene], m. p. 150° (picrate, m. p. 115°; dibromide, m. p. 102°), and 1:2:5:6:7:8-hexahydroanthracene [hexacene], m. p. 70°, respectively.

Reduction of III with sodium and alcohol affords no individual substance, whilst oxidation with permanganate gives phthalic and not naphthalene-2:3-dicarboxylic acid. When III is heated for a short time at its b. p. conversion into anthracene results. The phenylhydrazone, m. p. 116°, of III is



converted by heating with concentrated hydrochloric acid into the dihydrocarbazole derivative (annexed formula), m. p. 245°, dehydrogenated by distillation with lead oxide or boiling with nitrobenzene into the corresponding carbazole, m. p. 325°, and oxidised by chromic and

acetic acids to the corresponding o-quinone, not melted at 360°.

H. BURTON.

Thermal and hydrolytic decomposition of basic and phenolic diphenylmethane derivatives and synthesis of optically active aromatic compounds. J. VON BRAUN [with E. ANTON, W. HAENSEL, and G. WERNER] (Annalen, 1929, 472, 1—89).—Ketones condense with aromatic primary, secondary, and tertiary amines in presence of concentrated hydrochloric acid (cf. Dobner, A., 1879, 786; 1888, i, 278; also B.P. 204,722; B., 1924, 412) to give the corresponding diaminodiphenylmethane derivatives, $R' \cdot CH_2 \cdot CO \cdot R + 2C_6H_5 \cdot NR''_2 \longrightarrow R' \cdot CH_2 \cdot CR(C_6H_4 \cdot NR''_2)_2$, but a small amount of the unsaturated base, $R' \cdot CH:CR \cdot C_6H_4 \cdot NR''_2$, is also formed. This does not arise by thermal decomposition of the diamine, but can readily be obtained by heating the diamine with a small amount of hydrochloric or sulphuric acid (0.02—0.01 mol.) with subsequent distillation in a vacuum. The unsaturated base reacts with the original amine in presence of hydrochloric acid to give the diamine. Condensation occurs also with cyclic ketones, and the mechanism of the reaction is: $R' \cdot CH_2 \cdot CO \cdot R + C_6H_4 \cdot NR' \longrightarrow R' \cdot CH_2 \cdot CR(OH) \cdot C_6H_4 \cdot NR'_2 \rightleftharpoons H_2O +$

$R' \cdot CH:CR \cdot C_6H_4 \cdot NR''_2 \xrightarrow{C_6H_5 \cdot NR''_2} R' \cdot CH_2 \cdot CR(C_6H_4 \cdot NR''_2)_2$. Thus, cyclohexanone (1 mol.), aniline (2 mols.), and aqueous-alcoholic hydrochloric acid (2 mols.) yield after several days at 100°, 1:1-pp'-diaminodiphenylcyclohexane (I), b. p. 248°/0.1 mm., m. p. 114° (hydrochloride, m. p. 235°; acetyl derivative, m. p. 266°; phenylthiocarbimide derivative, m. p. 163°), and a small amount of p-Δ¹-cyclohexenylaniline (II), b. p. 175°/14 mm. (hydrochloride, m. p. 228°; picrate, decomp. 170°; acetyl derivative, m. p. 152°; benzoyl derivative, m. p. 177°; phenylthiocarbimide derivative, m. p. 144°; benzylidene derivative, m. p. 82°). When I is heated for a short time at 100° with hydrochloric acid no change occurs, but after several days an appreciable amount of II results. Distillation of I under ordinary pressure effects little change, but conversion into II proceeds readily by the above acid-distillation treatment (general method of preparation). Reduction of II with a large excess of sodium and alcohol gives p-cyclohexylaniline, and conversion into I is effected by heating with aniline and hydrochloric acid or, better, with dry aniline hydrochloride. cycloHexanone and methylaniline afford 1:1-pp'-dimethyldiaminodiphenylcyclohexane, b. p. 250—252°/0.3 mm., m. p. 124° (hydrochloride, m. p. 220°; picrate, m. p. 105°; diacetyl derivative, m. p. 185°; bisphenylthiocarbimide derivative, m. p. 165°), and p-Δ¹-cyclohexenylmethyl-aniline, b. p. 184°/14 mm. (hydrochloride, m. p. 212°; picrate, m. p. 114°; acetyl derivative, m. p. 85°; nitroso-derivative, m. p. 89°). 1:1-p:p'-Tetramethyldiaminodiphenylcyclohexane, b. p. 282—283°/12 mm., m. p. 164° (hydrochloride, m. p. 180°; picrate, m. p. 148°; dimethiodide, m. p. 178°), and p-Δ¹-cyclohexenyl dimethylaniline (III), b. p. 190°/14 mm., m. p. 56° (hydrochloride, m. p. 195°; picrate, m. p. 162°; methiodide, m. p. 190°), are obtained similarly from dimethylaniline. Treatment of III with aniline, diethylaniline, and α-naphthylamine hydrochlorides gives 1-p-aminophenyl-1-p-dimethylaminophenylcyclohexane, b. p. 250—255°/0.3 mm., m. p. 101° (hydrochloride, m. p. 195°; acetyl derivative, m. p. 115°), decomposed by the acid-distillation treatment into dimethylaniline and II, 1-p-dimethylaminophenyl-1-p-diethylaminophenylcyclohexane, b. p. 260—265°/0.1 mm., m. p. 108° (hydrochloride, m. p. 141—142°), and the compound b. p. 270—280°/0.1 mm., m. p. 152°, respectively. Treatment of III with cold, fuming hydrobromic acid during several days yields about 10% of a difficultly isolated additive compound (probably a tertiary bromide), C₁₄H₂₀NBr, m. p. 95°, which when warmed with water and magnesium carbonate yields a halogen-free substance, m. p. 45—48°, readily converted by dilute acid into III. Tetrahydroquinoline and cyclohexanone yield 1:1-ditetrahydroquinolylcyclohexane, b. p. 265—267°/0.1 mm., m. p. 114° (dinitroso-derivative, m. p. 85°; dibenzoyl derivative, m. p. 154°; bisphenylthiocarbimide derivative, m. p. 92°), and 6-Δ¹-cyclohexenyltetrahydroquinoline, b. p. 163—165°/0.1 mm. (hydrochloride, m. p. 120°; picrate, m. p. 90°), m-Toluidine and cyclohexanone do not condense in the above manner, but at 160° form a small amount of 4:6-di-Δ¹-cyclohexenyl-m-toluidine, b. p. 230—235°/12 mm. (picrate, m. p. 176—177°). Similarly, p-toluidine

yields 2:6-di- Δ^1 -cyclohexenyl-*p*-toluidine, m. p. 60° (picrate, m. p. 192°; benzoyl derivative, m. p. 69°), whilst small amounts of the compounds $C_{24}H_{25}N$ and $C_{18}H_{22}N_2Cl$, b. p. 200—205°/1 mm., and about 180°/1 mm., respectively, are formed from *p*-cyclohexyl- and *p*-chloro-anilines. 3-Methylcyclohexanone and aniline yield a mixture of 1:1-*pp'*-diaminodiphenyl-3-methylcyclohexane (IV), b. p. 285—290°/14 mm. (hydrochloride, m. p. 214°; bisphenylthiocarbimide derivative, m. p. 127°), and *p*- Δ^1 -3(or 5)-methylcyclohexenylaniline (V), b. p. 187—190°/14 mm. (acetyl derivative, m. p. 127°; benzoyl derivative, m. p. 178°; phenylthiocarbimide derivative, m. p. 143°). The amount of V produced is about ten times as great as of the corresponding base from cyclohexanone. Treatment of V with aniline gives IV. Dimethylaniline and 3-methylcyclohexanone afford 1:1-*pp'*-tetramethyldiaminodiphenyl-3-methylcyclohexane, b. p. 295°/13 mm., m. p. 109° (picrate, m. p. 164°; dimethiodide, m. p. 186°), and *p*-3-methylcyclohexenyldimethylaniline, b. p. 194—196°/14 mm., m. p. 38° (picrate, m. p. 162°; methiodide, m. p. 159°). 2-Methylcyclohexanone and aniline condense with difficulty, yielding a small amount of *p*-2-methylcyclohexenylaniline, b. p. 160°/14 mm. [chloroplatinate (?), m. p. 211—212°]. cyclopentanone and dimethylaniline at 150° furnish *p*-cyclopentenyl dimethylaniline, b. p. 160°/12 mm., m. p. 10° (hydrochloride, m. p. 170°; picrate, m. p. 129°; methiodide, decomp. 180°) [reduced by sodium and alcohol to *p*-cyclopentyl dimethylaniline, b. p. 156°/12 mm. (hydrochloride, m. p. 175°; picrate, m. p. 134°; methiodide, m. p. 179°)], and 1:1-*p*:*p'*-tetramethyldiaminodiphenylcyclopentane, m. p. 128° (hydrochloride, m. p. 213°; picrate, m. p. 181°; dimethiodide, decomp. 195°).

When aniline is heated with acetone in hydrochloric acid solution at 150° (B., 1924, 412) the main product is $\beta\beta$ -*pp'*-diaminodiphenylpropane (VI); a very small amount of *p*-isopropenylianiline (VII), b. p. 125—130°/vac., d_4^{20} 1.0320 (hydrochloride, m. p. 230—235°; picrate, m. p. 180°; acetyl derivative, m. p. 110—111°; phenylthiocarbimide derivative, m. p. 137°), is produced at the same time. Conversion of VI into VII is effected by the acid-distillation treatment. Polymerisation of VII occurs very readily at the ordinary temperature, forming a dimeride (VIII), probably

$NH_2 \cdot C_6H_4 \cdot CMe \cdot CH \cdot CH_2 \cdot CHMe \cdot C_6H_4 \cdot NH_2$, m. p. 173° (hydrochloride, m. p. 228°; picrate, m. p. 172°; phenylthiocarbimide derivative, m. p. 117°). Reduction of the diacetyl derivative, m. p. 205°, of VIII with hydrogen in presence of palladium and methyl alcohol gives the diacetyl derivative, m. p. 121—123°, of the base, $C_{18}H_{24}N_2$, b. p. 205—210°/0.1 mm., m. p. 50—52° (picrate, m. p. 213°; hydrochloride, not melted at 275°; bisphenylthiocarbimide derivative, m. p. 178°), converted by the usual method into the diphenol, $C_{18}H_{22}O_2$, m. p. 106—107° (dibenzoate, m. p. 117°; dimethyl ether, b. p. 192°/1.5 mm.). Acetone and methylaniline afford about 50% of -dimethyldiaminodiphenylpropane, b. p. 190°/1.5 mm., m. p. 138° (hydrochloride, m. p. 218°; acetyl derivative, m. p. 139°; bisphenylthiocarbimide derivative, m. p. 170°), converted into *p*-isopropenylmethylaniline, b. p. 123—125°/14 mm., d 0.9675 (picrate, m. p. 147°),

which does not polymerise readily even at 100°. isoPropenyldimethylaniline (hydrochloride, m. p. 122°; picrate, m. p. 96°) has b. p. 120—122°/15 mm., m. p. 74°. Acetone and *m*-toluidine at 150—160° yield small amounts of 4:6-diisopropenyl-*m*-toluidine, b. p. 225—230°/8 mm. (hydrochloride, m. p. 218°; picrate, m. p. 204°), and 4-isopropenyl-*m*-toluidine, b. p. 150—155°/8 mm. (hydrochloride, m. p. 217°; picrate, m. p. 224°), reduced by Ladenburg's method to 4-isopropyl-*m*-toluidine, b. p. 141—145°/13 mm. (hydrochloride, m. p. 211°). Methyl ethyl ketone condenses with aniline, methyl- and dimethylanilines forming $\beta\beta$ -*pp'*-diaminodiphenyl-, b. p. 210°/3 mm., $\beta\beta$ -*pp'*-dimethyldiaminodiphenyl-, b. p. 240°/4 mm., m. p. 98° (bisphenylthiocarbimide derivative, m. p. 142°; diacetyl derivative, m. p. 121°), and $\beta\beta$ -*p*:*p'*-tetramethyldiaminodiphenyl-*n*-butane, b. p. 210—212°/0.8 mm. (hydrochloride, m. p. 125°; picrate, m. p. 80—90°; methiodide, m. p. 202°), respectively. These are converted into *p*-isobutenylaniline, b. p. 140—145°/14 mm. (?), d_4^{20} 0.9899 (hydrochloride, m. p. 238°; picrate, m. p. 196°; phenylthiocarbimide derivative, m. p. 131°; acetyl derivative, m. p. 121°), *p*-isobutenylmethylaniline, b. p. 145—150°/14 mm., and *p*-isobutenyldimethylaniline, b. p. 138—142°/14 mm., d_4^{20} 0.9561 (picrate, m. p. 125°; methiodide, m. p. 175°), respectively. Methyl *n*-butyl ketone and dimethylaniline afford 15% of $\beta\beta$ -*pp'*-tetramethyldiaminodiphenyl-*n*-hexane, b. p. 230—234°/4 mm. (dimethiodide, m. p. 196°), and 5% of *p*-isohexenyldimethylaniline, b. p. 160—162°/12 mm. (methiodide, m. p. 175°); with acetophenone, 20% of *pp'*-tetramethyldiaminotriphenylethane, m. p. 134° (dimethiodide, m. p. 188°), and 7—8% of *p*- α -phenylvinyl dimethylaniline, b. p. 208—211°/13 mm., d_4^{20} 1.0409 (hydrochloride, m. p. 144°; methiodide, m. p. 170°), result. *n*-Butaldehyde and dimethylaniline yield $\alpha\alpha$ -*p*:*p'*-tetramethyldiaminodiphenyl-*n*-butane, b. p. 225—227°/0.3 mm., convertible into *p*-*n*-butenyldimethylaniline, b. p. 140—142°/12 mm., d_4^{20} 0.9395 (picrate, m. p. 99—100°), which on treatment with aniline hydrochloride gives some α -*p*-aminophenyl- α -*p*-dimethylaminophenyl-*n*-butane, b. p. 205—210°/0.2 mm.

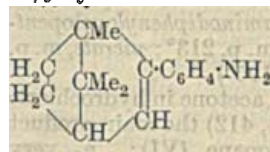
When aromatic aldehydes (1 mol.) are treated with aromatic bases (2 mols.) in presence of hydrochloric acid (2 mols.) the triphenylmethane derivative is generally formed considerably faster than from the amine (1 mol.) and the diphenylcarbinol (1 mol.), indicating in the first change an active intermediate. The change is formulated $C_6H_5 \cdot NR_2 \cdot HCl + R' \cdot CHO \rightarrow C_6H_5 \cdot NR_2 \cdot Cl \cdot CHR' \cdot OH \rightarrow CHR' \cdot C_6H_4 \cdot NR_2 \cdot Cl \rightarrow CHR' (C_6H_4 \cdot NR_2 \cdot HCl)_2$.

The condensation of ketones and phenols is best carried out in presence of hydrochloric acid (cf. Schmidlin and Lang, A., 1910, i, 836), but at a lower temperature than with amines. When the *pp'*-dihydroxydiphenylmethane derivatives are distilled under ordinary pressure decomposition into phenol and an unsaturated phenol usually occurs. Thus, cyclohexanone (1 mol.) and phenol (2 mols.) yield after 60 hrs. at 36°, 65% of the theoretical amount of 1:1-*pp'*-dihydroxydiphenylcyclohexane (IX) (dimethyl ether, b. p. 260—263°/16 mm., m. p. 82°; diacetate, m. p. 122°), which when distilled under

ordinary pressure decomposes into phenol, *p*-cyclohexylphenol (X) (methyl ether, m. p. 58°; acetate, b. p. 170°/15 mm., m. p. 35°), *p*-cyclohexenylphenol (XI), m. p. 123° (methyl ether, b. p. 155°/14 mm., m. p. 35°; acetate, m. p. 52°), and resinous products. Treatment of XI with hydrochloric acid at 100° gives X and resinous material. Hydrogenation of IX in presence of a nickel catalyst at 230–250° affords cyclohexanol, a substance, $C_{18}H_{26}O_2$ (probably 1-*p*-hydroxyphenyl-1-4-hydroxycyclohexylcyclohexane), and a mixture, b. p. 155–156°/15 mm., m. p. 92–93°, of *cis*- and *trans*-4-cyclohexylcyclohexanols (cf. Schrauth and Gorig, A., 1923, i, 1084) (acetate, b. p. 158–160°/15 mm.). This mixture yields two phenylcarbimide derivatives, m. p. 156° and 105°, respectively, and is oxidised by chromic acid to 4-cyclohexylcyclohexanone, b. p. 145°/14 mm., m. p. 31° (lit. 28–29°) [semicarbazone, m. p. 216° (lit. 206°)]. *m*-Cresol and cyclohexanone afford a small amount of 4-cyclohexenyl-*m*-cresol, b. p. 175°/12 mm., converted by hot hydrochloric acid into 4-cyclohexyl-*m*-cresol and resinous material. 2-Methylcyclohexanone and phenol yield small amounts of methylcyclohexenylphenol, b. p. 173–175°/12 mm., and 1:1-*pp'*-dihydroxydiphenyl-2-methylcyclohexane, b. p. 280°/12 mm., m. p. 135–137°. 1:1-*pp'*-Dihydroxydiphenylcyclopentane (XII), b. p. 270°/12 mm., m. p. 155–156° (dimethyl ether, b. p. 240–245°/12 mm., m. p. 115°; diacetate, m. p. 79°), is decomposed by hydrochloric acid at 100° yielding *p*-cyclopentylphenol (XIII), b. p. 155°/12 mm., m. p. 63–65° (methyl ether, b. p. 143°/12 mm.; acetate, b. p. 150–152°/12 mm.), and thermally giving *p*-cyclopentenylphenol (XIV), m. p. 148–150° (methyl ether, m. p. 90°; acetate, m. p. 72°). Catalytic hydrogenation of XIII and XIV affords a mixture of 4-cyclopentylcyclohexanols, b. p. 135°/12 mm., oxidised to 4-cyclopentylcyclohexanone, b. p. 125°/12 mm., n_D^{20} 1.4860 (semicarbazone, m. p. 195–197°). Acetone and phenol give a quantitative yield of $\beta\beta$ -*pp'*-dihydroxydiphenylpropame (XV), b. p. 250–252°/13 mm., which on thermal decomposition yields phenol, *p*-isopropylphenol, b. p. 112–115°/12 mm., m. p. 61°, and a dimeride, $C_{18}H_{20}O_2$ (probably a cyclobutane derivative), b. p. 255–256°/14 mm., m. p. 181° (diacetate, m. p. 165°; dimethyl ether, m. p. 115°), of *p*-isopropenylphenol. The same compound is obtained by treatment of XV with hydrochloric acid. Reduction of XV in presence of an active nickel catalyst at 260° affords cyclohexanol, 4-isopropylcyclohexanol, β -*p*-hydroxyphenyl- β -4-hydroxycyclohexylpropane, b. p. 244–248°/12 mm. [diacetate, b. p. 234–237°/16 mm.; monomethyl ether (XVI), b. p. 170–175°/1 mm.], and $\beta\beta$ -4:4'-dihydroxydicyclohexylpropane, b. p. 230–234°/14 mm. Oxidation of the last-named compound with chromic and acetic acids yields the diketone, $C_{18}H_{24}O_4$, m. p. 158–160° (disemicarbazone, m. p. 222°), whilst XVI furnishes the ketone, $C_{16}H_{22}O_2$, b. p. 205–210°/15 mm. (semicarbazone, m. p. 184°). Oxidation of XVI with cold alkaline permanganate gives 45% of β -(α -*p*-methoxyphenyl- α -methyl)ethyladipic acid, m. p. 116°. $\beta\beta$ -4:4'-Dihydroxy-di-*o*-tolylpropane has b. p. 230–235°/12 mm. $\beta\beta$ -*pp'*-Dihydroxydiphenyl-*n*-butane, b. p. 250–253°/12 mm. (cf. Zincke and Goldemann, A., 1908, i, 780), is decomposed to a mixture of phenol, *p*-isobutyl- and *p*-isobutenyl-

phenol, m. p. 86° (acetate, b. p. 148°/15 mm.). Catalytic reduction of the last-named substance yields 4-isobutylcyclohexanol, b. p. 128°/20 mm., oxidised by chromic and acetic acids to 4-isobutylcyclohexanone, b. p. 104–106°/13 mm. (semicarbazone, m. p. 190°). $\alpha\alpha$ -*pp'*-Dihydroxydiphenyl-*n*-butane (XVII), b. p. 270°/12 mm., on thermal decomposition yields *p*-*n*-butylphenol, b. p. 138–141°/15 mm. (acetate, b. p. 138–141°/15 mm.). Catalytic hydrogenation of XVII at 220° affords the substance, $C_{18}H_{24}O_2$, b. p. 235–240°/15 mm. (diacetate, b. p. 230–234°/15 mm.), and small amounts of cyclohexanol and 4-*n*-butylcyclohexanol, b. p. 120–122°/15 mm., d^{20} 0.9106, 1.4691 (phenylcarbimide derivatives, m. p. 124° and 42°). 4-*n*-Butylcyclohexanone (semicarbazone, m. p. 175°) has b. p. 101–102°/15 mm. (?). *n*-Butaldehyde and *m*-cresol afford 4-butenyl-*m*-cresol, b. p. 150°/12 mm. (methyl ether, b. p. 130–133°/12 mm.; acetate, b. p. 140°/12 mm.), and $\alpha\alpha$ -4:4'-dihydroxy-di-*o*-tolyl-*n*-butane, b. p. 250°/12 mm. (diacetate, b. p. 230–235°/11 mm.), converted by treatment with hydrochloric acid into 4-*n*-butyl-*m*-cresol, b. p. 140–145°/14 mm. Catalytic hydrogenation of $\alpha\alpha$ -*pp'*-dihydroxydiphenylethane gives a small amount of α -*p*-hydroxyphenyl- α -4-hydroxycyclohexylethane, b. p. 240°/12 mm. (monomethyl ether, b. p. 175–178°/0.2 mm.), and $\alpha\alpha$ -4:4'-dihydroxydicyclohexylethane, b. p. 230°/12 mm., m. p. 140–146°, oxidised to the corresponding diketone, $C_{14}H_{22}O_4$, b. p. 225–230°/16 mm., m. p. 55–56° (semicarbazone, m. p. 215–217°).

Camphor condenses with aniline in presence of 20% hydrochloric acid at 100° after 14 days yielding

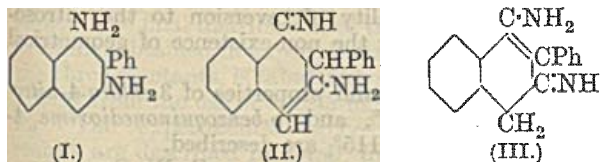


the compound $C_{16}H_{20}N$ (annexed structure), b. n. 140°/0.8 mm., $[\alpha]_D^{25} +9.49^\circ$ in alcohol, whilst menthone and dimethylaniline give after 10 hrs. at 180° 1-*p*-dimethylaminophenyl-5-methyl-2-isopropyl- Δ^1 -cyclohexene, b. p. 195–205°/12 mm., $[\alpha]_D^{25} +13^\circ$ in chloroform. From *d*-3-methylcyclopentanone and -cyclohexanone and the appropriate base or phenol the following are prepared: 1:1-*pp'*-tetramethyldiaminodiphenyl-3-methylcyclopentane, m. p. 95°, $[\alpha]_D^{25} +22.5^\circ$ in chloroform; *p*-3-methylcyclopentenyl-dimethylaniline, m. p. 64°; 1:1-*pp'*-dihydroxydiphenyl-3-methylcyclohexane, b. p. 235–236°/2 mm., m. p. 153–155°, $[\alpha]_D^{25} -18.74^\circ$ in alcohol, converted by concentrated hydrochloric acid at 100° into phenol and *p*-3-methylcyclohexenylaniline, b. p. 170°/14 mm., m. p. 60–75°, $[\alpha]_D^{25} -6.94^\circ$ in benzene; 1:1-*pp'*-diaminodiphenyl-3-methylcyclohexane, $[\alpha]_D^{25} -11.78^\circ$ in chloroform; *p*-3-methylcyclohexenylaniline, $[\alpha]_D^{25} +54.21^\circ$ in alcohol, reduced by sodium and alcohol to *p*-3-methylcyclohexylaniline (XVIII), b. p. 176–178°/18 mm., $[\alpha]_D^{25} -4.78^\circ$ in alcohol; *p*-3-methylcyclohexenylmethylaniline, b. p. 192–195°/15 mm., m. p. 33°, $[\alpha]_D^{25} +47.63^\circ$ in chloroform [hydrochloride, m. p. 180°; nitroso-derivative (XIX), m. p. 50°]; 1:1-*pp'*-dimethyldiaminodiphenyl-3-methylcyclohexane, b. p. 260–265°/1.5 mm., $[\alpha]_D^{25} -15.26^\circ$ in chloroform (hydrochloride, m. p. 185°; bisphenylthiocarbimide derivative, m. p. 105°); *p*-3-methylcyclohexenylmethylaniline, m. p. 48°, $[\alpha]_D^{25} -46.69^\circ$ in chloroform, and 1:1-*pp'*-tetramethyldiaminodi-

phenyl-3-methylcyclohexane, $[\alpha]_D^{20}$ -20.94° in chloroform. There are obtained from XVIII, by the usual methods, *p-3-methylcyclohexyl-phenol*, $[\alpha]_D^{20}$ -6.9° in benzene; *-benzene* (XX), b. p. $123-124^\circ/14$ mm., d_4^{20} 0.9304, n_D^{20} 1.5176, $[\alpha]_D^{20}$ -5.26° (cf. Kursanov, A., 1907, i, 600); *-bromobenzene*, b. p. $165-167^\circ/14$ mm., d_4^{20} 1.210, $[\alpha]_D^{20}$ -2.23° ; *-benzonitrile*, b. p. $166-168^\circ/14$ mm., d_4^{20} 1.0058, $[\alpha]_D^{20}$ -1.62° , and *-phenylhydrazine*, m. p. $84-85^\circ$, $[\alpha]_D^{20}$ -4.99° in alcohol (*hydrochloride*, m. p. 210° ; *phenylcarbimide* derivative, m. p. $217-218^\circ$; *phenylthiocarbimide* derivative, m. p. 175°). Reduction of XIX with zinc dust and aqueous-alcoholic acetic acid gives *p-3-methylcyclohexenyl-phenylmethylhydrazine*, $\text{Me}\cdot\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NH}_2$, b. p. $174-176^\circ/1$ mm., m. p. 34° , $[\alpha]_D^{20}$ $+39.12^\circ$ in alcohol (*phenylthiocarbimide* derivative, m. p. 181° ; *methylene* derivative, m. p. 121° ; *benzylidene* derivative, m. p. 108°), whilst XX is converted by acetyl chloride in presence of aluminium chloride and carbon disulphide into *p-3-methylcyclohexylacetophenone*, b. p. $182-185^\circ/14$ mm., d_4^{20} 0.9986, $[\alpha]_D^{20}$ -3° (*semicarbazone*, m. p. 211° ; *oxime*, m. p. $96-98^\circ$).

H. BURTON.

Isomerism of derivatives of 2-phenylnaphthyl-ene-1 : 3-diamine. M. S. LESSLIE and E. E. TURNER (J.C.S., 1929, 1512-1517).—Previous work on the derivatives of 2-phenylnaphthylene-1 : 3-diamine (I) (Lees and Thorpe, J.C.S., 1907, 91, 1282; Gibson, Kentish, and Simonsen, A., 1928, 1128) is reviewed. The authors consider that the isomerism is structural in character and not stereochemical (cf. Gibson, Kentish, and Simonsen, *loc. cit.*), and it is shown that 2-phenylnaphthylene-1 : 3-diamine probably has the structure II, containing an asymmetric carbon atom, since it has been resolved. When an aqueous solution of the diamine (1 mol.) in *d*-camphorsulphonic acid (2.2 mols.) was kept, *d*-2-phenylnaphthylene-1 : 3-diamine di-*d*-camphorsulphonate, $[\alpha]_{5461}^{20}$ $+40.5^\circ$, $[M]_{5461}^{20}$ $+282.9^\circ$ (in alcohol), separated, from which dilute aqueous ammonia liberated the free *d*-base, m. p. $109-111^\circ$, $[\alpha]_{5461}^{20}$ $+14.8^\circ$ in alcohol. By using *l*-camphorsulphonic acid, *l*-2-phenylnaphthylene-1 : 3-diamine di-*l*-camphorsulphonate, $[\alpha]_{5461}^{20}$ -40.7° , $[M]_{5461}^{20}$ -284.3° , was obtained.



It is suggested that on the basis of the tautomeric forms I, II, and III, by assuming that in hot acid media the diamine behaves as I, and that in cold alkaline media it behaves as III, the chemistry of the substance receives a simple and satisfactory explanation.

An improved preparation of I, m. p. $112.5-113.5^\circ$, is described.

C. W. SHOPPEE.

Derivatives of 2 : 4-dichloro-, 2 : 4 : 6-trichloro-, and 2-chloro-4-nitro-phenylhydrazines with aldehydes and ketones, particularly sugars. E. VOTOCEK and L. RYS (Coll. Czech. Chem. Comm., 1929, 1, 346-351).—2 : 4 : 6-Trichlorophenylhydrazine, m. p. 143° , and 2-chloro-4-nitrophenylhydrazine, m. p.

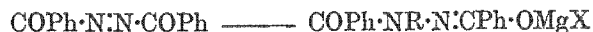
144° , are obtained by reduction of the requisite diazonium compound with stannous chloride and hydrochloric acid. 2 : 4-Dichlorophenylhydrazones, the following are described: arabinose, m. p. 161° ; galactose, m. p. 181° ; laevulose, m. p. 120° ; acetone, m. p. 44° ; benzaldehyde, m. p. 107° ; salicylaldehyde, m. p. 148° ; rhamnose and dextrose (gelatinous products). 2 : 4 : 6-Trichlorophenylhydrazones of rhamnose, m. p. $87-88^\circ$; dextrose, m. p. 174° ; galactose, m. p. 135° ; laevulose, m. p. 155° ; benzaldehyde, m. p. 90° ; acetone, m. p. 58° (formed in dilute aqueous solution), and 2-chloro-4-nitrophenylhydrazones of rhamnose, m. p. 135° ; dextrose, m. p. 130° ; galactose, m. p. 194° ; laevulose, m. p. $185-5^\circ$; acetone, m. p. 121.5° (also obtained with dilute solutions), and benzaldehyde, m. p. 156° , are described. The 2 : 4-dichlorophenylosazones of rhamnose, m. p. 155° ; dextrose, m. p. 209° ; galactose, m. p. 150° ; laevulose, m. p. 209° , and the 2-chloro-4-nitrophenylosazones of rhamnose, m. p. 190° ; dextrose, m. p. 210° ; galactose, m. p. 205° , and laevulose, m. p. 210° , are obtained in presence of 30% acetic acid. 2 : 4 : 6-Trichlorophenylosazones could not be obtained.

H. BURTON.

Preparation of organic reagents in the analytical laboratory. I. Diphenylcarbazine and diphenylcarbazone. K. H. SLOTTA and K. R. JACOBI (Z. anal. Chem., 1929, 77, 344-348).—To prepare diphenylcarbazine, 14 g. of finely-divided carbamide and 40 g. of freshly-distilled phenylhydrazine are heated at 155° for 2-25 hrs.; 250 c.c. of hot 96% alcohol are then added and the solution is boiled for about 15 min. After filtering and cooling in a freezing mixture the crystalline mass is collected, washed with ether, and air-dried. By evaporation of the mother-liquor a further yield may be obtained, bringing the total yield to 89%, calculated on the phenylhydrazine used. Diphenylcarbazone is prepared by rapidly adding, with stirring, 20 g. of finely-powdered potassium hydroxide, followed by 20 c.c. of 3% hydrogen peroxide solution, to 200 c.c. of a boiling alcoholic solution of 24 g. of diphenylcarbazine. After 5 min., 250 c.c. of 2*N*-sulphuric acid solution are added and the resulting pasty mass is diluted with 1500 c.c. of water, cooled, and filtered. The material should be recrystallised from 70-75 c.c. of alcohol, giving a yield of 50% of the theoretical.

H. F. GILLBE.

Action of magnesium alkyl and aryl halogen compounds on azodibenzoyl and benzoylazo-benzene. R. STOLLE and W. REICHERT (J. pr. Chem., 1929, [ii], 122, 344-349).—By the action of the appropriate Grignard reagent on azodibenzoyl a series of substituted derivatives of *s*-dibenzoylhydrazine has been prepared in accordance with the scheme



$\longrightarrow \text{COPh}\cdot\text{NR}\cdot\text{N}\cdot\text{CPh}\cdot\text{OH} \longrightarrow \text{COPh}\cdot\text{NR}\cdot\text{NH}\cdot\text{CPh}$, where R is ethyl, *n*-propyl (30% yield), isopropyl (poor yield), isobutyl, isoamyl (40%), phenyl (30%), and benzyl (30%). Similarly, from benzoylazo-benzene a 50% yield of *NN*-diphenyl-*N'*-benzoylhydrazine is obtained, whilst the action of magnesium phenyl bromide on methyl azodicarboxylate furnishes a poor yield of methyl phenylhydrazine-

s-dicarboxylate, m. p. 116°, identical with a specimen obtained in a similar manner to that previously used for the ethyl ester (Rupe and Labhardt, A., 1899, i, 356).

J. W. BAKER.

Relationship between quinonehydrazones and *p*-hydroxyazo-compounds. VI. *p*-Quinonedihydrazones from *p*-hydroxyazo-compounds. W. BORSCHKE, W. MÜLLER, and C. A. BODENSTEIN (Annalen, 1929, 472, 201—216).—Oxidation of *p*-anisylsemicarbazide with chromic oxide in acetic acid solution gives 4-methoxybenzeneazofornamide (I), $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{CO} \cdot \text{NH}_2$, m. p. 157° (decomp.), which on treatment with semicarbazide hydrochloride in aqueous methyl alcohol affords *p*-benzoquinone-disemicarbazone, m. p. 251° (decomp.) (cf. A., 1904, i, 1056). With 2:4-dinitro- and 2-nitro-4-cyanophenylhydrazines in presence of methyl-alcoholic hydrochloric acid I furnishes *p*-benzoquinonesemicarbazone-2:4-dinitrophenylhydrazone (II), m. p. 242° (decomp.), and *p*-benzoquinonesemicarbazone-2-nitro-4-cyanophenylhydrazone, decomp. about 240°, respectively. Treatment of I with *p*-nitrophenylhydrazine in absence of hydrochloric acid causes reduction to *p*-anisylhydrazofornamide, and similar treatment of *p*-bromobenzenazofornamide gives *p*-bromophenylsemicarbazide. 4-Phenoxybenzeneazofornamide has m. p. 165°. 2:4:6-Trinitro-4'-hydroxyazobenzene and 2:4-dinitrophenylhydrazine (III) react in aqueous methyl-alcoholic hydrochloric acid solution yielding *p*-benzoquinone-2:4-dinitrophenylhydrazone-2:4:6-trinitrophenylhydrazone, m. p. 204—206°. Similarly, 2:4-dinitro-4'-hydroxyazobenzene (IV) and III give *p*-benzoquinonebis-2:4-dinitrophenylhydrazone, m. p. 267—268° (decomp.), also formed from *p*-benzoquinone and III, by the action of hot, dilute hydrochloric acid on IV, and by the action of III on the benzoate, m. p. 164°, and methyl ether, m. p. 177—178°, of IV in presence of hydrochloric acid. Semicarbazide hydrochloride and phenylsemicarbazide hydrochloride convert IV into II and *p*-benzoquinonephenylsemicarbazone-2:4-dinitrophenylhydrazone, m. p. 248—250° (decomp.) (obtained also from 4-hydroxybenzeneazofornanilide and III), respectively, whilst with 2-nitrophenylhydrazine hydrochloride *p*-benzoquinone-2-nitrophenylhydrazone-2:4-dinitrophenylhydrazone, m. p. 236—238° (decomp.) (formed also from 2-nitro-4'-hydroxyazobenzene and III), results. From the appropriate 4-hydroxyazobenzene derivative and the hydrochloride of III the following were prepared: *p*-toluquinonebis-2:4-dinitrophenylhydrazone, m. p. 269°; *p*-toluquinone-2-nitrophenylhydrazone-2:4-dinitrophenylhydrazone, m. p. 246—247° (decomp.); thymoquinone-2-nitrophenylhydrazone-2:4-dinitrophenylhydrazone, m. p. 258—260°; *p*-benzoquinone-3- and -4-nitrophenylhydrazone-2:4-dinitrophenylhydrazone, m. p. 223—225° and 215° (decomp.), respectively. Diazotised anthranilic acid condenses with phenol forming 4-hydroxyazobenzene-2'-carboxylic acid, m. p. 206—207°, which with methyl sulphate gives 4-methoxyazobenzene-2'-carboxylic acid, m. p. 170—172° (methyl ester, m. p. 105—106°). Both these acids react with III in methyl-alcoholic hydrochloric acid solution yielding *p*-benzoquinone-2:4-dinitrophenylhydrazone-2-carboxyphenylhydrazone, m. p. 226—228°.

4-Hydroxyazobenzenes react, therefore, as *p*-benzoquinonehydrazones. Elimination of the methyl group from the 4-methoxy-derivatives occurs presumably through an intermediate of the type $\text{NHR} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OMeCl}$; this loses methyl chloride, yielding a *p*-benzoquinonehydrazone. *p*-Benzoquinonedihydrazones are formulated with a symmetrical structure (cf. Thiele and Barlow, A., 1899, i, 47).

H. BURTON.

Manufacture of water-insoluble azo-dyes [from new 6-acylamino-*m*-4-xylidines]. I. G. FARBENIND. A.-G.—See B., 1929, 637.

Nitrosation of phenols. VI. *m*-Chlorophenol. H. H. HODGSON and A. KERSHAW (J.C.S., 1929, 1553—1557).—The reported existence of 3-chlorobenzoquinone-4-oxime in stereoisomeric forms (Hodgson and Moore, *ibid.*, 1923, 123, 2499) is fallacious, and differences described are due to impurity.

The mechanism of the conversion of 3-chloro-4-nitrosophenol, m. p. 133°, into 3-chlorobenzoquinone-4-oxime is discussed from the point of view of electronic theory, the efficiency of both hydrogen and hydroxyl ions in promoting the change being satisfactorily accounted for. The action of hydriodic acid on nitroso-compounds (cf. Earl, Ellsworth, Jones, and Kenner, A., 1928, 1352) is also considered. The 3-chlorobenzoquinone-4-oxime has m. p. 184° (decomp.) (cf. Hodgson and Moore, *loc. cit.*) when obtained in either acid or alkaline media; the mol. wts. of the products and the parent nitrosophenol, determined cryoscopically in phenol and in naphthalene, are normal; the benzoate, m. p. 189.5°, and the methyl ether, m. p. 113°, are described.

The effect of the 3-chlorine atom is probably responsible for the slowness of the change of 3-chloro-4-nitrosophenol into the corresponding oxime, which is in striking contrast to the rapid action of hot acids on *p*-nitrosophenol; the behaviour of 3-bromo- and 3-iodo-nitrosophenols is similar. It is suggested that co-ordination of the chlorine atom, or its direct electronic effect, or steric hindrance, or some association of these influences, may be responsible for the apparent impossibility of reversion to the nitroso-compound, and for the non-existence of geometrical isomerides.

The preparation and properties of 3-chloro-4-nitroanisole, m. p. 60°, and *p*-benzoquinonedioxime 4-methyl ether, m. p. 115°, are described.

C. W. SHOPPEE.

[Preparation of] anisole. G. S. HERS and F. D. HAGER (Organic Syntheses, 1929, 9, 12—14).

[Preparation of] γ -phenoxypropyl bromide. C. S. MARVEL and A. L. TANENBAUM (Organic Syntheses, 1929, 9, 72—73).

Substitution in the benzene ring. 3:4-Dibromo-*o*-anisidine and some of its derivatives. E. BURES and M. SOUCEK (Casopsis Ceskoslov. Lék., 1928, 8, 295—299, 317—325; Chem. Zentr., 1929, i, 1098—1099).—Bromination of *o*-acetanisidine in acetic acid affords 3:4-dibromo-*o*-acetanisidine, m. p. 146°, hydrolysed by potassium hydroxide at 100° in 4 days to 3:4-dibromo-*o*-anisidine, m. p. 103° (hydro-

chloride, decomp. 192°; sulphate, decomp. 159—160°. 3:4-Dibromo-*N*-methyl-*o*-anisidine has b. p. 162°, and the 2-benzamido-compound has m. p. 137—138°. 3:4-Dibromo-2-hydroxyanisole has m. p. 94° (*O*-benzoyl derivative, m. p. 114°; *O*-acetyl derivative, m. p. 90°); 3:4-dibromoanisole, b. p. 127°, 2-chloro-3:4-dibromoanisole, m. p. 98°, 2:3:4-tribromoanisole, m. p. 101°, 3:4-dibromo-2-iodoanisole, m. p. 94°. A. A. ELDRIDGE.

Chaulmoogryl-aminophenols and -benzylamine. I. DE SANTOS and A. P. WEST (Phil. J. Sci., 1929, 38, 445—449).—Treatment of chaulmoogrylamine with appropriate chlorophenols or benzyl chloride in the presence of metallic copper gave: *chaulmoogryl-o*-, m. p. 104.9—105.9°; -*m*-, m. p. 105.9—108°; and -*p*-aminophenol, m. p. 97.8—101.9°; *chaulmoogrylbenzylamine*, m. p. 92.7—95.8°.

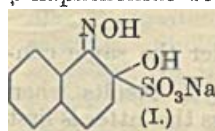
R. J. W. LE FÈVRE.

Reactions of a mixture of ethyl ether, acetyl bromide, and naphthol. H. L. BASSETT and K. F. TAYLOR (J.C.S., 1929, 1568—1578).—The reaction between acetyl chloride and various alcohols in ethereal solution has been examined, and found to be bimolecular, the values obtained for the velocity coefficients agreeing with the known order of reactivity of the alcohols used. With the naphthols, acetyl chloride reacted too slowly, and acetyl bromide, which was shown not to react with the solvent under the conditions used, gave the following results. The primary and most rapid reaction consists in the formation of naphthyl acetate, but secondary reactions quickly set in, which involve the solvent, and decompose the naphthyl acetate first formed. The reactions taking place may be represented by the equations: (1) $C_{10}H_7\cdot OH + AcBr = C_{10}H_7\cdot OH\cdot AcBr$; (2) $C_{10}H_7\cdot OH\cdot AcBr = C_{10}H_7\cdot OAc + HBr$; (3) $2HBr + Et_2O = 2EtBr + H_2O$; (4) $C_{10}H_7\cdot OAc + H_2O = C_{10}H_7\cdot OH + AcOH$; (5) $2AcOH + Et_2O = 2AcOEt + H_2O$, which are in the main consecutive, and are given in order of their velocities, (1) being the most rapid. The foregoing equations, and the evidence on which they are based, are discussed *seriatim*, and it is shown that no equilibrium is ever reached, but that the reactions gradually become immeasurably slow. The final distribution of the acetyl radical and bromine, obtained in experiments with 1 mol. each of the three reactants, is tabulated, and small differences arising from the use of α - or β -naphthol are accounted for. The experimental procedure and numerical results are described in detail, for which the original should be consulted. C. W. SHOPPEE.

Mechanism of hydrogen sulphite reaction with naphthol derivatives. N. N. VOROSHOV [with A. G. KASATKIN] (J. Russ. Phys. Chem. Soc., 1929, 61, 483—496).—Sulphur dioxide is passed through a 25% solution of the disodium salt of β -naphthol-1-sulphonic acid; on saturation, crystals of disodium 2-hydroxy-1:2-dihydronaphthalene-1:2-disulphonate separate. The latter substance undergoes hydrolytic dissociation in dilute solutions, sulphurous acid and the monosulphonic acid being formed. This hydrolysis amounts to 0.89% in 0.1*N*- and to 50.17% in 0.0005*N*-solutions. Hydroxyl ions augment this hydrolysis, which attains 78.8% in 0.01*N*-solutions of

the disulphonate and of sodium hydrogen carbonate. The disulphonate is stabilised by hydrogen ions, dissociation amounting to only 4.64% in the presence of 0.001*N*-hydrochloric acid. R. TRUSZKOWSKI.

Action of sodium hydrogen sulphite on nitroso-naphthols. N. N. VOROSHOV and S. V. BOGDANOV (J. Russ. Phys. Chem. Soc., 1929, 61, 497—514).—Sodium 2-hydroxy-1-nitroso-1:2-dihydronaphthalene-2-sulphonate (I) is prepared by the addition of saturated sodium hydrogen sulphite solution to sodium 1-nitroso- β -naphthoxide solution, and similar compounds are



obtained using the methyl ether of the latter substance and 2-hydroxy-1-nitrosodiphenylmethane-6-sulphonic acid. β -Nitroso- α -naphthol

can be separated from the α -nitroso-isomeride by the formation of a soluble compound of the latter with sodium hydrogen sulphite, the α -nitroso-form being then regenerated by the action of alkalis. R. TRUSZKOWSKI.

β -Naphthyl sulphide as a by-product in preparation of β -naphthonitrile. N. A. LANGE and H. S. HAUPT (J. Amer. Chem. Soc., 1929, 51, 2277—2278).—Crude sodium naphthalene-2-sulphonate contains di- β -naphthylsulphone, which is reduced by fusion with sodium cyanide to β -naphthyl sulphide. This is the by-product obtained by Colver and Noyes (A., 1921, i, 409) in the alkaline hydrolysis of β -naphthonitrile prepared by this method.

H. E. F. NOTTON.

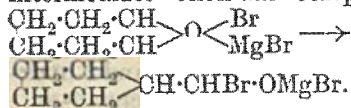
[Preparation of] phenyl- β -hydroxy- α -naphthylmethylamine. M. BETTI (Organic Syntheses, 1929, 9, 60—63).

Derivatives of 2-hydroxyfluorene. C. RUIZ (Anal. Asoc. Quím. Argentina, 1928, 16, 170—186).—The course of nitration and coupling of diazo-compounds with 2-hydroxyfluorene is analogous to that with 4-hydroxydiphenyl under the same conditions. 2-Hydroxyfluorene is prepared in 80% yield by adding fluorenc-2-diazonium chloride solution slowly to boiling dilute sulphuric acid. Nitration in acetic acid (cf. Raiford and Colbert, A., 1925, i, 808) yields 1(or 3)-nitro-2-hydroxyfluorene, m. p. 145.6°, which is reduced by sodium hyposulphite to 1(or 3)-amino-2-hydroxyfluorene, m. p. 246° (acetyl derivative, m. p. 215°). The aminophenol cannot be diazotised. It yields phthalic acid on oxidation. Nitration of 2-hydroxyfluorene under vigorous conditions (cf. García Banús and Guiteras, A., 1923, i, 770) yields 1:3-dinitro-2-hydroxyfluorene, m. p. 174°, and the 1:3:7-trinitro-compound, m. p. 233°. Nitration of 2-*p*-toluenesulphonyloxyfluorene, m. p. 174°, in acetic acid and hydrolysis of the product (cf. Bell and Kenyon, A., 1927, 145) yields 7-nitro-2-hydroxyfluorene, m. p. 219—220° (Novelli, Revista Farm., 1927, 68, 244). This is reduced by aluminium amalgam to 7-amino-2-hydroxyfluorene, m. p. 291—292° (decomp., darkening at 190°), which is oxidised by dichromate and sulphuric acid to (?):2:7-fluorenoquinone. The action of nitrous acid on 2-hydroxyfluorene yields only traces of the 1(or 3)-nitro-compound. 1(or 3)-Benzeneazo-2-hydroxyfluorene is obtained by coupling diazotised aniline with 2-hydroxy-

fluorene and is reduced to 1(or 3)-amino-2-hydroxy-fluorene.

R. K. CALLOW.

Conversion of a six-ring into a five-ring with magnesium bromide etherate. P. BEDOS (Compt. rend., 1929, 189, 255—257).—By the action of magnesium bromide etherate (2 mols.) in dry ether, benzene, or toluene on cyclohexene oxide and decomposition of the product with water a 34% yield of cyclopentanaldehyde is obtained, the formation of an intermediate oxonium compound being assumed:



Under the same conditions only a trace of the aldehyde results when 1-chlorocyclohexan-2-ol is used unless the latter is first treated with magnesium ethyl bromide to convert it into the magnesium alcoholate. In this case a 40% yield of cyclopentanaldehyde is obtained. The reaction also proceeds at the ordinary temperature and it is concluded that the transition from a six- to a five-ring is always effected through the intermediate formation of cyclopentanaldehyde (cf. Bedos and Ruyer, this vol., 558).

J. W. BAKER.

Esters of cyclohexane-1:4- and -1:3-diols (quinitol and resorcitol). L. PALFRAY and B. ROTHSTEIN (Compt. rend., 1929, 189, 188—189).—The following esters of quinitol have been prepared by the action of the acid chlorides in pyridine and chloroform: trans-dipropionate, m. p. 75.5—76.5°; cis-dipropionate, m. p. 39.5—40°; diisovalerate (mixture of isomerides), d_4^{20} 0.9867, n_D^{20} 1.4477; trans-cinnamate, m. p. 189°; cis-cinnamate, m. p. 122°. The following esters of cyclohexane-1:3-diol are also described: diacetate, b. p. 130.5—131.5°/15 mm., d_4^{20} 1.0790, n_D^{20} 1.4494; dipropionate, b. p. 154°/15 mm., d_4^{20} 1.0355, n_D^{20} 1.4478; diisovalerate, b. p. 159—160°/6 mm., d_4^{20} 0.9806, n_D^{20} 1.4458; di(phenylacetate), b. p. 215—217°/1 mm., d_4^{20} 1.1235, n_D^{20} 1.5390; di(ethyl-oxalate), b. p. 187°/2 mm., d_4^{20} 1.1988, n_D^{20} 1.4604; trans-dibenzoate, m. p. 122.5°; cis-dibenzoate, m. p. 65.5°; trans-di-p-nitrobenzoate, m. p. 176.5°; cis-di-p-nitrobenzoate, m. p. 154—154.5°. By the reaction of 1:3-di(chloromethoxy)cyclohexane with Grignard reagents the following resorcitol ethers are obtained: dipropyl, b. p. 113°/15 mm., d_4^{20} 0.9006, n_D^{20} 1.4430; diisobutyl, b. p. 160—162°/16 mm., d_4^{20} 0.9006, n_D^{20} 1.4489; dibenzyl, b. p. 205—207°/1 mm., d_4^{20} 1.0739, 1.5440.

R. K. CALLOW.

Reaction of resorcinol and a new coloured indicator. L. BEY and M. FAULLEBIN (Compt. rend., 1929, 188, 1679—1681).—The blue colour produced by the action of dilute ammonia on resorcinol in the presence of various cations (Cd^{++} , Zn^{++} , Cu^{++} , Pb^{++} , Sn^{++++}) results from oxidation, catalysed by the foregoing cations, which all afford the same colour. The coloured substance appears to be a loose compound of a colouring matter with one or more of the substances present in solution. The coloured substance, isolated by acidification and extraction with an organic solvent (amyl alcohol), acts as an indicator, being red in acid solution and turning green at p_H 9.8°; it is transformed irreversibly by concentrated ammonia solution into a second substance, which also functions

as an indicator, blue in alkaline and rose-red in acid media, the colour change occurring in the interval p_H 5.9—4.3; the substance is neither a lacmoid nor a lacmosol.

C. W. SHOPPEE.

Hoesch syntheses with thiocyanobenzene. W. BORSCHKE and J. NIEMANN (Ber., 1929, 62, [B], 1743—1745).—Thiocyanobenzene and resorcinol are converted by hydrogen chloride and zinc chloride in presence of ether into 2:4-dihydroxybenziminiothiophenyl ether hydrochloride, m. p. (hydrated) 80—82° (anhydrous) decomp. 222°. The free base, m. p. 150—152°, and its triacetyl derivative, m. p. 115°, are described. Orcinol similarly gives the compound $(\text{OH})_2\text{C}_6\text{H}_2\text{Me}(\text{SPh})\cdot\text{NH}_2\cdot\text{HCl}$, m. p. 220° after softening. 2:4:6-Trihydroxybenziminiothiophenyl ether hydrochloride, m. p. 232—233° (decomp.), the free base, and the tetra-acetyl compound, m. p. 96—98°, are described. The hydrochloride is hydrolysed by N-hydrochloric acid to thiophenol and 2:4:6-trihydroxybenzamide ($+\text{H}_2\text{O}$), decomp. 255° after softening.

H. WREN.

New sulphonephthaleins. W. C. HARDEN and N. L. DRAKE (J. Amer. Chem. Soc., 1929, 51, 2278—2279).—Tetrabromo-phenoltetrabromo-sulphonephthalein (this vol., 441), for which the name "tetrabromophenol-blue" is proposed, is a better indicator than bromophenol-blue, since it shows a colour change from yellow to blue, which is not obscured by dichromatism.

H. E. F. NOTTON.

[Preparation of] phloroglucinol. H. T. CLARKE and W. W. HARTMAN (Organic Syntheses, 1929, 9, 74—76).

Constitution of "olivil" from olive resin. B. L. VANZETTI (Monatsh., 1929, 52, 163—168).—Olivil is obtained in above 50% yield by extraction of olive resin with boiling ethyl or methyl alcohol and crystallises with 1 mol. of alcohol. By heating the crystals in carbon dioxide or hydrogen, olivil is obtained as a glassy, amorphous solid, m. p. 66—70°, crystallising anhydrous, m. p. 142.5°, from acetone, trimethylcarbinol, and benzyl alcohol. The following derivatives of olivil are described: hydrate, m. p. about 105°; methyl alcoholate, m. p. about 97°; ethyl alcoholate, m. p. about 120°; n-propyl alcoholate, m. p. about 104°; isopropyl alcoholate, m. p. about 101.5°; and allyl alcoholate, m. p. 100—105°. In saturated aqueous solution, olivil has $[\alpha]_D^{20}$ —127°. It dissolves readily in strong alkalis, from which it is precipitated by carbon dioxide. Olivil contains two phenolic hydroxyl and two methoxy-groups. Dry distillation yields cresol, whilst concentrated aqueous alkali hydroxide gives vanillin; it dissolves in sulphuric acid with an intense reddish-brown colour and is precipitated on addition of water. Warming with dilute organic acids, especially acetic and formic acids, causes complete conversion into the isomeric isoolivil, m. p. 167°, whilst warming with dilute mineral acids (2:1000) results in complete resinification. Potassium permanganate in boiling acetic acid solution gives an almost quantitative yield of acetylvanillic acid. The following alkylated derivatives of olivil are readily prepared, exhibit greater stability than the parent substance, and are not convertible into the isomeric isoolivil derivatives: dimethyl-, m. p. 156°; diethyl-,

m. p. 182°; *dipropyl*-, m. p. 133.5°; *dibenzyl*-, m. p. below 150°; *ethyl*-, m. p. 145°, and *methyl-olivil*, m. p. 238°. Isomeric monoalkylated olivils could not be prepared, the products, m. p. 169°, obtained by the ethylation of methyl- and methylation of ethyl-olivil being identical; hence the molecule possesses a symmetrical structure. Oxidation of dimethylolivil with potassium permanganate (11—12 atoms of oxygen) in alkaline solution at 100° gave about equal quantities of veratric and veratroylformic acids and also some oxalic acid; ozone had no action. Dimethyl-olivil and bromine gave two substitution products, a *monobromo*-, m. p. 128°, and a *dibromo-dimethyl-olivil*, m. p. 132°; the latter is oxidised by potassium permanganate to 3-bromoveratric and 3-bromoveratroylformic acids. It is concluded that in olivil two vanillin residues are connected by means of a six-carbon chain thus: $\text{O} < \text{C}_3\text{H}_4(\text{OH}) \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{OMe} \cdot \text{C}_3\text{H}_4(\text{OH}) \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{OMe}$.

isoOlivil in saturated aqueous solution has $[\alpha]_D^{25} +352^\circ$, and gives the following alkylated derivatives: *dimethyl*-, m. p. 184.5°; *diethyl*-, m. p. 179.5°; *methyl*-, $2\text{H}_2\text{O}$, m. p. about 150°, and *ethyl-isoolivil*, m. p. about 150°. In contradistinction to olivil, it yields two isomeric *methylethyl* derivatives, m. p. 168° and 192°, respectively. No conversion of *isoolivil* into olivil or its derivatives has yet been observed.

A. I. VOGEL.

Condensation products from *p*-halogenated phenols and aldehydes. [di-*o*-hydroxydi- and -tri-phenylmethane derivatives]. M. WEILER, B. WENK, and H. STÖTTER, Assrs. to I. G. FARBEIND. A.-G.—See B., 1929, 636.

Salts of β -naphtholsulphonic acids, their manufacture and separation. M. L. CROSSLEY and G. S. SIMPSON, Assrs. to CALCO CHEM. CO.—See B., 1929, 637.

Manufacture of arylaminonaphthalene derivatives. I. G. FARBEIND. A.-G.—See B., 1929, 590.

Photochemical oxidising power of cholesterol and ergosterol after irradiation with mercury arc light. E. ROUSSEAU (Compt. rend. Soc. Biol., 1928, 99, 1844—1847; Chem. Zentr., 1929, i, 849).—The sterols and their aqueous and alcoholic solutions differ in their oxidising power towards iodide, but the reaction admits of determination whether or not the sterol has been irradiated. Mercury radiation of short wave-length is most effective in producing oxidation.

A. A. ELDRIDGE.

Transformations of ergosterol. A. WINDAUS and E. AUHAGEN (Annalen, 1929, 472, 185—194; cf. A., 1927, 557).—When ergosterol is heated with finely-divided nickel at 225° in an atmosphere of carbon dioxide a mixture of *ergostadienone* (I), $\text{C}_{27}\text{H}_{42}\text{O}$, m. p. 182—183°, $[\alpha]_D^{25} +2^\circ$ (all rotatory powers are in chloroform) (*oxime*, decomp. 240—250°), and an impure isomeric *ketone* (II) (termed *u-ergostadienone*), results. Reduction of I with sodium and alcohol gives dihydroergosterol, whilst II yields *u-ergostadienol*, $\text{C}_{27}\text{H}_{44}\text{O}$, m. p. 170°, $[\alpha]_D^{25} +42^\circ$, purified through its *acetate* (III), m. p. 128°, $[\alpha]_D^{25} +58^\circ$. Reduction of III with hydrogen in presence of platinum and acetic acid at 60° affords the *acetate* (IV), m. p. 96°, $[\alpha]_D^{25} +39^\circ$, of *u-ergostanol*, $\text{C}_{27}\text{H}_{48}\text{O}$,

m. p. 184°, $[\alpha]_D^{25} +34^\circ$. These *u*-alcohols are not precipitated by digitonin. Similar treatment of dehydroergosterol (A., 1928, 1372) with nickel gives a mixture of *ergostatrienone-D* (V), $\text{C}_{27}\text{H}_{40}\text{O}$, m. p. 199—200°, $[\alpha]_D^{25} +56^\circ$ (*oxime*, decomp. about 245°), and the isomeric *u-ergostatrienone* (VI), m. p. 130—131°, $[\alpha]_D^{25} +53^\circ$. Etheral solutions of V and VI show absorption maxima at about 240° and 250 μ , respectively. Reduction of V with sodium and alcohol yields *ergostatrienol-D*, m. p. 165—166°, $[\alpha]_D^{25} +22^\circ$ (*acetate*, m. p. 171°, $[\alpha]_D^{25} +17.5^\circ$), precipitable by digitonin and formed also by the dehydrogenation of dihydroergosterol with mercuric acetate in alcoholic solution. Similar reduction of VI affords *u-ergostatrienol*, $\text{C}_{27}\text{H}_{42}\text{O}_2$, m. p. 154°, $[\alpha]_D^{25} +88^\circ$, not precipitable by digitonin. Catalytic reduction of the *acetate*, m. p. 151°, $[\alpha]_D^{25} +103^\circ$, of the last-named substance yields IV. The *isoergosterol* of Reindel, Walter, and Rauch (A., 1927, 241) is termed *ergosterol-B*, and the isomeride described by Windaus and Rygh (Nachr. Ges. Wiss. Gottingen, 1928, 212) is named *ergosterol-C*.

H. BURTON.

Transformations of ergosterol peroxide. A. WINDAUS, W. BERGMANN, and A. LUTTRINGHAUS (Annalen, 1929, 472, 195—201).—When ergosterol peroxide (I), $\text{C}_{27}\text{H}_{42}\text{O}_3$ (Windaus and Brunken, A., 1928, 424), is distilled at 180—215°/0.0007 mm. an isomeric *substance* (II), m. p. 159—160°, $[\alpha]_D^{25} +55.5^\circ$ (all rotatory powers in chloroform), is obtained. This does not give any peroxide reactions, contains one hydroxyl group (Zerewitinov determination), a keto-group, and one double linking (perbenzoic acid titration, whereby the *oxide*, $\text{C}_{27}\text{H}_{42}\text{O}_4$, m. p. 218°, $[\alpha]_D^{25} +94.6^\circ$, results). The *monoacetate*, m. p. 168—169°, $[\alpha]_D^{25} +41^\circ$, and the *oxime*, m. p. 260° (decomp.), are described. Magnesium methyl iodide converts II into the tertiary *alcohol*, $\text{C}_{28}\text{H}_{46}\text{O}_3$, m. p. 190°, whilst reduction with hydrogen in presence of palladium-black and alcohol gives the saturated *compound*, $\text{C}_{27}\text{H}_{44}\text{O}_3$, m. p. 152—153°, $[\alpha]_D^{25} +94.6^\circ$ (*monoacetate*, m. p. 161°, $[\alpha]_D^{25} +74.6^\circ$). Reduction of I with zinc dust and alkali furnishes the trihydric *alcohol* (III), $\text{C}_{27}\text{H}_{44}\text{O}_3$, $[\alpha]_D^{25} -13.7^\circ$ in pyridine (cf. Windaus and Linsert, A., 1928, 1372). Energetic reduction of III with sodium and alcohol gives dihydroergosterol, whilst reduction with hydrogen in presence of palladium-black and alcohol yields *ergostendiol* (IV), $\text{C}_{27}\text{H}_{46}\text{O}_2$, m. p. 234°, $[\alpha]_D^{25} +14.7^\circ$ [the *monoacetate* (V), m. p. 227°, $[\alpha]_D^{25} +14.7^\circ$, contains one double linking (perbenzoic acid titration)]. This furnishes an additive compound with digitonin, and distils unchanged in a high vacuum. Reduction of V with hydrogen in presence of platinum-black and acetic acid gives *allo- α -ergostanyl acetate*. Similar reduction of I and III affords *allo- α -ergostanol*, whilst with a palladium catalyst I yields IV. H. BURTON.

Reaction between magnesium phenyl bromide and phenylglycide. D. R. BOYD and G. J. C. VINEALL (J.C.S., 1929, 1622).—The reaction mixture from phenylglycide and etheral magnesium phenyl bromide is freed from solvent, heated at 100° until frothing occurs, and then decomposed with water. Removal of volatile products by steam distillation and subsequent acidification of the residue affords

75% of the theoretical amount of γ -phenoxy- α -phenylisopropyl alcohol (I), m. p. 92.5°. When the heating at 100° is not carried out the yield of I is negligible and an oil (probably α -bromo- γ -phenoxyisopropyl alcohol), b. p. 165°/15 mm., is isolated from the steam distillate. Phosphorus trichloride converts I into a product which with ice gives an ester of phosphorous acid, soluble in ammonia and less stable than the corresponding derivative of $\alpha\gamma$ -diphenoxyisopropyl alcohol (Boyd, J.C.S., 1901, 79, 1221).

H. BURTON.

Amino-alcohols. I. Phenyl- and *p*-tolyl-propylamine. W. H. HARTUNG and J. C. MUNCH (J. Amer. Chem. Soc., 1929, 51, 2262—2266).—Phenyl α -oximinoethyl ketone is hydrogenated almost quantitatively in presence of hydrogen chloride (3 mols.) and palladised charcoal (cf. this vol., 184) to α -hydroxy- α -phenyl- β -propylamine hydrochloride. *p*-Tolyl α -oximinoethyl ketone, m. p. 125°, is similarly reduced to the hydrochloride, m. p. 205°, of α -hydroxy- α -*p*-tolyl- β -propylamine, m. p. 112°, which is converted by nitrous acid into a product which after, but not before, distillation, gives with semicarbazide the semicarbazone of tolyl ethyl ketone. The pharmacological properties of the amino-alcohols are compared with those of ephedrine.

H. E. F. NOTTON.

Synthesis of ephedrine and related amino-alcohols. A. SKITA and F. KEIL (Z. angew. Chem., 1929, 42, 501—503).—See this vol., 808.

Preparation of β -methylamino- α -phenyl-*n*-propyl alcohol. W., K., L., W., and F. MERCK.—See B., 1929, 622.

Elimination of the amino-group from tertiary amino-alcohols. VII. Wandering of hydrocarbon radicals in derivatives of the optically active desylamines. A. MCKENZIE and A. K. MILLS (Ber., 1929, 62, [B], 1784—1794; cf. this vol., 317).—The exclusive wandering of the phenyl group during the de-amination of *l*- β -amino- $\alpha\beta$ -diphenyl- α -methylethanol is established by the optical inactivity of the product of the change. The product derived from *l*- β -amino- $\alpha\beta$ -diphenyl- α -1-naphthylethanol contains a small amount of *l*-1-naphthyldeoxybenzoin, but the migratory tendency of the phenyl group is much greater than that of the 1-naphthyl residue. Similarly, the action of nitrous acid on *d*- β -amino- $\alpha\beta$ -diphenyl- α -anisylethanol affords anisyl diphenylmethyl ketone containing a very small proportion of *d*-anisyldeoxybenzoin. Steric factors appear to affect the migratory tendencies of the aryl groups.

l- β -Amino- $\alpha\beta$ -diphenyl- α -methylethanol, m. p. 73—74°, feebly laevorotatory in ethyl alcohol, is obtained by the addition of *l*-desylamine hydrochloride to magnesium methyl iodide; the hydrochloride has m. p. 266—267°, $[\alpha]_{D}^{25} + 68^\circ$ in methyl alcohol, $[\alpha]_{D}^{25} + 56^\circ$ in methyl alcohol (amongst other values). The *l*-alcohol is also obtained by resolution of the *r*-alcohol by *d*-camphorsulphonic acid in aqueous solution. *d*-Desylamine hydrochloride and magnesium 1-naphthyl bromide yield *l*- β -amino- $\alpha\beta$ -diphenyl- α -1-naphthylethanol, m. p. 177—178°, $[\alpha]_{D}^{17} - 381^\circ$ in acetone [hydrochloride, m. p. 219—220° (decomp.), $[\alpha]_{D}^{15} - 236^\circ$ in ethyl alcohol]. *r*- β -Amino- $\alpha\beta$ -diphenyl- α -anisylethanol, m. p. 161—162° (hydrochloride, m. p. 211—

212°), from *r*-desylamine hydrochloride and magnesium anisyl bromide, is converted by nitrous acid into anisyl diphenylmethyl ketone, m. p. 130—131°, and by boiling dilute hydrochloric acid into anisyldeoxybenzoin, m. p. 87.5—88° (oxime, m. p. 139—140°). *l*- β -Amino- $\alpha\beta$ -diphenyl- α -anisylethanol, m. p. 146—147°, —259° in methyl alcohol (hydrochloride, m. p. 204—206°, $[\alpha]_{D}^{18} - 142^\circ$ in methyl alcohol), is prepared from *d*-desylamine hydrochloride. Resolution of the *r*-alcohol by *d*-camphorsulphonic acid in 96% alcohol affords *d*- β -amino- $\alpha\beta$ -diphenyl- α -anisylethyl *d*-camphorsulphonate, m. p. 220—221° (decomp.), $[\alpha]_{D}^{15} + 97^\circ$ in methyl alcohol, from which the homogeneous *d*-alcohol, m. p. 146—147°, $[\alpha]_{D}^{15} + 259^\circ$ in methyl alcohol, is derived. *l*- β -Amino- $\alpha\beta$ -diphenyl- α -anisylethyl *d*-camphorsulphonate, m. p. 211—213° (decomp.), $[\alpha]_{D}^{15} - 66^\circ$ in methyl alcohol, is isolated from the mother-liquors of the resolution and yields the homogeneous *l*-alcohol. H. WREN.

Reaction between carboxylic halides and organomagnesium halides. H. GILMAN, R. E. FOTHERGILL, and H. H. PARKER (Rec. trav. chim., 1929, 48, 748—751).—Good yields of tertiary alcohols (or their ethylenic dehydration products) are obtained by the action of the Grignard reagent on carboxylic halides in appropriate proportions. Thus by the action of benzoyl chloride (0.2 mol.) on magnesium phenyl bromide (0.5 mol.) at the ordinary temperature and without refluxing the reaction mixture a 91.5% yield of pure triphenylcarbinol is obtained. From the appropriate reagents under similar conditions the following were also prepared: diphenylmethylcarbinol (39% yield), diphenylethylcarbinol (57%) $\alpha\alpha'$ -diphenyl- Δ^4 -butene (84%), phenyldiethylcarbinol (93%), phenyldi-*n*-propylcarbinol (81%). An attempt to prepare secondary alcohols by the action of magnesium phenyl bromide on a suspension of cuprous chloride in dry ether saturated with dry hydrogen chloride and carbon monoxide was unsuccessful, the only products being diphenyl (31%), copper (39%), and some phenol. By the interaction of 0.3 mol. of magnesium phenyl bromide and 0.5 mol. of benzoyl chloride, a 45% yield of benzophenone is obtained, with 32.6% of triphenylcarbinol and 10.8% of diphenyl. J. W. BAKER.

Triarylmethyl carbonates: catalytic decomposition in presence of copper. J. O. HALFORD (J. Amer. Chem. Soc., 1929, 51, 2157—2162).—The formation of triphenylmethyl ether and carbon dioxide from triphenylmethyl carbonate (Gomberg, A., 1913, i, 257) in boiling xylene in presence of copper powder is practically quantitative. Diphenyl- α -naphthylmethyl carbonate, m. p. 228—230° (decomp.), is also completely decomposed, but secondary reactions prevent the isolation of the resulting ether. Diphenyl-*p*-tolylmethyl carbonate, m. p. 193—195° (decomp.), yields a trace of the impure ether. 9-Phenyl-9-fluorenyl carbonate, m. p. 218—220° (decomp.), is not decomposed under these conditions, but with copper in boiling mesitylene it gives carbon dioxide, but no phenylfluorenyl ether. The decomposition of triphenylmethyl carbonate is unimolecular at 139°, and the rate of reaction is increased only to a small extent by increasing the amount of catalyst. The effect

cannot, therefore, be explained by adsorption on a small fraction of the catalyst surface. It is suggested that the catalyst acts by increasing the concentration of some reactive intermediate product, the concentration approaching a limiting value as the amount of catalyst is increased. H. E. F. NOTTON.

Heteropolar compounds of carbon. VII. Formulation of dye salts. W. DILTHEY and R. DINKLAGE (Ber., 1929, 62, [B], 1834—1839).—Since in all the groups of dyes salts free from water can readily be obtained, the introduction of solvent into the formulæ of these compounds is arbitrary. The relationship between colourless and coloured salts is expressed: (I) $R_3C \cdot Cl$ (colourless) \rightarrow (II) $[R_3C]Cl$ (coloured, dipolar) $\xrightarrow{H_2O}$ $[R_3C, C_5H_5N]Cl$ (colourless, dipolar) $\rightarrow R_3C \cdot OH$ (colourless). The coloured (II) and colourless (III) carbonium salts are distinguished by the presence or absence of an unsaturated state of the central carbon atom. It is proposed to term III and II carbonium and carbenium salts, respectively. The following salts are free from water: *malachite-green perchlorate*, $C_{23}H_{25}O_4N_2Cl$; the *perchlorates* of brilliant-green, rhodamine, decomp. about 150°, crystal-violet, decomp. 190—200°, Victoria-blue, decomp. about 260—265°, pararosaniline, methylene-blue, *p*-aminotriphenylcarbinol, m. p. 209—210°; *picrate* of *p*-dimethylaminotriphenylcarbinol, m. p. 169—170°. H. WREN.

Trisubstituted stereoisomeric glycols. A. MCKENZIE, E. M. LUIS, M. TIFFENEAU, and P. WEILL (Bull. Soc. chim., 1929, [iv], 45, 414—422).—In continuation of earlier work (J.C.S., 1910, 97, 473; A., 1924, i, 825; this vol., 317) stereoisomeric glycols, $Ar \cdot CH(OH) \cdot CRR' \cdot OH$, containing the anisyl radical have been obtained by varying the order of introduction of the radicals. *p*-Anisylpropionylcarbinol (*p*-methoxyphenylhydroxymethyl ethyl ketone), b. p. 175°/15 mm., $d_{20} 1.11$, $n_D^{20} 1.531$ (*semicarbazone*, m. p. 220—222°; *oximes*, m. p. 128° and 88—89°), obtained in 48% yield from *p*-methoxyphenylglycollamide and magnesium ethyl bromide, affords with magnesium phenyl bromide 30% of α -*p*-anisyl- β -phenylbutane- $\alpha\beta$ -diol, m. p. 90° (α -isomeride). The β -isomeride, m. p. 112—113°, is similarly prepared (yield 25%) from magnesium ethyl bromide and benzoyl-*p*-anisylcarbinol (*p*-methoxybenzoin), m. p. 100—101° (*semicarbazone*, m. p. 206°; *oxime*, m. p. 132°), obtained in 25% yield from *p*-methoxyphenylglycollamide (cf. Asahina and Terasaka, A., 1923, i, 1023). Similarly, the α -*p*-anisyl- β -ethylhexane- $\alpha\beta$ -diol obtained from magnesium butyl bromide and *p*-anisylpropionylcarbinol has m. p. 74°, whilst magnesium ethyl bromide and *p*-anisylvalerylcarbinol, b. p. 204—208°/24 mm. (from *p*-anisylglycollamide) gives an isomeride, m. p. 65.5—66.5°. *p*-Anisylhydrobenzoin ($\alpha\beta$ -diphenyl- β -*p*-anisylethane- $\alpha\beta$ -diol), m. p. 203—204°, obtained by Tiffeneau and Orekhov (A., 1921, i, 565) from magnesium *p*-anisyl bromide and *r*-benzoin, is isomeric with the compound, m. p. 155—156°, obtained by the action of magnesium phenyl bromide on *p*-methoxybenzoin, m. p. 105.5—106.5° (*semicarbazone*, m. p. 185—186°; *phenylhydrazone*, m. p. 149.5—150.5°; *oxime*, m. p. 136—138°). The

last-named was obtained by adding a mixture of benzaldehyde and *p*-anisaldehyde to an aqueous-alcoholic solution of potassium cyanide (cf. Ekecrantz and Ahlqvist, A., 1908, i, 991); with copper sulphate in aqueous pyridine it affords *p*-methoxybenzil, m. p. 62—63°. Both *p*-anisylhydrobenzoins yield *p*-anisyldeoxybenzoin, m. p. 85—86°, on dehydration with sulphuric acid at 50°. R. BRIGHTMAN.

Halogen-substituted aromatic pinacols: formation of ketyl radicals, $CR_2(OMgI)$. M. GOMBERG and J. C. BAILAR, jun. (J. Amer. Chem. Soc., 1929, 51, 2229—2238).—Quantitative experiments show that *m*- and *p*-halogenated benzophenones are reduced by magnesium and magnesium iodide to the corresponding pinacols (cf. A., 1927, 1190). *o*-Substituted derivatives undergo, in addition, dehalogenation. Reduction proceeds much more slowly than with the ketones previously examined and magnesium bromide cannot be substituted for the iodide. The following benzophenones were prepared: *p*-chloro-*p'*-bromo-, m. p. 150°; *o*-bromo-*p'*-phenyl-, m. p. 88.5°; *m*-bromo-*p'*-phenyl-, m. p. 119°, and *p*-bromo-*p'*-phenyl-, m. p. 188°, also the following derivatives of ethylene glycol: $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-*p*-bromophenyl- (I), $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-*m*-bromophenyl-, tetra-*p*-bromophenyl-, tetra-*m*-bromophenyl-, m. p. 152—156°; $\alpha\beta$ -di-*m*-bromophenyl- $\alpha\beta$ -di-*p*-bromophenyl-, m. p. 160—163°; $\alpha\beta$ -di-*p*-chlorophenyl- $\alpha\beta$ -di-*p*-bromophenyl- (II), m. p. 169°; $\alpha\beta$ -di-*p*-bromophenyl- $\alpha\beta$ -di-*p*-diphenyl- (III), m. p. 158—159°; and $\alpha\beta$ -di-*m*-bromophenyl- $\alpha\beta$ -di-*p*-diphenyl- (IV), m. p. 175°. 1:4-Di-*m*-bromobenzoylbenzene has m. p. 217—220°, and 1:3-di-*m*-bromobenzoylbenzene, m. p. 172°. The iodomagnesium pinacoloxides $[CR^1R^2(OMgI)]_2$, derived from I, II, and III, are colourless in the solid state, but give coloured solutions which do not obey Beer's law (in complete absence of oxygen). This indicates that they are in equilibrium with highly coloured ketyl radicals. The comparative migratory tendencies of the *p*-diphenyl-, *p*-bromophenyl, and *m*-bromophenyl groups in the pinacol-pinacol rearrangement, calculated indirectly, are 16.5:1.0:0 (cf. Montagne, A., 1910, i, 323, 324; Koopal, A., 1915, i, 693). The ratio given by the following experiments is 21.5:1.0:0. The pinacol, III, is converted to the extent of 96.5% by acetyl chloride in benzene and acetic acid into *p*-bromophenyl *p*-bromophenylbis-*p*-diphenylmethyl ketone, m. p. 227°, and to the extent of 4.5% into the isomeric ketone (not isolated). IV is converted almost completely into *m*-bromophenyl *m*-bromophenylbis-*p*-diphenylmethyl ketone, m. p. 202—203°. The pinacols are hydrolysed by alcoholic potassium hydroxide to *p*-bromo-, m. p. 186°, and *m*-bromo-, m. p. 143°, -phenylbis-*p*-diphenylmethanes, respectively, which were synthesised for comparison from *p*-bromo-, m. p. 248—250°, and *m*-bromo-, m. p. 304°, -phenylbis-*p*-diphenylcarbinols. H. E. F. NOTTON.

Geometrical isomerides of tetraphenylbutenediol. J. SALKIND and V. TETERIN (Ber., 1929, 62, [B], 1746—1750).—The individuality of the β -form of tetraphenylbutenediol is established by the determination of the solubilities of it, tetraphenylbutanediol, and tetraphenylbutinenediol in benzene and ethyl alcohol and the possibility that it is a mixture of the

saturated glycol with the acetylenic or α -ethylenic glycol is excluded, since such mixtures are readily separated into their components; this is not the case with a mixture of the β -compound and the saturated glycol. Catalytic hydrogenation of tetraphenylbutenediol in presence of colloidal palladium gives the highest yields of the β -tetraphenylbutenediol, m. p. 195—196°, when the reaction occurs slowly. Treatment of tetraphenylbutenediol with bromine in chloroform yields 3:4-dibromo-2:2:5:5-tetraphenyl-2:5-dihydrofuran, m. p. 198° (cf. Kruglov, unpublished work). Under similar conditions, tetraphenylbutenediol affords tetraphenyltetrahydrofuran, m. p. 182°, and $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -butadiene, m. p. 192—193°. α -Tetraphenylbutenediol gives 2:2:5:5-tetraphenyl-2:5-dihydrofuran and a dibromide, $C_{23}H_{20}Br_2$ or $C_{23}H_{22}Br_2$, m. p. 192°, also obtainable from the furan; when very cautiously treated a (?) pentabromide, m. p. 110°, can be isolated which passes when warmed into the dibromide. β -Tetraphenylbutenediol reacts rather more readily than the α -compound with bromine, giving the dibromide, m. p. 192°. Oxidation of the β -isomeride with permanganate yields benzophenone and benzoic acid. Hydrogenation of either butenediol affords tetraphenylbutanediol, m. p. 202°.

H. WREN.

[Preparation of] *o*-chlorobenzoyl chloride. H. T. CLARKE and E. R. TAYLOR (Organic Syntheses, 1929, 9, 34—35).—*o*-Chlorobenzaldehyde is treated with chlorine.

A. A. ELDRIDGE.

[Preparation of] ammonium hydrogen sulphobenzoate. H. T. CLARKE and E. E. DREGER (Organic Syntheses, 1929, 9, 1—2).

[Preparation of] *o*-sulphobenzoic anhydride. H. T. CLARKE and E. E. DREGER (Organic Syntheses, 1929, 9, 80—82).

[Preparation of] ethyl cinnamate. C. S. MARVEL and W. B. KING (Organic Syntheses, 1929, 9, 38—40).

[Preparation of] hydrocinnamic acid. A. W. INGERSOLL (Organic Syntheses, 1929, 9, 42—45).

Preparation of β -naphthoic acid from magnesium β -naphthyl bromide. H. GILMAN and N. B. ST. JOHN (Rec. trav. chim., 1929, 48, 743—744).—Contrary to the statement of Loevenich and Loeser (A., 1927, 348) magnesium β -naphthyl bromide (prepared in 80% yield) is converted by the action of carbon dioxide in ether-benzene solution into β -naphthoic acid in 62.7% yield.

J. W. BAKER.

Mixed glycerides of salicylic acid. I. II. W. HUMNICKI (Rocz. Chem., 1929, 9, 390—395, 396—401).—See this vol., 811.

Mixed glycerides of salicylic acid. III. W. HUMNICKI and (Mlle.) J. ŁUNKIEWICZ (Rocz. Chem., 1929, 9, 402—409, and Bull. Soc. chim., 1929, [iv], 45, 422—428).—The following mixed aromatic-aliphatic glycerides are prepared by the reaction between the appropriate dichlorohydrin ester and the sodium or silver salt of the acid used: $\alpha\alpha'$ -diisovaleryl β -salicyl, b. p. 237—238°; $\alpha\alpha'$ -dihexoyl β -salicyl, b. p. 256—257°/12 mm.; $\alpha\alpha'$ -dilauryl β -salicyl, m. p. 52—53°; $\alpha\alpha'$ -dimyristyl β -salicyl, m. p. 55—57°;

$\alpha\alpha'$ -disalicyl β -acetyl, m. p. 96—97°, $\alpha\alpha'$ -disalicyl β -isovaleryl, m. p. 52—53°, $\alpha\alpha'$ -disalicyl β -hexoyl, b. p. 268—270°/12 mm., $\alpha\alpha'$ -disalicyl β -lauryl, d^{20}_4 1.118, $\alpha\alpha'$ -disalicyl β -myristyl, m. p. 34—35°, and $\alpha\alpha'$ -disalicyl β -stearyl, m. p. 42—44°. $\alpha\beta$ -Disalicyl α -monochlorohydrin, m. p. 82—83°, is prepared by the addition of salicyl chloride to excess of α -monochlorohydrin.

R. TRUSZKOWSKI.

Reduction of semicarbazones of α -ketonic acids. Semicarbazides substituted in α -position by acid residues. J. BOUGAULT and L. POPOVICI (Compt. rend., 1929, 189, 186—188).—Reduction of the semicarbazones of phenylglyoxylic and phenylpyruvic acids by sodium amalgam yields, respectively, the semicarbazide acids, $CHPh(CO_2H) \cdot NH \cdot NH \cdot CO \cdot NH_2$, m. p. 208°, and $CH_2Ph \cdot CH(CO_2H) \cdot NH \cdot NH \cdot CO \cdot NH_2$, m. p. 164°. The same compounds are obtained by reduction of the diketotriazines formed from the semicarbazones (A., 1914, i, 1004, 1205). The semicarbazide acids reduce Nessler's reagent quantitatively, and are oxidised by iodine and sodium carbonate to the semicarbazones of the decarboxylated aldehydes.

R. K. CALLOW.

Synthesis of tropic acid. M. CHAMBER (Bull. Soc. chim., 1929, [iv], 45, 524—528).—See A., 1928, 884.

Isomeric monohydroxyphenylalanines. I. New synthesis of the *o*- and *m*-isomerides and a comparison of their properties with those of tyrosine. W. P. DICKINSON and P. G. MARSHALL (J.C.S., 1929, 1495—1498).—Glycine anhydride, prepared by a modification of Fischer's method (A., 1906, i, 808), condenses with salicylaldehyde in the presence of anhydrous sodium acetate and acetic anhydride at 125—135° to give 2:5-diketo-3:6-di-*o*-acetoxybenzylidenepiperazine (I), m. p. 272° (yield 15%). A better yield (46%) of piperazine derivative is obtained by replacement of salicylaldehyde by salicylaldehyde methyl ether, obtained by using methyl sulphate and 2*N*-sodium hydroxide at 100° (cf. lit.); 2:5-diketo-3:6-di-*o*-methoxybenzylidenepiperazine (II) has m. p. 268°, and 2:5-diketo-3:6-di-*o*-ethoxybenzylidenepiperazine (III), similarly prepared from salicylaldehyde ethyl ether, has m. p. 205—206°. By reduction of I, II, or III with hydriodic acid (d 1.7) and red phosphorus for 7 hrs., *o*-hydroxyphenylalanine, m. p. 249—250° (cf. Blum, A., 1908, ii, 1052), is obtained. Glycine anhydride also condenses with *m*-hydroxybenzaldehyde in the presence of sodium acetate and acetic anhydride at 135—140° to afford 2:5-diketo-3:6-di-*m*-acetoxybenzylidenepiperazine, m. p. 272° (yield 90%), which by reduction with hydriodic acid (d 1.7) and red phosphorus for 12 hrs. yields *m*-hydroxyphenylalanine, m. p. 275° (cf. Blum, loc. cit.) (yield 62%).

With Folin and Ciocalteu's modified form of Millon's reaction (A., 1927, 892), *o*-hydroxyphenylalanine gives a much less orange shade, intensity roughly 35%, of that produced by tyrosine. *m*-Hydroxyphenylalanine gives a shade (intensity 60%) identical with that given by tyrosine. With Folin's phenol reagent (loc. cit.) by comparison in the colorimeter, and using tyrosine as standard, the following results are obtained: tyrosine, 100%; *o*-hydroxyphenylalanine,

126.5%; *m*-hydroxyphenylalanine, 123.5%; tryptophan, 84.7% (Folin and Ciocalteu give 84.3%).

C. W. SHOPPEE.

Isomerisation of phenylglycidic and phenylhydroxyglycidic esters. M. Tiffeneau and J. Levy (Anal. Assoc. Quim. Argentina, 1928, 16, 144—157).—An attempt has been made to study the relative migratory tendencies of groups in the isomerisation of esters of phenylglycidic acids. When the vapour of ethyl phenylglycidate is passed over infusorial earth at 310° it yields a mixture, b. p. 150—151°/18 mm., n_D^{21} 1.532, of *ethyl formylphenylacetate*, $\text{CHO}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$, and *ethyl phenylhydroxymethyleneacetate*, $\text{CH}(\text{OH})\cdot\text{CPh}\cdot\text{CO}_2\text{Et}$, which are tautomeric. The mixture yields a *semicarbazone* of the first compound, m. p. 162—165°. Treatment of the product with perbenzoic acid in chloroform yields *ethyl β -hydroxy- α -phenylglycidate*, b. p. 165—170°/26 mm., n_D^{15} 1.527. When distilled with zinc chloride this yields ethyl hydrogen phenylmalonate. Similarly, from methyl phenylglycidate may be prepared a mixture of *methyl formylphenylacetate* and *phenylhydroxymethyleneacetate*, b. p. 153—155°/18 mm., n_D^{20} 1.52425, and *methyl β -hydroxy- α -phenylglycidate*, b. p. 160—162°/25 mm. Ethyl α -phenyl- α -methylglycidate yields, when the vapour is passed over heated infusorial earth, *ethyl phenylmethylpyruvate*, b. p. 256—258°/760 mm., n_D^{20} 1.5115 (*semicarbazone*, m. p. 162—163°), which is hydrolysed by alcoholic potassium hydroxide to give hydratropic acid, or by dilute sulphuric acid to give the aldehyde. The mechanism of these two isomerisations is discussed, and it is concluded that the first occurs by migration of the phenyl group from the β - to the α -position.

R. K. CALLOW.

Hydrogenation of unsaturated compounds.
IV. Hydrogenation of conjugated systems:
piperic acid. S. V. Lebedev and A. O. Yakubchik (J. Russ. Phys. Chem. Soc., 1929, 61, 551—560).—See this vol., 442.

Alkoxy-esters of polybasic organic acids [phthalic acid]. R. H. Van Schaack, jun., and R. Calvert, Assrs. to Van Schaack Bros. Chem. Works, Inc.—See B., 1929, 636.

Methylated gallic acids. R. L. Shriner and P. McCutchan (J. Amer. Chem. Soc., 1929, 51, 2193—2195).—5-Bromovanillin is converted through 5-bromoveratraldehyde into 5-bromoveratric acid, hydrolysed by 8% sodium hydroxide and copper powder at 200° to 5-hydroxyveratric acid, m. p. 184—185° (cf. Herzig and Pollak, A., 1902, i, 482) (*acetyl* derivative, m. p. 137—138°). 5-Bromovanillin is simultaneously hydrolysed and oxidised by 8% sodium hydroxide and copper powder at 200—210° to 5-methoxyprotocatechuic acid, m. p. 102—103° (Vogl, A., 1899, i, 697, gives 199—200°), which gives a light green colour with ferric chloride.

H. E. F. NORTON.

Synthesis of substantive dyes of the dicinnamoylmethane group. W. Lampe (Rocz. Chem., 1929, 9, 144—463).—[With R. Nelken.].—The *copper salt* of ethyl α -(4-isopropylcinnamoyl)acetoacetate, m. p. 210°, yields on treatment with sulphuric acid 4-isopropylcinnamoylacetone, m. p. 45—47°

(*copper salt*, m. p. 236—238°), which on further condensation yields *di*-(4-isopropylcinnamoyl)methane, m. p. 136—138°.

[With M. Tokarska-Kozłowska.] *m*-Carbomethoxycinnamic acid, m. p. 151—152°, is converted into the *chloride*, m. p. 68—70°, which is condensed with ethyl sodioacetoacetate to yield *ethyl α -m-carbomethoxycinnamoylacetate*, m. p. 81—83°, which, on treatment with sodium hydroxide, gives *ethyl α -m-hydroxycinnamoylacetate*, m. p. 115—117°, and when heated with water in an autoclave gives *m-carbomethoxycinnamoylacetone*, m. p. 77—79°; this, on hydrolysis with sodium hydroxide, yields *m-hydroxycinnamoylacetone*, m. p. 132—134°. *Sodio-m-carbomethoxycinnamoylacetone* gives on condensation with *m-carbomethoxycinnamoyl chloride* and subsequent hydrolysis *di-m-carbomethoxycinnamoylmethane*, m. p. 120—122°, which on hydrolysis with sodium hydroxide yields *di-m-hydroxycinnamoylmethane*, m. p. 193—195°.

[With C. Sieradzka.] 2:4-Dicarbomethoxycinnamic acid, m. p. 184—186°, is converted into the *chloride*, m. p. 87—89°, which is condensed with ethyl sodioacetoacetate to yield *ethyl α -2:4-dicarbomethoxycinnamoylacetate*, m. p. 95—97°, which decomposes when heated to produce 2:4-dicarbomethoxycinnamoylacetone, m. p. 110—112° (*copper salt*, m. p. 205—207°). *Sodicinnamoylacetone* condenses with 2:4-dicarbomethoxycinnamoyl chloride to yield *cinnamoyl-2:4-dicarbomethoxycinnamoylmethane*, m. p. 132—134°; it was not possible to accomplish this condensation using dihydroxycinnamoylacetone. The above product yields on hydrolysis *cinnamoyl-2:4-dihydroxycinnamoylmethane*, m. p. 158—161°.

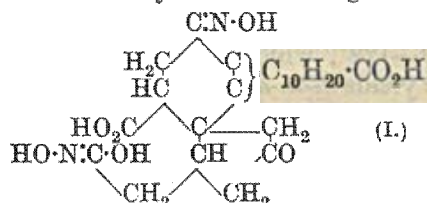
[With E. Gliksman-Korngold.] 2:5-Dicarbomethoxycinnamic acid, m. p. 184—186°, is converted into the *chloride*, m. p. 104—106°, which is condensed with ethyl sodioacetoacetate to yield *ethyl α -2:5-dicarbomethoxycinnamoylacetate*, m. p. 95—97°, whence is prepared 2:5-dicarbomethoxycinnamoylacetone, m. p. 108—110°. The sodium salt of the latter substance yields on condensation with 2:5-dicarbomethoxycinnamoyl chloride *di-2:5-dicarbomethoxycinnamoylmethane*, m. p. 194—196° (corresponding *dihydroxy*-derivative, m. p. 174—176°).

[With Z. Buczkowska.] *Ethyl 3:4-piperonylacrylacetate*, m. p. 98—100°, is converted into 3:4-piperonylacrylacetone, m. p. 123—125°, the sodium salt of which is condensed with the appropriate chloride to yield *di*-(3:4-piperonylacryl)methane, m. p. 198—200°.

[With J. Frenkiel.] 4-Carbomethoxy-1-naphthaldehyde, m. p. 124—126°, condenses with malonic acid to yield 4-carbomethoxy-1-naphthylidenemalonic acid, m. p. 193°, which on fusion loses carbon dioxide, giving rise to 4-carbomethoxy-1-naphthylacrylic acid, m. p. 230—235°, the *chloride* of which (m. p. 152—154°) is condensed with ethyl sodioacetoacetate to yield *ethyl α -(4-carbomethoxy-1-naphthylacryl)acetoacetate*, m. p. 110—112°; this substance is converted on heating into 4-carbomethoxy-1-naphthylacrylacetone, m. p. 104—106°, which is as before converted into *di*-(4-carbomethoxynaphthylacryl)methane, m. p. 120—124°. The end-products of the above syntheses

are substantive dyes for cotton, the intensity of coloration depending on the number and position of auxochrome (hydroxyl) groups. R. TRUSZKOWSKI.

Bile acids. XXIV. M. SCHENCK and H. KIRCHHOFF (Z. physiol. Chem., 1929, 183, 88—97).—Treatment of α -diketocholanic acid dioxime (this vol., 187) with nitric acid (d 1.4) at the ordinary temperature affords deoxybilanic acid in small yield. Reduction of the nitrohydroxamic acid, $C_{24}H_{34}O_8N_2$ (this vol., 558), with zinc dust and 9% ammonia affords the compound (I), $C_{24}H_{36}O_8N$, decomp. 224 — 226° after previous sintering, oxidised by nitric acid (d 1.4) to the nitroso-compound, $C_{24}H_{33}O_8N$ (A., 1928, 1007), previously obtained from bilanic acid dioxime. Partial hydrolysis of I with hydrochloric acid gives hydroxyl-



amine and the acid, $C_{24}H_{35}O_8N$ (I, where upper N:OH=O), decomp. 225° after previous sintering. This is hydrolysed further, with difficulty, to bilanic acid. H. BURTON.

[Preparation of] ammonium aurintricarboxylate. G. B. HEISIG and W. M. LAUER (Organic Syntheses, 1929, 9, 8—10).

Influence of ultra-violet light on aldehydes. Hexahydrophenylacetaldehyde, hexahydro- β -phenylpropaldehyde, and n -dodecaldehyde. F. SIGMUND (Monatsh., 1929, 52, 185—191).—The aldehydes were exposed in quartz vessels to the light from a quartz-mercury vapour lamp. Hexahydrophenylacetaldehyde (from its dimethylacetal) yielded, after 6 hrs.' exposure, a gas containing 88% of carbon monoxide, hexahydrotoluene, b. p. 100 — 110° , and small quantities of polymerised products. Hexahydro- β -phenylpropaldehyde (semicarbazone, m. p. 133° ; lit. 128°), which rapidly forms a trimeride, m. p. 100° , on keeping, prepared from the diethylacetal, b. p. 205° or 93 — $95^\circ/15$ mm., similarly yielded, after 10 hrs.' exposure, carbon monoxide, but more slowly and in smaller quantity, and highly polymerised products from which only the above trimeride, m. p. 100° , and no hexahydroethylbenzene could be isolated in the pure state. n -Dodecaldehyde, b. p. 227 — 235° , from the semicarbazone, m. p. 101 — 102° , after 8 hrs.' exposure, afforded a gas (80% CO) and undecane, b. p. 190 — 200° . A. I. VOGEL.

Isomerism of dicyclohexylacetaldehyde into the ketone. E. D. VENUS-DANILOVA (J. Russ. Phys. Chem. Soc., 1929, 61, 53—70).—The isomerisation of dicyclohexylacetaldehyde into cyclohexylcyclohexylmethyl ketone, in the presence of sulphuric acid or an alcoholic solution of mercurous chloride, is investigated.

The aldehyde was obtained from ethyl ethoxyacetate and magnesium cyclohexyl bromide, the resulting dicyclohexylethoxymethylcarbinol, m. p. 53° , b. p. 170 — $171^\circ/9$ mm., being oxidised by heating with

oxalic acid. In the preparation of the carbinol, both ethyl cyclohexylacetate, m. p. 31° , b. p. 211 — 211.5° , and cyclohexylethoxymethylcarbinol, b. p. $108^\circ/13$ mm., were obtained as by-products. The aldehyde has b. p. 153 — $153.5^\circ/10$ mm., d_4^{20} 0.9808, d_4^{25} 0.9676, d_4^{30} 0.9621, and gives a semicarbazone, m. p. 184 — 184.5° , and oxime, m. p. 108 — 109° . It oxidises on keeping in air, with the formation of dicyclohexylacetic acid, m. p. 134 — 135° (amide, m. p. 188 — 189° ; anilide, m. p. 202 — 202.5°). When the semicarbazone of the aldehyde is heated with moderately concentrated sulphuric acid, cyclohexyl cyclohexylmethyl ketone is obtained, b. p. 172 — $173^\circ/26$ mm. (oxime, m. p. 112 — 113° ; semicarbazone, m. p. 190 — 191°). The structure of the ketone was determined by synthesising $\alpha\beta$ -dicyclohexylethanol, m. p. 64 — 65° , b. p. 162 — $164^\circ/17$ mm., from magnesium cyclohexylmethyl iodide and hexahydrobenzaldehyde, and oxidising it to the ketone by chromic acid. The identity of the ketone was also confirmed by its decomposition products, since it gave cyclohexane and cyclohexylacetic acid on treatment with alcoholic potassium hydroxide.

M. ZVEGINTZOV.

2:4-Dinitrobenzaldehyde as a reagent. G. M. BENNETT and W. L. C. PRATT (J.C.S., 1929, 1465—1468).—2:4-Dinitrobenzaldehyde is a valuable reagent for the characterisation of amines (cf. A., 1920, i, 440; 1921, i, 337; 1923, i, 578) and for revealing the reactive methyl or methylene group in heterocyclic bases. Condensation with amines occurs readily in hot alcoholic solution containing a few drops of acetic acid to yield the following dinitrobenzylidene compounds: dinitrobenzylidene- m -chloroaniline, m. p. 137° ; - o -chloroaniline, m. p. 164.5° ; - p -chloroaniline, m. p. 158° ; -3:5-dibromoaniline, m. p. 181° ; - p -iodoaniline, m. p. 163° ; - p -aminophenol, m. p. 158° ; - p -aminoacetanilide, m. p. 199° ; bisdinitrobenzylidene- o -phenylenediamine, m. p. 158° ; -3:4-tolylenediamine, m. p. 153.5° ; -4:4'-diaminodiphenylamine, m. p. 263° (decomp.); 6-aminoquinoline, m. p. 206° .

Condensation of 2:4-dinitrobenzaldehyde with substances possessing a reactive methyl or methylene group proceeds rapidly in boiling acetic anhydride, the products crystallising from the reaction mixture. 2-Methylpyridine gives 2-dinitrostyrylpyridine, m. p. 159° , and 2:6-dimethylquinoline yields 2-dinitrostyryl-6-methylquinoline, m. p. 213° . After 0.5—1 hr. 2:4-dimethylquinoline affords 2-dinitrostyryl-4-methylquinoline, m. p. 163.5° , but with excess of the reagent for 6—8 hrs. this compound or the original base furnishes tetranitro-2:4-distyrylquinoline, m. p. 270° (decomp.). 5:8-Dichloro-2-dinitrostyryl-4-methylquinoline has m. p. 198.5° , and 5:6:8-trichloro-2-dinitrostyryl-4-methylquinoline, m. p. 225.5° . 2:4:6-Trimethylquinoline rapidly gives 2-dinitrostyryl-4:6-dimethylquinoline, m. p. 195° , and 2-methylbenzimidazole affords 2-dinitrostyrylbenzimidazole, m. p. 215° . Condensation also occurs with p -nitrophenylacetonitrile giving 2:4:4'-trinitro- α -cyanostilbene, m. p. 149° , but no reaction could be detected with dibenzylsulphoxide or dibenzylsulphone.

An improved method of preparation of the reagent is described (cf. Sachs and Kempf, A., 1902, i, 682).

C. W. SHOPPEE.

Substitution in resorcinol derivatives. II. Bromo-derivatives of β -resorcyaldehyde and their orientation. M. G. S. RAO, C. SRIKANTIA, and M. S. IYENGAR (J.C.S., 1929, 1578—1581; cf. A., 1925, i, 675).—When a solution of 2-hydroxy-4-methoxybenzaldehyde in formic acid (d 1.20) is treated with bromine in the presence of anhydrous potassium acetate, 5-bromo-2-hydroxy-4-methoxybenzaldehyde, m. p. 120—121° (oxime, m. p. 148—149°; phenylhydrazone, m. p. 177—178°), is obtained; the same substance is produced when 5-nitro-2-hydroxy-4-methoxybenzaldehyde is reduced with sodium hyposulphite, and the reduction product diazotised in the presence of cuprous bromide. The bromoaldehyde may be obtained on a larger scale by working in glacial acetic acid, and passing bromine vapour diluted with carbon dioxide through the solution. Using 2 mols. of bromine in glacial acetic acid, 3:5-dibromo-2-hydroxy-4-methoxybenzaldehyde, m. p. 97—98° (oxime, m. p. 215°; phenylhydrazone, m. p. 131—132°), is obtained; if the period of bromination is unduly prolonged and an excess of bromine employed, a large quantity of a white solid, m. p. above 250°, is formed (cf. Davies, J.C.S., 1923, 123, 1575). All attempts to prepare a tribromo-derivative failed, although small quantities of tribromoresorcinol monomethyl ether were produced. By nitration at 100° in glacial acetic-sulphuric acid with nitric acid (d 1.52), the dibromoaldehyde affords 2:6-dibromo-4-nitroresorcinol 1-monomethyl ether, m. p. 127—128°, also obtained by partial methylation by the Purdie method of 2:6-dibromo-4-nitroresorcinol, m. p. 148°, and previously prepared by Kohn and Löff (A., 1925, i, 1264). Both specimens, by further methylation with methyl iodide, yielded the same dimethyl ether, m. p. 81°, the constitution of which is known definitely (Jackson and Fiske, A., 1903, i, 688).

By bromination in acetic acid in the presence of sodium acetate, 2:4-dimethoxybenzaldehyde, 2-ethoxy-4-methoxybenzaldehyde, and methyl *p*-methoxysalicylate gave respectively: 5-bromo-2:4-dimethoxybenzaldehyde, m. p. 136—137° (oxime, m. p. 175—176°), identical with the product obtained by methylating 5-bromo-2-hydroxy-4-methoxybenzaldehyde, and oxidised by hot potassium permanganate in the presence of magnesium sulphate to 5-bromo-2:4-dimethoxybenzoic acid, m. p. 195—196°; 5-bromo-2-ethoxy-4-methoxybenzaldehyde, m. p. 126—127° (oxime, m. p. 169—170°), identical with the ethylated product of 5-bromo-2-hydroxy-4-methoxybenzaldehyde, and oxidised by permanganate to 5-bromo-2-ethoxy-4-methoxybenzoic acid; methyl 5-bromo-4-methoxysalicylate, hydrolysed by alcoholic potassium hydroxide to 5-bromo-4-methoxysalicylic acid, identical with that obtained by bromination of 4-methoxysalicylic acid (cf. Fries and Saftien, A., 1926, 849).

C. W. SHOPPEE.

Chemistry of the three-carbon system. XXI. Some cycloheptane compounds. W. E. HUGH, G. A. R. KON, and T. MITCHELL (J.C.S., 1929, 1435—1440).—The point of equilibrium between cycloheptylideneacetic acid (*anilide*, m. p. 90—91°) and Δ^1 -cycloheptenylacetic acid found by Kon and May (A., 1927, 853) has been confirmed; under the standard conditions used by Linstead (A., 1927, 1167) and by

Goldberg and Linstead (A., 1928, 1214), the equilibrium mixture contains 26% of the $\alpha\beta$ -acid, but this value may be 2—3% low: the mobility $(k_1 + k_2) \times 10$ is 0.66. The preparation of pure Δ^1 -cycloheptenylacetic acid (cf. Wallach, A., 1901, i, 155) is described; the acid has b. p. 153°/17 mm., 107°/2.5 mm., d_4^{20} 1.01155, n_D^{20} 1.48820 (*anilide*, m. p. 79—80°; ethyl ester, b. p. 104—107°/12 mm., $d_4^{15.4}$ 0.97172, $n_D^{15.4}$ 1.44689).

cycloHeptylideneacetone, b. p. 96°/10 mm., 0.94852, n_D^{18} 1.49518, was obtained from cycloheptylideneacetyl chloride, b. p. 120—121°/13 mm., by the Blaise-Maire reaction, and was regenerated from the semicarbazone, m. p. 172—173°, which was identical with the compound previously described by Kon (J.C.S., 1921, 119, 810) as cyclohexenylacetonesemicarbazone. The ketone afforded suberone by oxidation. cycloHeptenylacetone, b. p. 95°/13 mm., d_4^{18} 0.93558, n_D^{18} 1.47595, after regeneration from the semicarbazone, m. p. 128—129°, was obtained similarly from cycloheptenylacetyl chloride, b. p. 100—104°/13 mm.; the equilibrium mixture obtained under standard conditions contains 65% of the $\alpha\beta$ -ketone. In contrast with the acids described above, the mobility of the ketones is extremely high, being greater than 3500, whilst the period of half-change is less than 2 min.

C. W. SHOPPEE.

[Preparation of] *p*-bromophenacyl bromide. W. D. LANGLEY (Organic Syntheses, 1929, 9, 20—21).

Dicymyl. E. BOEDTKER and R. KERLOV (Compt. rend., 1929, 188, 1681—1683).—*p*-Tolyl methyl ketone reacts with magnesium methyl iodide to give *p*-tolyl dimethylcarbinol, which cannot be distilled in a high vacuum without dehydration; by treatment with a saturated solution of hydriodic acid in glacial acetic acid at 15° for some hours, it is converted into α -*p*-tolyl isopropyl iodide, which with zinc dust yields *s*-pp'-ditolyl tetramethylethane, m. p. 157°, identical with the dicymyl obtained by Ciamician and Silber (A., 1910, i, 489) from benzophenone and *p*-cymene in sunlight.

C. W. SHOPPEE.

Additive reactions of phenyl vinyl ketone. I. Phenyl nitromethane. C. F. H. ALLEN and M. P. BRIDGES (J. Amer. Chem. Soc., 1929, 51, 2151—2157).—Phenyl vinyl ketone, isolated as described by Mannich (A., 1922, i, 351), or formed in solution, as required, from phenyl β -chloroethyl ketone and potassium carbonate, gives with phenyl nitromethane and sodium methoxide phenyl γ -nitro- γ -phenylpropyl ketone, m. p. 72°. The sodio-derivative of this is hydrolysed by dilute hydrochloric acid to $\alpha\beta$ -dibenzoyl ethane (I), and brominated in methyl alcohol to phenyl γ -bromo- γ -nitro- γ -phenylpropyl ketone, m. p. 146°, decomposing at a higher temperature, mainly into 3-bromo-2:5-diphenylfuran. The bromonitroketone is converted by alcoholic sodium hydroxide into I; by boiling glacial acetic acid into 3-bromo- and a little 3:4-dibromo-2:5-diphenylfuran, and by prolonged refluxing with potassium acetate in methyl alcohol into 1-nitro-2-benzoyl-1-phenylcyclopropane, m. p. 131°, together with a mixture, m. p. 80°, probably containing a stereoisomeride. These are both stable towards bromine, hydrogen bromide, and acetyl chloride, but are converted by sodium methoxide

into I. The mechanism of this new type of reaction is discussed (cf. Kohler, A., 1919, i, 330, 582; 1920, i, 59, 61; 1928, 523).

H. E. F. NOTTON.

Stereochemistry of the phenyl styryl ketones. The stereoisomerism of phenyl α -bromo- β -ethoxystyryl ketone. C. DUFRAISSE and R. NETTER (Compt. rend., 1929, 189, 299—301).—A substance, m. p. 85°, noted by Dufraisse and Gillet (this vol., 700), is shown to be a stereoisomeride of phenyl α -bromo- β -ethoxystyryl ketone and not a fourth polymorphic variety of the original compound. The isomerides are interconvertible, the change being accelerated by light, heat, and acids. Their properties are very similar and their separation is difficult.

A. A. GOLDBERG.

Polymorphism of organic substances. C. WEYGAND (Annalen, 1929, 472, 143—179).—Inoculation of the supercooled fused mass from stable (m. p. 74·5°) *p*-tolyl styryl ketone (A) with *p*-ethylphenyl styryl ketone (I), m. p. 61·5°, causes instantaneous crystallisation of modification III of A (=AIII; for notation see this vol., 815), and of the seven principal modifications of A (*loc. cit.*) only AIII causes spontaneous crystallisation of a supercooled fused mass of I. AIII and I are, therefore, corresponding forms. A new, metastable modification, m. p. 64° (II), of the enol form of benzoyl-*p*-toluoylmethane (III), m. p. 84° (A., 1928, 291), is described: the velocity of the transformation II \rightarrow III is more rapid than AII \rightarrow AIV, and inoculation experiments show that II and AIII and III and AII are corresponding pairs. Inoculation of the fused mass from II or III with metastable phenyl *p*-methylstyryl ketone, m. p. 91° (A., 1928, 180), affords a further metastable modification, m. p. 42°, of III; occasionally a fourth form, m. p. 38°, is obtained. The less fusible forms are polymorphic modifications of the enol, $C_6H_4Me \cdot CO \cdot CH : CPh \cdot OH$, whilst the more fusible forms are similarly related to the enol, $COPh \cdot CH : C(OH) \cdot C_6H_4 \cdot Me$. The following, not hitherto described modifications of a series of chalkones have been obtained: phenyl styryl ketone, m. p. 58—49°, 56—57°, 28°, 18° (β -ethoxy-derivative, m. p. 43°; α -bromo-derivative, m. p. 45°); phenyl *p*-methylstyryl ketone, m. p. 96·5°, 91°, 86° (β -ethoxy-derivative, m. p. 91°; α -bromo-derivative, m. p. 66—67°); *p*-tolyl *p*-methylstyryl ketone, m. p. 128—129° (β -hydroxy-derivative, m. p. 127—129°; β -ethoxy-derivative, m. p. 80—81°); *p*-tolyl β -ethoxystyryl ketone, m. p. 73°, 56—58°; *p*-tolyl α -bromostyryl ketone, m. p. 66—67°, 58°. The crystallisation velocities of the various forms have been determined and the various transformations studied.

H. BURTON.

Condensation of piperonaldehyde with certain pinacolins. E. PACE (Atti R. Accad. Lincei, 1929, [vi], 9, 778—782).—3:4-Methylenedioxystyryl *tert*-butyl ketone, $CH_2 \begin{smallmatrix} \diagup O \diagdown \end{smallmatrix} C_6H_3 \cdot CH : CH \cdot CO \cdot CMe_3$, m. p. 98°, d_4^{20} 1·0765, n_D^{20} 1·34825, is obtained by the condensation of piperonaldehyde with methyl *tert*-butyl ketone (this vol., 538) in presence of sodium hydroxide. Piperonylidene-ethyl *tert*-amyl ketone, m. p. 106°, d_4^{20} 1·0883, n_D^{20} 1·36132, and piperonylidenepropyl *tert*-hexyl ketone, m. p. 117°, d_4^{20} 1·0928, n_D^{20} 1·38576, are

obtained from piperonaldehyde with ethyl *tert*-amyl ketone and propyl *tert*-hexyl ketone, respectively.

T. H. POPE.

Bivalency of carbon. II. Displacement of chlorine from desyl chloride. Benzoin diethylacetal. A. M. WARD (J.C.S., 1929, 1541—1553; cf. A., 1927, 1061).—Desyl chloride, m. p. 67°, obtained by an improvement of the method of Darzens (A., 1911, i, 513), is completely stable in lime-dried alcoholic or aqueous-alcoholic solution at 25°, but the halogen is very rapidly displaced in the presence of sodium hydroxide or ethoxide at 15°. Quantitative experiments, carried out in an atmosphere of hydrogen to minimise side and subsequent reactions, show that the velocity coefficients of the displacements are those of a bimolecular reaction; their values are dependent, however, on the concentrations of the reactants. These results are in marked contrast with those previously obtained (*loc. cit.*) for diphenylchloromethane, and are not in accordance with the hypothesis of Schroeter (A., 1909, i, 617, 773), that the elimination of chlorine from desyl chloride proceeds through a phase involving bivalent carbon. This conclusion is supported by the products formed in the foregoing reaction. When the final reaction mixture was added to cold dilute hydrochloric acid, benzoin only was obtained; no trace of benzoin ethyl ether, which is stable to dilute hydrochloric acid at 15°, could be detected. The exclusive production of benzoin is found to be due to the prior formation of benzoin diethylacetal, m. p. 68° (crystallographic data), which is rapidly decomposed by dilute hydrochloric acid at 15° giving benzoin. A mechanism is put forward based on the above results, in which the primary reaction in the displacement consists in the addition of an ethoxide ion to the carbonyl group in desyl chloride.

C. W. SHOPPEE.

Dioximes. LIII. M. MILONE (Gazzetta, 1929, 59, 266—272).—A survey of previous work on the arylglyoxime peroxides (cf. Ponzio and others, A., 1927, 470, etc.), and a further application of the cryoscopic method (this vol., 334) to the study of their structure. Oximinophenyl- and oximino-*p*-tolyl-acetonitrile oxides, and phenyl- and *p*-tolyl-glyoxime peroxides (m. p. 112°, 117°, 108—109°, and 100—101°, respectively) all give normal mol. wt. values in 3-phenyl- and 3-*p*-tolyl-1:2:5-oxadiazoles as solvents, and are thus not to be regarded as themselves having an oxadiazole structure (cf. Ponzio, *loc. cit.*).

E. W. WIGNALL.

Dioximes. G. PONZIO (Ber., 1929, 62, [B], 1750).— β -*p*-Methoxybenzildioxime has m. p. 185° (Meisenheimer and others record m. p. 176°). It is dehydrogenated by sodium hypochlorite to a substance, m. p. 106—107°, identical in m. p. with the " α -phenylanisilfuroxan" of Meisenheimer (A., 1925, i, 1075).

H. WREN.

Catalytic reduction of $\alpha\beta$ -diketones and their derivatives. J. S. BUCK and S. S. JENKINS (J. Amer. Chem. Soc., 1929, 51, 2163—2167).—Modifications of the method and apparatus of Adams (A., 1922, ii, 558) suitable for the hydrogenation of about 0·01 g.-mol. of material are described. The following reductions have been effected with almost quant-

ative yields: benzil, anisil, and piperil to the corresponding benzoin and hydrobenzoin derivatives; furil to furoin; phenyl benzyl ketone to phenylbenzylcarbinol; anisyl *p*-methoxybenzyl ketone to $\alpha\beta$ -di-*p*-anisylethyl alcohol, m. p. 110–4° (Wiechell, A., 1894, i, 507, gives m. p. 170°), and *piperonyl mp-methylene-dioxybenzyl ketone*, m. p. 114–5°, to $\alpha\beta$ -di-*piperonylethyl alcohol*, m. p. 154–155°. The phenylbenzylcarbinols are dehydrated by acetic and hydrochloric acids to stilbenes, which are readily hydrogenated to the corresponding $\alpha\beta$ -diarylethanes. Attempts to hydrogenate veratril were unsuccessful. H. E. F. NOTTON.

Synthesis of ephedrine and structurally similar compounds. III. New synthesis of $\alpha\beta$ -diketones. H. W. COLES, R. H. F. MANSKE, and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 2269–2272).—Propiophenone is oxidised by nitrogen peroxide at 60° in alcoholic hydrogen chloride in presence of calcium chloride to α -phenylpropane- $\alpha\beta$ -dione. The method, described in detail, is also applicable to the preparation of α -phenylbutane- $\alpha\beta$ -dione, b. p. 130–132°/20 mm., α -*p*-ethylphenylpropane- $\alpha\beta$ -dione, b. p. 138–140°/20 mm., and α -2:5-dimethylphenylpropane- $\alpha\beta$ -dione, b. p. 140–144°/20 mm., but α -hydrindone gives 2-oximino-1-hydrindone and, on further treatment, resinous products, and α -ketotetrahydronaphthalene gives no crystalline product. H. E. F. NOTTON.

Reactions of oximes with metallic salts. III. Complex-chemical behaviour of stereoisomeric oximes. W. HIEBER and F. LEUTERT (Ber., 1929, 62, [B], 1839–1846).—The occurrence of a reaction between metallic salts and oximes is conditioned by the presence of an oximino-nitrogen atom capable of subsidiary valency action. Transformation or conversion into an internally complex salt usually follows as a consequence of greatly enhanced stability, but this is not universal. Copper acetate and α -benzildioxime in aqueous-alcoholic suspension in the presence of ammonia give the compound $[\text{CPh}(\text{N}\cdot\text{OH})\cdot\text{CPh}(\text{NO})]_2\text{Cu}$, converted by hydrogen chloride into the additive product of cupric chloride and α -benzildioxime and the free dioxime. The additive compound is also obtained from γ -benzildioxime and cupric chloride in chloroform. The β -oxime of benzoylformic acid gives adducts with cupric and cobalt chloride, also obtained from the α -oxime (in consequence of isomerisation). The copper, nickel, and cobalt salts, $\text{Cu}(\text{Co}, \text{Ni})[\text{CPh}(\text{N}\cdot\text{OH})\cdot\text{CO}_2]_2\cdot 2\text{H}_2\text{O}$, and the potassium copper salt, $\text{K}_2\text{Cu}[\text{CPh}(\text{NO})\cdot\text{CO}_2]_3$, are described. anti-Chloroglyoxime shows much less tendency than aromatic anti-dioximes towards the formation of complex compounds. Potassium nickel amphi-chloroglyoxime, $\text{K}_2\text{Ni}[\text{Cl}(\text{NO})\cdot\text{CH}(\text{NO})]_2$, is described in which potassium may be replaced by barium, lead, or silver. H. WREN.

Reduction of aromatic $\alpha\beta$ -diketones by the binary system, magnesium-magnesium iodide (or bromide). M. GOMBERG and F. J. VAN NATTA (J. Amer. Chem. Soc., 1929, 51, 2238–2245).—Equilibrium in the reversible reaction, $(\cdot\text{CR}\cdot\text{O})_2 + 2\text{MgI}_2 \rightleftharpoons (\cdot\text{CR}\cdot\text{OMgI})_2 + \text{I}_2$ (cf. A., 1927, 1190), has been approached from both sides in the case of several

benzil derivatives. In presence of magnesium, the reduction proceeds quantitatively and the products give high yields of benzoin when hydrolysed in absence of air. Many of the resulting glycoloxides are deeply coloured in solution, probably owing to the production of free valencies by the partial opening of the double linking. *p*-Tolil is reduced to toluoin in 90% yield using magnesium iodide, and in 82% yield using the bromide. The intermediate *magnesium glycoloxide* is oxidised by dry air to the polymeric *anhydride* (28% of the theoretical yield), m. p. above 360°, of di-*p*-tolylglycollic acid, and to *p*-tolil (45%). *p*-Anisil is quantitatively reduced to a *glycoloxide* which is oxidised by air to the polymeric *anhydride* (31% yield), m. p. above 360°, of di-*p*-anisylglycollic acid. *pp'*-Dichlorobenzil yields a *glycoloxide* which is oxidised by air to the polymeric *anhydride*, decomp. 320–340°, of *pp'*-dichlorobenzilic acid. The last two benzils cannot be reduced by means of magnesium bromide, since they form insoluble compounds with it. α -Naphthil (2:3-di- α -naphthylquinoxaline, m. p. 203–204°), conveniently prepared from α -naphthoin, copper sulphate, and pyridine, is reduced to a *glycoloxide*, which gives di- α -naphthylglycollic acid, m. p. 137–138° (40% yield), but no anhydride, when oxidised by air. *p*-Phenylbenzaldehyde and potassium cyanide in boiling aqueous alcohol give *pp'*-di-phenylbenzoin, m. p. 168–170°, oxidised to *pp'*-di-phenylbenzil, m. p. 141–142° (2:3-bisdiphenylquinoxaline, m. p. 209–210°). This is quantitatively reduced to a *glycoloxide*, oxidised by air to the polymeric *anhydride*, decomp. 250°, of *pp'*-diphenylbenzilic acid. Benzyl *p*-diphenyl ketone is oxidised by potassium permanganate in pyridine to *p*-phenylbenzil, m. p. 105°, which is reduced by magnesium and magnesium iodide, or, better, bromide, to a *p*-phenylbenzoin, m. p. 148–151°. The glycoloxides are converted by benzoyl chloride into the following derivatives of $\alpha\beta$ -dibenzoyloxystilbene: *pp'*-dimethyl-, m. p. 135°; *pp'*-dichloro-, m. p. 200–202°, and *pp'*-diphenyl-, m. p. 180°, resolidifying with conversion into an *isomeride*, m. p. 200–203°.

H. E. F. NOTTON.

Oximino-derivatives of *p*-bromobenzoyl-acetone and the corresponding dioxime. J. HANUS, A. JÍLEK, and J. LUKAS (Coll. Czech. Chem. Comm., 1929, 1, 392–396).—*p*-Bromoacetophenone, treated with sodium and ethereal ethyl acetate, gives *p*-bromobenzoylacetone, m. p. 94–96° (corr.). With aqueous sodium nitrite and acetic anhydride it affords oximino-*p*-bromobenzoylacetone, m. p. 169–170°, which yields with hydroxylamine an oxime, m. p. 189–190°. Attempts to prepare the corresponding trioxime gave an isomeric dioxime (?), m. p. 147–148°. Characteristic reactions of the first and second oxime derivatives with metallic cations are recorded.

R. J. W. LE FEVRE.

Conjugated systems. Factors disturbing valency fields. V. Action of compounds with a reactive methylene group on carbindogenides. V. IONESCU and A. GEORGESCU (Bull. Soc. chim., 1929, [iv], 45, 428–435).—In continuation of previous work (A., 1928, 422, 1026) the three isomeric chlorobenzylideneindandiones have been shown to react with ethyl malonate, dimethyldihydroresorcinol, and

1-phenyl-3-methyl-5-pyrazolone analogously with the toluylideneindandiones, the additive product,

$C_6H_4 \begin{smallmatrix} \diagup & \diagdown \\ CO & \end{smallmatrix} CH \cdot CH(C_6H_4Cl) \cdot R$, being first formed by addition of one mol. of the reagent, from which further complex products are formed in the case of dimethyldihydroresorcinol and phenylmethylpyrazolone, either by displacement of the indandione group or by reaction of the di-indone formed with unchanged chlorobenzylideneindandione to give mono- or di-substituted derivatives. Small quantities of truxenequinone formed by auto-condensation of the di-indone were present in all cases.

With *o*-, *m*-, and *p*-chlorobenzylideneindandiones in alcohol, ethyl malonate affords the corresponding ethyl chlorobenzylindandionylmalonates, which were not obtained pure and when heated are decomposed into the original indogenide. Dimethyldihydroresorcinol in presence of piperidine yields *o*-chlorobenzylidenebisdimethyldihydroresorcinol, m. p. 203—205°, and -indandionedi-indone, m. p. 288° (decomp.). *m*-Chlorobenzylidene-, m. p. 265—267° (decomp.), and *p*-chlorobenzylideneindandionedi-indones, m. p. 275° (decomp.), are similarly obtained, but the *m*- and *p*-chlorobenzylidenebisdimethyldihydroresorcinols were not obtained pure. *o*-Chlorobenzylidene-, m. p. 229—231°, *m*-chlorobenzylidene-, m. p. 206—207°, and *p*-chlorobenzylidenebis-1-phenyl-3-methyl-5-pyrazolones, m. p. 208°, are accompanied by traces of anhydrobis-1-phenyl-3-methyl-5-pyrazolone (A., 1927, 880).

R. BRIGHTMAN.

Migration of the acyl group in partly acylated phenolic compounds. II. Synthesis of anthragallol 1:2- and 1:3-dimethyl ethers. A. G. PERKIN and C. W. H. STORY (J.C.S., 1929, 1399—1421; cf. A., 1925, i, 1159; 1928, 293).—When anthragallol 2-methyl ether is treated with acetic anhydride and powdered potassium acetate at 15°, 3-acetylanthragallol 2-methyl ether, m. p. 167—169.5°, is obtained; it is converted by diazomethane in ether suspension into a mixture of anthragallol trimethyl ether, m. p. 167—169° (15%), and 3-acetylanthragallol 1:2-dimethyl ether, m. p. 177—179°. Hydrolysis of the latter yields anthragallol 1:2-dimethyl ether, m. p. 230—232°, identical with that present in Chay root (Perkin and Hummel, J.C.S., 1893, 63, 1160; Perkin, *ibid.*, 1907, 91, 2066). Benzoylation of 2:3-diacetylanthragallol in pyridine suspension at 0° affords a mixture of 2-benzoyl-3-acetylanthragallol (I), m. p. 203—206°, and 1- or 3-benzoyl-2-acetylanthragallol (II), m. p. 189—190°, which both yield 2-benzoylanthragallol (III), m. p. 241—243°, by hydrolysis with acetic and hydrochloric acids at 100°, migration of the benzoyl group occurring in the case of II. By acetylation with boiling acetic anhydride and pyridine, III affords triacetylanthragallol, but at 0° both I and III yield 2-benzoyl-1:3-diacetylanthragallol, m. p. 211—213°, whilst II furnishes an isomeric benzoyldiacetylanthragallol, m. p. 203—205°, partial acetylation of III with acetic anhydride in the presence of potassium acetate at 15° yields I. When methylated with ethereal diazomethane, 2-benzoylanthragallol gives 1-benzoylanthragallol 2:3-dimethyl ether (IV), m. p. 216—218° (60%), hydrolysed by boiling 1% methyl-alcoholic potassium hydroxide to

anthragallol 2:3-dimethyl ether, m. p. 160—162°, together with 3-benzoylanthragallol 1:2-dimethyl ether (15.5%) and 2-benzoylanthragallol 1:3-dimethyl ether (V) (13%); the two last-named compounds were not isolated, but their presence was indicated by hydrolysis to anthragallol 1:2-dimethyl ether and anthragallol 1:3-dimethyl ether (acetyl derivative, m. p. 218—220°; cf. Perkin and Hummel, *loc. cit.*). These results involve migration of the benzoyl group from the 2 to the 1, and from the 2 to the 3 position. Anthragallol 2:3-dimethyl ether by hydrolysis with sulphuric acid at 100° yields anthragallol 3-methyl ether (VI), m. p. 242—245° (acetyl derivative, m. p. 204—206°) (cf. *lit.*), identical with the anthragallol methyl ether obtained by Kubota and Perkin (A., 1925, i, 1159), whose preparation from 2:3-diacetylanthragallol, which involves migration of both acetyl groups, is confirmed. By treatment of a mixture of VI and benzoyl chloride with a solution of pyridine in chloroform at 0° 2-benzoylanthragallol 3-methyl ether (VII), m. p. 221—223°, is obtained; it is converted by boiling with acetic anhydride and pyridine into two isomeric benzoylacetylanthragallol 3-methyl ethers, m. p. 195—196° and 214—217°, which are considered to arise by migration of the benzoyl group. When methylated with ethereal diazomethane, VII affords a mixture of IV (76%) and V (15%).

By digestion of 2:3-thionylanthragallol (cf. Green, A., 1926, 1041) with boiling acetic acid 2-acetylanthragallol, m. p. 219—220°, is obtained [described by Green (*loc. cit.*) as the 3-acetyl compound]; when methylated with ethereal diazomethane it affords 1-acetylanthragallol 2:3-dimethyl ether (69%), 2-acetylanthragallol 1:3-dimethyl ether (15%), and 3-acetylanthragallol 1:2-dimethyl ether (15%), with migration of the acetyl group from the 2 to the 1, and from the 2 to the 3 position. A boiling acetone solution of 1:3-diacetylanthragallol 2-methyl ether on treatment with excess of aqueous ammonia yields 1-acetylanthragallol 2-methyl ether, m. p. 205—208°, hydrolysed to anthragallol 2-methyl ether, m. p. 218—220°, and affording by methylation with ethereal diazomethane 1-acetylanthragallol 2:3-dimethyl ether, m. p. 168—170°; no substance other than anthragallol 2:3-dimethyl ether could be obtained by hydrolysis of the methylation product. Hydrolysis of triacetylpuropuroxanthin with ammonia in boiling acetone solution yields 1-acetylpuropuroxanthin, m. p. 231—235°, hydrolysed by hydrochloric acid to purpuroxanthin, m. p. 268—270° (cf. *lit.*), which by reacylation affords 3-acetylpuropuroxanthin, m. p. 144° (cf. *lit.*). Similar treatment of triacetylpuropurin and triacetylanthragallol yields respectively 1:3-diacetylpuropurin, m. p. 203—205°, and 2:3-diacetylanthragallol, m. p. 223—224°.

3-Nitroalizarin dimethyl ether, m. p. 168—171°, obtained by methylating the potassium salt of 3-nitroalizarin with methyl sulphate at 140°, by reduction with sodium sulphide affords 3-aminoalizarin dimethyl ether, m. p. 203—205° (acetyl derivative, m. p. 237—240°). By diazotisation in sulphuric acid solution, dilution, and boiling, anthragallol 2-methyl ether is obtained [1:3-diacetyl derivative, m. p. 146—150° (cf. *lit.*)], partial demethylation occurring in the latter process.

2 : 3-Ditoluene-*p*-sulphonylanthragallol (VIII), m. p. 196—198° (acetyl derivative, m. p. 212—215°), obtained by treatment of anthragallol with toluene-*p*-sulphonyl chloride in pyridine at 0—15°, furnishes with diazomethane in acetone solution 2 : 3-ditoluene-*p*-sulphonylanthragallol 1-methyl ether, m. p. 210—213°, hydrolysed by 10% alcoholic potassium hydroxide to anthragallol 1-methyl ether, m. p. 248—250° (compound +1MeOH; diacetyl derivative, m. p. 165—166°; barium and lead salts). By treatment with 1% methyl-alcoholic potassium hydroxide in acetone solution, VIII yields monotoluene-*p*-sulphonylanthragallol 1-methyl ether, m. p. 289—291°, which is converted by diazomethane in acetone into 2-toluene-*p*-sulphonylanthragallol 1 : 3-dimethyl ether, m. p. 175—177°, and 3-toluene-*p*-sulphonylanthragallol 1 : 2-dimethyl ether, giving by hydrolysis anthragallol 1 : 3- and 1 : 2-dimethyl ether, respectively, migration of the toluene-*p*-sulphonyl group having occurred.

When 2-ethylcarbonatoalizarin (IX) is acetylated with acetic anhydride and pyridine in the usual manner, diacetylalizarin, m. p. 188—189°, is obtained, but if the pyridine solution of IX is cooled prior to the addition of acetic anhydride 2-ethylcarbonato-1-acetylalizarin, m. p. 177—179°, separates. Reduction of IX with stannous chloride and acetic and hydrochloric acids gives 2-ethylcarbonato-1-hydroxyanthrone (X), m. p. 130—133° after sintering at 120°, affording by acetylation with acetic anhydride and pyridine in the cold 2-ethylcarbonato-1 : 9-diacetylanthranol, m. p. 177—180°, and yielding 1 : 2-dihydroxyanthrone, m. p. 149—151°, by treatment with alcoholic potassium hydroxide in boiling methyl alcohol in an atmosphere of hydrogen. With diazomethane in benzene solution in an atmosphere of hydrogen X affords a mixture of 2-ethylcarbonato-1-methoxyanthrone and 1-ethylcarbonato-2-methoxyanthrone (not isolated, but identified by their respective hydrolysis to alizarin 1- and 2-methyl ethers); in acetone solution, 2 : 2'-diethylcarbonatodianthrone, m. p. above 290°, oxidised by chromic acid to alizarin 1-methyl ether, accompanies the foregoing compounds. Similarly, 3 : 4-dihydroxyanthranol (deoxyalizarin) with diazomethane in tetrachloroethane affords 4 : 4'-dihydroxy-3 : 3'-dimethoxydianthrone, m. p. 290—292°, giving alizarin 2-methyl ether by chromic acid oxidation; replacement of the tetrachloroethane by ether increases the yield of the dianthrone, but by using benzene in an atmosphere of hydrogen its presence could not be detected; in the foregoing methylation experiments 4-hydroxy-3'-methoxyanthranol and 3 : 4-dimethoxyanthranol are produced but were not isolated.

5 : 6-Dihydroxy-1-benzylidenecoumaran-2-one (XI) (diacetyl derivative, m. p. 202—203°), obtained in almost theoretical yield by condensing 5 : 6-dihydroxycoumaranone with benzaldehyde, is converted by treatment with excess of toluene-*p*-sulphonyl chloride and pyridine in chloroform into 5 : 6-ditoluene-*p*-sulphonyloxy-1-benzylidenecoumaran-2-one, m. p. 178—180°, but under special conditions into two isomeric monotoluene-*p*-sulphonyloxy-1-benzylidenecoumaran-2-ones, m. p. 217—219° (fluorescent in alkaline solution; acetyl derivative, m. p. 177—180°), and m. p. 237—240° (acetyl derivative, m. p. 145—146°); the latter compound, together with XI, is obtained when the

ditoluene-*p*-sulphonyl derivative is treated with 2 mols. of alcoholic potassium hydroxide in the cold. By treatment with ethyl chloroformate and pyridine in chloroform solution, XI affords a monoethylcarbonato-derivative, m. p. 177—180°, giving by acetylation 5 : 6-diacetoxy-1-benzylidenecoumaran-2-one, m. p. 200—202°, and in the presence of excess of ethyl chloroformate, 5 : 6-diethylcarbonato-1-benzylidenecoumaran-2-one, m. p. 104—107°.

The theory of acyl migration in phenolic compounds (cf. Perkin and Storey, A., 1928, 293), under the influence of diazomethane, is further discussed.

C. W. SHOFFER.

[Di- and tri-quinones of the anthracene series.] R. E. SCHMIDT, B. STEIN, and C. BAMBERGER (Ber., 1929, 62, [B], 1884—1889).—Contrary to Heller and others (this vol., 701), *ψ*-nitropurpurin is not a "quinonenitronic acid," but a nitrohydroxyanthradiquinone, converted by reducing agents which do not affect the nitro-group, into 3-nitro-1 : 2 : 4-trihydroxyanthraquinone. Similarly, Heller's "1 : 2 : 5 : 6-tetrahydroxyanthraquinone-4 : 3, 8 : 7-diquinone-nitronic acid" is 3 : 7-dinitro-2 : 5 : 6 : 8-tetrahydroxyanthradiquinone, reduced to 3 : 7-dinitro-1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone, from which it is obtained by gentle oxidation. The phenylhydrazine salt of the supposed "quinonenitronic acid" is the salt of dinitrohexahydroxyanthraquinone, the production of which is due to the reducing action of phenylhydrazine. Heller's "third yellow variety" is 3 : 7-dinitro-2 : 6-dihydroxyanthratricquinone, reduced successively to 3 : 7-dinitro-2 : 5 : 6 : 8-tetrahydroxyanthradiquinone and 3 : 7-dinitro-1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone.

H. WREN.

Condensation products of the pyrenequinone series. I. G. FARBERIND. A.-G.—See B., 1929, 590.

Santenol. G. KOMPPA (Ber., 1929, 62, [B], 1751—1752).—Santenol is converted by diphenic anhydride at 140—150° or in presence of pyridine at 100° into *santenyl hydrogen diphenate*, m. p. 119—120°, from which homogeneous santenol, m. p. 86°, is derived.

H. WREN.

Bixin. P. KARRER, A. HELFENSTEIN, R. WIDMER, and T. B. VAN ITALLIE (Helv. Chim. Acta, 1929, 12, 741—756).—A review of analytical results given by previous workers for bixin, together with those of the present authors for bixin, perhydrobixin, *bixin methyl ester* (obtained from bixin by methylation in chloroform solution with diazomethane), m. p. 163—164°, and *perhydrobixin methyl ester* (prepared from perhydrobixin either by the action of diazomethane or by treatment with alkali and methyl sulphate), b. p. 203—205°/0.3—0.4 mm., d_4^{20} 0.924, n_D^{20} 1.45597, supports the bixin formula $C_{24}H_{27}O_3 \cdot OMe$.

Hydrolysis of bixin by methyl-alcoholic potassium hydroxide at 65° affords a *norbixin*, m. p. 255° after sintering at 250°; this, by reduction with titanium trichloride, sodium hydroxide, and ammonia, gives successively *dihydronorbixin*, sintering at 197°, and *tetra- or hexa-hydronorbixin*, an oil. Bixin is similarly reduced to *dihydrobixin*, m. p. 207—208° after sintering at 190°.

Hydrolysis of bixin by boiling alcoholic potassium hydroxide leads to *isonorbixin*, m. p. above 300°

(sodium and pyridine salts), methylation of which yields the same isobixin methyl ester as is obtained from bixin methyl ester by heating with iodine in acetic acid solution. *isoBixin*, m. p. 216—217° (methyl ester, m. p. 200—201°), is obtained from bixin by treatment with iodine in chloroform solution. *Perhydronorbixin diamide* (prepared from perhydronorbixin through the *dichloride*) has m. p. 111°.

R. J. W. LE FÈVRE.

Isomerisation and catalytic hydrogenation of Sandaraco-pimaric acid. F. BALAS and J. BRZÁK (Coll. Czech. Chem. Comm., 1929, 1, 352—359; cf. this vol., 811).—Isomerisation of the *pimaric acid* (I) is not effected by boiling with acetic acid, alcoholic sulphuric acid, or 50% potassium hydroxide solution. Distillation at 0.3 mm. gives mainly unchanged material together with a small amount of an acid, m. p. 182°, $[\alpha]_D^{25}$ -34.9° in alcohol. When heated at 240° in carbon dioxide, I furnishes an *isomeride*, m. p. 156°, $[\alpha]_D^{25}$ +64.5° in alcohol (crystalline *ammonium salt*); at 310° considerable decomposition occurs and there are formed an amorphous acid, m. p. 125—130°, $[\alpha]_D^{25}$ +32.5°, and a *hydrocarbon*, $C_{15}H_{28}$, b. p. 195°/12 mm., d_4^{20} 0.9784, n_D^{20} 1.5465. Reduction of I with hydrogen in presence of colloidal platinum and acetic acid at 60° yields a *dihydropimaric acid*, $C_{20}H_{32}O_2$, m. p. 180°, $[\alpha]_D^{25}$ +23.9° in alcohol (crystallographic data by NOVÁČEK). Dehydrogenation of I with sulphur gives indefinite products. The *i*-*pimaric acids* of Henry and Tschirch are probably impure specimens of I, and it is probable that I differs constitutionally from *abietic* and *d*- and *l*-*pimaric acids*.

H. BURTON.

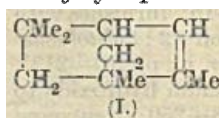
[Preparation of] *l*-menthone. L. T. SANDBORN (Organic Synthesis, 1929, 9, 52—53).

α -Pinene oxide in Grignard's reaction. N. PRILESCHAEV and V. VERSCHUK (J. Russ. Phys. Chem. Soc., 1929, 61, 473—482).— Δ^1 ⁶. *Menthenol*, b. p. 109—110°/13 mm., is prepared by the action of magnesium methyl iodide on *l*- α -pinene oxide. The above alcohol yields the corresponding oxy-alcohol on oxidation with perbenzoic acid, whilst reduction by the Sabatier method gives a saturated *alcohol*, b. p. 223—224°/756 mm.; hydrogenation does not take place when other methods are used. The product of interaction of *l*- α -pinene oxide with magnesium ethyl iodide is *ethylisopropylhexen- α -ol*, b. p. 142—143.5°/50 mm. With magnesium isopropyl chloride an *alcohol*, $C_{12}H_{22}O$, b. p. 133°/17 mm., is obtained, whilst with the corresponding bromide a mixture of products results, from which an *alcohol*, $OH \cdot C_{10}H_{16} \cdot C_4H_9$, b. p. 140—143°/17 mm., was isolated. With magnesium phenyl bromide an *alcohol*, $C_{10}H_{16} \cdot Ph \cdot OH$, b. p. 189—190°/17 mm., was obtained.

R. TRUSZKOWSKI.

Fenchene series. II. Homologue of *isofenchene*. G. KOMPPA (Annalen, 1929, 472, 179—184).—Magnesium methyl iodide and *isofenchene* give *methylisofenchol*, b. p. 82°/10 mm., m. p. 47°, dehydrated by sodium hydrogen sulphate at 155—160° in carbon dioxide to a mixture of hydrocarbons, $C_{11}H_{18}$, b. p. 157—162°, separable into a small fraction, b. p. 157—160°, d_4^{20} 0.84848, n_D^{20} 1.46082, and a main fraction, b. p. 160—162°, d_4^{20} 0.85205, n_D^{20} 1.46261. Treatment of the mixture with ozone in acetic acid

solution with subsequent decomposition by warming gives, after removal of the solvent, 4-*acetyl*-2 : 2 : 4-*tri-methylcyclopentanal*, together with the corresponding



acid. Oxidation of this last substance with sodium hypobromite affords *dl-cis-fenchocamphoric acid*. The hydrocarbon mixture is, therefore, essentially *methylisofenchene* (I). No Wagner rearrangement occurs during the dehydration.

H. BURTON.

Auto-oxidation of cedrene. A. BLUMANN, W. HELLRIEGEL, and L. SCHULZ (Ber., 1929, 62, [B], 1697—1700).—Cedrene, d_4^{20} 0.938, α_D^{25} -52° 30', is converted by protracted treatment with moist oxygen at 30—35° in presence of a cobalt drier into the *alcohol*, $C_{15}H_{24}O$, m. p. 103.5—104°, b. p. 160°/12 mm., d_4^{20} 0.821, $[\alpha]_D^{25}$ -217.5° in alcohol, converted by acetic anhydride and sodium acetate mainly into a doubly unsaturated *sesquiterpene*, $C_{15}H_{22}$. Oxidation of the alcohol with chromic acid affords cedrene, b. p. 157—159°/12 mm., m. p. 32—33°, d_4^{20} 1.014, n_D^{25} 1.51293, $[\alpha]_D^{25}$ -91.67° in alcohol (semicarbazone, m. p. 239—241°).

H. WREN.

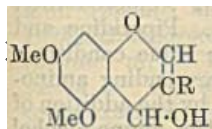
***iso*Flavone group. V. General method applicable to synthesis of derivatives of 7-hydroxyisoflavone.** W. BAKER, A. POLLARD, and R. ROBINSON (J.C.S., 1929, 1468—1473).—*m*-Methoxyphenol reacts with phenacyl bromide in presence of acetone and aqueous sodium hydroxide, forming ω -*m*-methoxyphenoxyacetophenone (I), m. p. 85—86°, converted by sulphuric acid at -5° into 6-methoxy-3-phenylcoumarone, m. p. 43°. Treatment of an ethereal solution of I with aqueous potassium cyanide and 30% sulphuric acid affords α -*m*-methoxyphenoxy-methylmandelonitrile (II), m. p. 84—85.5°, converted by treatment with ethereal methyl-alcoholic hydrogen chloride and subsequent hydrolysis with aqueous-alcoholic potassium hydroxide into a mixture of α -*m*-methoxyphenoxy-methylmandelic acid, $+H_2O$, m. p. 74—76°, m. p. (anhydrous) 96—97° [*methyl ester* (III), m. p. 48—49°, by the action of diazomethane on the acid], and its *amide*, m. p. 122—123°. Treatment of III with 80% sulphuric acid at 60° affords 7-methoxy-3-phenylcoumarin in poor yield. When II is treated with hydrogen chloride in presence of ether and anhydrous zinc chloride and the reaction product hydrolysed with water, 3-hydroxy-7-methoxyisoflavanone, m. p. 133—135°, results. This is reduced by sodium amalgam and methyl alcohol to 3 : 4-dihydroxy-7-methoxyisoflavane, m. p. 153°, whilst treatment with sulphuric acid gives 7-methoxyisoflavone (IV), m. p. 156°.

Oxidation of 7-methoxy-2-styrylisoflavone in pyridine solution with aqueous potassium permanganate below 40° (cf. A., 1925, i, 1299) gives 7-methoxyisoflavone-2-carboxylic acid, m. p. 241° with loss of carbon dioxide. Thermal decomposition of this acid also yields IV (cf. *loc. cit.*).

H. BURTON.

Substances derived from anhydrocatechin tetramethyl ethers. W. BAKER (J.C.S., 1929, 1593—1604).—Anhydrocatechin tetramethyl ether (I) (cf. Drumm, A., 1923, i, 1221) is oxidised by potassium permanganate in slightly diluted acetone

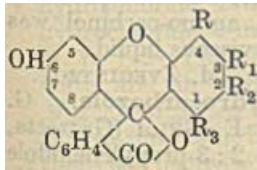
at 12—22°, yielding about 12% of 5:7:3':4'-tetramethoxy-3-phenylcoumarin (II), m. p. 177°, and a substance which when boiled with hydrochloric acid gives 5:7:3':4'-tetramethoxyisoflavylum chloride (III) (about 8%). Demethylation of II with hydriodic acid (*d* 1.7) at 140° produces 5:7:3':4'-tetrahydroxy-3-phenylcoumarin, m. p. 337° (decomp.). Phloroglucinaldehyde reacts with sodium homoveratrate in presence of acetic anhydride, forming the diacetyl derivative, m. p. 151°, of 5:7-dihydroxy-3':4'-dimethoxy-3-phenylcoumarin, m. p. about 327° (decomp.). Methylation of the last-named substance with methyl sulphate yields II. Oxidation of I with potassium permanganate in slightly diluted pyridine affords about 25% of II and a trace of III. 5:7:3':4'-Tetramethoxyisoflavylum bromide is identical with the bromide described by Drumm (*loc. cit.*) and formulated as a pyrylium salt. Oxidation of the ψ -base from III with potassium permanganate in slightly diluted acetone or pyridine gives a trace of II and 2-hydroxy-4:6-dimethoxybenzoic acid; the major part of the material is unchanged. The annexed constitution [$R=C_6H_3(OMe)_2$] is assigned to the ψ -base. It is improbable that isoflavones are derived from catechin-like substances:



stances:

The "hydrochloride" of anhydrocatechin tetramethyl ether (Freudenberg, Carrara, and Cohn, A., 1926, 73) is identical with III and is conveniently prepared by saturating a solution of I in acetic acid and anhydride with hydrogen chloride. When this is carried out in an atmosphere of hydrogen, III is formed only slowly and in small amount, indicating that aerial oxidation takes place during the change I \rightarrow III. The "hydrochloride" of anhydroepicatechin tetramethyl ether (Freudenberg, Fikentscher, and Wenner, A., 1925, i, 692) is identical with tetramethyl-luteolinidin chloride (Pratt, Robinson, and Williams, A., 1924, i, 306), now shown to be 5:7:3':4'-tetramethoxyflavylum chloride hydrochloride dihydrate, $C_{19}H_{19}O_5Cl \cdot HCl \cdot 2H_2O$, m. p. 161—162° (decomp.). H. BURTON.

Fluoresceins and rhodamines of mixed type. N. N. GHATAK and S. DUTT (J. Indian Chem. Soc., 1929, 6, 465—471).—A number of unsymmetrically substituted phthaleins have been prepared by condensing *o*-2':4'-dihydroxybenzoylbenzoic acid with phenols or aminophenols, generally by heating with concentrated sulphuric acid or stannic chloride. Condensation always occurs in the *o*-position of the phenol to give the fluoran (annexed formula). The colours of the products deepen when the substituent hydroxy- or amino-groups are nearer to the bridge oxygen atom (cf. Dutt, A., 1927, 1006). The following fluorans



are described, and their absorption maxima, shades on silk and wool, and colour and fluorescence in solution tabulated: 6-hydroxy-, m. p. 181°; 4:6-dihydroxy-, m. p. 179°; 1:6-dihydroxy-, m. p. above

280°; 2:6-dihydroxy-, m. p. 177°; 3:4:6-trihydroxy-, m. p. 189°; 1:3:6-trihydroxy-, m. p. above 285°; 6-hydroxy-4-methyl-, m. p. 135°; 6-hydroxy-3-methyl-, m. p. 143°; 6-hydroxy-2-methyl-, m. p. 152°; 6-hydroxy-1-methyl-4-isopropyl-, m. p. 166°; 6-hydroxy-4-methyl-1-isopropyl-, m. p. 134°; 6-hydroxy-3:4-benzo-, m. p. 117°; 6-hydroxy-2:3-benzo-, m. p. 113°; 6-hydroxy-2:3-(4'-hydroxy)benzo-, m. p. 183°; 3-dimethylamino-6-hydroxy-, m. p. 169°; 3-diethylamino-6-hydroxy-, m. p. 163°. R. K. CALLOW.

Plant colouring matters. Carotinoid pigment from maize: zeaxanthin. P. KARRER, H. SALOMON, and H. WEHRLI (Helv. Chim. Acta, 1929, 12, 790—792).—Extraction of maize with ethyl alcohol and light petroleum gives zeaxanthin, $C_{40}H_{56}O_2$, m. p. 201—202°, and a yellow pigment (flavone derivative?). With sulphuric acid zeaxanthin gives a stable deep blue coloration. R. J. W. LE FEVRE.

Mononitro- and dinitro-thiophens. II. Vapour pressures. V. S. BABASINIAN and J. G. JACKSON (J. Amer. Chem. Soc., 1929, 51, 2147—2151).—The vapour pressures of pure (a) nitro- and (b) dinitro-thiophens (cf. A., 1928, 1378) have been measured by an improved dynamic method at (a) 105—170°, (b) 115—250°. The calculated b. p., molecular latent heats of vaporisation, and entropies of vaporisation (cf. Hildebrand, A., 1915, ii, 416), respectively, are (a) 218.2°, 12,300 g.-cal., 14.7, and (b) 293.3°, 14,300 g.-cal., and 14.8. Nitrothiophen is stable at 170°; dinitrothiophen decomposes at 250° and reacts with mercury at 195°. H. E. F. NOTTON.

Thionaphthen derivatives. G. KOMPPA (J. pr. Chem., 1929, [ii], 122, 319—331).—In the nitration of thionaphthen with nitric and acetic acids an intermediate substance, m. p. 154.5°, is obtained if a deficiency of nitric acid is used for a short period. Reduction of nitrothionaphthen with stannous chloride yields the double lin salt, m. p. 204°, of aminothionaphthen. The free base is obtained by steam distillation of the basified reduction product and is isolated from the aqueous distillate as its acetyl, m. p. 166—167°, or benzoyl derivative, m. p. 132°, since the free base is unstable and, moreover, cannot be converted into hydroxythionaphthen (cf. Friedlander, A., 1907, i, 335). Sulphonation of pure thionaphthen obtained by reduction of 2-hydroxythionaphthen yields a monosulphonic acid isolated as its sodium salt, but with commercial thionaphthen only a mixture of mono- and di-sulphonic acids could be obtained, whence a pure disulphonic acid was isolated as its sodium salt. Thionaphthen and bromine in carbon tetrachloride give 2-bromothionaphthen, b. p. 136—137°/13 mm., d_4^{20} 1.6294, the bromine atom of which is not replaced by hydroxyl either by boiling 30% aqueous sodium hydroxide or methyl-alcoholic potassium hydroxide at 200—210°, although in the latter case an acidic substance, $C_8H_{10}O_2S$, m. p. 125°, is obtained. Dibromothionaphthen, m. p. 57.5° (Komppa, A., 1894, i, 130), is also stable to 30% alkali, nitric and hydrochloric acids. Chlorination of thionaphthen in carbon tetrachloride yields 1:2(?)-dichlorothionaphthen, b. p. 125—127°/10 mm., m. p. 54°. 2-Thionaphthenyl methyl ketone, m. p. 64° (semicarbazone, m. p. 244—

245°), is obtained in 30% yield by the action of anhydrous aluminium chloride on acetyl chloride and thionaphthen in carbon disulphide solution, and is oxidised by sodium hypobromite to *thionaphthen-2-carboxylic acid*, m. p. 174—175°. J. W. BAKER.

Thiophen analogues of di-, tri-, and tetraphenylmethane compounds. W. MINNIS (J. Amer. Chem. Soc., 1929, 51, 2143—2147).—The thiophen derivatives are obtained by the methods applicable to their benzene analogues, but usually in smaller yield. Phenyl 2-thienyl ketone (Covey, A., 1884, 1168) and phosphorus pentachloride at 60—80° give *dichlorophenylthienylmethane*, which cannot be distilled at 20 mm., whilst aluminium amalgam and ammonia give *phenyl-2-thienylcarbinol*, m. p. 57—58°. Diphenylthienylcarbinol (cf. Gomberg, A., 1913, i, 641), from phenyl thienyl ketone and magnesium phenyl bromide, is reduced by formic acid to diphenylthienylmethane and a bimolecular substance, m. p. 174°, and converted by hydrogen bromide in benzene into *diphenylthienylmethyl bromide*, m. p. 110—111° (decomp. when kept), and by hydrogen chloride into *diphenylthienylmethyl chloride*, m. p. 80—81°. *Diphenylthienylmethylaniline* has m. p. 118—119°. The chloride or bromide reacts quantitatively with molecular silver in benzene, giving red solutions of *diphenylthienylmethyl*, from which a pink solid, m. p. 157—162°, was obtained. This radical resembles phenylthioxanthyl in its reactions (cf. A., 1921, i, 163). An attempt to prepare triphenylthienylmethane from triphenylmethyl chloride and magnesium thienyl iodide gave instead 5:5'-*bistriphenylmethyl-2:2'-dithienyl*, m. p. 277° (*dibromo-derivative*, m. p. 287°), also formed from triphenyl-2-iodothienylmethane and copper powder at 200—250°. Magnesium thienyl iodide gives with fluorenone 9-thienylfluoren-9-ol, m. p. 81—82°, with phenyl α -naphthyl ketone, *phenyl- α -naphthylthienylcarbinol*, m. p. 131°, and with xanthone, 9-thienylxanthen-9-ol, m. p. 168—169°. This gives with hydrogen chloride in ethyl acetate 9-chloro-9-thienylxanthen, from which a ferrichloride, m. p. 198°, mercurichloride, m. p. 182—198° (decomp.), and zincichloride, m. p. 225—227°, are obtained.

H. E. F. NOTTON.

Synthesis of hexahydro- β -collidine. M. DE MONTMOLLIN and M. MARTENET (Helv. Chim. Acta, 12, 1929, 604—609).—*n*-Propyl alcohol is oxidised catalytically (Sabatier-Senderens) to *n*-propaldehyde, converted by saturated potassium carbonate solution into the corresponding aldol. Reduction of the crude aldol is carried out *in situ* by aluminium turnings. From the resulting β -methylpentane- α -diol α - *dibromo- β -methylpentane*, b. p. 80—82°/12 mm., and a *bromohydroxy- β -methylpentane*, b. p. 86—94°/12 mm., are obtained by the action of phosphorus tribromide in benzene solution.

The related β -methylpentane- α -dicarboxylonitrile, b. p. 189—193°/12 mm., is reduced by sodium and boiling alcohol to γ -methyl- β -ethylpentamethylene-diamine, b. p. 100—103°/12 mm., which gives hexahydro- β -collidine hydrochloride when its ethereal solution is treated with dry hydrogen chloride. Catalytic hydrogenation (pyrophoric nickel) of β -methylpentane- α -dicarboxylonitrile results in the

direct production of about 30% of the disubstituted piperidine owing to simultaneous hydrogenation and cyclisation.

R. J. W. LE FÈVRE.

[Preparation of] benzoylpiperidine. C. S. MARVEL and W. A. LAZIER (Organic Synthesis, 1929, 9, 16—19).

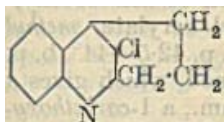
Action of piperidine and piperazine on the α -oxides of ethylene, isobutylene, and trimethylethylene. K. A. KRASUSKI and K. G. KOSENKO (Ukraine Chem. J., 1929, 4, 38—59).—The action of piperidine and piperazine on ethylene, isobutylene, and trimethylethylene α -oxides with the formation of α -amino-alcohols was investigated. The reaction was much more vigorous with piperidine than with piperazine, in accordance with the rule, suggested by the author, that the rate depends on the electrolytic dissociation constant of the amine. Piperidine and isobutylene oxide reacted in a sealed tube at 100° to give piperidinotrimethylcarbinol, b. p. 202—202.5°, d_4^{20} 0.9114 (hydrochloride, m. p. 191—192°; chloroaurate, m. p. 118—119°; picrate, 111.5°). Piperidine and trimethylethylene oxide under the same conditions gave only a 12% yield of the corresponding amino-alcohol, but this was raised to 70% by the addition of water to the reaction mixture. The amino-alcohol was dimethylpiperidinoethylcarbinol, b. p. 219.5—220.5° (hydrochloride, m. p. 187—179°; chloroaurate, m. p. 73—74.5°; picrate, m. p. 83—84°).

Piperazine reacted with 2 mols. of the oxides in every case, to give dihydroxy-carbinols; the monohydroxy-compounds could not be obtained. Piperazine and isobutylene oxide gave 1:4-di- β -hydroxyisobutylpiperazine, m. p. (+2H₂O) 78—79°, m. p. (anhydrous), 102—102.5° [hydrochloride, m. p. 224° (decomp.); chloroaurate, m. p. 198° (decomp.); picrate, decomposes above 200°]. With trimethylethylene, piperazine reacted less readily to give a 40% yield of 1:4-di- β -hydroxy- α - β -dimethylpropylpiperazine, (OH·CMe₂·CHMe)₂·C₄H₈N₂, b. p. 124—124.5° [hydrochloride, does not melt at 300°; chloroaurate, m. p. 180—182° (decomp.); picrate, decomposes above 220°]. Considerable quantities of trimethylethylene glycol, b. p. 176—178°, which yielded a hexahydrate, m. p. 23.5—24° were also obtained. If the reaction was carried out at 160—180° the yield of the carbinol was not increased, but methyl isopropyl ketone was obtained, owing apparently to the decomposition of the amino-carbinol, as the olefine oxide does not isomerise to the ketone in alkaline solution. From the higher fraction of the reaction mixture, a compound which did not form a hydrochloride, chloroaurate, or picrate, and was probably a dehydration product of the amino-carbinol was isolated in an impure state as a viscous liquid.

M. ZVEGINTZOV.

Homologues of tetrahydrocarbazole. G. PLANCHER, B. CECCHETTI, and E. GHIGI (Gazzetta, 1929, 59, 334—347).—When 2:3-propyleneindole (dihydropentindole; Perkin and Plant, J.C.S., 1923, 123, 3243) in alcoholic sodium ethoxide solution is treated with chloroform a vigorous reaction takes place in which it is assumed that the dichloromethyl group enters the 11 position and the pyrrole ring is

enlarged with the formation of 3-chloro 2:4-cyclopropylenequinoline (annexed formula), m. p. 208°. 2:3-Pentamethyleneindole, m. p. 143° (picrate, m. p. 140°), is obtained by heating cycloheptanonephenylhydrazone with 10% sulphuric acid. Only a



trace of basic product is obtained by treatment of this with chloroform and sodium ethoxide. cyclo-Heptanone-p-nitrophenylhydrazone has m. p. 137°. cycloHeptanone condenses with *as*-methylphenylhydrazine, and the product, treated with 10% sulphuric acid, yields *N*-methyl-2:3-pentamethyleneindole, m. p. 50° (picrate, m. p. 78°), which on long heating with methyl iodide yields the *hydriodide*, m. p. 249° (decomp.), of a base, $C_{15}H_{19}N$, m. p. 55° (picrate, m. p. 138°). When tetrahydrocarbazole is heated in a sealed tube with excess of ethyl iodide, 9:11-diethyl- $\Delta^{10,1}$ -carbazolenine *hydriodide* (I), m. p. 190—200° (decomp.), is obtained. The phenylhydrazone of 2-ethylcyclohexanone yields with sulphuric acid a mixture of 11-ethyl- Δ^8 -carbazolenine, b. p. 190—195°/12 mm. (picrate, m. p. 138°) (II), and acid-soluble 1-ethyltetrahydrocarbazole, b. p. 160—175°/17 mm. (picrate, m. p. 145°) (III). With ethyl iodide, II yields I. The *as*-ethylphenylhydrazone of 2-ethylcyclohexanone yields with sulphuric acid a mixture of 1:9-diethyltetrahydrocarbazole, b. p. 200—210°/15 mm. (picrate, m. p. about 65°), and I (picrate, m. p. 131°). The postulated course of these reactions is supported by a similar series with methyl derivatives. The phenylhydrazone of 2-methylcyclohexanone, b. p. 220°/35—40 mm., yields 1-methyltetrahydrocarbazole, b. p. 208°/25 mm., m. p. 65° (picrate, m. p. 145°) (IV), and 11-methyl- Δ^8 -carbazolenine, b. p. 176—177°/25 mm., m. p. 65° (picrate, m. p. 169°) (V). Reduction of IV by tin and hydrochloric acid yields 1-methylcarbazoline hydrochloride, m. p. 268°. Reduction of V yields 11-methylcarbazoline hydrochloride, m. p. 220°. With methyl iodide IV yields 1:9:11-trimethylcarbazole (picrate, m. p. 157°), whilst V yields 9:11-dimethyl- $\Delta^{10,1}$ -carbazolenine *hydriodide*, m. p. 211°. The phenylosazone of 2-hydroxycyclohexanone yields with sulphuric acid 1-ketotetrahydrocarbazole, m. p. 167° [picrate, m. p. 162°; semicarbazone, m. p. 227° (decomp.)]; semicarbazone picrate, m. p. 182°].

R. K. CALLOW.

Natural rotation of polarised light by optically active bases. III. Rotation, refraction, and volume of organic bases in solution. W. LEITHE (Monatsh., 1929, 52, 151—162; cf. A., 1928, 1022; this vol., 647).—The rotatory powers, refractive indices, and densities of α -pipecoline and its hydrochloride, α -phenylethylamine, *r*-phenylethylamine hydrochloride, tetrahydro-2-methylquinoline and its hydrochloride, α -methylindoline and its *hydrochloride*, m. p. 142—143°, have been determined in the pure state and in various solvents and the values of $M_{\text{solution}} - M_{\text{substance}}$ and $V_{\text{solution}} - V_{\text{substance}}$ calculated. With α -pipecoline in water, alcohol, and methyl alcohol there is a decrease in the value of M , in carbon tetrachloride, ether, heptane, and acetone there is an increase, whilst benzene, chloroform, ethyl acetate, and pyridine have little or no influence. For com-

parison the effect of solvent on cyclohexane is examined: here the values increase throughout the series, indicating that the differences with α -pipecoline are due to solvent action on the imino-group. With phenylethylamine all the solvents used except benzene, pyridine, and water, cause generally an increase; similar differences are shown by ethylbenzene except in heptane and halides. The phenyl group has also a considerable influence on the rotatory power. Tetrahydro-2-methylquinoline and α -methylindoline give increased values, again due to the phenyl group. Ether exerts an abnormal effect on the molecular volume of the bases examined, but apart from this the variation in the rotatory powers and V is more in agreement than with the rotatory power and M . The rotatory power of α -pipecoline hydrochloride is much lower in chloroform than in water or alcohols.

H. BURTON.

Two *ms*-tetrahydro-9:9'-diacridyls (?). K. LEHMSTEDT and H. HUNDERTMARK (Ber., 1929, 62, [B], 1742—1743).—The constitution of 9:9'-diacridyl (Lehmstedt and Wirth, A., 1928, 1259) is confirmed by its conversion by zinc dust and acetic acid into tetrahydrodiacridyl, m. p. 214° with decomposition into acridine and acridan. This latter compound is not identical with the tetrahydrodiacridyl, m. p. 279°, of Schlenk and Bergmann (A., 1928, 1031 *seq.*). The "insoluble hydroacridine" of Graebe and Caro has the composition $C_{26}H_{22}ON_2$ and hence differs from Schlenk's compound; under certain conditions it loses water with formation of 9:10:9':10'-tetrahydro-10:10'-diacridyl, m. p. 220°.

H. WREN.

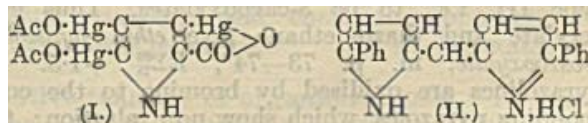
[Preparation of] pyrrole. S. M. McELVAIN and K. M. BOLLIGER (Organic Syntheses, 1929, 9, 78—79).

Inner complex salts of 2-pyridyl methyl ketoxime. B. EMMERT and K. DIEHL (Ber., 1929, 62, [B], 1738—1742).—Cobaltic hydroxide is transformed by a boiling aqueous solution of 2-pyridyl methyl ketoxime into the compound,

$(Co(\overline{NC_5H_4} \xrightarrow{NO} CMe)_3)_3$ decomp. 275—280°. The nickel compound is isolated as the substances $2C_{14}H_{14}O_2N_4Ni, PhOMe$, $C_{14}H_{14}O_2N_4Ni, 4C_5H_5N$, and $C_{14}H_{14}O_2N_4Ni, 2C_5H_5N, 4H_2O$. The substances $C_{14}H_{14}O_2N_4Zn, H_2O$, $2C_{14}H_{14}O_2N_4Zn, ZnO$, and $C_{28}H_{30}O_4N_8Cd$, decomp. above 250° are described.

H. WREN.

Pyrrole derivatives. G. PLANCHER, G. ROSSI, and E. GHIGI (Gazzetta, 1929, 59, 347—355).—Interaction of pyrrole-2-carboxylic acid with mercuric acetate in aqueous-alcoholic solution in presence of a little acetic acid yields a compound to which the constitution I is assigned.



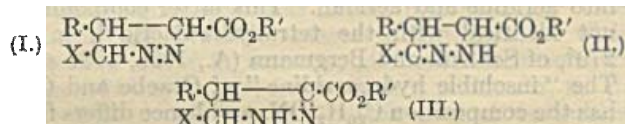
α -Phenylpyrrole-2-aldehyde, m. p. 138° (semicarbazone, m. p. 190°; *p*-nitrophenylhydrazone, m. p. 222°; azine, m. p. 240°; azlactone, m. p. 180°; compound with 1 mol. (?) 5-dimethylcyclohexane-1:3-

dione, m. p. 129°), is obtained in poor yield by the action of chloroform on 2-phenylpyrrole in aqueous-alcoholic potassium hydroxide solution, but in good yield by the Adams-Levine modification of the Gattermann synthesis (A., 1924, i, 860) from 2-phenylpyrrole. In the latter reaction (5-phenyl-2-pyrrolyl)-(5-phenyl-2-pyrrolyl)methane hydrochloride, blue (II) (perchlorate), is formed as a by-product.

R. K. CALLOW.

Action of piperazine on isosafrole oxide. T. S. KUSNER (Ukraine Chem. J., 1929, 4, 85—88; cf. A., 1928, 999).—An equimolecular mixture of piperazine and isosafrole oxide was kept in ethyl-alcoholic solution at the ordinary temperature. Slow combination occurred, giving a compound (2 oxide + 1 base), a white powder, m. p. 238—240° (decomp.), insoluble in most organic solvents. M. ZVEGINTZOV.

Δ^1 - and Δ^2 -Pyrazolines. K. VON AUWERS and E. CAUER (Annalen, 1929, 470, 284—312).—When a pyrazoline is formed by the addition of an aliphatic diazo-compound to an unsaturated ester, a nitrogen atom becomes attached to the α -carbon atom, and an intermediate compound of the type I is formed; this then changes, by migration of hydrogen, to give a



compound of type II or of type III (cf. Buchner, A., 1893, i, *passim*; von Pechmann, A., 1898—1901, i, *passim*). Buchner considered that compounds of type I (Δ^1 -pyrazolines) underwent immediate isomeric change; since in the cases investigated by him the groups X· and ·CO₂R' were identical, being the carbethoxyl group, types II and III (Δ^2 -pyrazolines) became identical. Compounds of each of the three types are now described.

There being no suitable chemical method, compounds of types II and III are distinguished by optical means. It has been shown (A., 1927, 1203) that 3-phenylpyrazolines, unlike the 5-phenyl isomerides, give a strong exaltation of the refractivity and dispersivity; since compounds of type III contain a conjugated system of double linkings, whilst those of type II do not, it can be assumed that compounds having exaltations comparable with that of 3-phenylpyrazoline are of type III. The author, as usual, employs the specific exaltation, EΣ, as the characteristic spectrochemical property.

Pyrazolines are prepared by the addition of diazomethane or diazoethane to a number of esters in ether at −5°, and the products are all found to be of type III, i.e., to be 3-carboxylates. Thus ethyl acrylate and diazomethane give ethyl pyrazoline-3-carboxylate, m. p. 73—74°, EΣ_D²⁰ +1.5. The pyrazolines are oxidised by bromine to the corresponding pyrazoles, which show no exaltation; thus the above compound yields ethyl pyrazole-3(5)-carboxylate, m. p. 157—158°, which hydrolyses to the known acid. The addition of diazomethane takes place readily, but that of diazoethane (obtained by the

gradual addition of methyl-alcoholic potassium hydroxide to a boiling ethereal solution of nitrosoethylurethane) is slower; with methyl acrylate, methyl 5-methylpyrazoline-3-carboxylate, m. p. 42.5—44°, b. p. 138°/12 mm., EΣ_D²⁰ +1.65°, is formed, which gives a 1-acetyl derivative, b. p. 140°/12 mm., a 1-carbethoxy-derivative, m. p. 84—85.5°, and, with sodium methoxide and methyl iodide, a 1-methyl derivative, b. p. about 105°/12 mm.

The preparation of conjugation-free compounds, of type II, is more difficult, but is effected by the condensation of unsaturated esters with hydrazine. With hydrazine itself, methyl β-acetylacrylate gives mainly the hydrazide of the acid, but when the hydrochloride is used, methyl 3-methylpyrazoline-5-carboxylate, b. p. 117°/12 mm., d₄²⁰ 1.139, n_D²⁰ 1.476, EΣ_D²⁰ +0.05, is obtained. This ester gives, with phenylcarbimide, a 1-phenylcarbamylyl derivative, m. p. 117.5—118.5°; the acetyl derivative has m. p. 52.5—55°; the 1-carbethoxy-derivative, m. p. 53—54.5°, would be expected to be formed by ring-closure from methyl β-acetylacrylate carbethoxyhydrazone, m. p. 127—127.5°, but actually the hydrazone is regenerated. The action of methylhydrazine on methyl β-acetylacrylate gives rise to a largely resinified product, identified as methyl 1:3-dimethylpyrazoline-5-carboxylate, b. p. 104°/11 mm., d₄²⁰ 1.152, n_D²⁰ 1.501, EΣ_D²⁰ −0.05.

Similarly, methyl crotonate with diazomethane (cf. von Pechmann and Burkard, A., 1901, i, 167) yields methyl 4-methylpyrazoline-3-carboxylate, m. p. 33—35°, b. p. 139°/13 mm., EΣ_D²⁰ +1.5 (benzoyl derivative, m. p. 89—90°), which is oxidised to methyl 4-methylpyrazole-3(5)-carboxylate, m. p. 170—171°, hydrolysed to the acid. With diazoethane, methyl 4:5-dimethylpyrazoline-3-carboxylate, b. p. 139—140°/14 mm., d₄²⁰ 1.101, n_D²⁰ 1.506, EΣ_D²⁰ +1.55, is formed, which gives a 1-phenylcarbamylyl derivative, m. p. 111—113°; methyl 4:5-dimethylpyrazole-3-carboxylate and its parent acid will be described later. Methyl crotonate reacts very slowly with phenyldiazomethane, to give an impure pyrazoline, oxidised and hydrolysed to 3(5)-phenyl-4-methylpyrazole-5(3)-carboxylic acid, m. p. 234—236° (decomp.).

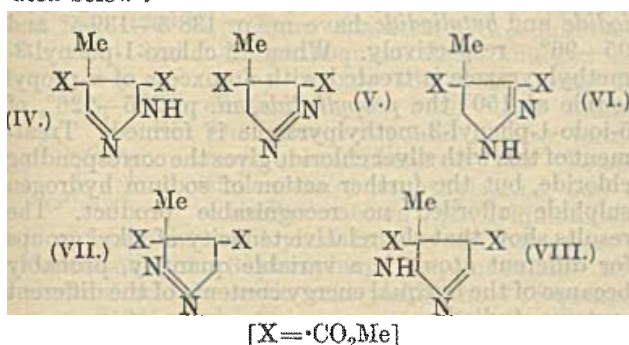
Ethyl cinnamate and diazomethane give ethyl 4-phenyl pyrazoline-3-carboxylate, m. p. 100—100.5°, oxidised to ethyl 4-phenylpyrazole-3(5)-carboxylate, m. p. 162—162.5°. From amyl cinnamate, amyl 4-phenylpyrazoline-3-carboxylate, m. p. 109—111°, d₄²⁰ 1.095, n_D 1.617, EΣ_D²⁰ +1.05 (in quinoline, which may be responsible for the small relative deficiency of the exaltation).

—The product described by Gabriel and Colman (A., 1899, i, 390) as the hydrazone of benzoylacrylic acid, from which it is obtained by the action of hydrazine, is actually 3-phenylpyrazoline-5-carboxylic acid, m. p. 186°; with acetic acid this gives a 1-acetyl derivative, m. p. 216—217.5°, and with nitrous acid a 1-nitroso-compound, m. p. 133.5° (decomp.). Attempted esterification by methyl alcohol and sulphuric acid or hydrochloric acid gave resinous products, but by the action of diazomethane the methyl ester, b. p. 178°/12 mm., d₄²⁰ 1.179, n_D²⁰ 1.578, EΣ_D²⁰ +1.35, is obtained; although this is a 5-carboxylate, it gives an exaltation, since there is a phenyl group in the 3-posi-

tion. The ester reacts with phenylcarbimide to give a 1-phenylcarbamyl derivative, m. p. 136.5—137.5°; the acid, with bromine to give 4-bromo-3(5)-phenylpyrazole-5(3)-carboxylic acid, m. p. 256—257°, identical with a specimen prepared by bromination of the parent acid.

Dimethyl maleate and diazoethane yield methyl 5-methylpyrazoline-3 : 4-dicarboxylate, b. p. 145—153°/2 mm., $E\sigma_D^{20} +1.4$, which is oxidised and hydrolysed to 5-methylpyrazole-3 : 4-dicarboxylic acid, m. p. 229—230°.

In the investigation of the possibility of the existence of compounds of type I (Δ^1 -pyrazolines), it was considered that such compounds would be most likely to have independent existence when the product to which they would invert would be non-conjugated. In the reaction between methyl citraconate and diazomethane, the conceivable products are as formulated below :



but of these IV and V can be excluded, since IV could be obtained only by inversion of V, and since V would itself invert in the opposite direction to give the conjugated compound VI. Von Pechmann and Burkard investigated the reaction (A., 1901, i, 167), and oxidised their product to the pyrazole; they considered the first product to be VII or VIII. The reaction is actually more complex, and the product from 18 g. of the original ester yields three fractions, A (3 g.), B (12 g.), and C (2 g.). A consists of methyl 1-methylcyclopropane-1 : 2-dicarboxylate, b. p. 104°/14 mm., d_4^{20} 1.112, n_D^{20} 1.4466, which shows exaltation of refractivity and of dispersivity, and is hydrolysed to the acid (mixed isomerides, m. p. 100—120°); the last is converted into the anhydride (cf. Ingold, A., 1925, i, 357), which takes up water from the atmosphere to form the *cis*-acid. The high-boiling fraction C is identified from its exaltation as the co-ordinated methyl 4-methylpyrazoline-3 : 4-dicarboxylate, m. p. 58—60°, b. p. 178°/12 mm., $E\sigma_D^{20} +0.95$ (the somewhat low value of the exaltation is attributed to the effect of the *gem*-grouping); with phenylcarbimide, the 1-phenylcarbamyl derivative, m. p. 148—149°, is formed. Oxidation and hydrolysis gives a methylpyrazoledicarboxylic acid, m. p. 313°; such an acid could be formed by the migration of either the 4-methyl or the 4-carbomethoxyl group to the 5-position, and could thus be either 4-methylpyrazole-3 : 5-dicarboxylic acid, or 5-methylpyrazole-3 : 4-dicarboxylic acid. The latter of these is formed (m. p. 229—230°) from methyl maleate (see above), and

the present substance has thus the former structure (cf. Klages, A., 1903, i, 528). The migration of the carbomethoxyl group in this oxidation is noteworthy; its elimination would have been expected.

The main fraction B, which is optically normal, must have one of the structures VII or VIII, and these can be distinguished chemically. All the Δ^2 -pyrazolines described above react vigorously with ethyl chloroformate or with phenylcarbimide; the present substance is indifferent to the former, and reacts only slowly with the latter, giving ill-defined products, and thus does not possess a secondary nitrogen atom. It must therefore be a Δ^1 -pyrazoline, namely, methyl 3-methyl- Δ^1 -pyrazoline-3 : 4-dicarboxylate, b. p. 148°/12 mm., d_4^{20} 1.200, n_D^{20} 1.464, $E\sigma_D^{20}$ 0.0. This is confirmed by the fact that the action of hydrogen chloride converts it into the hydrochloride, m. p. about 120°, of methyl 5-methylpyrazoline-4 : 5-dicarboxylate (the structure VIII above), b. p. 172°/20 mm., d_4^{20} 1.230, n_D^{20} 1.479, $E\sigma_D^{20} +0.05$, which reacts with phenylcarbimide, giving unidentified products. Oxidation of either the Δ^1 - or of this Δ^2 -pyrazoline gives 3(5)-methylpyrazole-4-carboxylic acid (cf. von Pechmann and Burkard, *loc. cit.*); carbomethoxyl has been eliminated from the *gem*-grouping.

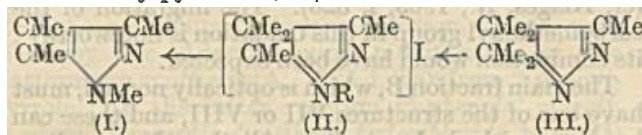
Methyl dimethylmaleate, b. p. 106°/17 mm., obtained from the anhydride (Ott, A., 1928, 1351), reacts with diazomethane to form a product which is optically normal, and is identified as methyl 3 : 4-dimethyl- Δ^1 -pyrazoline-3 : 4-dicarboxylate, m. p. 49—51°, b. p. 149°/11 mm., d_4^{20} 1.172, n_D^{20} 1.446, $E\sigma_D^{20}$ 0.0, since it reacts only very slowly with phenylcarbimide, and since it is converted by hydrogen chloride into the hydrochloride, m. p. about 160°, of methyl 4 : 5-dimethyl- Δ^2 -pyrazoline-4 : 5-dicarboxylate, m. p. 71—73°, $E\sigma_D^{20} -0.05$, which reacts more rapidly with phenylcarbimide, forming the same product as the Δ^1 -compound, a 1-phenylcarbamyl derivative, m. p. 136—137°. An attempt to oxidise the Δ^1 -compound by bromine yielded the hydrobromide of the isomeride.

It was hoped that methyl 4-phenyl-3-methyl- Δ^1 -pyrazoline-3-carboxylate might be obtained by the interaction of methyl α -methylcinnamate and diazomethane, but the product was unstable and lost nitrogen to give a substance which from spectrochemical evidence could not be a cyclopropane derivative, and was considered to be a methyl $\alpha\beta$ -dimethylcinnamate (probably the *cis*-form, since hydrolysis gave an oil), b. p. 134°/17 mm., d_4^{20} 1.051, n_D^{20} 1.5347, of exaltation comparable with that of ethyl *trans*- $\alpha\beta$ -dimethyleinnamate (von Auwers, A., 1917, i, 267).

A tabular conspectus is given of various spectrochemical properties of the Δ^1 - and Δ^2 -pyrazolines described above; an investigation of the stereochemistry, stability, and chemical properties of Δ^1 -pyrazolines is promised. E. W. WIGNALL.

Relative tenacity of organic radicals. K. VON AUWERS and F. BERGMANN (Annalen, 1929, 472, 287—314).—Knorr and Oettinger's observation (A., 1894, i, 546; Diss., Jena, 1894) that 1 : 3 : 4 : 5-tetramethylpyrazole (I) is formed by thermal decomposition of the methiodide (II, R—Me) of 3 : 4 : 4 : 5-

tetramethylpyrazole (III) is confirmed. Similar de-



composition of a series of iodides corresponding with II, namely, *ethyl* (II, R=Et), m. p. 167°; *n-propyl*, m. p. 142—142.5°; *isopropyl*, m. p. 157—158.5°; *allyl*, m. p. 165°, and *benzyl*, m. p. 132—133°, shows that with the exception of the *isopropyl* derivative elimination of both R and 4-methyl groups occurs. The percentages of 4-methyl group eliminated in the above series are 74, 89, 100, 35, and 33.5, respectively. The strength of attachment of the Pr^β group to nitrogen is greater than that of the Pr^α group (cf. A., 1928, 306). 1-*Ethyl*-, b. p. 192—193° (*picrate*, m. p. 156—157°); 1-*n-propyl*-, b. p. 94—95°/15 mm. (*picrate*, m. p. 107—107.5°); 1-*isopropyl*-, b. p. 89—91°/15 mm. (*picrate*, m. p. 137—138.5°); 1-*allyl*-, b. p. 94—96°/13 mm. (*picrate*, m. p. 119—120°), and 1-*benzyl*-3:4:5-trimethylpyrazoles, b. p. 163°/16 mm. (*picrate*, m. p. 148—148.5°), are prepared by the action of the requisite alkyl iodide and benzyl chloride on 3:4:5-trimethylpyrazole. In order to determine the difference in the attachment of methyl and ethyl groups to carbon, decompositions of the following quaternary iodides of 3:5-dimethyl-4:4-diethylpyrazole, b. p. 130—133°/17 mm., m. p. 52—53° and 72—73.5° (when kept in a desiccator) (*picrate*, m. p. 193° after previous softening) (obtained from diethylacetylacetone and hydrazine), were carried out: *methyl*, m. p. 186°; *n-propyl*, m. p. 106—112°; *isopropyl*, m. p. 161.5—162°; *allyl*, m. p. 123.5—125°, and *benzyl*, m. p. 148.5—149°. The percentages of 4-ethyl group eliminated are 79, 100, 100, 90, and 75.5, respectively, indicating a stronger attachment of methyl than of ethyl to carbon. In both these series of decompositions the temperature has an effect on the ratio C-alkyl:N-alkyl obtained; the amount of C-alkyl fission is usually lowered with rise of temperature. Hydrazine hydrate and ethylacetylacetone yield 3:5-dimethyl-4-ethylpyrazole (IV), b. p. 133—135°/15 mm., m. p. 53.5—54.5° (*picrate*, m. p. 211—212°); with methylhydrazine, 1:3:5-trimethyl-4-ethylpyrazole, b. p. 84—86°/12 mm. (*hydrochloride*, m. p. 114.5—115°; *picrate*, m. p. 134.5—135.5°), results. 1-*Ethyl*-, b. p. 86—89°/13 mm. (*picrate*, m. p. 108—109°); 1-*n-propyl*-, b. p. 98—100°/12 mm. (*picrate*, m. p. 116.5—117°); 1-*isopropyl*-, b. p. 90—92°/13 mm. (*picrate*, m. p. 112.5—113.5°); 1-*allyl*-, b. p. 100—103°/14 mm. (*picrate*, m. p. 75—76°), and 1-*benzyl*-3:5-dimethyl-4-ethylpyrazoles, b. p. 162—164°/12 mm. (*picrate*, m. p. 126—127.5°), are prepared by the action of the requisite alkyl iodide and benzyl chloride on IV. $\gamma\gamma$ -Dibenzoyl-*n*-pentane reacts with hydrazine, yielding 3:5-diphenyl-4:4-diethylpyrazole, m. p. 155.5° (*picrate*, m. p. 160—161°). Thermal decomposition of the *methiodide*, m. p. 196.5°, of this gives 3:5-diphenyl-1-methyl-4-ethylpyrazole, m. p. 80—82° (*picrate*, m. p. 138—139°), also obtained by methylation of 3:5-diphenyl-4-ethylpyrazole, m. p. 167°. 3:5-Diphenyl-1:4-diethyl-, m. p. 63—64°

(*picrate*, m. p. 122.5—123.5°), and 3:5-diphenyl-1-benzyl-4-ethylpyrazole, m. p. 83—83.5° (*picrate*, m. p. 111.5—112.5°), are also described. 3:5-Diphenylpyrazole *picrate* has m. p. 161—163°.

Knorr's observation (A., 1897, i, 108) that thermal decomposition of antipyrine ψ -ethiodide yields ethyl iodide and antipyrine, is also confirmed. From this and various observations recorded in the literature it is concluded that the strength of attachment of alkyl groups to oxygen is much less than that to nitrogen. Decomposition of a series of thiopyrine ψ -alkiodides (V) (cf. Michaelis, A., 1904, i, 780), shows that elimination of both R and R' occurs. Thus when R=Me and R'=Et, Pr, Bu, and C₃H₅, the percentages of R eliminated are 13—28, 45—46, 55, and 10.5, respectively. When R'=Me and R=Et and C₃H₅, the corresponding elimination is 89—94 and 87%, respectively. Thiopyrine ψ -*propyl*-iodide and *butyl*iodide have m. p. 138.5—139.5° and 95—96°, respectively. When 5-chloro-1-phenyl-3-methylpyrazole is treated with an excess of *n*-propyl iodide at 150° the *propyl*iodide, m. p. 225—226°, of 5-iodo-1-phenyl-3-methylpyrazole is formed. Treatment of this with silver chloride gives the corresponding chloride, but the further action of sodium hydrogen sulphide afforded no recognisable product. The results show that the relative tenacity of alkyl groups for different atoms is a variable quantity, probably because of the unequal energy contents of the different systems studied.

Spectrochemical data for 1-phenyl-3-methyl-2-ethyl-, 1-phenyl-2:3:4-trimethyl-, and 1-phenyl-3:4:4-trimethyl-5-pyrazolones, and 5-methoxy- and 5-methylthiol-1-phenyl-3-methylpyrazoles, are given. These support Knorr's structure for antipyrine but do not afford a certain proof. 1-Phenyl-4-ethyl-5-pyrazolone has m. p. 114—115.5° (lit. 78°).

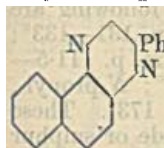
H. BURTON.

Isomerism of diphenylmethylpyrazoles. K. VON AUWERS and K. SCHAUM (Ber., 1929, 62, [B], 1671—1677).—In the cases of the isomeric 1:5-diphenyl-3-methylpyrazoles, m. p. 63° and 72°, respectively, and 1:3-diphenyl-5-methylpyrazoles, m. p. 47° and 77°, respectively, it is found that the stable modification causes transformation of the isomeric as well as its own labile form. The existence of isomeric forms of 3-phenylindazole, 5-chloro-, 5-bromo-, and 7-acetamido-5-methyl-indazoles, can be explained by assuming structures analogous to C₆H₄<^{CPh}/_{NH}>N and C₆H₄<^{CPh}/_N>NH but the validity of the hypothesis is rendered doubtful by its non-applicability to the diphenylmethylpyrazoles in which a free imino-hydrogen atom is not present. The capacity of transformation of the diphenylmethylpyrazoles in the crystalline state appears to consign this case of isomerism to the large group of polymorphism. The main types of the latter phenomenon are considered at length under the headings: physical polymorphism, chemical polymorphism, cryptochemical polymorphism, cryptochemical-metameric polymorphism, and cryptochemical-polymeric polymorphism. H. WREN.

Inner complex salts of pyrrole derivatives. B. EMMERT, K. DIEHL, and F. GOLLWITZER (Ber., 1929, 62, [B], 1733—1738; cf. A., 1927, 1204).—

Nickel pyridylpyrrole, $\text{Ni}(\text{C}_5\text{H}_4\text{N})_2$, m. p. 165°, is prepared by the action of nickel oxide on 2-2'-pyridylpyrrole in boiling naphthalene. The corresponding *aluminum salt*, m. p. about 310°, and *cadmium compound* are described. Pyrrole-2-aldehyde affords a *copper compound*, $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2\text{Cu}$. The aldehyde is converted by aqueous methylamine into the corresponding *methylimide*, $\text{C}_4\text{H}_4\text{N}\cdot\text{CH}\cdot\text{NMe}$, m. p. 57°, which yields a *copper salt*, $\text{C}_{12}\text{H}_{14}\text{N}_4\text{Cu}$, m. p. 163—165°, and a *cobalt compound*, $\text{C}_{18}\text{H}_{21}\text{N}_6\text{Co}$, m. p. 250—252° (additive compound, $\text{C}_{25}\text{H}_{29}\text{ON}_6\text{Co}$, with anisole). H. WREN.

Formation of the quinoxaline nucleus. G. B. CRIPPA (Gazzetta, 1929, 59, 330—334).—Benzene-azo- β -naphthylamine condenses with acetophenone at 165—170° in presence of a little hydrochloric acid to yield 3-phenylnaphthoquinoxaline (annexed formula), m. p. 161—162°, with the



elimination of water and aniline. The same compound is also formed from *m*-nitrobenzene- or 1-naphthalene-azo- β -naphthylamine, and by a similar reaction 2-phenylquinoxaline is obtained in small yield from *o*-aminoazobenzene. Oxidation of 3-phenylnaphthoquinoxaline with chromic acid in acetic acid yields the 7:8-quinone, m. p. 210°, which condenses with *o*-phenylenediamine to yield the *azine*, m. p. 272°. R. K. CALLOW.

Complexes derived from triazinetricarboxylic acid. P. PASCAL and R. LECUIR (Compt. rend., 1929, 189, 49—51; cf. A., 1925, i, 984).—The following complex derivatives of triazinetricarboxylic acid were prepared by adding the appropriate heavy metal salt to a solution of the potassium salt of the acid until the precipitate formed just ceases to redissolve in the excess of the alkali salt [$\text{X} = \text{C}_3\text{N}_3(\text{CO}_2)_3$]: $\text{K}_6\text{Fe}(\text{FeX}_2)_2\cdot 24\text{H}_2\text{O}$, greyish-violet; $\text{K}_2\text{Mn}(\text{MnX}_2)_2\cdot 6\text{H}_2\text{O}$, yellow; $\text{K}_3\text{Cr}(\text{CrX}_2)_2\cdot 40\text{H}_2\text{O}$, greyish-violet; $\text{K}_3\text{Co}(\text{CoX}_2)_2\cdot 24\text{H}_2\text{O}$, pale violet; $\text{K}_3\text{Fe}(\text{FeX}_2)_2\cdot 3\text{K}_3(\text{FeX}_2)_2\cdot 40\text{H}_2\text{O}$, orange-yellow; $\text{K}_2\text{Ni}(\text{NiX}_2)_2\cdot \text{H}_2\text{O}$, green; $\text{K}_6\text{Co}(\text{CoX}_2)_2\cdot 8\text{H}_2\text{O}$, yellow. By adding the potassium salt to that of the heavy metal with the latter always in excess, there were formed the complexes $\text{Fe}(\text{FeX}_2)_2\cdot 24\text{H}_2\text{O}$, yellow; $\text{Co}_2(\text{CoX}_2)_2\cdot 9\text{H}_2\text{O}$, yellow; and $\text{Ni}_2(\text{NiX}_2)_2\cdot 4\text{H}_2\text{O}$, green; but not the corresponding derivatives of manganese or chromium. Using concentrated solutions containing a large excess of the potassium salt, the following derivatives were separated by the addition of alcohol: $\text{K}_4(\text{FeX}_2)_2$, wine-red, and $\text{K}_3(\text{FeX}_2)_2\cdot 20\text{H}_2\text{O}$, orange-yellow. The yellow compound, $\text{Co}_2(\text{CoX}_2)_2\cdot 9\text{H}_2\text{O}$, already mentioned, undergoes internal hydrolysis of the triazinetricarboxylic chain, in presence of a slightly acid solution, to form the pink isomeric double salt, $\text{Co}_2(\text{CoX}_2)_2\cdot 9(\text{NH}_4)_2(\text{Co}[\text{C}_2\text{O}_4]_2)$. B. W. ANDERSON.

Poly-membered ring system. B. EMMERT and F. MEIXNER (Ber., 1929, 62, [B], 1731—1733).—

4:4'-Dipiperidyl is converted by benzaldehyde in the presence of alcohol into *dibenzylidenedipiperidyl*, $\text{CHPh}(\text{NC}_5\text{H}_9)_2\text{CHPh}$, m. p. 189°, readily hydrolysed to its components by dilute hydrochloric acid. Formaldehyde and dipiperidyl afford the compound $(\text{C}_{11}\text{H}_{20}\text{N}_2)_2$, m. p. about 285° after darkening, whilst with *p*-hydroxybenzaldehyde the substance $[\text{C}_5\text{H}_9\text{N}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{OH}]_2$, m. p. 153°, is produced. H. WREN.

Alkylxanthines. D. W. MACCORQUODALE (J. Amer. Chem. Soc., 1925, 51, 2245—2251).—8-Chloroxanthine, prepared by Fischer's method (A., 1898, i, 48), is converted by ethyl iodide and *N*-potassium hydroxide at 90—95° into 8-chloro-3:7-diethylxanthine (I), m. p. 207° (all m. p. corr.) (cf. Biltz and Peukert, A., 1925, i, 1462). This with 10% potassium hydroxide in absolute alcohol gives 8-ethoxy-3:7-diethylxanthine, m. p. 212°, hydrolysed by hydrochloric acid to 3:7-diethyluric acid, m. p. 371—376°. Methylation of I gives 8-chloro-1-methyl-3:7-diethylxanthine, m. p. 114.5°, from which 8-ethoxy-1-methyl-3:7-diethylxanthine, m. p. 112°, and 1-methyl-3:7-diethyluric acid are prepared, and ethylation of I gives 8-chloro-1:3:7-triethylxanthine, m. p. 79—80°, reduced by hydriodic acid at 100° to 1:3:7-triethylxanthine. 8-Chloroxanthine, *n*-butyl iodide, and potassium hydroxide at 130° give 8-chloro-3:7-dibutylxanthine, m. p. 145°, from which 3:7-dibutylxanthine, m. p. 127°, 8-chloro-1:3:7-tributylxanthine, b. p. 232—240°/10 mm. (uncorr.), and 1:3:7-tributylxanthine, m. p. 41—42° (hydrochloride, m. p. 131—134°), are prepared. H. E. F. NOTTON.

Hæmin synthesis. H. FISCHER (Naturwiss., 1929, 17, 611—617).—See this vol., 333.

Amino-derivatives of 1-thio- and furo-3:4-diazoles. R. STOLLE and K. FEHRENBACH (J. pr. Chem., 1929, [ii], 122, 289—318).—Treatment of 2-amino-1:3:4-thiodiazole (Freund and Meinecke, A., 1897, i, 122) with nitrous acid yields a diazonium salt which couples with phenol to yield 2-*p*-hydroxybenzeneazo-1:3:4-thiodiazole, decomp. 270°. Similarly, from the corresponding 5-methyl compound (*loc. cit.*) is obtained 2-*p*-hydroxybenzeneazo-5-methyl-1:3:4-thiodiazole, decomp. 270°. The action of nitrous acid on 2:5-diamino-1:3:4-thiodiazole (I) (Fromm, A., 1923, i, 1239) in 12% acetic acid converts it into the 2-nitrosoamino-derivative, identical with the compound erroneously described as di-iminotetrahydrothiodiazole by Busch and Lotz (A., 1915, i, 317). This is reduced by stannous chloride to 2-hydrazino-5-amino-1:3:4-thiodiazole dihydrochloride, decomp. 207° [benzylidene derivative of the free base, m. p. 232° (decomp.)]; hydrochloride of benzylidene derivative, m. p. 250° (decomp.), converted by nitrous acid into the 2-azido-compound. Diazotisation of I in concentrated hydrochloric acid yields the 2-diazonium chloride, which couples with phenol to yield 2-*p*-hydroxybenzeneazo-5-amino-1:3:4-thiodiazole hydrochloride, decomp. 260° [ON-diacetyl derivative of the free base, m. p. 315° (decomp.)], and by heating

in hydrochloric acid solution is converted into the *hydrochloride*, m. p. 110°, of 2-chloro-5-amino-1:3:4-thiodiazole, m. p. 192° (decomp.), which is oxidised with bleaching powder to 2:2'-dichloro-5:5'-azo-1:3:4-thiodiazole, m. p. 274° (decomp.). Diazotisation of I with sodium nitrite and concentrated hydrochloric acid at -10° yields the bisdiazonium salt, since on warming the solution 2:5-dichloro-1:3:4-thiodiazole, m. p. 74°, is obtained. If, however, nitrogen trioxide is passed into the boiling diazonium solution the product is 2-chloro-5-hydroxy-1:3:4-thiodiazole, m. p. 107°. Similar diazotisation of I in 40% hydrobromic acid at -10° yields the corresponding 2:5-dibromo-derivative, m. p. 111°. The action of nitrous acid on 2-thiol-5-amino-1:3:4-thiodiazole (Freund and Imgart, A., 1895, i, 400; cf. Busch and Lotz, *loc. cit.*) in dilute hydrochloric acid yields *bis*-(5:5'-nitrosoamino-1:3:4-thiodiazole) 2:2'-disulphide, decomp. 120°, reduced by stannous chloride to 2-thiol-5-hydrazino-1:3:4-thiodiazole *hydrochloride*, decomp. 212° (benzylidene derivative of the free base, decomp. 255°). Corresponding amino-furodiazoles are prepared by the action of lead oxide on the appropriate acylthiosemicarbazide, hydrogen sulphide being eliminated. Thus acetylthiosemicarbazide, +H₂O, m. p. 105°, and anhydrous, m. p. 165° (cf. Freund and Meinecke, *loc. cit.*), yields 2-amino-5-methyl-1:3:4-furodiazole, m. p. 183° [acetyl derivative, m. p. 180°, identical with that obtained by the action of acetic anhydride on 5-amino-1:2:3:4-tetrazole (Stollé, this vol., 828)]. Benzoylthiosemicarbazide yields 2-amino-*o*-phenyl-1:3:4-furodiazole (II), decomp. 245° (*hydrochloride*, decomp. 177°; *acetyl* derivative, m. p. 223°; *benzoyl* derivative, m. p. 203°); the same compound is prepared from 1:4-dibenzoylthiosemicarbazide, m. p. 176°, obtained by the action of benzoylhydrazine on benzoylthiocarbimide, one benzoyl group being eliminated. By the action of nitrous acid in dilute hydrochloric acid II yields the 2-nitrosoamino-derivative, decomp. 101°, reduced by zinc dust and water to the 2-hydrazino-compound, which is isolated as its *benzylidene* derivative, m. p. 242° (decomp.) (decomposed by boiling dilute hydrochloric acid to benzoic acid, benzaldehyde, and carbohydrazide), or is converted by the further action of nitrous acid (in acetic acid) into 2-azido-5-phenyl-1:3:4-furodiazole, m. p. 89°. Oxidation of II with bleaching powder yields 5:5'-diphenyl-2:2'-azo-1:3:4-furodiazole, m. p. 330° (decomp.), reduced by alcoholic ammonium sulphide to the corresponding *hydrazo*-derivative, m. p. 233° (decomp.). An attempt to prepare 2:5-diamino-1:3:4-furodiazole by the action of lead oxide on hydrazothiodicarbonylamine yielded only hydrazodicarbonylamine.

J. W. BAKER.

Formation and stability of 2-thio-1:2-dihydrobenzothiazoles. E. W. McCLELLAND, L. A. WARREN, and (Miss) J. H. JACKSON (J.C.S., 1929, 1582—1588).—2-Dithiobenzoyl (improved method of preparation given) reacts with phosphorus pentasulphide in boiling xylene yielding 2:3-dithiosulphindene, m. p. 94—95° (lit. 98°), which when treated with primary amines, usually in alcoholic

solution, gives 1-substituted 2-thio-1:2-dihydrobenzothiazoles, $C_6H_4 \begin{smallmatrix} S \\ \diagup \diagdown \\ CS \end{smallmatrix} NR$ (I). The following are described: 1-methyl-, (I, R=Me), m. p. 138—139°; 1-ethyl-, m. p. 63—64°; 1-benzyl-, m. p. 122—123°, and 1-phenyl-, m. p. 77°. These compounds are converted by treatment with hydrogen sulphide into 2:3-dithiosulphindene, but are unaffected by sulphur dioxide. 2-Keto-1-methyl-1:2-dihydrobenzothiazole (I, CS=CO, R=Me) and 2-keto-1-phenyl-1:2-dihydrobenzothiazole are reduced by sulphur dioxide to 2:2'-dithiobenzomethylamide and 2:2'-dithiobenzanilide, respectively (cf. McClelland and Longwell, J.C.S., 1923, 123, 3310). Replacement of oxygen by sulphur in these benzothiazoles thus causes an increase in the stability of the N-S linking. Oxidation of the above thiodihydrobenzothiazoles with hydrogen peroxide in acetic acid solution at 100° gives *N*-substituted *o*-benzoic sulphinides, $C_6H_4 \begin{smallmatrix} SO_2 \\ \diagup \diagdown \\ CO \end{smallmatrix} NR$ (II), also formed by similar oxidation of 2:2'-dithiobenzamides. The following are described: *N*-methyl-, (II, R=Me), m. p. 131—133°; *N*-ethyl-, m. p. 94—94.5°; *N*-benzyl-, m. p. 111.5—113.5° (lit. 118°); *N*-phenyl-, m. p. 191°; *N*-propyl-, m. p. 75—76°, and *N*-*o*-tolyl-, m. p. 173°. These are also unaffected by hydrogen sulphide or sulphur dioxide. 2:2'-Dithiobenzonitrile (from the corresponding amide by dehydration with phosphoric oxide in boiling xylene) is converted by treatment with hydrogen sulphide in presence of alcohol and a small amount of sodium ethoxide into 2:3-dithiosulphindene. 2-Thio-1:2-dihydrobenzothiazole could not be prepared.

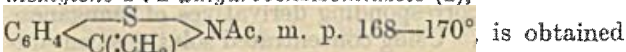
The increased stability of the S-N linking in I and II is probably due to an increase in the positive character of the *o*-sulphur atom; if this effect is due to an electronic displacement the CS group must exert a greater influence than the CO group in series I.

H. BURTON.

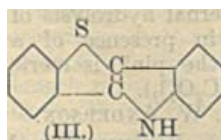
Determination of methylene-blue. M. FRANÇOIS and L. SEGURN (J. Pharm. Chim., 1929, [viii], 10, 5—9).—Methylene-blue can be determined by precipitation with picric acid as *methylene-blue picrate trihydrate*.

R. J. W. LE FEVRE.

Thionaphthindole. E. W. McCLELLAND (J.C.S., 1929, 1588—1593).—When 2-keto-1:2-dihydrobenzothiazole is treated with acetic anhydride and anhydrous potassium acetate at 120°, 1-acetyl-2-methylene-1:2-dihydrobenzothiazole (I),



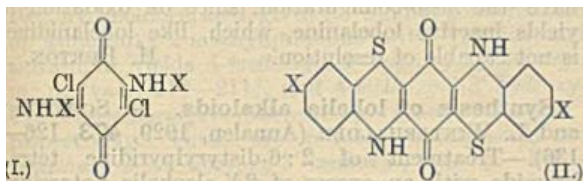
is obtained together with *o*-thiolacetophenone (II) [*semicarbazone*, m. p. 235° (decomp.)], and 2-acetyl-3-oxy-1-thionaphthen. Formation of I occurs presumably by loss of carbon dioxide from the intermediate



unsaturated carboxylic acid. Hydrolysis of I with 2*N*-hydrochloric acid affords 3-oxy-1-thionaphthen, whilst treatment with bromine in chloroform solution gives a *bromo*-derivative, m. p. 201—202°. Treatment of II with phenyl-

hydrazine in warm, glacial acetic acid solution yields *thionaphthindole* (III), m. p. 252—253° (N-*acetyl* derivative, m. p. 160—161°), also obtained from 2-thioacetophenone synthesised from *o*-aminoacetophenone by Leuckart's method (G.P. 198,509). Treatment of *o*-thiolbenzoic acid with *o*-nitrobenzyl chloride in presence of alcoholic potassium ethoxide, subsequent treatment of the product formed with alcoholic potassium ethoxide, and further reduction of the intermediate thionaphthen so formed with zinc dust and acetic acid also yields III. The ready formation of III from II indicates that a sulphur atom *ortho* to carbonyl promotes enolisation, thus rendering the indole transformation facile. H. BURTON.

Derivatives of dibenzodithiazinequinone—vat dyes. II. R. SHIBATA, S. TESHIMA, and Y. ASAGI (Tech. Rep. Tôhoku, 1929, 8, 279—295).—Condensation of chloranil in boiling alcoholic solution with *p*-chloroaniline or *p*-bromoaniline gives *dichloro-* or *dibromo-*condensation products (I; X=C₆H₄hal.), m. p. 305—307° (after decomp. and sublimation at about 287°) and m. p. 285—289° (with sublimation at about 275°), respectively. Both substances give



amorphous *mercaptans* by treatment with aqueous sodium sulphide solution; those, by oxidation with boiling nitrobenzene, yield *dichloro-* and *dibromo-dibenzodithiazinequinone* (II; X=Cl or Br), both decomp. above 360°.

Condensation of chloroanil with *p*-aminophenol similarly gives a *product* (I; X=C₆H₄·OH), m. p. 264° (decomp.), from which is derived, through the corresponding *mercaptan*, *dihydroxydibenzodithiazinequinone* (II; X=OH) (also obtained by treatment of the analogous *ethoxy-*derivative [*sulphoxide* described] from *p*-phenetidine with aqueous hydrobromic acid under pressure; the *ethoxy-*intermediate compound [I; X=C₆H₄·OEt], decomp. 263°). *p*-Aminophenyl acetate condenses with chloroanil in boiling alcoholic solution giving a *compound* (I; X=C₆H₄·OAc), decomp. 280°; treatment of this with aqueous sodium sulphide solution gives the *mercaptan* derived from the substance, m. p. 264° (decomp.), above.

From the condensation of chloroanil with β -naphthylamine *dinaphthodithiazinequinone* (corresponding *sulphoxide* and its sodium *salt*) is obtained, a *compound* (I; X=C₁₀H₇), decomp. 273°, being obtained immediately. R. J. W. LE FEVRE.

Ketosulphonic acids. I. Synthesis of 1 : 2 : 3-thiodiazole derivatives. P. MAZAK and J. SUSZKO (Rocz. Chem., 1929, 9, 431—443).—Phenylmethylidihydrothiodiazole dioxide (see this vol., 829) is extremely resistant to the action of acids, and the nitrogen atoms possess no tendency towards salt-formation with acids. Alkali hydroxides, on the other hand,

hydrolyse it to acetonesulphonic acid phenylhydrazone. The m. p. of the dioxide is 84—85°, and of the 5-bromo-derivative, 123°. R. TRUSZKOWSKI.

Alkaloids of chinese *Corydalis ambigua*, Cham. et Sch. (Yen-Hu-So). III. *Corydalis-I* and monomethyl ethers of *corydalis-F* and *-G*. T. Q. CHOU (Chinese J. Physiol., 1929, 3, 301—305).—In addition to the eight alkaloids previously obtained from the tubers of this plant (cf. A., 1928, 927; this vol., 477), another has now been isolated, *corydalis-I*, m. p. 104°, [α]_D²⁵ in alcohol +112.5° (*hydrogen oxalate*, m. p. 185°; *hydrochloride*, m. p. 236°; *hydrobromide*, m. p. 241°), which appears to act as a depressor towards the central nervous system. The monomethyl ether, C₂₁H₂₅O₄N, m. p. 140°, [α]_D²⁵ —275° (in alcohol), of *corydalis-F*, prepared by the action of nitrosomethylurethane in presence of sodium hydroxide on *corydalis-F*, appears to be *l*-tetrahydropalmatine (Spath, Mosettig, and Trothandl, A., 1923, i, 593). The monomethyl ether, m. p. 135°, [α]_D²⁵ +300°, of *corydalis-G*, prepared similarly, is identical with *corydaline* (*corydalis-A*), whence *corydalis-G* is the *corybulbine* of Freund and Josephi (A., 1894, i, 100). C. C. N. VASS.

Lobelia alkaloids. III. Constitution of lobelia alkaloids. H. WIELAND and O. DRAGENDORFF (Annalen, 1929, 473, 83—101).—Oxidation of lobelanidine and lobeline with chromic oxide in acetic acid solution gives lobelanine (I), which when treated with phenylhydrazine in presence of 50% acetic acid affords an additive compound, C₂₂H₂₅O₂N₂·2NH₂·NHPh, m. p. 187° (decomp.). Oxidation of I with hydrogen peroxide in acetic acid solution yields lobelanine N-oxide, m. p. 84—86° (not sharp; *hydrochloride*, m. p. 169°), reduced by sulphurous acid to I and unaffected by heating with 20% sulphuric acid. Distillation of lobelanine hydrochloride (II), m. p. 196°, with zinc dust gives rather more than 1 mol. of acetophenone, indicating the presence of two phenacyl groups in I. *Lobelaninedioxime*, m. p. 209° (decomp.; prepared in not very good yield from II, hydroxylamine hydrochloride, and potassium acetate in aqueous solution), probably exists in stereoisomeric forms, and is converted by treatment with cold thionyl chloride in chloroform into the *dianilide*, m. p. 218—219°, of lobelinic acid [1-methylpiperidine-2 : 6-diacetic acid], m. p. 225—228° (decomp.; *chloroaurate*, decomp. 215—217°). Oxidation of I with chromic oxide and 33% sulphuric acid affords benzoic and scopolinic [1-methylpiperidine-2 : 6-dicarboxylic] acids. Treatment of I with methyl iodide and dissolution of the product in methyl alcohol affords a small amount of the hydriodide of I, together with a soluble quaternary iodide, which on treatment with silver oxide eliminates trimethylamine. Extraction of the residue with hydrochloric acid affords 50% of unchanged material together with a *hydrochloride*, C₂₃H₂₉O₃N·HCl, m. p. 236° (decomp.) [the free *base*, m. p. 164°, is probably CH₂Bz·CHNMe₂·[CH₂]₃·CH(OH)·CH₂Bz], and a neutral fraction (A). Hydrogenation of A in presence of palladium-black and alcohol affords $\alpha\gamma$ -dibenzoyl-*n*-heptane (III), m. p. 56—57° (lit. 44°),

oxidised by chromic oxide in acetic acid solution to ζ -benzoyl-*n*-heptoic acid, m. p. 84–85°, benzoic and impure pimelic acids. Catalytic reduction of *I* in presence of acetic acid gives α -diphenyl-*n*-nonane- α -diol, oxidised by chromic oxide and acetic acid to *III*.

Lobelanine is, therefore, 2 : 6-diphenacyl-1-methylpiperidine, whilst lobeline and lobelanidine are respectively the mono- and di-alcohols derived by successive reduction of the keto-groups in *I* (cf. A., 1925, i, 1087). Since *I* is a β -aminoketone, hydrolysis (with ring fission) occurs readily and the formation of diphenylcarbinol and fluorene during alkaline and acid hydrolysis of *I* (*loc. cit.*) is readily explained by assuming successive elimination of acetophenone and methylamine, and subsequent ring closure to partly hydrogenated benzophenone derivatives. Ring fission occurs also during the action of methyl iodide on *I*.

H. BURTON.

Lobelia alkaloids. IV. Synthesis of lobelia alkaloids. H. WIELAND and I. DRISHAUS (Annalen, 1929, 473, 102–118).—Reduction of 2 : 6-distyrylpyridine with sodium and alcohol gives a mixture of stereoisomeric 2 : 6-di- β -phenylethylpiperidines, separable through the hydrochlorides into *meso*-norlobelan, $C_{21}H_{27}N$ [hydrochloride, m. p. 195°; the methiodide, $C_{22}H_{29}N, MeI$, m. p. 234°, obtained by the action of methyl iodide is identical with lobelan methiodide (A., 1925, i, 1087)], and *trans*-norlobelan (hydrochloride, m. p. 162–165°; hydriodide, m. p. 187–189°; methiodide, $C_{22}H_{29}N, MeI$, m. p. 217–219°, also obtained by the action of methyl iodide on the base). Condensation of ethyl glutarate and acetophenone in presence of ether and sodamide gives α -*dibenzoyl-n-heptane*- β -*dione* (*I*), m. p. 72°, and δ -keto- ϵ -benzoyl-*n*-hexoic acid, m. p. 130° [methyl ester (*II*), m. p. 43°], together with a base, $C_{19}H_{15}N$, m. p. 64–5° (picrate, m. p. 185°), and a substance, $C_{27}H_{29}O$, m. p. 135°. Similar condensation of *II* and acetophenone affords *I*. When *I* is treated at 100° with dry ammonia 2 : 6-di(benzoylmethylene)piperidine (*III*), m. p. 237° with coloration (tetrabromide, m. p. 183°), results. Reduction of *III* with hydrogen in presence of platinum oxide and pyridine at 40–50° yields the isomeric unsaturated glycols, α (racemic)- and β (*meso*)-norlobelanidienes, $C_{21}H_{23}O_2N$, m. p. 148° and 173°, respectively, together with a substance, $C_{21}H_{21}O_2N$, m. p. 125°. Further reduction of the β -form with aluminium amalgam and moist ether affords norlobelanidine, m. p. 120° (hydrochloride, m. p. 244°), but the main product is an oil, oxidised by chromic oxide in acetic acid to norlobelanine (*IV*), m. p. 120° [hydrochloride, m. p. 195° (cf. *loc. cit.*)]. Similar reduction of the α -form gives a mixture of bases oxidised by chromic acid to *IV*. The stereochemistry of the above bases is discussed.

H. BURTON.

Lobelia alkaloids. V. Bases accompanying lobeline and the mutual relationships of the lobelia alkaloids. H. WIELAND, W. KOSCHARA, and E. DANE (Annalen, 1929, 473, 118–126).—The substance previously described (A., 1921, i, 802) as lobelidine is now shown to be dl-lobeline (*I*), $C_{22}H_{27}O_2N$, m. p. 110° (hydrochloride, m. p. 170° with

coloration; nitrate, decomp. 159–160°), oxidised by chromic oxide in acetic acid solution to lobelanine [nitrate, m. p. 160° (cf. A., 1925, i, 1087)]. *iso*Lobelanine (A., 1925, i, 1087) is now formulated as norlobelanine (*II*) [2 : 6-diphenacylpiperidine] (*N*-benzoyl derivative, m. p. 125–126°). Reduction of *II* with 1% sodium amalgam and dilute acetic acid affords norlobelanidine (*III*), m. p. 120° (hydrochloride, m. p. 244° with slight coloration and decomp.; nitrate, m. p. 179–180°; hydriodide, m. p. 211°), methylated by methyl *p*-toluenesulphonate to lobelanidine (*IV*). Oxidation of *III* with chromic oxide in acetic acid solution gives *II*, whilst oxidation of *IV* with potassium permanganate and *N*-sulphuric acid yields *I*. Treatment of the hydrochloride of *I* with sodium *d*-tartrate affords the not very soluble *l*-lobeline *d*-tartrate, from which *l*-lobeline, m. p. 130–131°, $[\alpha]_D -38.6^\circ$ in alcohol, is obtained. Separation of *III* from the minor alkaloids of lobelia is effected through its hydrochloride.

Of the five chief alkaloids of the lobelia group only lobeline occurs in an optically active form. The asymmetric ring carbon atoms in this compound have the *meso*-configuration, since on oxidation it yields inactive lobelanine, which, like lobelanidine, is not capable of resolution.

H. BURTON.

Synthesis of lobelia alkaloids. G. SCHEUING and L. WINTERHALDER (Annalen, 1929, 473, 126–136).—Treatment of 2 : 6-distyrylpyridine tetrabromide with an excess of 2*N*-alcoholic potassium hydroxide solution affords 2 : 6-di- β -phenylethynylpyridine (*I*), m. p. 137–138°, reduced by hydrogen in presence of palladised barium sulphate and methyl alcohol to 2 : 6-distyrylpyridine. Treatment of *I* with 50% sulphuric acid gives 2 : 6-diphenacylpyridine (*II*), m. p. 92° [sulphate, m. p. 197°; hydrochloride, m. p. 223° (decomp.)], reduced by hydrogen in presence of platinum oxide, barium sulphate, and methyl alcohol to 2 : 6-di- β -hydroxy- β -phenylethylpiperidine. Similar catalytic reduction of the hydrochloride, m. p. 219° (decomp.), of the last-named compound gives norlobelanidine [2 : 6-di- β -hydroxy- β -phenylethylpiperidine], m. p. 120°, methylated to lobelanidine. Catalytic reduction of norlobelanine with 1 mol. of hydrogen gives dl-norlobeline, m. p. 104°, reduced further to norlobelanidine. Treatment of *I* with methyl *p*-toluenesulphonate in benzene solution affords the corresponding meth-*p*-toluenesulphonate, m. p. 168°, converted by treatment with slightly diluted sulphuric acid at 125° into the meth-*p*-toluenesulphonate, m. p. 224°, of *II*. Reduction of this with hydrogen (5 mols.) in presence of platinum oxide, barium sulphate, and methyl alcohol affords lobelanidine (*III*). With 3 mols. of hydrogen lobelanine results; this is reduced further to *III*. 2- β -Phenylethynylpyridine, b. p. 148–150°/1 mm., is converted by treatment with 50% sulphuric acid into 2-phenacylpyridine (*IV*), b. p. 159°/1 mm., m. p. 59°, also obtained by oxidation of 2- β -hydroxy- β -phenylethylpyridine (*V*) with chromic oxide in acetic acid solution. Reduction of *IV* with hydrogen in presence of platinum oxide, barium sulphate, and methyl alcohol affords *V*; in acetic acid as solvent

the product is 2- β -hydroxy- β -phenylethylpiperidine, b. p. 165°/4 mm., m. p. 85°. H. BURTON.

Phenol bases from *Angostura* bark. Synthesis of galipoline. E. SPATH and G. PAPAIOANOU (Monatsh., 1929, 52, 129—140).—Galipoline (I), $C_{19}H_{19}O_3N$, m. p. (vac.) 193°, has been isolated in a yield of 3 g. from the phenolic bases of the alcoholic extract of 16 kg. of *Angostura* bark. The presence of two methoxyl groups in I and the formation of galipine (Spath and Eberstaller, A., 1924, i, 1335) by methylation with diazomethane indicates that I is a hydroxy-dimethoxy-2- β -phenylethylquinoline. It is shown to be 4-hydroxy-2- β -3':4'-dimethoxyphenylethylquinoline by the following synthesis. 4-Chloro-2-methylquinoline condenses with veratraldehyde in presence of zinc chloride at 120° yielding 4-chloro-2-3':4'-dimethoxystyrylquinoline, m. p. 144—145°, which with sodium benzyloxide affords 4-benzyloxy-2-3':4'-dimethoxystyrylquinoline, m. p. 138—139°. Reduction of the last-named substance with hydrogen in presence of palladised charcoal, alcohol, and acetic acid, and subsequent hydrolysis of the product formed with 10% hydrochloric acid, gives I. Similar condensation of 4-methoxy-2-methylquinoline with vanillin and isovanillin yields 4-methoxy-2-4'-hydroxy-3'-methoxy-, m. p. (vac.) 210—211°, and 4-methoxy-2-3'-hydroxy-4'-methoxy-styrylquinoline, m. p. (vac.) 267—268°, respectively. These are reduced catalytically to 4-methoxy-2- β -4'-hydroxy-3'-methoxy-, m. p. 186—187°, and 4-methoxy-2- β -3'-hydroxy-4'-methoxy-phenylethylquinoline, m. p. 147—148°, respectively. 4-Hydroxy-2-methylquinoline, m. p. (vac.) 241—242° (lit. 230—231°), is converted by phosphoryl chloride into 4-chloro-2-methylquinoline, m. p. 25—26° (lit. 42—43°), which when treated with methyl-alcoholic sodium methoxide at not too high a temperature yields 4-methoxy-2-methylquinoline, b. p. 79—81°/1 mm., m. p. 84—85° (lit. 63—65° and 82°). Treatment of the last-named substance with methyl-alcoholic sodium methoxide at 150—155° gives 4-hydroxy-2-methylquinoline. 4-Methoxy-2:6-, -2:7-, and -2:8-dimethylquinolines are similarly converted into the corresponding 4-hydroxy-derivatives.

H. BURTON.

Quaternary bases from *Berberis vulgaris*. E. SPATH and N. POLGAR (Monatsh., 1929, 52, 117—128).—The dry root is extracted with methyl alcohol, the extract freed from solvent, re-extracted with water, and separated by acid into (a) basic and (b) non-basic constituents. An amorphous substance was isolated from b; it does not contain any appreciable quantity of oxyberberine. Treatment of a with an excess of sodium carbonate solution and subsequent extraction with ether removes tertiary bases (3.9% of dry material; separation not carried out), and the remaining quaternary bases were converted, by treatment with acetic acid and potassium iodide, into the corresponding iodides. The mixture is separated further by washing with a mixture of potassium iodide and hydroxide into (c) phenolic (2.03% of dry material) and (d) non-phenolic (9.4%) fractions. Fraction d consists mainly of berberine iodide together with a small amount of palmatine iodide, since reduction

of the residue from the crystallisation liquor with zinc dust and acetic acid affords tetrahydroberberine (I) and tetrahydropalmatine. Similar reduction of the berberine chloride obtained from the above iodide and silver chloride, yields small amounts of an amorphous substance and tetrahydrojatrorrhizine, in addition to I, indicating incomplete removal of phenolic bases by the potassium iodide-hydroxide washing. Treatment of c with hydrochloric and sulphurous acids gives a crystalline product, which when reduced affords tetrahydrojatrorrhizine, tetrahydrocolumbamine, m. p. (vac.) 221—223°, and a small amount of tetrahydroberberrubine.

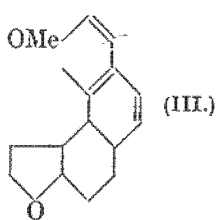
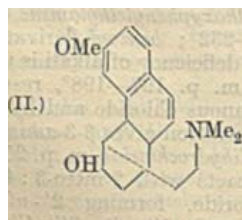
H. BURTON.

Synthetical experiments on aporphine alkaloids. VI. *iso*Thebaine. Attempted syntheses of 3:4:5-trimethoxyaporphine. R. K. CALLOW, J. M. GULLAND, and R. D. HAWORTH (J.C.S., 1929, 1444—1456).—Various unsuccessful attempts to synthesise 3:4:5-trimethoxyaporphine [Klee's *iso*-thebaine methyl ether (A., 1914, i, 1086)] are described. β -4-Methoxyphenylethylamine (I) (improved method of preparation given) reacts with 2-nitro-3:4-dimethoxyphenylacetyl chloride in presence of benzene and aqueous sodium hydroxide, forming 2'-nitro-3':4'-dimethoxyphenylaceto- β -4-methoxyphenylethylamide (II), m. p. 97.5—98°. Conversion of II into an *iso*quinoline by the action of various dehydrating agents is not possible, but when a solution of II in benzene or toluene is heated with a mixture of phosphoric oxide and chloride dehydration to 2'-nitro-3':4'-dimethoxyphenyl-(β -4-methoxyphenylethylamino)-acetylene, m. p. 143.5—144°, occurs. Nitration of the sulphate of I with nitric (*d* 1.4) and sulphuric acids affords β -3-nitro-4-methoxyphenylethylamine-5-sulphonic acid, +H₂O, dimorphous, m. p. 297° with effervescence after blackening at 293°; elimination of the sulpho-group with superheated steam was not practicable. Nitration of I with cold nitric acid (*d* 1.5) gives β -3:5-dinitro-4-methoxyphenylethylamine nitrate (III), m. p. 161° (decomp.), together with a small amount of impure β -3:5-dinitro-4-hydroxyphenylethylamine (picrate, m. p. 209—209.5°). It was not possible to obtain the free base from III, and hydrolytic dissociation and demethylation occurs when III is boiled with water. Nitration of β -4-methoxyphenylpropionic acid (improved method of preparation given) with nitric acid (*d* 1.42) at 10—25° yields β -3-nitro-4-methoxyphenylpropionic acid, m. p. 128—130.5°, together with a small amount of β -3:5-dinitro-4-hydroxyphenylpropionic acid, m. p. 136—139°. β -3-Nitro-4-methoxyphenylpropionamide, m. p. 123—127°, is converted by alkaline sodium hypochlorite into β -3-nitro-4-methoxyphenylethylamine (IV) (hydrochloride, m. p. 231—232°; benzoyl derivative, m. p. 129—130°); when a deficiency of alkali is used a substance, $C_{20}H_{22}O_7N_4$, m. p. 197—198°, results. Reduction of IV with stannous chloride and hydrochloric acid in acetic acid solution gives β -3-amino-4-methoxyphenylethylamine [dihydrochloride, m. p. 253—254° (decomp.)], which reacts with 2-nitro-3:4-dimethoxyphenylacetyl chloride, forming 2'-nitro-3':4'-dimethoxyphenylaceto- β -3-(2'-nitro-3':4'-dimethoxyphenylacetamido)-4-methoxyphenylethylamide,

m. p. 158—159°. Dehydration of this with phosphoric chloride in cold chloroform solution or with phosphoric oxide in boiling toluene affords a product which when hydrolysed with concentrated hydrochloric acid at 100° yields 2'-nitro-3':4'-dimethoxyphenyl-(β -3-amino-4-methoxyphenylethylamino)acetylene, m. p. 169.5—170° [picrate, m. p. 194—195° (decomp.)]; benzoyl derivative, m. p. 206—208°, together with a small amount of a substance, m. p. 168.5—170.5°. H. BURTON.

Constitution of sinomenine. H. KONDO and E. OCHIAI (Annalen, 1929, 470, 224—254).—A review of the properties of sinomenine (VII) (cf. Kondo and others, A., 1923, i, 1222; Goto, A., 1926, 1160; A., 1927, 146; this vol., 944), followed by new work. The oxime has (new) m. p. 254°; the semicarbazone, decomp. 264°, and methylsinomenine semicarbazone, decomp. 250—252°, were prepared. The dihydro-derivative, new m. p. 199°, $[\alpha]_D^{25} + 170.5^\circ$ (in alcohol—all values of $[\alpha]$ are in alcohol unless otherwise stated), forms a semicarbazone, m. p. 207°; the ketonic character thus persists. For the two bromosinomenines the new m. p. 138° and 205° are found. The iodine value of sinomenine appears to show the presence of two double linkings, but this is due to a substitution reaction, since benzoylsinomenine shows one only. Sinomenine reacts with ethyl chloroformate in chloroform to give a substance $C_{25}H_{32}O_8NCl$, m. p. 166—183° (decomp.), $[\alpha]_D^{25} - 108.4^\circ$ (in chloroform); this behaviour is characteristic of tetrahydroisoquinoline derivatives, as is that with benzoic anhydride, with which sinomenine gives dibenzoylsinomenol (cf. Goto, loc. cit.). These and earlier results show that sinomenine belongs to the morphine group.

Reduction of sinomenine by amalgamated zinc and hydrochloric acid yields deoxytetrahydrosinomenine, $C_{18}H_{25}O_2N \cdot 0.5H_2O$, (I), m. p. 150—151°, $[\alpha]_D^{25} + 48.2^\circ$, which has no phenolic properties, and reacts with phenylcarbimide. In general behaviour the substance closely resembles dihydrothebaine (Ia), $[\alpha]_D^{25} - 47.2^\circ$, obtained by Speyer and Siebert (A., 1921, i, 685) by the electrolytic reduction of dihydrothebaine, and now by the Clemmensen method. It is actually found that the two bases are optical antipodes; the racemic compound has m. p. 132° (decomp. after sintering at 125°), and $[\alpha]_D^{25} 0^\circ$. The hydriodides of the two bases have the same m. p., 250—251° (cf. Speyer and Siebert, loc. cit.). The methiodide of I, m. p. 265°, when treated with potassium hydroxide gives de-N-methyldeoxytetrahydrosinomenine, $C_{18}H_{27}O_2N$, (II), m. p. 140°, $[\alpha]_D^{25} - 41.59^\circ$ (in methyl alcohol); the methiodide of this compound



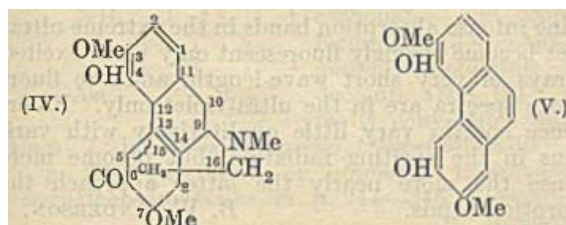
is prepared, converted into the methochloride, and treated with potassium hydroxide, when, with the

elimination of trimethylamine, the substance $C_{17}H_{20}O_2$, m. p. 93°, $[\alpha]_D^{25} - 181.6^\circ$, is obtained. This last substance contains no hydroxyl or vinyl group, and is stable towards potassium permanganate in the cold (giving, on heating, a product, m. p. 115°); it probably is III. Wieland and Kotake (A., 1925, i, 1093) have observed a similar reaction with dihydrode-N-methyl-dihydrothebaine. The elimination of the phenolic hydroxyl group during the Clemmensen reduction of sinomenine or dihydrothebaine is remarkable: it may be assumed that the group occupies the 4-position. This is confirmed by the reduction of dihydrosinomenine by sodium amalgam, when demethoxydihydrosinomenol, $C_{18}H_{25}O_3N$, m. p. 95—105° (decomp.), $[\alpha]_D^{25} + 32.02^\circ$ [unaffected by hydroxylamine; methiodide, m. p. 268—272°, $[\alpha]_D^{25} + 23.9^\circ$ (in methyl alcohol)], is formed, which is identified as an optical isomeride of dihydrothebaine (Speyer and Siebert, loc. cit.). This last, now prepared from dihydrothebaine by sodium amalgam reduction, has m. p. 144°, $[\alpha]_D^{25} - 46.2^\circ$, and forms a methiodide, m. p. 278° (decomp.), $[\alpha]_D^{25} - 24.25^\circ$ (in methyl alcohol); the racemic compound of the two methiodides has m. p. 270—272° and $[\alpha]_D^{25} 0^\circ$. Sinomenine reduced by sodium amalgam gives a substance, $C_{18}H_{25}O_3N$, m. p. 180°, $[\alpha]_D^{25} - 11.24^\circ$ (methiodide decomp. 250°), which does not form a semicarbazone.

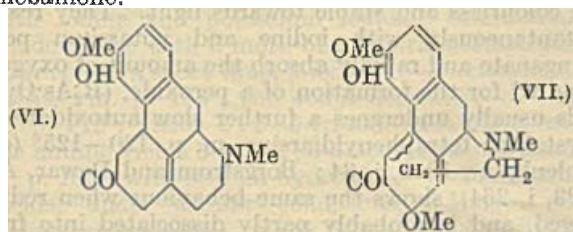
The phenolic hydroxyl group in sinomenine occupies the 4-position, and the keto-group the 6-position, in a phenanthrene skeleton. A methoxyl group probably occupies the 5- or the 7-position, and its actual situation is determined as follows. Sinomenol, obtained by the alkali fusion of sinomenine (Goto, loc. cit.), is a dihydroxydimethoxyphenanthrene; assuming this to have been formed by the enolisation of the keto-group of sinomenine, and by the loss of methyl-ethylamine, sinomenol dimethyl ether must be either 3:4:5:6- or 2:3:5:6-tetramethoxyphenanthrene. This is confirmed by the synthesis of these two compounds. When sodium homoveratrate is treated in acetic anhydride with o-nitroveratraldehyde, the product is 2-nitro-3:4-dimethoxy- α -3':4'-dimethoxyphenylcinnamic acid, m. p. 191—192°, which when reduced to the amino-compound, m. p. 146°, and treated in sulphuric acid and methyl alcohol with sodium nitrite, gives rise to the isomeric 3:4:5:6- and 3:4:6:7-tetramethoxyphenanthrene-9-carboxylic acids, m. p. 232—234° and 210°, respectively. The last heated at 250—260° in acetic acid gives 2:3:5:6-tetramethoxyphenanthrene, m. p. 124—125° (picrate, m. p. 123—125°), identical with dimethoxysinomenol. The actual differentiation between the above two isomerides was effected by synthesising the compound of m. p. 232—234° from 2-nitro-3:4-dimethoxy- α -6'-bromo-3':4'-dimethoxyphenylcinnamic acid, m. p. 216°; this was obtained by the interaction of sodium 6-bromohomoveratrate and o-nitroveratraldehyde in acetic anhydride at 100—110°, and was reduced to the amino-compound, m. p. 187°, and converted as before into 8-bromo-3:4:5:6-tetramethoxyphenanthrene-9-carboxylic acid, m. p. 187—188° (decomp.); this last was reduced by zinc in alcoholic sodium hydroxide to the bromine-free compound, identical with the compound of m. p. 232—234°.

This shows that sinomenine has a 7-methoxyl group,

and leads to the formulæ IV and V for dihydro-sinomenine and sinomenol, respectively. Sinomenine



is thus an optical isomeride of 7-methoxythebainone, and its structure is bound up with that of codeine. The formula for thebainone put forward by Gulland and Robinson (J.C.S., 1923, 123, 999) is now criticised, on the ground that when thebainone is neutralised and catalytically reduced in presence of palladium chloride, a new β -dihydrothebainone, m. p. 76° (after sintering at 62–64°), $[\alpha]_D^{25}$ –83.94°, is obtained [*picrate*, m. p. 245°; *semicarbazone*, m. p. 199–201° (decomp.)], and not thebainol. In order to explain this, Robinson's formula for thebainone is abandoned, and the formula VI is substituted; addition of hydrogen to the $\Delta^{8:14}$ double linking in different directions is considered to give either dextro-rotatory thebainol or laevorotatory β -dihydrothebainone.



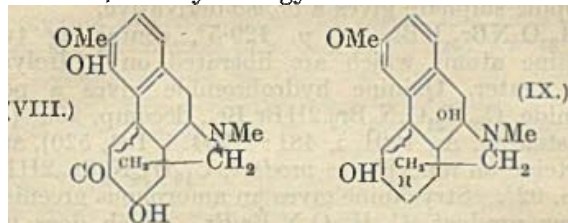
Sinomenine has a double linking; since it has none of the properties of an enol methyl ether, this linking must lie not between the atoms 7 and 8, but between 8 and 14. The formula VII is therefore proposed for sinomenine.

When sinomenine is reduced by sodium amalgam, isodemethoxydihydrosinomeninol, m. p. 180°, is formed; this is isomeric with demethoxydihydrosinomenol, and it is suggested that this is a case of *cis-trans*-isomerism.

Sinomenine is of particular interest as being the first alkaloid of the thebainone group to be found in nature.

A comparison of sinomenine with substances of the thebainone type leads to some further results. From the analogy between dihydrosinomenine and hydroxydihydrothebainone, which Speyer (A., 1923, i, 128) obtained by the sodium amalgam reduction of hydroxydihydrocodeinone, and to which he ascribed the formula VIII, the 7-hydroxyl group in the second substance would be expected to be very labile; it is not, however, removed in the above reduction process. When now hydroxydihydrocodeinone is reduced by Clemmensen's method, the product is not dihydrothebaine, as would be expected if the hydroxyl group were in the 7-position, but *hydroxydihydrothebaine*, m. p. 138–139°, $[\alpha]_D^{25}$ –58.15° (in acetone), which contains two free hydroxyl groups. It is

therefore concluded that Speyer's formula VIII is incorrect, and by analogy with Gulland and Robin-



son's formula for hydroxycodeinone, the formula IX is proposed for hydroxydihydrothebaine.

Silver nitrate acts on sinomenine to form *dehydrosinomenine nitrate*, not decomp. at 280°, from which *dehydrosinomenine*, $(C_{19}H_{23}O_4N)_2$ (cf. Goto, J. Chem. Soc. Japan, 1925, 44, 821), m. p. 218–220°, $[\alpha]_D^{25}$ +97.38° (in methyl alcohol), is obtained. The changed sign of the rotation, due to the action of silver nitrate, is to be noted. Catalytic reduction of dehydrosinomenine in presence of palladium gives rise to an isomeride of dihydrosinomenine, *isodihydrosinomenine*, which sinters at 220° (decomp. 271°), has $[\alpha]_D^{25}$ +171.16°, and forms a *methiodide*, and an *oxime*, m. p. 245–250° (decomp.). Dihydrosinomenine is oxidised by silver nitrate to *isodihydrosinomenine*, together with a bimolecular product, $(C_{19}H_{25}O_4N)_2$, m. p. 270°, $[\alpha]_D^{25}$ +113.8° (in methyl alcohol). Thebainone is converted by silver nitrate into ψ -thebainone, $C_{18}H_{21}O_3N$, decomp. 227°, $[\alpha]_D^{25}$ –339.5° (in acetone) (*semicarbazone*, decomp. 290°), which is reduced by hydrogen in presence of palladium to *dihydro- ψ -thebainone*, m. p. 270° (decomp.), $[\alpha]_D^{25}$ –71.77° (in acetone). E. W. WIGNALL.

Reduction of disinomenine and ψ -disinomenine. K. Goro (Bull. Chem. Soc. Japan, 1929, 4, 129–132).—Reduction of disinomenine by hydrogen in presence of colloidal palladium gave *tetrahydrosinomenine*, $(C_{19}H_{24}O_4N)_2$, m. p. 247–252° (decomp.), $[\alpha]_D^{25}$ +264.41° [*oxime*, m. p. 227°; *methiodide*, m. p. 275° (decomp.); *semicarbazone*, m. p. above 290°]. Similarly, ψ -disinomenine yielded *ψ -tetrahydrosinomenine*, m. p. 271° (decomp.), $[\alpha]_D^{25}$ +167° [*oxime*, m. p. 242°; *methiodide*, m. p. 285° (both decomp.); *semicarbazone*, m. p. above 290°]. These bases were also obtained by mild oxidation of dihydrosinomenine. B. W. ANDERSON.

Preparation and properties of some double chlorides of bismuth and quinine. H. LENORMAND (J. Pharm. Chim., 1929, [viii], 10, 69–74).—The following compounds are described:

$BiCl_3 \cdot (C_{20}H_{24}N_2O_2 \cdot 2HCl)_2$,
 $(BiCl_3)_3 \cdot (C_{20}H_{24}N_2O_2 \cdot 2HCl)_4$,
 $BiCl_3 \cdot C_{20}H_{24}N_2O_2 \cdot 2HCl$; all of them are decomposed by water and are sparingly soluble in most organic solvents. E. H. SHARPLES.

Bromination of natural alkaloids by acidified hydrogen peroxide. A. MOREL, A. LEULIER, and P. DENOYEL (Bull. Soc. chim., 1929, [iv], 45, 435–456).—In the action of a mixture of 2% hydrogen peroxide and hydrobromic acid on natural alkaloids, bromine derivatives of the alkaloids are obtained, unaccompanied by amine oxides. Cocaine hydrochloride yields a dibromo-derivative,

$C_{17}H_{21}O_4NBr_2 \cdot 2HBr$, m. p. 130° , probably identical with the product obtained by Jong (A., 1906, i, 301). Atropine sulphate gives a bromo-derivative, $C_{17}H_{23}O_3NBr_3 \cdot HBr$, m. p. 129.5° , containing two bromine atoms which are liberated on hydrolysis with water. Quinine hydrobromide gives a perbromide, $C_{20}H_{24}O_3N_2Br_3 \cdot 2HBr \cdot Br_2$, decomp. 200° (cf. Christensen, A., 1901, i, 481; 1904, i, 184, 520), and sparteine an amorphous product, $C_{15}H_{26}N_2Br_3 \cdot 2HBr$, m. p. 92° . Strychnine gives an amorphous greenish-yellow product, $C_{21}H_{21}O_2N_2Br \cdot Br_2$, which does not give the characteristic strychnine colorations with ammonium sulphovanadate or Denigès' reagent. Morphine hydrochloride affords the monobromo-derivative, $C_{17}H_{19}O_3NBr \cdot HBr \cdot 3H_2O$, m. p. 221° (decomp.), $[\alpha] -1.25^\circ$, which gives the intense violet coloration with Marquis' reagent, characteristic of morphine, and is free from hydroxydimorphine, and with excess of both reagents, the β -tetra-bromo-derivative, $C_{17}H_{15}O_3NBr_4 \cdot HBr$, decomp. 200° . Heroin yields the hydrobromide of bromodiacetylmorphine. The toxicity towards white mice of bromomorphine hydrobromide is about twice and of bromoheroin about eight times as great as that of morphine hydrochloride. R. BRIGHTMAN.

Bromination of novocaine by acidified hydrogen peroxide. A. MOREL, A. LEULIER, and P. DENOYEL (Bull. Soc. chim., 1929, [iv], 45, 457—463).—Bromination of novocaine by the hydrogen peroxide-hydrobromic acid method (cf. preceding abstract) yields a dibromo-derivative, $C_{13}H_{18}O_2N_2Br_2 \cdot HBr$, m. p. 217° , probably 3:5-dibromo-4-aminobenzoyldiethylaminoethyl alcohol, which with cold sulphuric acid in presence of sodium nitrite gives on warming an intense yellow coloration. Dibromonovocaine hydrobromide has an anaesthetic power on rabbits about ten to thirteen times as great as novocaine and about equal to that of cocaine hydrochloride. Addition of adrenaline slightly increases the anaesthetic power. Towards white mice dibromonovocaine hydrobromide is ten times as toxic as novocaine and three times as toxic as cocaine.

R. BRIGHTMAN.

Relations between the chemical constitution, absorption [spectra], and fluorescence of alkaloids. A. ANDANT (Compt. rend., 1929, 189, 98—100; cf. A., 1927, 538, 1124).—Alkaloids may be divided into four groups in accordance with their fluorescence spectra: (1) alkaloids with weak or non-present fluorescence spectra (morphine, cocaine, strychnine, brucine), (2) those with spectra in the visible region (hydrastinine), (3) those with spectra only in the ultra-violet (atropine, hyoscyamine), (4) those with spectra in the visible and ultra-violet regions (caffeine, quinine, hydrastine, etc.). Isomeric alkaloids have identical or very similar fluorescence; substitution of a methyl or methoxyl group for a hydrogen atom intensifies the fluorescence and causes displacement towards the red, as is the case with benzene derivatives. Etherification of a phenol group in the nucleus also intensifies the fluorescence, but causes displacement towards the violet. The salts of alkaloids have a slightly more intense fluorescence than the corresponding free bases; the spectra are

more spaced out towards the red and the maxima displaced in the same sense. Similar variations have been observed with absorption spectra. Alkaloids having intense absorption bands in the extreme ultra-violet become strongly fluorescent only when excited by rays of very short wave-length, and the fluorescence spectra are in the ultra-violet only. Fluorescence spectra vary little qualitatively with variations in the exciting radiation, but become more intense the more nearly the latter approach the absorption bands. B. W. ANDERSON.

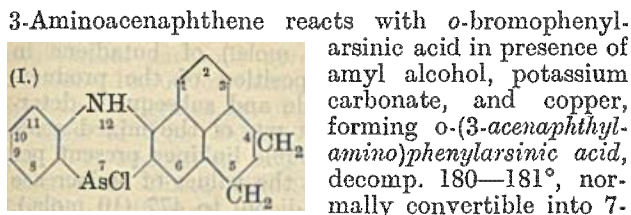
Action of ammonia on halogenated arsines. V. IPATIEV, G. RAZUBAIEV, and V. STROMSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 3—12).—See this vol., 584.

Action of arsenic acid and its derivatives on nitrophenols. O. R. PEPE (Rev. Fac. Cien. quim. La Plata, 1928, 5, I, 105—179; Chem. Zentr., 1929, i, 643).—Attempts to prepare nitrohydroxyphenyl-arsinic acids failed. A. A. ELDRIDGE.

Tetra-aryldiarsines. I. F. F. BLOCHE and F. D. SMITH (J. Amer. Chem. Soc., 1929, 51, 2272—2276).—Iododiarylsarsines (cf. this vol., 833) in ether or benzene react readily with mercury and more slowly with finely-divided silver or zinc, giving quantitatively tetra-aryldiarsines. In solution these are colourless and stable towards light. They react instantaneously with iodine and potassium permanganate and rapidly absorb the amount of oxygen required for the formation of a peroxide, $(R_2AsO)_2$. This usually undergoes a further slow autoxidation. Crystalline tetraphenyldiarsine, m. p. $120—125^\circ$ (cf. Schlenk, A., 1913, i, 34; Borgstrom and Dewar, A., 1923, i, 264), shows the same behaviour when redissolved, and is probably partly dissociated into free radicals. Iododiphenylarsine and triphenylmethyl bromide in bromobenzene give bromodiphenylarsine and the strongly dissociated triphenylmethyl iodide, but the solution absorbs more oxygen than is accounted for by the amount of triphenylmethyl produced. H. E. F. NOTTON.

10-Chloro-5:10-dihydrophenarsazine and its derivatives. X. 1- and/or 3-Methyl derivatives. Condensation of arsenious chloride and phenyl-*m*-tolylamine. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1929, 1473—1476).—Phenol reacts with *N*-*m*-tolylbenzimidochloride in presence of sodium ethoxide solution yielding *N*-*m*-tolylbenzimidophenyl ether, m. p. 60° , which at $280—300^\circ$ gives the benzoyl derivative, m. p. $104—106^\circ$, of phenyl-*m*-tolylamine (I), b. p. $183—184^\circ/17$ mm., m. p. 27.5° . This benzoyl derivative is obtained similarly from *N*-phenylbenzimidino-*m*-tolyl ether, m. p. 65° . Arsenious chloride and I in boiling *o*-dichlorobenzene give 10-chloro-1- and/or 3-methyl-5:10-dihydrophenarsazine (II), m. p. $215—216^\circ$ (this vol., 710). Razubaiev's "10-chloro-2(4)-methyl-9:10-dihydrophenarsazine," m. p. $195—196^\circ$ (this vol., 834), is an impure specimen of II. H. BURTON.

Substances of phenarsazine type containing the acenaphthene nucleus. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1929, 1621—1622).—



chloro-7:12-dihydroisoacenaphthabenzarsazine (I), m. p. 241° (decomp.), or 7-bromo-7:12-dihydroisoacenaphthabenzarsazine, m. p. 244—246° (decomp.).

H. BURTON.

[Preparation of] mercury diphenyl. H. O. CALVERY (Organic Syntheses, 1929, 9, 54—55).

Position occupied by acetatomercuri ($\text{Hg} \cdot \text{OAc}$)-groups in anilines containing in the nucleus a halogen group or a hydrocarbon residue. IV. L. VECCHIOTTI and G. SPERANZINI (Gazzetta, 1929, 59, 363—372; cf. A., 1928, 655, 783).—Substitution by the acetatomercuri-group in *m*-halogeno-anilines generally yields, according to the proportion of mercuric acetate used, 4-mono-, 4:6-, or occasionally 2:5-, di-, and 2:4:6-tri-acetatomercuri-derivatives. As a by-product in the preparation of 3-iodo-4-acetatomercurianiline (A., 1927, 1098) 3-iodo-4:6-di-acetatomercurianiline, m. p. 190°, separates very slowly from the mother-liquors. The acetyl derivative, m. p. 202°, yields 2:4:5-tri-iodoacetanilide with iodine and potassium iodide. Interaction of 3-iodoaniline with 2 mols. of mercuric acetate yields, however, in a short time, 3-iodo-2:5-di-acetatomercurianiline, m. p. 163°, the acetyl derivative of which, m. p. 212°, yields 2:3:5-tri-iodoacetanilide, whilst the aniline yields 3-iodo-2:5-dihydroxymercurianiline, m. p. 186°, with sodium hydroxide. *m*-Bromoaniline yields, under similar conditions, 3-bromo-4:6-di-acetatomercurianiline, m. p. 172° (acetyl derivative, m. p. 198°, yielding 3:4:6-tribromoacetanilide). The 2:5-derivative could not be obtained.

R. K. CALLOW.

Mercuration in alkaline solution. A. L. FOX and F. C. WHITMORE (J. Amer. Chem. Soc., 1929, 51, 2196—2197).—3-Hydroxy-2-naphthoic acid is mercurated by mercuric acetate more rapidly in alkaline than in acid solution to anhydro-3-hydroxy-4-hydroxymercuri-2-naphthoic acid. Salicylic acid in alkaline solution yields hydroxymercurisalicylic acid and phenol yields anhydrohydroxymercuriphenol, but α -naphthol, *o*-nitrophenol, and anthranilic, sulphanilic, benzenesulphonic, α -naphthoic, and phthalic acids are not mercurated.

H. E. F. NOTTON.

Organo-alkali compounds. I. Reaction between unsaturated hydrocarbons and alkali metal alkyls. K. ZIEGLER, F. CROSSMANN, H. KLEINER, and O. SCHAFER. II. Schlenk's addition of alkali metals to unsaturated hydrocarbons. K. ZIEGLER, H. COLONIUS, and O. SCHAFER. III. Polymerisation of unsaturated hydrocarbons under the influence of alkali metals and alkali metal alkyls. K. ZIEGLER and H. KLEINER (Annalen, 1929, 473, 1—35, 36—56, 57—82).—I. Alkali metal alkyls are of three types. (1) Colourless and insoluble in organic media (e.g., simple sodium and potassium alkyls and aryls). In

combination with zinc alkyls they are electrolytes and even in the solid state are probably heteropolar. (2) More or less intensively coloured, usually soluble in organic solvents, especially ether, and such solutions are conductors (e.g., NaCH_2Ph and KCM_2Ph). (3) Colourless and mostly soluble. They usually distil or sublime unchanged, are non-electrolytes, and slight conductors only in presence of zinc alkyls. Compounds of type 1 are readily decomposed by ether, those of type 2 are usually stable towards ether and react instantaneously with alkyl halides, whilst those of type 3 are very slowly decomposed by ether and react only slowly with alkyl halides. Potassium phenylisopropyl, $\text{K} \cdot \text{CM}_2\text{Ph}$, prepared by the action of potassium-sodium alloy (5:1) on phenylisopropyl methyl ether (cf. Ziegler and Bahr, A., 1928, 404), does not react with ethylene or triphenylethylene. When addition of the metal does occur reaction is almost instantaneous. Decomposition of the additive product first with dry carbon dioxide and then with dilute alkali gives an acid, formed by replacement of the potassium atom with carboxyl. Thus, benzylidenefluorene yields an acid, $\text{C}_{30}\text{H}_{26}\text{O}_2$, m. p. 205—206° with elimination of carbon dioxide; propenylbenzene gives an acid, $\text{C}_{19}\text{H}_{22}\text{O}_2$, m. p. 146—147° (silver salt); isopropenylbenzene affords an isomeric acid, an oil (silver salt), and ethylidenefluorene furnishes an acid, $\text{C}_{25}\text{H}_{24}\text{O}_2$, m. p. 113° (silver salt). In the remainder of the cases studied substitution takes place (usually in a methyl group) and reaction occurs only slowly. Thus, $\omega\omega$ -dimethylstyrene yields an unsaturated acid, $\text{C}_{11}\text{H}_{12}\text{O}_2$ (β -benzylidene-*n*-butyric acid), m. p. 80—81° (silver salt), reduced by hydrogen in presence of palladised barium sulphate and alcohol to β -benzyl-*n*-butyric acid; $\alpha\alpha$ -diphenyl- Δ^a -propylene gives the acid, $\text{C}_{16}\text{H}_{14}\text{O}_2$ ($\gamma\gamma$ -diphenyl- Δ^b -butenoic acid), m. p. 112—113°, reduced to $\gamma\gamma$ -diphenylbutyric acid; $\alpha\alpha$ -diphenyl- $\beta\beta$ -dimethylethylene affords a mixture of impure β -diphenylmethylene-glutaric acid, m. p. 153—154° (silver salt), and an acid, m. p. 108°, reduced to β -benzhydryl-*n*-butyric acid, m. p. 113°; $\alpha\alpha$ -diphenyl- Δ^a -butylene furnishes an acid, $\text{C}_{17}\text{H}_{16}\text{O}_2$ (silver salt); $\alpha\alpha\gamma$ -triphenyl- Δ^a -propylene yields $\alpha\gamma\gamma$ -triphenyl- Δ^b -butenoic acid, m. p. 166—167° (silver salt), also obtained by the action of potassium on $\alpha\alpha\gamma$ -triphenyl- γ -methoxy- Δ^a -propylene with subsequent decomposition by carbon dioxide. $\alpha\gamma\gamma$ -Triphenylbutyric acid has m. p. 111—112°, whilst $\alpha\alpha\gamma$ -triphenylbutyric acid has m. p. 181°. α -Methylstilbene gives β -phenyl- β -benzylidenepropionic acid, m. p. 168° (silver salt). With $\alpha\delta$ -diphenyl- Δ^a -butylene addition of potassium phenylisopropyl occurs, the acid $\text{C}_{26}\text{H}_{28}\text{O}_2$ (silver salt) being finally isolated. With $\alpha\delta$ -diphenyl- Δ^b -butylene substitution of potassium occurs in one or both methylene groups, and the decomposition products are $\alpha\delta$ -diphenyl- Δ^b -pentenoic acid (silver salt) and $\alpha\delta$ -diphenyl-dihydromuconic acid, m. p. 233—234° (silver salt). This last acid is probably stereoisomeric with the acid described by Schlenk and Bergmann (A., 1928, 1031). Addition also takes place with $\alpha\delta$ -diphenyl- $\Delta^a\gamma$ -butadiene yielding the acid $\text{C}_{26}\text{H}_{26}\text{O}_2$ (silver salt), but with $\alpha\delta$ -dibenzyl- $\Delta^a\gamma$ -butadiene substitution of potassium occurs in both methylene groups, affording $\alpha\gamma$ -diphenyl- Δ^b -hexadiene- $\alpha\gamma$ -dicarboxylic acid, m. p. 240—

242° (silver salt). Standardisation of solutions of potassium phenylisopropyl is readily effected by treatment with butyl bromide and subsequent determination of bromide ions by the Volhard method. The rates of addition of lithium ethyl, propyl, and butyl to *as*-diphenylethylene in benzene solution have been determined at 50°; the velocity coefficients are 1.5, 3.4, and 2.8, respectively. The additive compound from lithium butyl is decomposed by carbon dioxide to $\alpha\alpha$ -diphenyl-*n*-heptioic acid, m. p. 104–105°, obtained also by the action of potassium–sodium alloy on $\alpha\alpha$ -diphenyl-*n*-hexyl methyl ether, m. p. 58°, and subsequent decomposition with carbon dioxide. $\alpha\alpha$ -Diphenyl-*n*-hexyl alcohol, m. p. 46.5–47.5°, is obtained from ethyl hexoate and excess of magnesium phenyl bromide. Addition of lithium butyl to stilbene occurs in ethereal solution and decomposition of the product with carbon dioxide affords $\alpha\beta$ -diphenyl-*n*-heptioic acid, m. p. 102°. Benzene solutions of lithium butyl containing ether do not alter appreciably after 3–4 hrs. The determination of simple lithium alkyls in solution is carried out by addition of butyl bromide and then, in small portions, mercury dibenzyl. The lithium benzyl formed reacts immediately with the butyl bromide.

II. Treatment of *as*-diphenyldimethylethylene with potassium–sodium alloy (5 : 1) in concentrated ethereal solution and decomposition of the product with carbon dioxide affords $\alpha\alpha$ -diphenylisovaleric acid (I), m. p. 168–169°, obtained also by the successive action of potassium and carbon dioxide on the methyl ether, b. p. 124–126°/0.5 mm., of diphenylisopropylcarbinol. In dilute ethereal solution both I and β -diphenylmethylene-*n*-butyric acid (II), m. p. 108° (cf. Part I), are formed. The reactions taking place are: $\text{CPh}_2\cdot\text{CMe}_2 \rightarrow \text{CKPh}_2\cdot\text{CKMe}_2$ ($\text{CPh}_2\cdot\text{CMe}_2$).

$\text{CKPh}_2\cdot\text{CHMe}_2 + \text{CPh}_2\cdot\text{CMe}\cdot\text{CH}_2\text{K}$ (cf. Schlenk and Bergmann, A., 1928, 1031). The thioanilides of I and II, m. p. 144–145° and 161°, respectively, are obtained by the action of phenylthiocarbimide on the potassium derivatives. Treatment of a solution of *as*-diphenylethylene in toluene with a solution of sodium in liquid ammonia at a low temperature, and decomposition of the red sodium derivative formed with ammonium chloride affords $\alpha\alpha$ -diphenylethane. No trace of $\alpha\alpha\delta\delta$ -tetraphenylbutane is formed (cf. Schlenk and Bergmann, loc. cit.). Decomposition of the above sodium derivative with benzyl chloride gives $\alpha\beta\beta$ -triphenylpropane. The reactions taking place are, therefore, $\text{CPh}_2\cdot\text{CH}_2 \xrightarrow{\text{NH}_2} \text{CNaPh}_2\cdot\text{CH}_2\text{Na} \xrightarrow{\text{NH}_2} \text{CNaPh}_2\cdot\text{CH}_3 + \text{NaNH}_2$. When sodium is added in small portions, with good stirring, to a mixture of *as*-diphenylethylene, toluene, and liquid ammonia, a small amount of $\alpha\alpha\delta\delta$ -tetraphenylbutane is probably formed. $\alpha\alpha$ -Diphenyl- β -benzylethylene affords $\alpha\alpha\gamma$ -triphenylpropane, whilst cyclohexene is unaffected by potassium in liquid ammonia. Aryl-substituted ethylenes add primarily two atoms of alkali metal across the double linking. This additive product can either remain unchanged (e.g., stilbene, tetraphenylethylene) or undergo secondary reactions, which can occur under the influence of excess of the hydrocarbon used. These consist of addition or substitution processes.

III. A series of experiments has been carried out

on the addition of potassium phenylisopropyl to varying amounts (1–10 mols.) of butadiene in ethereal solution. Decomposition of the products formed with carbon dioxide and subsequent determination of the equivalent wt. of the mixed acids (A) and the number of double linkings present per equivalent (B), shows that the values of A increase from 218 (2 mols. of butadiene) to 477 (10 mols.), whilst the values of B increase correspondingly from 1.32 to 5.55. Maximum values are given with 8 mols. of butadiene, namely, 493 and 6.04. The following primary reactions are presumed to occur (1:4-addition is assumed arbitrarily): (1) $\text{CKPhMe}_2 + \text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2 \rightarrow \text{CPhMe}_2\cdot\text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2\text{K}$; (2) $2\text{CKPhMe}_2 + \text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2 \rightarrow \text{CH}_2\text{K}\cdot\text{CH}=\text{CH}\cdot\text{CH}_2\text{K} + 2\text{CPhMe}_2$. H. BURTON.

Lead aryl-alkyl compounds. H. GILMAN, O. R. SWEENEY, and J. E. KIRBY (Iowa State Coll. J. Sci., 1928, 3, 1–4).—By interaction of lead triphenyl bromide with the appropriate Grignard reagent, lead triphenyl butyl, m. p. 47°, isobutyl, m. p. 68–68.5°, sec.-butyl, m. p. 84°, and tert.-butyl, m. p. 150–150.5°, have been obtained.

CHEMICAL ABSTRACTS.

Metallic derivatives of thiophen. II. Thallium, silicon, bismuth, tellurium, and mixed tin and lead thienyls. E. KRAUSE and G. RENWANZ (Ber., 1929, 62, [B], 1710–1716; cf. A., 1927, 891).—Thiophen is converted by bromine in glacial acetic acid into 2-bromothiophen, b. p. 42–46°/13 mm. Addition of ethereal magnesium 2-thienyl bromide to ethereal thallium chloride affords thallium di-2-thienyl bromide, $\text{Tl}(\text{C}_4\text{H}_3\text{S})_2\text{Br}$, decomp. 270° after darkening at 250°. Silicon tetrachloride and magnesium 2-thienyl iodide yield silicon tetra-2-thienyl, m. p. 135.5° (corr.). Bismuth tri-2-thienyl, m. p. 137.5° (corr.), is more advantageously prepared from magnesium 2-thienyl bromide than from the corresponding iodide. Tellurium di-2-thienyl dibromide, m. p. 195° (corr.), decomp. about 220°, is reduced by stannous chloride and hydrochloric acid to tellurium di-2-thienyl, from which tellurium di-2-thienyl dichloride, m. p. 189.5°, decomp. about 250° after darkening at 210°, and the corresponding di-iodide, m. p. 126.5° (corr.), decomp. about 190°, are prepared. Magnesium 2-thienyl bromide and tellurium di-2-thienyl dibromide afford tellurium tri-2-thienyl bromide, m. p. 253° (corr. decomp.) [corresponding iodide]. Tin triphenyl 2-thienyl, m. p. 206° (corr.), is prepared from magnesium 2-thienyl iodide and tin triphenyl bromide; it is converted by bromine in pyridine at –48° into tin triphenyl bromide. Lead triphenyl 2-thienyl, m. p. 208° (corr.), decomp. 305°, is converted by bromine into lead triphenyl bromide. H. WREN.

Mol. wt. of edestin. T. SVEDBERG and A. J. STAMM (J. Amer. Chem. Soc., 1929, 51, 2170–2185).—The solubility of edestin in aqueous sodium chloride and in phosphate buffer solutions, with and without sodium chloride, has been determined. Three independent methods give p_H 5.5 as its isoelectric point (cf. Michaelis and Mendelssohn, A., 1914, i, 1007). Its partial specific vol. is 0.744 at 19.8°, and its ultraviolet absorption spectrum shows a maximum at 276 μ and a minimum at 254 μ . Determinations by the sedimentation velocity and sedimentation

equilibrium methods give a normal mol. wt. of $212,000 \pm 10,000$ (cf. Cohn, A., 1925, ii, 641) and show that the molecules are of uniform size (a) at concentrations of 1.38—0.155%, (b) over a p_H range of 5.5—9.7, and (c) in salt solutions of varying concentration. Small quantities only of non-centrifugable matter are present. These results indicate that the methods are applicable to proteins in salt solutions of considerable concentration. At p_H 3.1 and p_H 11.3, and in neutral solutions at concentrations below 0.1%, edestin dissociates, or decomposes into smaller molecules.

[With O. LAMM.]—A modification (to be described later; cf. this vol., 129) of the sedimentation velocity method, involving the measurement of changes in the refractive index of the sedimenting solution, shows that a 0.487% solution at p_H 11.3 contains edestin (15%) and dissociation products of one half (30%) and one third (55%) its mol. wt., approximately in the proportions stated. It is significant that both edestin and its dissociation products have, like most of the proteins hitherto examined, mol. wts. which are integral multiples (6, 3, and 2 times, respectively) of that of egg-albumin (cf. this vol., 26, 203, 458). The edestin molecules are practically spherical.

H. E. F. NOTTON.

Combination between basic dyes and proteins. L. M. C. RAWLINS and C. L. A. SCHMIDT (J. Biol. Chem., 1929, 82, 709—716).—Titration of gelatin, caseinogen, and edestin with three basic dyes shows that, at p_H 11, gelatin combines with 70×10^{-5} , caseinogen with 210×10^{-5} , and edestin with 70×10^{-5} equivalents of dye. The results can be correlated with the base-binding capacity of the proteins, and support the previous conclusion that combination of acid dyes with proteins takes place in stoichiometric proportions (cf. A., 1927, 686). C. R. HARRINGTON.

Fractionation of casein. K. LINDERSTRÖM-LANG (Compt. rend. Lab. Carlsberg, 1929, 17, 1—116).—Casein previously purified by the usual methods has been separated into several fractions by mild treatment, e.g., by warming with 60% alcoholic hydrochloric acid (0.002*N*), when one part is obtained as an alcohol-soluble and the other as an alcohol-insoluble fraction. The fractions, which are not claimed to be chemically pure, have been subjected to thorough examination by chemical and physical methods, including the determination of phosphorus, nitrogen, arginine, tyrosine, tryptophan, specific rotation, and solubility, and titration of acid and basic groups. Probably no irreversible processes are involved in the fractionations, as mixing the fractions in their proper proportions produces a substance physically and chemically identical with the original casein. It is concluded that casein consists of at least three fractions, one of which is alcohol-soluble and contains no phosphorus. The bearing of these results on the rennin reaction is discussed.

W. O. KERMACK.

Determination of tyrosine and tryptophan in 0.1 g. of protein. Colorimetric determination of cystine in protein. Preparation of uric acid reagent free from phenol reagent. O. FOLIN and A. D. MARENZI (J. Biol. Chem., 1929, 83, 89—102,

103—108, 109—113).—The precipitation of tyrosine from protein hydrolysates with mercuric acetate and sodium chloride recommended by Hanke (A., 1928, 1389) is incomplete and variable, and the results of this author are criticised on this and other grounds. A modification of the method of Folin and Ciocalteu (A., 1927, 892) in which the error in the tyrosine determinations due to the presence of cystine is eliminated is described; it is applicable to 0.1 g. of protein (except caseinogen) after hydrolysis with 20% sodium hydroxide at 100°. Figures are given for the tyrosine and tryptophan content of a number of proteins. The method of Folin and Looney (A., 1922, ii, 539) for the determination of cystine has been modified by reducing the cystine in acid solution, which enables the amount of sodium sulphite, and hence the blank, to be diminished, and by using an improved uric acid reagent (cf. A., 1924, ii, 634), in the course of preparation of which traces of molybdate are removed by treatment with hydrogen sulphide and extraction with alcohol. C. R. HARRINGTON.

Determination of nitrogen by Dumas' method. I. MAREK [with KRAJČINOVIC and G. ZALJESOV] (Bull. Soc. chim., 1929, [iv], 45, 555—560).—See A., 1928, 1346.

Determination of iodine in organic substances which lose iodine with ease. E. I. VAN ITALLIE (Pharm. Weekblad, 1929, 66, 629—632).—The substance (10—200 mg.) is heated with 8—10 c.c. of sulphuric acid in a small retort and the iodine evolved is absorbed in 30—50 c.c. of 5% sodium hydroxide solution. The iodine may be determined either by titration or by reduction to iodide by hydrogen peroxide and precipitation as silver iodide.

H. F. GILLBE.

Determination of sulphur in organic liquids. S. LANDA (Coll. Czech. Chem. Comm., 1929, 1, 397—400).—The liquid is burnt in a lamp (substantially the procedure of petroleum testing is followed), the combustion products are passed into hydrogen peroxide, and the sulphuric acid is titrated with alkali hydroxide.

R. J. W. LE FEVRE.

Analysis of organic mixtures. E. BENESCH (Chem.-Ztg., 1929, 53, 566—567).—A semi-mathematical paper in which it is indicated how the composition of appropriate mixtures of organic substances may be determined from a combination of analytical determinations.

J. S. CARTER.

Colorimetric determination of butyric acid. R. J. ALLGEIER, W. H. PETERSON, and E. B. FRED (J. Bact., 1929, 17, 79—87).—The solution is treated with a solution containing cupric chloride dihydrate (85.26 g.) in *N*-hydrochloric acid (1000 c.c.), shaken with chloroform, and the solution compared with controls. Acetic or formic acid does not interfere.

CHEMICAL ABSTRACTS.

Colour reaction of adrenaline. A. ORRÙ (Annali Chim. Appl., 1929, 19, 239—240).—When a trace of either natural or synthetic adrenaline, suspended in 1 c.c. of water, is heated to boiling with 2 drops of a solution of 0.1 g. of triketohydrindene hydrate in 300 c.c. of water, a blue colour is obtained. The reaction is given only by the free base. T. H. POPE.

Biochemistry.

Determination of carbon monoxide in blood. W. M. M. PILAAR (J. Biol. Chem., 1929, 83, 43—50).—See A., 1928, 1149.

Physico-chemical system of blood in relation to respiration and circulation. I. M. HOCHREIN, D. B. DILL, and L. J. HENDERSON. II. **Determination of blood circulation during rest and work.** M. HOCHREIN, J. H. TALBOTT, D. B. DILL, and L. J. HENDERSON. III. **Ionic distribution during rest and work.** H. T. EDWARDS, M. HOCHREIN, D. B. DILL, and L. J. HENDERSON. IV. **Carbonic acid respiration and hyperpnœa.** M. HOCHREIN, D. B. DILL, and L. J. HENDERSON (Arch. exp. Path. Pharm., 1929, 143, 129—146, 147—160, 161—169, 170—183).—I. A number of tables and curves summarise the changes of the physico-chemical properties of arterial and venous blood and respiratory changes of normal individuals at rest and during work.

II. The Haldane-Bock method is applied to determine the blood circulation in normal individuals at rest and during work, and it is shown how the position of the arterial and venous lines in the Hender-son nomogram can be fixed by this method.

III. In experiments with twelve normal individuals it is shown that during slight fatigue the difference between the value of r_{Cl} (ratio of chlorine in cell to that in serum) at rest and during work is smaller than for r_{HCO_3} . During exhaustion the value of r_{Cl} is twice and of r_{HCO_3} four times as great as in the condition of slight fatigue. If lactic acid is added to the blood *in vitro*, both r_{Cl} and r_{HCO_3} increase and $r_{lactate}$ decreases, the degree of change depending on the concentration of lactic acid added. From these experiments *in vitro*, approximate values of $r_{lactate}$ during work can be calculated.

IV. The physico-chemical composition of blood during inspiration of a gas mixture of 6% of carbon dioxide, 20% of oxygen, and 74% of nitrogen and during hyperpnœa is indicated by a series of tables and nomograms. P. W. CLUTTERBUCK.

Cataphoretic velocity of mammalian red blood-corpuscles. H. A. ABRAMSON (J. Gen. Physiol., 1929, 12, 711—725; cf. this vol., 478).—The sus-pensions of blood cells were made up in *M*/15-phos-phate, 7.35 ± 0.03 , which had a specific resistance of 126 ± 1 ohms at 25°. The temperatures used varied from 22° to 27° and results were corrected to 25°. The mean velocity for ten normal white adults was found to be $1.31 \pm 0.02 \mu/\text{sec./volt/cm.}$, and that for negroes $1.30 \pm 0.05 \mu$. Results found on the same day were constant to within about 5%, but varied con-siderably over several weeks in the same individual. The cataphoretic velocity of mammalian red cells was found to be constant for all ages in the same species, and no variation in the average value was detected in various types of anæmia. No direct relationship appeared to hold between mobility and sedimentation velocity.

The relative mobilities of some different species were as follows: (in $\mu/\text{sec./volt/cm.}$) rabbit 0.55, pig 0.98, guinea-pig 1.11, man 1.31, monkey 1.33, mouse 1.40, dog 1.65. No appreciable change in mobility occurred

in 24 hrs. in the phosphate buffer used. Unlike cholesterol, red cells did not adsorb gelatin even in 24 hrs. and retained their original velocity.

P. G. MARSHALL.

Structure of the hæmoglobin molecule. I, II. A. POLJAKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 173—182, 183—191).—See this vol., 338.

New inorganic factor as supplement to iron in hæmoglobin building. E. B. HART (Wisconsin Med. J., 1929, 28, 60).—Experiments with anæmic rats indicate that copper plays a definite and specific part as a supplement to iron in the production of hæmoglobin. No evidence of the existence in liver of an indispensable organic factor for hæmoglobin production in anæmia was found.

CHEMICAL ABSTRACTS.

Influence of hæmocyanin on distribution of chloride between sea-water and blood of *Limulus polyphemus*. G. W. THOMAS (J. Biol. Chem. 1929, 83, 71—77).—The ratio Cl in *Limulus* blood-serum : Cl in sea-water is 0.981, concentrations being expressed as g. per kg. of water; the difference in concentration in the two fluids can be largely accounted for by the Donnan equilibrium due to the hæmocyanin of the blood. C. R. HARRINGTON.

Hæmochromogen and related compounds. H. F. HOLDEN and M. FREEMAN (Austral. J. Exp. Biol., 1929, 6, 79—89).—The relative dissociation of a number of hæmochromogens and the quantitative relationships between reduced hæmatin and certain proteins are determined. The effect of treatment with nitrous acid on the ability of proteins to form hæmochromogens and parahæmatins is described. Some hæmochromogens are dissociated by formalde-hyde. Native proteins do not form hæmochromogens.

P. W. CLUTTERBUCK.

Reduced hæmatin and hæmochromogen. R. HILL (Proc. Roy. Soc., 1929, B, 105, 112—130).—Hæmochromogens are formed by the union of 1 mol. of reduced hæmatin with 2 mols. of a nitrogenous compound. This conclusion is supported by spectro-scopic observations on solutions containing reduced hæmatin in presence of pyridine, nicotine, or cyanide. Reduced hæmatin also forms a compound with 1 mol. of cyanide, but this compound combines with a second molecule of cyanide to form the true cyan-hæmochromogen or with 1 mol. of nicotine to form a mixed nicotine-cyan-hæmochromogen. It is therefore proposed to call the equimolecular compound of reduced hæmatin and cyanide cyan-reduced hæmatin and to reserve the name cyan-hæmochromogen for the compound containing 2 mols. of cyanide (cf. Anson and Mirsky, this vol., 87). The dis-sociation constants of the pyridine-, cyan-, and nicotine-hæmochromogens are, respectively, 8.9×10^{-6} , 4.8×10^{-8} , and 1.1×10^{-7} . The mixed nicotine-cyan-hæmochromogen has a dissociation constant of 0.38×10^{-8} and the cyan-reduced hæmatin of 1.3×10^{-9} .

W. O. KERMACK.

Inhibition by hydrogen sulphide of catalysis by hæmatin. H. A. KREBS (Biochem. Z., 1929, 209, 32—33).—The rapid oxidation which occurs when

hæmin is added to linoleic acid is almost completely checked when sodium sulphide is added also.

W. MCCARTNEY.

Blood-catalase. E. SCHILLING (Klin. Woch., 1928, 7, 2202; Chem. Zentr., 1929, i, 760).—Catalase, by protecting tissue from the oxidising action of peroxide, is considered a protective enzyme.

A. A. ELDRIDGE.

Is fibrinogen in natural plasma present in the free state or as a complex? E. HEKMA (Biochem. Z., 1929, 209, 90—102).—A discussion of theories of the coagulation of the blood, the author's views being contrasted particularly with those of Pickering (cf. Pickering, "The Blood Plasma in Health and Disease," London, 1928).

W. MCCARTNEY.

Existence, in plasmatic liquids, of fibrinogen-containing complexes together with free fibrinogen. E. HEKMA (Biochem. Z., 1929, 209, 128—133; cf. preceding abstract).—Examination of the appearance of the precipitates produced when plasmatic fluids are treated with suitable precipitants leads to the conclusion that both free fibrinogen and a complex containing it may be present together in the fluids.

W. MCCARTNEY.

Chemical characterisation of serum-proteins. H. K. BARRENSCHEEN and L. MESSINER (Biochem. Z., 1929, 209, 251—262).—When serum-protein is phosphorylated by Rimington's method (A., 1927, 581) more phosphoric acid is taken up by the globulin than by the albumin. When serum-protein is methylated by methyl sulphate in alkaline solution the methoxyl values of the fractions are analogous to but rather higher than the phosphorylation values, and the methylated protein can be further phosphorylated. The methylimide and the *N*-methyl values show with globulin (except pseudoglobulin) lower values than with albumin.

P. W. CLUTTERBUCK.

Influence of hydrogen-ion concentration on the precipitation of serum-proteins by salts. II. D. VON KLOBUSITZKY (Biochem. Z., 1929, 209, 304—311).—Electrodialysed serum-albumin and -globulin are precipitated by saturated sodium chloride only below their isoelectric points, p_H 4.8 and 5.4, respectively (distinction from the albumin and globulin of whole serum), when the precipitating power and the concentration of hydrogen ions run parallel. Pseudo-globulin-euglobulin mixtures are stable at the isoelectric point.

P. W. CLUTTERBUCK.

Concentration of protein in serum and the reactions of coagulation. L. BLAS and M. MAGALLÓN (Anal. Fís. Quím. [Techn.], 1929, 27, 129—134).—The concentration of protein in blood-serum exerts a definite influence on coagulation reactions. Irregularities occasionally observed in the Wassermann and Meinecke reactions are ascribed to this influence.

H. F. GILLBE.

Determination of hydrogen-ion concentration in circulating blood. K. GOLLWITZER-MEIER and W. STEINHAUSEN (Klin. Woch., 1928, 7, 2426—2428; Chem. Zentr., 1929, i, 1030).—The effect on the results of the velocity of flow is pointed out.

A. A. ELDRIDGE.

Determination of the alkaline reserve of blood-plasma and determination of acetoacetic acid in blood. P. CRISTOL (Bull. Soc. Chim. biol., 1929, 11, 731—744).—The methods at present in use for the determination of the alkaline reserve of the blood-plasma are subject to an error due to decarboxylation of acetoacetic acid when applied to the blood of acetonic subjects. If sodium fluoride is substituted for hydrochloric acid in the method of Lescœur and Manjean (A., 1928, 724) no decarboxylation occurs and a true measure of the carbon dioxide is obtained. By using the original and the modified method the acetoacetic acid of the blood may be determined.

J. H. BIRKINSHAW.

Bile-acid content of blood under various physiological conditions. M. CHARLET (Biochem. Z., 1929, 210, 42—69).—The method of Aldrich and Bledsoe (A., 1928, 788) with slight modification (principally the use of "norit" for decolorisation) was used to determine bile acids. These were shown to be present in the blood of normal men, rats, and cats. In rats the bile-acid content of the blood is a function of the activity of the liver. It is increased after protein and thyroid feeding. Thus the view that the liver supplies to the blood a hormone regulating the heart's activity receives new support.

J. H. BIRKINSHAW.

[Serum]-nitrogen coefficient in the normal state. M. LABBE, F. NEPVEUX, and A. HIERNAX (Compt. rend. Soc. Biol., 1928, 99, 1492—1493; Chem. Zentr., 1929, i, 667).—The ratio urea-nitrogen : total nitrogen in the serum is normally 40—48 (average 44.2) mg.-%.

A. A. ELDRIDGE.

Colorimetric micro-determination of residual nitrogen in blood and serum. B. GROAK (Biochem. Z., 1929, 209, 148—153).—If gum arabic is added to the solution obtained after the trichloroacetic acid filtrate from blood or serum has been digested with sulphuric acid and hydrogen peroxide, residual nitrogen can be determined accurately by the Nessler method.

W. MCCARTNEY.

Determination of iron in blood. P. FLEURY (J. Pharm. Chim., 1929, [viii], 9, 561—568).—The blood is ashed in the presence of magnesium nitrate, the product dissolved in hydrochloric acid, and after dilution with water a little orthophosphoric acid is added. The ferric salt is reduced with zinc, the solution filtered, and titrated against potassium permanganate in the presence of phosphomolybdic acid and manganese sulphate.

F. C. HAPPOLD.

Determination of iron in blood. P. FLEURY and J. MARQUE (J. Pharm. Chim., 1929, [viii], 9, 568—570).—The ferric salt is reduced with mercury (see preceding abstract).

F. C. HAPPOLD.

Determination of phosphorus in blood. A. IONESCO-MATTU and M. VITNER (Bull. Soc. Chim. biol., 1929, 11, 776—781).—The colorimetric method of Bordeiano (B., 1927, 422) is applied to the micro-determination of inorganic and total phosphorus in blood. The inorganic phosphorus is determined directly in the filtrate after precipitation of the blood with trichloroacetic acid. The total phosphorus is determined after oxidation with nitric acid and permanganate.

J. H. BIRKINSHAW.

Inorganic phosphoric acid content of arterial and venous blood. A. HOFF (Biochem. Z., 1929, 209, 195—199).—In dogs the inorganic phosphoric acid content of the venous blood is higher than that of the arterial blood. W. McCARTNEY.

Biometry of calcium, inorganic phosphorus, cholesterol, and lipid phosphorus in the blood of rabbits. II. A. R. HARNES (J. Exp. Med., 1929, 49, 287—301).—Values for animals kept in the laboratory or in the open air are recorded. Mean values are: calcium 15.7 ± 0.05 , inorganic phosphorus 4.65 ± 0.05 mg. per 100 c.c. of serum; cholesterol 58.2 ± 0.39 , lecithin 118.4 ± 1.13 mg. per 100 c.c. of whole blood. C. R. HARRINGTON.

Distribution of copper in blood. C. A. ELVEHJEM, H. STEENBOCK, and E. B. HART (J. Biol. Chem., 1929, 83, 21—25).—Horse blood contains about 0.05 mg. of copper per 100 c.c., the larger proportion being in the red blood-corpuscles. Haemoglobin contains amounts of copper which, on the basis of the accepted mol. wt. of this protein, are so small as to indicate that the metal does not form a part of the haemoglobin molecule. C. R. HARRINGTON.

Combined sugar and its ratio to total nitrogen in the normal Japanese [blood?] K. KITAMURA (Kyoto Ikwad. Zasshi, 1928, 2, 241—246).—The following values [? for the blood] are recorded: combined sugar 0.067—0.107, average 0.091%; total nitrogen: combined sugar 9.15—10.70 (average 10.10), free: combined sugar 0.83—1.37 (1.15), combined: total sugar 0.420—0.545 (0.485), free: total sugar 0.455—0.578 (0.518). CHEMICAL ABSTRACTS.

Fixation of dextrose by blood-corpuscles. F. HOGLER, A. THOMANN, and K. ÜBERRACK (Biochem. Z., 1929, 209, 1—31).—The analysis of a large number of experimental results shows that, in Loewi's phenomenon, the influence of swelling must be taken into account and that even so the method is not sufficiently accurate to enable definite conclusions to be reached. There is evidence that the uptake of sugar by erythrocytes is chiefly or entirely the result of a process of diffusion. W. McCARTNEY.

Salts and blood-sugar. H. MASAMUNE (Fukuoka Ikwad. Zasshi, 1927, 20, 1437—1522).—Potassium phosphate, magnesium salts, and to some extent calcium salts produce hyperglycaemia; sodium salts, or potassium acetate, chloride, or sulphate, have no effect. Ammonium chloride produces acidosis and magnesium salts alkalosis. CHEMICAL ABSTRACTS.

Dependence of the blood-sugar curve on the sugar preparation used. P. NIEDERHOFF (Biochem. Z., 1929, 210, 226—230).—Oral administration to fasting dogs or men of a paste of dextrose freshly crystallised from water with mother-liquor adhering gives a less marked initial hyperglycaemia than ordinary dextrose moistened with water. A secondary hyperglycaemia is observed with the freshly crystallised sugar. J. H. BIRKINSHAW.

Gasometric determination of fermentable sugar in blood and urine. D. D. VAN SLYKE and J. A. HAWKINS (J. Biol. Chem., 1929, 83, 51—70).—Fermentable sugar is determined in protein-free blood-filtrates or in urine cleared with Lloyd's reagent,

by application of the authors' ferricyanide method (A., 1928, 1358) before and after removal of dextrose with yeast. Normal urine contains 0.05—0.25% of total reducing substances, of which about one tenth is fermentable. This fermentable fraction is not affected, in normal individuals, by ingestion of 1 g. of dextrose per kg. The extra carbon dioxide produced by the action of yeast carboxylase on amino- and keto-acids introduces an error into the determination of fermentable sugar by direct measurement of carbon dioxide production in normal urines; in urines from glycosuric patients this error is insignificant. C. R. HARRINGTON.

Folin's micro-method for determination of blood-sugar. Blood-sugar and fermentable blood-sugar determined by different methods. O. FOLIN and H. MALMROS (J. Biol. Chem., 1929, 83, 115—120, 121—127).—Filtration of the light through filter-paper stained with picric acid eliminates the disturbing effect of the unchanged ferricyanide, and enables the colour comparisons in the method of Folin (A., 1928, 786) to be made over wider ranges of concentration.

Comparative determinations of total and fermentable sugar have been made in a large number of samples of blood by different methods. C. R. HARRINGTON.

Nature of blood-sugar. II. M. SOMOGYI (J. Biol. Chem., 1929, 83, 157—164).—The previous conclusions of Somogyi and Kramer (this vol., 207) as to the identity of the true blood-sugar determined by different methods are confirmed by experiments with four different methods on protein-free blood-filtrates prepared by the author's zinc technique (Proc. Soc. Exp. Biol. Med., 1929, 26, 353) which removes non-fermentable reducing substances. Folin's criticism (this vol., 462) of the author's work fails to take into account that in the application of Folin's recent method (A., 1928, 786) the oxidation of non-fermentable reducing substances in the tungstic acid blood-filtrate is, under the conditions prescribed by him, inhibited by the competing effect of the dextrose. The assumption of a second fermentable sugar in blood is unnecessary. C. R. HARRINGTON.

Determination of sugar in blood. S. R. BENEDICT (J. Biol. Chem., 1929, 83, 165—168).—Experimental results are given in disproof of the validity of Everett's criticism (this vol., 837) of the author's method (A., 1928, 438). C. R. HARRINGTON.

Hyperglycaemia associated with anaphylactic shock in the dog. I. T. ZECKWER and J. E. NADLER (J. Exp. Med., 1929, 49, 481—495).—The factors responsible for the condition are discussed. CHEMICAL ABSTRACTS.

Blood-nitrogen in sensitised animals. Z. M. DIENERSTEIN and S. GUENES (Zhur. exp. Biol. Med., 1929, 10, 520—529).—Anaphylactic shock, or any disturbance of the nitrogen of the tissues, does not disturb the nitrogen balance of the blood. CHEMICAL ABSTRACTS.

Haemolytic action of some hydrolysis products of lecithin, lecithides, and phosphatides. I. Products of intermediary hydrolysis. H. MAGIS-

TRIS (Biochem. Z., 1929, 210, 85—119).—The hydrolytic action of cobra or bee-sting poison on egg-lecithin and kephalin liberates a fatty acid giving a lysolecithin and a lysokephalin. The former has a strong hæmolytic power (active at 1 in 26,000), the latter very little. The pure lysokephalin is probably inactive. Similar products were prepared from various animal and vegetable lecithides. A lysokephalin and a lysosphingomyelin from brain showed little hæmolytic power; a lysolecithin from the same source showed marked activity. Lysolecithins from horse pancreas, horse brain, or ox testes all showed fair hæmolytic activity, although much less than the product from egg-yolk. Active lysolecithins were also obtained from peas, oats, and soya beans. From the last-named, two products (α - and β -lysolecithin) differing widely in activity were obtained.

Irradiation of lecithin with ultra-violet light eliminates choline, and the lysolecithin derived from it is much less active. A slight diminution in activity is also observed on irradiation of lysolecithin. It seems that the hæmolytic activity depends on the presence of the choline radical, and it is suggested that in the hydrolysis of lecithin to lysolecithin the nitrogen atom of the choline radical becomes linked through oxygen to the free glycerol-hydroxyl group.

J. H. BIRKINSHAW.

Influence of hydrogen-ion concentration on hæmolytic by solanine. R. FISCHER (Biochem. Z., 1929, 209, 319—325).—The hæmolytic action of solanine at p_H 5.5 is very slight and rapidly lost on diluting, but at p_H 10 is retained down to dilutions of 1 in 266,000.

P. W. CLUTTERBUCK.

Mechanism of hæmolytic by complement.
I. **Complement fixation as an essential preliminary to hæmolytic.** H. EAGLE and G. BREWER (J. Gen. Physiol., 1929, 12, 845—862).—The influence of electrolytes on the hæmolytic of sensitised cells by complement is studied. For sodium chloride the two zones of inhibition are (1) below a concentration of 0.025—0.03*N*, (2) above 0.4*N*, a partial destruction of complement also occurring in the lower zone. The observation of Muir and Browning that hypertonic saline allows complement to pass through a Berkefeld filter is explained on a physical basis, viz., that adsorption of complement by the minute particles of the filter is inhibited by the saline. Increase in the valency of the cation has a marked effect in increasing the degree of inhibition of complement; barium chloride exhibits an effect twenty times as powerful as that of sodium chloride in a concentration of 0.07*N*. Electrolytes are shown (within the limits of experimental error) to produce an inhibition of complement fixation exactly similar to that of hæmolytic (same optimum p_H etc.), and the authors therefore regard it as proved that adsorption is an essential preliminary to hæmolytic.

Variations of p_H are also shown to produce zones of inhibition of hæmolytic and complement fixation, the optimal range being p_H 6.5—8.0, but in addition to these zones an irreversible inactivation takes place below p_H 4.8 or above p_H 8.8. It is assumed that the adsorption demonstrated is of the "midpiece" fraction of complement.

P. G. MARSHALL.

Titration of complement. H. EAGLE (J. Gen. Physiol., 1929, 12, 821—823).—A convenient and rapid method for the determination of complement, based on the fact that the time required for hæmolytic is a function of the amount of complement, under standard conditions of temperature and volume, is described. A time-complement reference curve is given and the complement content of an unknown solution is determined by interpolation. P. G. MARSHALL.

Mechanism of complement fixation. H. EAGLE (J. Gen. Physiol., 1929, 12, 825—844).—A fixation of complement by sensitised red cells is shown to occur, just as has previously been demonstrated with agglutinated bacteria and an immune precipitate. Complement fixation precedes hæmolytic. The degree of complement fixation by a globulin suspension can be altered by variation of the amounts of either globulin or complement. The rapid initial rise and the change in slope of the fixation curves on approach to the equilibrium point are difficult to explain, although widely differing adsorption processes show a similar phenomenon on increasing either constituent. Evidence of the effect of temperature on complement fixation by globulin suspensions, agglutinated bacteria, and sensitised red cells shows that the process is essentially the same in all three cases. The temperature coefficient, however expressed, averages only about 1.3 between 0° and 40°, and this is taken as evidence that the process is a physical rather than a chemical one.

In a quantitative study of the complement fixation reactions the same type of deviation from Freundlich's empirical rule is encountered as is the case with adsorption from dilute solutions. Experiments are described which indicate that complement fixation is determined entirely by some change in the cell surface, both in the case of bacteria and with red cells, such change being proportional to the degree of sensitisation. It is considered that during sensitisation an aggregation of immune-serum globulin occurs on the surface of the cells, and that this aggregation is responsible for complement fixation by adsorption. In support of this, the optimum p_H for agglutination of sensitised bacteria is the same (p_H 5.0) for *Pneumococcus*, *B. typhosus*, and *B. pertussis*, and differs from that of the normal bacteria. Nevertheless the possibility of the existence of a thermo-labile substance with a chemical affinity for complement is admitted, although positive evidence is at present lacking. P. G. MARSHALL.

Occurrence and behaviour of methæmoglobin in cadavers. W. LAVES (Deut. Z. ges. gerichtl. Med., 1928, 12, 549—575; Chem. Zentr., 1929, i, 932).—Bacterial methæmoglobinæmia is relatively seldom observed. Poisoning with nitrite is characterised by a gradual post-mortal conversion of the methæmoglobin into nitric oxide-hæmoglobin; presence of the spectra of both substances affords a trustworthy diagnosis. Differentiation from spontaneously formed nitric oxide-hæmoglobin by nitrite-forming bacteria is based on the uniform distribution of the substance in cases of poisoning.

A. A. ELDRIDGE.

Biochemistry of the sense organs. F. BERENSTEIN (Russ. Fisiol. Zhur., 1926, 9, 205—216).—The

eyes of rabbits (1), sheep (2), cows (3), and dogs (4) contain the following enzymes: amylase, 1, 2, 4; invertase, 1, 2, 3; glucosidase, 4; erepsin, 2, 3, 4; trypsin, 1; catalase, 1, 2, 3, 4; reductase, 2, 3, 4; oxidase, 1, 2, 3, 4; peroxidase, 1, 2, 3, 4; lactolase, 3; chymosin, 2, 4. Lactase, maltase, urease, pepsin, lipase, lecithinase, alcoholase, and zymase were not found.

CHEMICAL ABSTRACTS.

Distribution of the enzymes in the organs and tissues of the animal body. F. BERENSTEIN (Russ. Fisiol. Zhur., 1926, 9, 383—394).—The testicles or ovaries of the dog (1), ram (2), bull (3), sow (4), ewe (5), and cow (6) contain the following enzymes: amylase, peroxidase, catalase, lipase, trypsin, and autolytic enzyme in all; invertase, 2, 6; glucosidase, 3; oxidase, 2, 3, 4, 5, 6; reductase, 2, 3, 4, 6; lecithinase, 2, 3, 4; erepsin, 2, 3, 4, 5, 6; pepsin, 1, 4; lactolase, 2, 3, 4, 6; alcoholase, 2. Lactase, maltase, urease, and zymase were not found.

CHEMICAL ABSTRACTS.

Composition of body and organs of homeotherms and poikilotherms. E. VORT (Z. Biol., 1929, 89, 114—138).—Analyses have been made for water, ash, fat, and nitrogen of the organs and whole bodies of various warm- and cold-blooded animals under varying physiological conditions. The results are discussed in relation to the fundamental nature of the metabolic processes concerned.

E. A. LUNT.

Presence of aluminium in plant and animal matter. L. KAHLENBERG and J. O. CLOSS (J. Biol. Chem., 1929, 83, 261—264).—Spectroscopic examination indicates the presence of aluminium in a number of samples of plant and animal material. The contrary conclusions of McCollum and others (A., 1928, 793) are therefore erroneous. C. R. HARRINGTON.

Iron content of the albino rat at different stages of the life cycle. C. V. SMYTHE and R. C. MILLER (J. Nutrition, 1929, 1, 209—216).—At birth, during suckling, and at 20—40 days (and after), rats contain 0.0055, 0.0026, and 0.0045% Fe, respectively. The iron content of females is depleted during pregnancy, but returns to the normal value during lactation.

CHEMICAL ABSTRACTS.

Iodine content of human organs. B. BUCHHOLZ (Z. ges. exp. Med., 1928, 63, 188—197; Chem. Zentr., 1929, i, 915).—Iodine was detected in all the organs examined; individuals exhibit differences. The thyroid gland contains most iodine; the adrenals, ovaries, thymus, and sometimes the spleen contain fairly large amounts. Chronic pathological conditions affect the values. The total iodine content of the human body varies considerably around 11 mg.

A. A. ELDRIDGE.

Nucleic phosphorus of tissues and its determination. M. JAVILLIER (Bull. Soc. Chim. biol., 1929, 11, 644—678).—A lecture.

Titanium in animals. G. BERTRAND and (MME.) VORONCA-SPIRT (Compt. rend., 1929, 189, 221—223).—The titanium has been determined in various organs of a large number of animals and fish by the method previously used for its detection in plants (this vol., 855). In the horse, cow, sheep, and pig the liver is richest in this element (0.5—

0.6 mg./kg.), the heart, lungs, and kidneys containing about one half of this amount, whilst the element is absent from the muscles, brain, and spinal cord. Titanium could not be detected, however, in the corresponding organs of a rabbit, but the fur contains 2.2 mg./kg. Small quantities (0.3—0.9 mg.) are found in most fish, whilst *Crustacea* and molluscs are relatively rich in this element, the combined head and thorax organs of the edible crab containing 32.5 mg./kg.

J. W. BAKER.

Sulphur content of melanotic pigments. F. SCHAAF (Biochem. Z., 1929, 209, 79—82).—A method by which melanotic pigments rich in sulphur can be freed almost completely from this element is described. The last traces of sulphur are almost as difficult to remove as are those of iron. The view that sulphur is not an integral part of the pigment is confirmed.

W. MCCARTNEY.

Determination of the mineral constituents of rabbit's and dog's muscle. BOUTIRON and GENAUD (Compt. rend. Soc. Biol., 1928, 99, 1730—1731; Chem. Zentr., 1929, i, 765).—Determinations of water, chlorine, potassium, sodium, and phosphorus are recorded.

A. A. ELDRIDGE.

Pyrophosphate fraction in muscle. K. LOHMANN (Naturwiss., 1929, 17, 624—625).—The pyrophosphate fraction of muscle can be isolated through the barium salt. Neutral hydrolysis of the complex salt results in the formation of pyrophosphoric acid and adenosinephosphoric acid (adenylic acid). Adenylpyrophosphoric acid, after brief treatment with hot dilute acid, yields 2 mols. of orthophosphoric acid and 1 mol. of adenine and pentose (ribose)-phosphoric acid. The results are discussed in relation to other work on muscle.

R. A. MORTON.

Enzymic action of the muscle of a mummy 3000 years old (precipitin reaction, glycolysis, and respiratory enzyme). E. SEHR (Arch. exp. Path. Pharm., 1929, 143, 35—45).—The glycolytic activity of a powder prepared from ox pancreas after extraction with acetone is distinct although weak, but a mixture of an acetone powder of mummy muscle, which itself has no appreciable glycolytic activity, with the acetone powder from ox pancreas possesses very considerable glycolytic activity, approximately equal to that of a similar mixture from fresh ox tissues. Powder from mummy muscle gives the indophenol oxidase reaction.

W. O. KERMAK.

Influence of hæmolysis on the secretion of bile. K. SUGIU and O. HISASI (Okayama Ig. Zasshi, 1927, 39, 1902—1913).—In dogs with gall bladder fistulas, splenectomy caused for 20—30 days a diminution in the iron and bilirubin contents of the bile. Injection of water or hæmolysin caused an increase in the biliary iron and bilirubin either before or after splenectomy. The effects of phenylhydrazine, nitrobenzene, and tolylenediamine were examined.

CHEMICAL ABSTRACTS.

Excretion of iodine by the gastric glands. L. HEILMEYER and A. STURM (Klin. Woch., 1928, 7, 2381—2383; Chem. Zentr., 1929, i, 555).—A few minutes after intravenous administration of iodine the gastric juice contains considerable amounts of

iodine and an increased quantity of free hydrochloric acid. Iodine appears in the stomach soon after inhalation of ethyl iodide vapour.

A. A. ELDRIDGE.

Phosphorus, calcium, and potassium contents of artificially induced peritoneal exudates. X. CHAHOVITCH and M. VICHNJITCH (Compt. rend. Soc. Biol., 1928, 99, 1267—1270; Chem. Zentr., 1929, i, 552).—The values do not correspond with those of the blood.

A. A. ELDRIDGE.

Normal day-to-day variability of yield of milk and fat of individual cows. S. BARTLETT (J. Agric. Sci., 1929, 19, 438—451).—A statistical study of the variability of milk and fat yield of cows as affected by such factors as stage of lactation and season of the year is presented.

E. HOLMES.

Variations in the composition of the milk of an abnormal cow. H. T. CRANFIELD and E. R. LING (J. Agric. Sci., 1929, 19, 491—499).—Details are recorded of a cow which, during three lactation periods, gave milk of which the fat percentages were very variable; the solids-not-fat were consistently low, the value exceeding 8.5% in only 2% of the total number of samples analysed. Protein, lactose, phosphoric acid, and lime percentages were much below normal, whilst the soluble portion of the ash was high and the insoluble low. Porcher's contention that there is a definite lactose-chlorine ratio in milk is supported. Feeding first with "non-mineralised" and later with "mineralised" cake had no apparent effect, but these abnormalities may have been incipient signs of disease affecting the milk-secreting organs, for the cow was eventually found to be suffering from tuberculosis.

E. HOLMES.

Buffer intensities of milk and milk constituents. I. Buffer action of caseinogen. E. O. WHITTIER (J. Biol. Chem., 1929, 83, 79—88).—Titration curves were obtained for skimmed milk and for whey, and the curve for the caseinogen was constructed by difference. Milk showed maximum buffering at p_H 5.5 and the caseinogen at p_H 5.2, whence it appears that caseinogen is one of the predominant buffers of milk. Curves obtained for different samples of purified caseinogen showed different characteristics. The curve for milk lost its characteristic form on addition of rennet, owing to the conversion of the caseinogen into casein.

C. R. HARRINGTON.

Effect of diet on copper content of milk. C. A. ELVEHJEM, H. STEENBOCK, and E. B. HART (J. Biol. Chem., 1929, 83, 27—34).—Cow's milk contains about 0.15 mg. of copper per litre with no significant geographical variation. The copper content of cow's and goat's milk was not increased by 5-fold increase in the dietary intake of copper (in the form of copper sulphate).

C. R. HARRINGTON.

Is the iron content of milk increased by the ingestion or injection of iron salts? V. HENRIQUES and A. ROCHE (Bull. Soc. Chim. biol., 1929, 11, 679—692; cf. this vol., 93).—Daily ingestion of 0.5 g. of ferrous sulphate by women and of 5 g. of ferrous lactate by goats does not cause any change in the iron content of the blood, which is normally 1 mg.

per litre in each case. Intravenous injection of lactate in the goat likewise produces no increase.

J. H. BIRKINSHAW.

Aroma of butter. C. B. VAN NIEL, A. J. KLUYVER, and H. G. DERX (Biochem. Z., 1929, 210, 234—251).—The aroma of butter is parallel with its content of acetylmethylcarbinol, and *Streptococcus cremoris*, *S. citrovorus*, and *S. paracitrovorus*, which produce the aroma, all produce the carbinol. Pure acetylmethylcarbinol has no odour, whereas diacetyl in dilute solution possesses the characteristic butter aroma. The aroma of butter is due to the presence of chemically undetectable amounts (0.0002—0.0004%) of diacetyl formed by the oxidation of acetylmethylcarbinol.

J. H. BIRKINSHAW.

Volumetric determination of potassium in urine. A. BOLLIGER and E. M. DAY (Austral. J. Exp. Biol., 1929, 6, 91—95).—A method for determination of urinary potassium depending on its precipitation as perchlorate from the unashed urine and titration with methylene-blue is described.

P. W. CLUTTERBUCK.

Colorimetric determination of small amounts of sugar in urine. C. STICH (Pharm. Zentr., 1929, 70, 437).—Urine is heated with Fehling's solution and the precipitated copper oxide separated by centrifuging, dissolved in pure nitric acid, and suitably diluted. The colour produced by the addition of ferrocyanide and ammonia is then compared with that produced from a standard solution of dextrose treated in a similar way.

W. O. KERMAK.

Determination of dextrose in urine. F. JUSTEN (Apoth.-Ztg., 1928, 43, 1436; Chem. Zentr., 1929, i, 565).—Addition of excess of Fehling's solution and titration of the excess with iodine and thiosulphate is preferred to Meyer's direct method.

A. A. ELDRIDGE.

Test for protein in urine. C. BOSE (Indian Med. Gaz., 1929, 64, 17—19).—A supersaturated aqueous solution of saccharin is employed, the test being performed in the same manner as Heller's nitric acid test. The reagent has the advantage of failing to precipitate mucin, urea, or urates.

CHEMICAL ABSTRACTS.

Iron in nutrition. VIII. Ineffectiveness of large doses of iron in curing anaemia in the rat. J. WADDELL, H. STEENBOCK, and E. B. HART [with E. VAN DONK]. **IX. Deficiency of copper as cause of anaemia.** J. WADDELL, H. STEENBOCK, C. A. ELVEHJEM, and E. B. HART [with E. VAN DONK] (J. Biol. Chem., 1929, 83, 243—250, 251—260).—VIII. Relief of nutritional anaemia in young rats was obtained by heavy dosage with iron salts only when the latter contained traces of copper.

IX. Anaemia in young rats on a diet of milk and pure iron salts could be cured by addition of liver extracts, the acid-insoluble sulphides of the ash of such extracts, and copper sulphate, all additions containing equivalent amounts of copper.

C. R. HARRINGTON.

Xanthine calculi in sheep. T. H. EASTERFIELD, T. RIGG, H. O. ASKEW, and J. A. BRUCE (J. Agric. Sci., 1929, 19, 573—585).—Xanthine calculi in the kidneys of sheep, reported on certain poor pastures on the Moutere Hills in the Nelson district, N.Z.,

occur where the soils and pasture are notably deficient in lime and phosphate. Samples of pasture show a great deficiency of iron and an abnormally high content of manganese. "Bush" sickness, definitely associated with iron deficiency, is unknown in the district. Calculus formation does not occur on the small areas where good pastures have been established by lime and phosphate treatment. E. HOLMES.

Vitamin-B in cancer. H. JACKSON, jun., and C. I. KRANTZ (J. Clin. Invest., 1929, 6, 609—612).—Malignant tissue contains less vitamin-B than normal liver. CHEMICAL ABSTRACTS.

Action of various proteins on blood-sugar [in diabetes]. H. GLATZEL (Arch. exp. Path. Pharm., 1929, 143, 234—245).—In diabetics after oral administration of protein, a strong tendency to hyperglycæmia is obtained. The hyperglycæmia after a single administration of 20 g. of dextrose by mouth to a diabetic after an egg-protein diet is less and lasts for a shorter time than after a pure fat-vegetable diet. If the egg-protein be replaced by a corresponding amount of flesh-protein, the hyperglycæmia is greater and lasts longer. P. W. CLUTTERBUCK.

Effect of oral administration of bile acids on the sugar metabolism of the diabetic. H. HORSTERS and H. ROTHMANN (Arch. exp. Path. Pharm., 1929, 142, 261—270).—Oral and intravenous administration of bile acids or salts lowers the blood-sugar of normal and diabetic individuals; the action is comparable with that of insulin. In the fasting diabetic the lowering is greater than that produced by lack of food alone; when food is taken the usual rise in blood-sugar is suppressed. In mild cases of diabetes an improvement in the carbohydrate tolerance is observed, in severe diabetes mellitus there is frequently no improvement. The bile acids probably act by stimulating the portion of pancreas tissue which is still active.

J. H. BIRKINSHAW.

Blood-sugar in insulin-treated diabetes. N. A. NIELSEN (Z. klin. Med., 1929, 109, 636—646; Chem. Zentr., 1929, i, 1229).—Determination of blood-sugar before, and 5 hrs. after, the injection is recommended.

A. A. ELDRIDGE.

Effect of insulin on the properties of the blood in diabetes mellitus. E. ZUCKERSTEIN and A. STREICHER (Deut. Arch. klin. Med., 1928, 161, 323—337; Chem. Zentr., 1929, i, 1229).

Hyperinsulinism. F. N. ALLAN (Arch. Int. Med., 1929, 44, 65—70).—It has been definitely established that spontaneous hypoglycæmia, due to over-production of insulin by the pancreas or perhaps, in some cases, to failure of the liver, sometimes occurs in man. Distinction between the two causes may be difficult.

W. MCCARTNEY.

"Oxantin" (dihydroxyacetone); relation between metabolism and blood-sugar changes. A. LÖW and A. KRCMA (Klin. Woch., 1928, 7, 2432—2435; Chem. Zentr., 1929, i, 1019).—Dihydroxyacetone, orally administered, passes into the blood of diabetics, but not of normal individuals.

A. A. ELDRIDGE.

Phloridzin diabetes. III. Effect of phloridzin on glycogen storage in dogs with ligated ureters. T. P. NASH, jun. (J. Biol. Chem., 1929, 83, 139—155).—Procedures such as fasting, exposure to cold, and administration of adrenaline do not invariably reduce the glycogen stores of the dog to a significant extent. Phloridzin was without effect on the sugar, non-protein nitrogen, and acetone of the blood, and on the glycogen of the liver and muscles of dogs with ligated ureters. The results, however, fail to provide conclusive evidence that the site of action of phloridzin is exclusively renal. C. R. HARRINGTON.

Fructosuria. P. A. HEERES and H. Vos (Arch. Int. Med., 1929, 44, 47—64).—Experiments on a subject suffering from essential fructosuria gave the following results. Fructosuria at once disappears if only food free from lævulose is consumed. The quantity of lævulose excreted in the urine is constant (about 14%), and independent of the amount administered, whether in one large or several small doses, and whether orally or intravenously. Administration of lævulose causes a rise in the blood-sugar content due to fructosæmia. Inulin does not cause or influence fructosuria. Lævulose when given together with other sugars causes a fructosuria more severe than that produced when it is given alone. The metabolism of dextrose, galactose, maltose, and mannose is not disturbed, but when sorbose is administered it is largely excreted in the urine. There is no rise in the respiratory quotient following administration of lævulose. Freshly-dissolved lævulose produces a greater degree of fructosuria than lævulose which has been in solution for some time before administration. Crystalline lævulose, administered *per rectum*, produces a more severe fructosuria than lævulose given by the mouth. W. MCCARTNEY.

Decomposition of protein in fever. I. MA (Monatsschr. Kinderheilk., 1928, 36, 363—376; Chem. Zentr., 1929, i, 1031—1032).—In infection and fever (in children) the action of the serum-peptidase was increased. Comparison of the urinary nitrogen and peptidase did not suggest that the increase was due to cellular breakdown. A. A. ELDRIDGE.

Iodine and exophthalmic goitre. A. SPRINGBORN and A. GOTTSCHALK (Deut. Arch. klin. Med., 1928, 161, 338—352; Chem. Zentr., 1929, i, 1234).—The effect of administration of iodine in simple and in exophthalmic goitre is described. A. A. ELDRIDGE.

Calcium content of blood of normal and thyroidectomised sheep. P. V. BOTCHKAREFF and M. P. DANILOVA (Compt. rend., 1929, 189, 304—305).—The difference between the calcium content of the blood of normal sheep (10 mg. per 100 c.c.) and that of thyroid-parathyroidectomised sheep is negligible. A. A. GOLDBERG.

Changes in the alkali reserve and chloride content of the blood in experimental intestinal closure. F. D. ALSINA and J. R. PIJOAN (Compt. rend. Soc. Biol., 1928, 99, 1278; Chem. Zentr., 1929, i, 549).—Closure of the upper intestine increases the alkali reserve and reduces the blood-chlorine; closure of the lower intestine reduces the blood-chlorine without affecting the alkali reserve. A. A. ELDRIDGE.

Cholesterol content of Indian blood in health and leprosy. T. C. BOYD and A. C. ROY (Indian J. Med. Res., 1928, 15, 643—651).—Normal values range from 0.082 to 0.184 g. per 100 c.c.; values for early and advanced leprosy, respectively, are 0.070—0.109 and 0.080—0.130. CHEMICAL ABSTRACTS.

Blood-calcium in leprosy. M. C. CRUZ, C. B. LARA, and E. M. PARAS (J. Philippine Is. Med. Assoc., 1928, 8, 216—221).—Serum-calcium values are unchanged. CHEMICAL ABSTRACTS.

Effect of [intravenous injection of] calcium or ergotamine on the blood-sugar curve after administration of dextrose as a test of liver function. T. REDNIK (Z. klin. Med., 1929, 109, 720—724; Chem. Zentr., 1929, i, 1228—1229).—Injection of calcium or ergotamine diminishes the rise of the blood-sugar curve caused by administration of dextrose. A. A. ELDRIDGE.

Physico-chemical changes in the blood and histological changes in the kidneys in experimental nephritis. N. ISHIYAMA (Z. ges. exp. Med., 1928, 63, 699—716, 717—719; Chem. Zentr., 1929, i, 1119).—Excessive feeding of rabbits with vegetable protein leads to albuminuria and increase of the blood-residual nitrogen and plasma-protein, changes differing from those in man. Injection of mercuric chloride, cantharidin, or habu-poison, but not uranium, caused a diminution of the serum-albumin and an increase of the serum-globulin; these changes correspond with those observed in man. A. A. ELDRIDGE.

Chlorine ions in the blood in chloride retention of nephritis. H. THIERS (Bull. Soc. Chim. biol., 1929, 11, 693—709).—The chloride of plasma shows very variable values in nephritis. The acidity drives the chlorine ions from the plasma to the erythrocytes, lowering the ratio plasma-chloride/erythrocyte-chloride. Consequently when the total chlorine ions are insufficient in nephritis these are increased in the erythrocytes and tissues but reduced in the plasma, which then gives subnormal values. With strong acidosis the blood may show a reduced chloride content, the chloride being found in the tissues. J. H. BIRKINSHAW.

Blood-chlorides in conditions associated with pneumonia. C. A. L. BINGER, R. V. CHRISTIE, J. S. DAVIS, jun., and A. HILLER (J. Exp. Med., 1929, 49, 603—614).—Ingestion of much water, and experimental pneumococcal infection but not starvation, anoxemia, tissue destruction, anaphylactic shock, leucocytosis, or fever diminished the serum-chloride of dogs. CHEMICAL ABSTRACTS.

Determination of respiratory exchange of small animals. H. WU and T. T. CHEN (Chinese J. Physiol., 1929, 3, 307—313).—A simple closed-circuit method involving determinations of carbon dioxide and oxygen is described. C. C. N. VASS.

Basal metabolism of omnivorous and vegetarian rats. H. WU and T. T. CHEN (Chinese J. Physiol., 1929, 3, 315—323).—The basal metabolism of 95 vegetarian rats determined by means of the respiratory exchange method (preceding abstract)

was slightly lower than that of the 96 omnivorous rats examined. C. C. N. VASS.

Respiratory metabolism in eviscerated dogs. A. BORNSTEIN (Biochem. Z., 1929, 209, 172—180).—When fasting dogs are eviscerated but not decapitated the gaseous exchange always falls on the average about 45% and the respiratory quotient always rises but remains below 1.0 (average 0.8—0.9). The increase in the respiratory quotient is largely due, however, to over-ventilation of the lungs. It follows that, after evisceration, considerable amounts of fat can be burnt. If dextrose is injected into eviscerated dogs in amounts greater than that necessary for their calorie requirements the respiratory quotient rises to a value considerably higher than that found when no dextrose is injected. It is concluded that the fat and carbohydrate metabolism of eviscerated dogs depends mainly on the quantities of these substances present in the food supplied. W. MCCARTNEY.

Inorganic salt metabolism. I. Methods. W. BAUER and J. C. AUB (J. Amer. Dietet. Assoc., 1927, 3, 106—115).—Clinical routine for the study of calcium and phosphorus metabolism is described. New determinations of these elements in various foods are recorded. CHEMICAL ABSTRACTS.

Calcium metabolism in the human female. R. F. MATTERS (Austral. J. Exp. Biol., 1929, 6, 119—125).—The blood-calcium shows a pre-menstrual rise followed by a fall just prior to the onset of menstrual flow, the variation being 5—8% of the normal calcium level. P. W. CLUTTERBUCK.

Effect of intragastric administration of calcium on the urinary C:N quotient in rabbits. A. BICKEL and D. MARSHALKOWITZ (Z. ges. exp. Med., 1928, 62, 747—755; Chem. Zentr., 1929, i, 552).—Administration of 0.011—0.013 g. of calcium per kg., but not of greater doses, caused a transitory fall in the urinary C:N quotient. A. A. ELDRIDGE.

Cholesterol metabolism. M. WICHERT, S. POSPELOV, and A. JAKOVLEVA (Z. klin. Med., 1929, 109, 678—697; Chem. Zentr., 1929, i, 1233).—Increased ingestion of cholesterol increases the blood-cholesterol only when the lipid metabolism is seriously disturbed. There appears to be a relationship between the urinary bile acids and the excretion of cholesterol. A. A. ELDRIDGE.

Ageing of tissue. M. BURGER and G. SCHLOMKA (Z. ges. exp. Med., 1928, 63, 105—116; Chem. Zentr., 1929, i, 920).—The cholesterol content of the skin decreases with increasing age. Values for the dry matter and nitrogen content (g.-%), respectively, are: 5 weeks 24.6—35.5, 3.68—4.86; 5 years 29.7—42.1, 4.74—6.36; 60 years 35.4—44.1, 5.91—7.25. A. A. ELDRIDGE.

Ammonia metabolism of the kidneys and its relation to the acid-base balance. H. WASSERMEYER (Arch. exp. Path. Pharm., 1929, 143, 117—128).—Determinations of ammonia in blood from the carotid artery, vena cava, and kidney vein confirm the view that ammonia is produced by the kidneys. The probable source of this ammonia is adenosinephos-

phoric acid, from which it is formed during enzymic deamination.

W. O. KERMACK.

Protein metabolism of organs of animals kept in air under reduced pressure. H. ANGELESCU (Biochem. Z., 1929, 209, 236—239).—Lack of oxygen produces the following changes in the nitrogen content of the spleen, heart, liver, and muscles of guinea-pigs: a 2—7% decrease in the total nitrogen, with the greatest lack of oxygen investigated (barometric pressure, 230 mm.), an increase of total residual nitrogen amounting to about 9% for heart and muscle and to 100% for spleen and liver, and an increase of from 20% (muscle and heart) to almost 100% (spleen and liver) in the amino-acid fraction of the residual nitrogen. These changes appear first in the spleen, then in the liver, and finally, as rarefaction is increased to its greatest extent, in heart and muscle.

W. MCCARTNEY.

Embryonic metabolism. III. Nitrogen distribution in the developing hen's egg. H. O. CALVERY (J. Biol. Chem., 1929, 83, 231—241).—Figures are given for the analysis by the Van Slyke method of the alcohol-insoluble contents of the hen's egg at varying stages of development. The most conspicuous change is a decrease in the amino-nitrogen and a corresponding increase in the non-amino-nitrogen of the filtrate. Arginine shows a preliminary decrease, followed by an increase above the initial level; histidine shows considerable fluctuations.

C. R. HARRINGTON.

Production of choline from the suprarenal capsule. S. ONO (Fukuoka Ikwa. Zasshi, 1927, 20, 1187—1212).—Venous blood of the suprarenal capsule contains more choline than blood from any other abdominal organ. The formation of choline is regulated by the nervous system. Extirpation of the suprarenal capsule decreases the choline content of the serum.

CHEMICAL ABSTRACTS.

Urea content of frog muscle. J. HELLER (Biochem. Z., 1929, 209, 74—78).—The urea content of frog muscle varies widely from animal to animal and from species to species, being much higher in *Rana temporaria* than in *R. esculenta*. Changes in the urea content run parallel with changes in glycogen content. In frogs kept for several days with insufficient water or at temperatures above normal the urea content of the muscle rises. The urea in the muscle does not take part in the traumatic production of ammonia.

W. MCCARTNEY.

Purine metabolism. II. Effect of ingestion of glycine on excretion of endogenous uric acid. A. A. CHRISTMAN and E. C. MOSIER (J. Biol. Chem., 1929, 83, 11—19).—The previous conclusion of Lewis and others (A., 1918, i, 559) that ingestion of glycine is followed by increased excretion of uric acid is confirmed, the contrary results of Zwarenstein (A., 1928, 547) being explained by his employment of the method of Benedict and Franke (A., 1922, ii, 669), which gives low results for uric acid in presence of large amounts of amino-acids.

C. R. HARRINGTON.

Variation of acetone substances in the living organism. K. WATANABE (Aichi J. Med., 1928, 35, 381—534).—Administration of butyric, valeric,

or, particularly, isovaleric acid to rabbits increases the blood-acetone substances and causes the appearance of acetone substances in the urine; poisoning by yellow phosphorus has a similar effect, but causes no marked change in the blood-sugar. Injection of adrenaline, followed by that of butyric acid, has a specially marked effect. Adrenaline decreases the acetone concentration which has been increased by fatty acid. The combined use of fatty acid and insulin causes an increase in acetone concentration which is comparable with that produced by fatty acid alone, the urinary excretion being small. Insulin does not inhibit the formation of acetone substances. On injection of sodium butyrate and dextrose recovery is more rapid than with sodium butyrate alone. In phosphorus-poisoned rabbits the velocity of increase in the blood-acetone is retarded, its excretion in the urine being small.

CHEMICAL ABSTRACTS.

Behaviour of carbohydrates during muscle perfusions. A. BORNSTEIN and H. VOLKER (Biochem. Z., 1929, 209, 103—118).—In the isolated hind limbs of a dog perfused with dog's blood the amount of blood-sugar tends to fall, and addition of 0.225 g. of dextrose per kg. per hr. is necessary to maintain it at physiological level. The amount of laevulose necessary for the same purpose is 0.25 g. per kg. per hr., whilst additions of lactic acid or of alcohol have a slight sugar-saving effect. If insulin is added to the blood-stream along with sufficient sugar to produce an increase in blood-sugar, the amount of this falls considerably, the quantity of insulin required for the purpose being of the same order as is necessary in the whole animal. There is no constant relationship between the glycogen and the total carbohydrate content of the muscle and the amount of sugar administered, although the glycogen content usually increases during 1½—2 hrs. when sufficient sugar for maintaining a constant level of blood-sugar is given, and usually decreases without appearance of convulsions when insulin is given simultaneously. The amount of sugar necessary to maintain constancy of the blood-sugar level corresponds with about 50% more than the oxygen requirement of the limbs. Part of the sugar which disappears from the blood is stored as reserve carbohydrate or reserve fat.

W. MCCARTNEY.

Critical temperature of freezing. Living muscle. T. MORAN (Proc. Roy. Soc., 1929, B, 105, 177—197).—Experiments carried out on living sartorius and gastrocnemius muscles in the frog indicate that the effects of freezing are similar to those produced by desiccation. A 78% removal of water produces instant death and corresponds with freezing to equilibrium at -2° . Muscles frozen below -2° exhibit on thawing loss of osmotic properties and express an acid liquid. Super-cooling below -2° produces no changes. A freezing or desiccation resulting in a loss of water of not more than 40% of the original weight of muscle is shown to be completely reversible.

E. A. LUNT.

Formation of lactic acid in the muscles in the frozen state. E. C. SMITH (Proc. Roy. Soc., 1929, B, 105, 198—207).—The rates of accumulation of lactic acid have been determined in the case of the gastrocnemius of the frog exposed to temperatures between 0° and -10° . With falling temperature

of storage the rate of accumulation increases, reaching a maximum at -25° , and is negligible at -10° . Muscles frozen above -1.6° appear capable on thawing of returning to their normal lactic acid content, whilst in muscles frozen below this temperature the lactic acid on thawing increases to that of the normal rigor maximum. E. A. LUNT.

Oxidation of lactic acid in muscle. A. HAHN and E. FISCHBACH (*Z. Biol.*, 1929, 89, 149—158).—A review of current investigations on the existence of a thermostable co-enzyme for the oxidation of lactic acid in muscle suggests that admissible evidence for such an enzyme can only be obtained by establishing the identity of the respiration process in unwashed muscle with that occurring in washed muscle, the respiration of which has been restored by the addition of boiled aqueous extract of muscle which was thought by Meyerhof to contain the thermostable co-enzyme. Experiments are described in which finely-divided unwashed muscle and finely-divided washed muscle + boiled aqueous extract are shaken in a vacuum and in oxygen; the oxygen consumption and lactic acid contents are determined for various times of shaking. No sensible difference between the lactic acid content in oxygen and in a vacuum was observed in the experiments with washed muscle + extract; with unwashed muscle the lactic acid content after shaking was markedly higher in vacuum than in oxygen. The degree of restoration of respiration in these experiments ranged from 0.52 to 0.92 as measured by the ratio of the rate of oxygen consumption of washed muscle + extract to the corresponding rate for unwashed muscle. It is concluded that no detectable oxidation of lactic acid results from the restoration of the respiration of washed muscle by extract. Since it is thus shown that the original and the restored respiratory processes are essentially different, Meyerhof's assumption of a co-enzyme is held to be unnecessary. E. A. LUNT.

Oxidation of succinic acid. II. A. HAHN and W. HAARMANN (*Z. Biol.*, 1929, 89, 159—166).—A method has been developed for the analysis of mixtures containing succinic, malic, and fumaric acids. The fumaric acid is first determined by the authors' method (cf. A., 1928, 323) as mercurous salt; in a second sample the malic acid is converted into fumaric acid, from the amount of which the malic acid may be calculated. In a third sample the succinic acid is determined by means of the silver salt after the other two acids have been preferentially oxidised by neutral aqueous permanganate. Under the conditions described the conversion of malic into fumaric acid takes place to the extent of about 94%, and the mean error in the determination of succinic acid is about 2%.

This method has been used to investigate the oxidation of succinic acid by means of muscle in the presence of (a) methylene-blue, (b) oxygen. In (a) about 9% of fumaric acid and 25% of malic acid are produced, corresponding with about 40% decomposition of the original succinic acid. In (b) succinic acid is completely oxidised to fumaric and malic acids approximately in the ratio 1:2.5. If, however, the muscle be first washed with toluene-water, no sensible

oxidation takes place in the presence of oxygen, but the reaction velocity with methylene-blue remains approximately unchanged. E. A. LUNT.

Physical chemistry in the service of biology. F. G. DONNAN (*J.C.S.*, 1929, 1387—1398).—Liversidge lecture, delivered on Nov. 29, 1928.

Influence of certain water conditions, especially dissolved gases, on trout. J. S. GUTSELL (*Ecology*, 1929, 1, 77—96).—A study of the effect of variations in p_{H} and dissolved oxygen and carbon dioxide. Marked increase in the carbon dioxide and decrease in the oxygen content of spring- and brook-water as the warm season advanced is attributed to increased bacterial activity. CHEMICAL ABSTRACTS.

Basal and resting metabolism after irradiation with ultra-violet light. I. Resting metabolism of birds. II. Basal metabolism of man. III. Resting metabolism of rabbits. E. CROFTS (*Amer. J. Hyg.*, 1928, 8, 1014—1019, 1020—1023, 1024—1029).—With canaries a 14% fall in oxygen consumption, followed by a delayed rise of 21%, was observed; in the other cases no effect was observed. CHEMICAL ABSTRACTS.

Absorption by dyes and leuco-compounds as a pre-condition of photobiological sensitisation in the ultra-violet. W. HAUSMANN and O. KRUMHOLZ (*Biochem. Z.*, 1929, 209, 142—147).—The ultra-violet absorption spectra of a dye containing two pyrrole nuclei and of the corresponding leuco-compound as well as of mesoporphyrinogen have been studied and evidence has been obtained that photobiological sensitisation in the ultra-violet region may be caused by the uncoloured precursor of the dye (or porphyrin). W. MCCARTNEY.

Behaviour and action of undigestible substances (keratin, kaolin) in the organism of mammals. A. GOLDFEDER (*Biochem. Z.*, 1929, 209, 154—171).—Experiments on mice by which food containing up to 60% of keratin or 80% of kaolin was consumed show that these substances have practically no influence of any kind. Keratin has no mechanical influence (increase of length) on the intestine. W. MCCARTNEY.

Action of active iron oxide on blood formation and growth of white rats. W. LINTZEL (*Biochem. Z.*, 1929, 210, 76—84).—Only about 7% of active iron oxide ("siderac") was soluble in hydrochloric acid at the concentration of gastric juice. It had no specific action on the growth of rats. It was much inferior to ferric chloride weight for weight when added to an iron-free ration. J. H. BIRKINSHAW.

Histochemical investigations on the behaviour of various iron compounds in the organism. V. HENRIQUES and H. OKKELS (*Biochem. Z.*, 1929, 210, 198—225).—By the intravenous injection of various forms of iron into rabbits it is shown that iron exists in the cell in two forms often present together, the diffuse and the granular. When the histochemical (Turnbull) reaction is negative, this is due to the presence of iron in traces only, or in complex form, or as very slightly soluble compounds in colloidal solution. The examination of various organs shows that the question as to whether and how iron is taken up

by an organ depends largely on the physico-chemical structure of the iron compound used.

J. H. BIRKINSHAW.

Elimination of drugs introduced intravenously and subcutaneously. L. STRADA (Arch. Farm. sperim., 1929, 47, 36—55).—As regards elimination from the system, some drugs, such as sodium thio-sulphate, behave similarly whether administered intravenously or subcutaneously in similar doses. Others, such as sodium salicylate, are eliminated in slightly larger amounts in the former than in the latter case, whilst others again, like potassium iodide, show a similar but much more marked difference in this respect.

T. H. POPE.

Analogous action of sodium fluoborate and sodium perchlorate on skeletal muscle. G. BOEHM (Biochem. Z., 1929, 209, 489—491).—The analogous action of sodium fluoborate and sodium perchlorate on the frog's preparation in causing fibrillar contractions and rigidity is attributed to the similarity in constitution of the respective anions.

P. W. CLUTTERBUCK.

Effect of colloidal sulphur on blood-sugar. G. BUCCIARDI (Arch. Farm. sperim., 1928, 46, 90—96; Chem. Zentr., 1929, i, 1229).—Intraperitoneal administration of "sulfosol" (0.5% S) to guinea-pigs in doses less than 0.0005 g. per kg. does not affect the blood-sugar, in doses of 0.0007—0.01 g. per kg. causes a fall, and in doses of more than 0.013 g. per kg. causes a rise, in the blood-sugar.

A. A. ELDRIDGE.

Pathological formation of fat. I. Does fat arise from protein? G. ROSENFELD (Biochem. Z., 1929, 209, 312—318).—In phosphorus poisoning, migration, but not formation, of fat occurs.

P. W. CLUTTERBUCK.

Effect of acids and alkalis on the actual reaction of the tissue and blood. S. KAPLANSKI and N. TOLKATSCHEVSKAYA (Z. ges. exp. Med., 1928, 63, 90—101; Chem. Zentr., 1929, i, 918).

Influence of electrolytes on the activity of specific diuretics and on the normal secretion of urine. D. BERGER (Biochem. Z., 1929, 209, 218—235).—Intraperitoneal injection of urea (2.0—1.0% solution) into rabbits greatly reduces the characteristic action of a specific diuretic, but the addition of an electrolyte to the injected solution immediately increases that action to an extent proportional to the concentration of the added electrolyte. The theories of Curtis (*ibid.*, 1925, 163, 109) are confirmed.

W. MCCARTNEY.

Hypnotics and diuresis. Water and salt excretion in sleep with and without pituitrin. M. A. KUGEL (Arch. exp. Path. Pharm., 1929, 142, 166—188).—The effect of various hypnotics and pituitrin on the urine excretion of rabbits was observed. Paraldehyde increases the excretion of water and salt, "sandoptal" (isobutylallylbarbituric acid), urethane, and veronal increase the water and lessen the salt diuresis. "Luminal" decreases the water diuresis; this effect is nullified by veronal. "Chloretone" may increase the water and lessens the salt diuresis. Chloral hydrate and chloralose inhibit the water excretion in light, and increase it in deep, hypnosis. Pituitrin subcutaneously injected inhibits

the water diuresis in urethane, veronal, chloral hydrate, chloralose, chloretone, and sandoptal hypnosis, but not in deep paraldehyde hypnosis, and produces a general increase in the salt excretion.

J. H. BIRKINSHAW.

Influence of hypnotics and other drugs on thyroxine diuresis. E. Z. EPSTEIN (Arch. exp. Path. Pharm., 1929, 142, 214—235).—Subcutaneous injection of thyroxine after oral administration of water to rabbits produces an increased water excretion; the percentage salt excretion is only slightly increased. This diuresis is inhibited by subcutaneous injection of pituitrin, ergotamine, and hypertonic dextrose solution.

Paraldehyde, "sandoptal," and deep "chloretone" hypnosis increases the thyroxine water diuresis; luminal and light chloretone hypnosis inhibits it, veronal inhibits only when administered at the same time as the thyroxine. The thyroxine salt excretion is mostly lessened by luminal, veronal, sandoptal, and chloretone, and increased by paraldehyde. These substances probably act not only on the kidneys, but also on the central and sympathetic nervous system.

J. H. BIRKINSHAW.

Diuresis after oral and intravenous administration of liquid and changes produced by hypnotics. E. Z. EPSTEIN (Arch. exp. Path. Pharm., 1929, 142, 236—247).—Intravenous injection of physiological salt solution into rabbits produces only a small water excretion and a pronounced increase in salt elimination. This low water diuresis is increased by paraldehyde, "sandoptal," and "luminal" narcosis; veronal and urethane produce no change. The salt excretion is independent of the water excretion. The sudden hydraemia probably excites central regulatory processes which alter the normal fluid exchange between blood and tissue.

J. H. BIRKINSHAW.

Pharmacology of brominated valeric esters. E. RATH (Arch. exp. Path. Pharm., 1929, 142, 162—165).—Experiments on fishes and mice showed that the introduction of a bromine atom into the acid radical of *tert*-amyl isovalerate increased its hypnotic action more than when the bromine was introduced into the alkyl radical.

J. H. BIRKINSHAW.

Detoxication of chloroform. P. HOLTZ (Arch. exp. Path. Pharm., 1929, 142, 139—156).—The harmful after-effects of chloroform narcosis on a strain of white mice were lessened when the chloroform contained 10—20% of hexane. In the case of a more sensitive strain the addition of hexane merely delayed death and was not more effective than alcohol or acetone. Keeping the mice at a higher temperature after narcosis did not increase the number of survivors, but the food prior to narcosis had considerable influence. Repeated narcosis had a cumulative effect. 7% of alcohol in the chloroform lessened the blood-pressure lowering of cats and rabbits caused by chloroform alone.

J. H. BIRKINSHAW.

Toxicity of various hydrocarbon vapours. N. W. LAZAREV (Arch. exp. Path. Pharm., 1929, 143, 223—233).—The toxicity of 35 saturated and unsaturated cyclic and straight-chain hydrocarbons to white mice is tabulated. The toxicity decreases in the order aromatic hydrocarbons, cycloparaffins,

olefines, paraffins. The decrease in toxicity runs parallel with the decrease in solubility.

P. W. CLUTTERBUCK.

[Lack of] injurious effects to health of the methyl alcohol formed in alcoholic fermentations. O. WINDHAUSEN (Naturwiss., 1929, 17, 631—634).—The capacity to withstand the effects of consumption of methyl alcohol varies widely amongst individuals, but the small amounts which occur in spirits, beverages, tobacco, and vegetables are decomposed in the body at once or excreted and are harmless.

W. MCCARTNEY.

Comparison of lactones with santonin. I. Chemical constitution and pharmacological action. W. F. VON OETTINGEN (J. Pharm. Exp. Ther., 1929, 36, 335—354).—Butyro-, valero-, iso-hexo-, α - and β -angelica-lactones, valerolactone-carboxylic acid, and the dilactone of acetonediacetic acid have vermicidal effects on earthworms, the last three having, in 0.04M-concentration, *in vitro*, the same efficiency as santonin. At higher dilutions these three are less effective than santonin. The introduction of a double linking or of a carboxyl group into valerolactone (α - and β -angelicalactones, valerolactone-carboxylic acid) considerably increases efficiency. Of the seven compounds β -angelicalactone and the dilactone are the most effective vermicides.

W. MCCARTNEY.

Toxicity and vermicidal properties of the dilactone of acetonediacetic acid and β -angelicalactone in cats. Dilactone and β -angelicalactone as anthelmintics. W. F. VON OETTINGEN and F. GARCIA (J. Pharm. Exp. Ther., 1929, 36, 355—362; cf. preceding abstract).—The minimum lethal dose of β -angelicalactone is 0.7—1.25 g. per kg. in the cat: that of the dilactone of acetonediacetic acid is much higher and 2.6 g. per kg. produces only slight transient depression. In treating *Ascaris* in cats seven out of ten experiments with the dilactone were completely successful, a single dose of 0.3 g. per kg. being sometimes sufficient.

W. MCCARTNEY.

Salicylates. XVIII. [Pharmacological] actions of ammonium salicylate compared with [those of] sodium salicylate. C. C. JOHNSON and P. J. HANZLIK (J. Pharm. Exp. Ther., 1929, 36, 319—333).—The physiological properties of ammonium salicylate are very similar to those of sodium salicylate. The former salt shows no advantage over the latter.

W. MCCARTNEY.

Changes in the serum-inorganic phosphorus, -calcium, and -potassium in rabbits on intra-cardiac or subcutaneous injection of peptone. X. CHAHOVITCH and M. VICHENJITCH (Compt. rend. Soc. Biol., 1928, 99, 1264—1267; Chem. Zentr., 1929, i, 551).—A temporary fall in the blood-phosphorus, -calcium, and -potassium occurs, normal values being reached in a few days whether the injections are continued or discontinued.

A. A. ELDRIDGE.

Combination of curare with some proteins and dyes and dependence of this process on p_H . V. M. KARASSIK, A. PETRUNKINA, and M. PETRUNKIN (Biochem. Z., 1929, 210, 70—75).—Gelatin and brain proteins at high p_H have the power of removing curare

from its solutions, which lose their colour and toxic property, these being transferred to the protein. At low p_H there is no such action. The power of Congo-red to detoxicate curare is ascribed to its sulphonic acid groups.

J. H. BIRKINSHAW.

Ouabain (*g*-strophanthin or acocantherin) as a physiological standard for digitalis, strophanthus, and squill. E. W. SCHWARTZ, R. M. HANN, and G. L. KEENAN (J. Pharm. Exp. Ther., 1929, 36, 481—491).—Purification of ouabain for use as a physiological standard is facilitated by successive crystallisations from alcohol-ether and water. The substance has no definite m. p. Revised data concerning its crystalline forms, optical and crystallographic properties, degrees of hydration, and its specific rotation are given.

W. MCCARTNEY.

Relationship between pharmacological action and chemical constitution and configuration in optical isomerides of ephedrine and related compounds. K. K. CHEN, C. K. WU, and E. HENRIKSEN (J. Pharm. Exp. Ther., 1929, 36, 363—400).—Twenty-seven derivatives of β -phenylethylamine having the general formula $\text{CHPhH}'\cdot\text{CHR}\cdot\text{NR}'\text{R}''$ ($\text{H}'=\text{H}$ or OH and $\text{R}, \text{R}', \text{R}''=\text{H}$ or alkyl), including six optical isomerides of ephedrine, have been studied pharmacologically. The actions of the compounds related to ephedrine are similar to those of ephedrine itself. When H' is OH toxicity is reduced and mydriatic action is favoured. Most of the compounds studied inhibit the movements of the isolated rabbit's intestine, stimulate the isolated uterus of the virgin guinea-pig, and contract the congested nasal mucous membrane in man. With increase in the number of carbon atoms in R, R' , and R'' the cardiac depressant action increases, the pressor action becomes a depressor action, and the toxicity rises. When H' is OH , R'' is H , and R or R' becomes Me or Et , the sympathomimetic action is preserved, but weakened as compared with β -phenylethylamine, the ethyl being weaker than the methyl derivatives. Those compounds have mydriatic action. The primary amines are more active than the corresponding methylated secondary or tertiary amines, especially with reference to pressor action. When $\text{R}=\text{Me}$ or Et , the compound acquires a prolongation of action and loss of pressor response on repeated intravenous injections in animals. The methyl members are easily absorbed from the gastro-intestinal tract to produce systemic effects in men (ephedrine and nor-*d*- ψ -ephedrine). The ephedrines are qualitatively similar in their actions. The mydriatic action of *l*-ephedrine and *d*- ψ -ephedrine is greater than that of *d*-ephedrine and *l*- ψ -ephedrine, respectively. When indirectly compared for pressor action in pithed cats with adrenaline, *l*-ephedrine is found to be three times as strong as *d*-ephedrine and *d*- ψ -ephedrine seven times as strong as *l*- ψ -ephedrine. *l*-Ephedrine, the strongest isomeride, is thirty-five times as powerful as *l*- ψ -ephedrine, the weakest isomeride of the six. When orally administered to men in the same quantity, *d*-ephedrine and *l*- ψ -ephedrine do not raise the systolic blood pressure: the other isomerides do so. *d*-Ephedrine and *l*- ψ -ephedrine have the least toxicity of the two sets of isomerides.

W. MCCARTNEY.

[Physiological effects of] quaternary pyridine bases. O. Y. MAGIDSON and G. P. MENSCHIKOV (Trans. Sci. Chem.-Pharm. Inst. Moscow, 1926, No. 16, 7—22).—Pyridine benzyl chloride, methiodide, and amyl iodide, in order of decreasing effect, induced paralysis in the frog. Less effective were the propyl, isoamyl, ethyl, and allyl iodides. The compounds which show a strong paralytic effect have a low conductivity and a low dissociation constant.

CHEMICAL ABSTRACTS.

Effect of ergotamine on alimentary hyperglycæmia. E. COELHO and J. C. DE OLIVEIRA (Compt. rend. Soc. Biol., 1928, 99, 1527—1530; Chem. Zentr., 1929, i, 667).—In normal and diabetic individuals ergotamine reduces hyperglycæmia produced by dextrose or adrenaline. A. A. ELDRIDGE.

Inactivation of enzymes by tannins. A. OPARIN and A. KIRSANOV (Biochem. Z., 1929, 209, 181—194).—The inactivating effect of tannins on enzymes is due to the formation of protein precipitates on which the dissolved enzymes are adsorbed. Enzymes so inactivated can be completely regenerated by the addition of egg-albumin or of peptone. Determination of enzymes in the presence of tannins (*e.g.*, in leaves rich in tannins) can thus be carried out.

W. MCCARTNEY.

Oxidation-reduction potentials of mammalian tissues. E. A. H. FRIEDHEIM (Compt. rend., 1929, 189, 266—268).—The oxidation-reduction potentials of various macerated organs of different mammals (guinea-pig, rabbit, pig, ox, and mouse) have been determined with the rigid exclusion of oxygen with a mercury, platinum, gold, or gold-plated platinum electrode, the same values being obtained with each. All the values of E_h are negative and form series in which the value for the liver is the lowest and that for the spleen the highest. Contrary to the conclusion of Drew (Brit. J. Exp. Path., 1920, 1, 115), no diminution in reducing power is observed with cancerous tissue. All the values of r_H are less than 9.9, and thus, in agreement with other authors, all organs, in the absence of oxygen, reduce Clark's indicators. The values of r_H diminish exponentially with dilution of the suspension of the tissue, thus explaining the positive values obtained by some authors in dilute suspension.

J. W. BAKER.

Oxidation-reduction systems of biological importance. IV. Cysteine complexes with metals of the iron group. L. MICHAELIS and E. S. G. BARRON.—See this vol., 1011.

Catalase. A. MADINAVEITIA (Unters. Enzyme, 1928, 1, 381—399; Chem. Zentr., 1929, i, 1115).—On crystallisation of oxyhæmoglobin most of the catalase remains in the mother-liquor, although the yield is only 7%. Hæmolysed corpuscle mash affords 40% of the "hæmase" originally present. Attempts to purify the enzyme by precipitation or adsorption were unsuccessful. Battelli's method for the preparation of liver-catalase is preferred.

A. A. ELDRIDGE.

Peroxidase. VII. Soluble and insoluble peroxidase. R. WILLSTATTER and A. POLLINGER. VIII. Formation of peroxidase. R. WILLSTATTER, A. POLLINGER, and H. WEBER. IX.

Peroxidase from grain. R. WILLSTATTER and A. POLLINGER (Unters. Enzyme, 1928, 1, 512—515, 516—520, 521—525; Chem. Zentr., 1929, i, 1224—1225; cf. A., 1926, 1275).—Peroxidase occurs in the plant partly dissolved in the cell sap, and partly adsorbed. For complete dissolution of the peroxidase the plant-substance must be thoroughly ground with sand and kept for a long time in water. Preliminary treatment with sodium hydrogen carbonate or barium hydroxide solution is favourable. The fractions of peroxidase which are dissolved readily or with difficulty, when examined by adsorption on alumina, behave similarly. The increase in extractable enzyme occasioned by the use of sodium hydrogen carbonate is also observed with dialysed plant material. The increase observed when running water is used is attributed to the calcium hydrogen carbonate which it contains. The increase depends on the time and on the concentration of the reagent. A still greater increase is observed if the root is ground in a mill and well pressed. The turbid hydrogen carbonate extract or press-juice shows after several days an increase in peroxidase activity, owing to gradual dissolution of the enzyme from the colloidal carrier. Cereal grains, although exhibiting considerable individual variations, contain as much peroxidase as dehydrated horse-radish (800 units per kg.). The quantity varies irregularly when the grain is kept. The enzyme content increases during germination, reaching a maximum in about 4 days. The peroxidase extracted from cereal grains is less pure than that obtained from horse-radish. Purification can be effected by adsorption on kaolin from a solution in very dilute acetic acid, and elution with very dilute ammonia solution.

A. A. ELDRIDGE.

Effect of antiseptics on the action of salivary diastase. E. PRECHTL (Biol. gen., 1928, 4, 181—190; Chem. Zentr., 1929, i, 912).—The lower limits of interference with the action of salivary diastase are: toluene 0.2%, chloroform 2.0%, chloral hydrate 1.5%, sodium fluoride 1.0%. Thymol is without effect.

A. A. ELDRIDGE.

Qualitative test for invertase. Z. I. KERTESZ (Biochem. Z., 1929, 209, 492—494).—A small amount of invertase may be detected by allowing it to act on a solution of sucrose and testing for the presence of lævulose in the liquid by covering a small piece of sodium or potassium hydroxide with a few drops of the solution. If lævulose is present a brownish-red colour is produced.

P. W. CLUTTERBUCK.

Mechanism of the action of muscle-phosphatase, -cozymase, and insulin. J. BODNAR and B. TANKÓ (Biochem. Z., 1929, 210, 143—174).—A mixture of disodium hydrogen phosphate, sodium fluoride, glycogen, and muscle powder (from pigeon breast muscle) was used to study the esterification of phosphoric acid. The amount of phosphoric acid esterified increases considerably with the concentration of phosphate; boiled muscle juice scarcely increases the esterification, since the muscle powder already contains sufficient cozymase. When this is washed out with water at the ordinary temperature the esterification is greatly reduced. The washed powder is reactivated by boiled muscle juice or boiled yeast

juice. The enzyme is harmed less by washing the powder at 0°. The muscle powder, unlike fresh muscle, loses only 20% of its activity in 5 weeks. Insulin produces no effect on the activity of fresh muscle or muscle powder (whether washed or not). An apparent increase in the esterification in some cases is due to the inorganic phosphate present in insulin.

J. H. BIRKINSHAW.

Effect of skeletal muscle on blood-sugar *in vitro*. M. SARYUN and C. L. ALSBERG (J. Biol. Chem., 1929, 83, 129—136).—The extent of disappearance of dextrose from blood on incubation was not affected by normal muscle alone, but was increased by normal muscle in presence of insulin; the glycogen-free muscle obtained from animals treated with adrenaline caused increased glycolysis in blood in the absence of insulin, and also caused the disappearance of dextrose from a solution of the latter in dilute sodium chloride.

C. R. HARRINGTON.

Enzymic transformation of uric acid into allantoinic acid. R. FOSSE, A. BRUNEL, and R. DE GRÆVE (Compt. rend., 1929, 189, 213—215).—The pea, soya bean, and numerous other leguminous seeds contain enzymes capable of transforming uric acid into allantoinic acid. The action is accelerated in presence of ammonium carbonate. The existence of two enzymes is postulated, an oxidase which yields allantoin, and a second enzyme which transforms allantoin into allantoinic acid (cf. this vol., 847).

R. K. CALLOW.

Purification of pepsin. J. PLÉ (Rev. gen. Colloid., 1929, 7, 193—201).—The precipitating action of acetone and of alcohol on pepsin has been studied as a function of hydrogen-ion concentration, time, and temperature. The weight of precipitate obtained is always less than the amount taken initially. In strongly acid solution acetone causes an irreversible coagulation; at p_H 1.03, the precipitate is quite inactive. In agreement with the observations of Fenger and Andrew (A., 1927, 793), the most active pepsin is that precipitated at p_H 2.5, using 75% acetone. Alcohol is a less effective precipitating agent, the yield of precipitate being only about one half of that given by acetone. Applying these methods to the purification of pepsin, the following procedure is recommended: 1 g. of the pepsin is dissolved in 6 c.c. of water at 18° with the addition of 1 c.c. of *N*-hydrochloric acid, and water is added to 10 c.c.; 30 c.c. of pure, anhydrous acetone are added, the mixture is centrifuged, the supernatant liquid decanted off, and the purified pepsin dried in a vacuum. The yield is about 55% by weight, but the activity is increased by about 75%.

E. S. HEDGES.

Enzymic proteolysis. V. Structure of animal tissue substances. E. WALDSCHMIDT-LEITZ and G. VON SCHUCKMANN (Ber., 1929, 62, [B], 1891—1896).—The products of the degradation of keratin by hydrogen peroxide or bromine and glacial acetic acid are hydrolysed by trypsin, but not by erepsin, and therefore do not contain dipeptides but only polypeptides which cannot arise by fission of diketopiperazines. Similar treatment of silk fibroin yields only small amounts of soluble products which do not

suffer enzymic fission. Silk peptone, obtained by incomplete hydrolysis of silk fibroin by acids, suffers extensive hydrolysis by trypsin, yielding products which suffer fission with erepsin. Polypeptides with long chains therefore appear to be present in silk peptone.

H. WREN.

Optimum p_H for trypsin and the reaction of the intestinal contents. H. J. VONK and H. P. WOLVEKAMP (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 440—443).—The influence of bile on the digestion of fibrin by trypsin at p_H 6 has been studied. At volume concentrations from 0.25 to 0.025 the activity is doubled, but at lower concentrations the digestion is retarded. The bile thus appears to compensate for the low p_H value and this action may be considered as specific for the p_H of the intestinal contents. A similar influence is produced by multivalent anions, e.g., the ferrocyanide ion.

H. F. GILLBE.

Action of adrenal tissue on lecithin. A. DA CRUZ (Compt. rend. Soc. Biol., 1928, 99, 1530—1532; Chem. Zentr., 1929, i, 666).—Choline is produced in lecithin solutions by addition of adrenal tissue or minced liver. The decomposition is attributed to lecithinase; it is increased by addition of cholesterol.

A. A. ELDRIDGE.

Pyocyanase. S. HOSoya (Compt. rend. Soc. Biol., 1928, 99, 771—773; Chem. Zentr., 1929, i, 1010).—The preparation of pyocyanase, which may be identical with pyocyanolysin, is described.

A. A. ELDRIDGE.

Conditions of activation of washed zymin in relation to co-enzyme. A. A. STHEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 426—434).—Zymin inactivated by washing for a short period is reactivated by addition of acetaldehyde, methylene-blue, hexosediphosphate, or of a co-enzyme, but after washing for a longer period addition of the first two substances no longer has any effect. After more intensive washing neither of these nor hexosediphosphate produces reactivation, which can, however, be produced by addition of hexosediphosphate together with either a protein sol (prepared from zymin) free from co-enzyme or with the original washings, even after boiling. If the zymin be washed for a still longer period addition of the boiled wash-liquor is essential for the production of reactivation. Excessive washing causes irreversible inactivation of the enzyme.

H. F. GILLBE.

Soluble enzymes secreted by fungi. Phenolic constituents of essential oils and the anti-oxygenic function. L. LUTZ (Compt. rend., 1929, 189, 62—63).—Small quantities of various phenols and phenol ethers found in essential oils were added to cultures of *Stereum purpureum*, *S. hirsutum*, and *Coriolus versicolor* with methylene-blue as a reducible indicator. It was found that those phenolic constituents of essential oils which contain one or more free hydroxyl groups behave as antioxidants in regard to the oxido-reducing action provoked by the soluble enzymes secreted by *Hymenomyces*.

B. W. ANDERSON.

Soluble enzymes secreted by fungi. Comparison of the anti-oxygenic power of tannin and

of the phenolic constituents of essential oils. L. LUTZ (Compt. rend., 1929, 189, 134—135).—The development of colour which occurs when certain fungi (*Stereum hirsutum*, *S. purpureum*, and *Coriolus versicolor*) are grown in a medium containing a phenolic substance such as *m*-cresol, *p*-cresol, thymol, carvacrol, guaiacol, eugenol, anethole, creosole, or methyl salicylate is inhibited by the presence of tannin, which itself undergoes oxidation very readily. The antioxygenic property of tannin is probably of biological significance. W. O. KERMACK.

Enzyme action of *Alternaria Solani*. G. VON SZELÉNYI and G. VON BECZE (Zentr. Bakt. Par., 1929, II, 76, 121—124; Chem. Zentr., 1929, i, 760).—Invertase, lactase, and maltase are present; sucrose, lactose, and maltose are quickly attacked, raffinose and starch more slowly. Acid was not formed.

A. A. ELDRIDGE.

Penetration of luminous bacteria by ammonium salts of the lower fatty acids. I. Effects of strong acids and alkalis. S. E. HILL (J. Gen. Physiol., 1929, 12, 863—872).—*B. Fischeri* was grown on a calcium carbonate-buffered medium in Petri dishes and suspended in 0.5*M*-sodium chloride. Sucrose is nearly as efficient as sodium chloride for preserving the luminescence of the bacteria, thus showing that disappearance of light is merely an osmotic pressure phenomenon, due to rupture of the cells. Alcohol and glycerol penetrate the bacteria, although the effect is inhibited by presence of sufficient sodium chloride. Urea does not penetrate so readily. Decrease of oxygen pressure to less than 0.0053 mm. will cause disappearance of light and in these experiments the presence of sufficient oxygen has been assured. None of the ammonium salts used was more acid than p_H 5.0, and injury due to presence of hydrogen ions may be excluded, as may also any effect due to hydroxyl ions. Penetration by strong acids and alkalis takes place suddenly and does not occur until the cell membrane is destroyed, in sharp contrast to the effect of ammonium salts and weak acids. P. G. MARSHALL.

Fluorescent bacteria from water, soil, and plants. C. HURRIC (Ber. deut. bot. Ges., 1929, 47, 395—400).—The fluorescent bacteria isolated from the milk of cows fed on turnips feed have no denitrifying properties, whilst the strains isolated from pond-water are strongly denitrifying. The strains isolated from milk contain diastase, hydrolyse fats and proteins, have a low optimum temperature, and exhibit generally the characteristics of *B. fluorescens*, whilst those from pond-water do not. E. A. LUNT.

Bacterial oxidation of crude oils. V. O. TAUSSON (Neft. Choz., 1928, 14, 220—230; cf. A., 1928, 447).—*Bacillus fluorescens liquefaciens*, *B. pyocyaneus*, and *B. Stutzeri* and others utilise paraffins as well as kerosene. *Penicillium* develops on paraffins, *m. p.* 45—56°, utilising 80% of the hydrocarbon; *Aspergillus flavus* and bacteria from Baku can utilise both hard and soft paraffins and white vaseline. The paraffins are oxidised to carbon dioxide and water, there being no evidence of the production of fatty acids. Olefines, and probably terpenes, are also oxidised. The conditions of oxidation are: presence

of an aqueous solution of mineral salts (including nitrate, or ammonium salts and calcium carbonate), neutrality, and free access of oxygen. The oxidation of benzene, toluene, and xylene by *B. benzoli*, of naphthalene by *B. naphthalinicus liquefaciens*, *B. naphthalinicus*, and *B. naphthalinicus non-liquefaciens*, and of phenanthrene by *B. phenanthrenicus* is described. The facts that the soil in the oil-bearing regions is rich in a great variety of micro-organisms utilising hydrocarbons and displaying considerable specificity, and that the conditions are nearly optimal, indicate that they play an important part in effecting alterations of the crude oil *in situ*.

CHEMICAL ABSTRACTS.

Biochemical preparation of fats. V. KULIKOV (Oil Fat Ind. Russia, 1928, No. 4, 21—23).—In molasses-broth a non-virulent strain of *B. tuberculosus* produced 22—36% of fatty substances containing glyceryl palmitate and stearate (*m. p.* 66°) and waxes (*m. p.* 70°). CHEMICAL ABSTRACTS.

Lipins of tubercle bacilli. III. Phthioic acid. R. J. ANDERSON (J. Biol. Chem., 1929, 83, 169—175).—The phosphate obtained from tubercle bacilli (A., 1927, 1114) was hydrolysed with dilute sulphuric acid; the fatty acids were converted into lead soaps and the latter extracted with ether; the acids regenerated from the ether-soluble portion were hydrogenated, and again subjected to the lead soap fractionation. The ether-soluble portion, on decomposition, gave crude *phthioic acid*, a saturated acid having *mol. wt.* 313, $[\alpha]_D^{25} +1.6^\circ$.

C. R. HARRINGTON.

Metabolism of *Bacillus coli* and *paratyphosus*. B. H. BRAUN and R. GOLDSCHMIDT (Zentr. Bakt. Par., 1928, I, 109, 353—361; Chem. Zentr., 1929, i, 763).—The ease of aerobic or anaerobic growth in various media was studied. Sodium aspartate or glutamate or tryptophan with dextrose favours anaerobic growth. A. A. ELDRIDGE.

Proteolysis by *Streptococcus lactis*. L. T. ANDEREGG and B. W. HAMMER (J. Dairy Sci., 1929, 12, 114—128).—Certain cultures (particularly butter cultures) of *Streptococcus lactis* showed proteolytic activity in milk, especially in presence of calcium carbonate. Addition of peptone retarded the decomposition of protein. *S. citrovorus* and *S. paracitrovorus* did not exhibit proteolytic activity in milk.

CHEMICAL ABSTRACTS.

Action of streptococci on caseinogen. G. J. HUCKER (Zentr. Bakt. Par., 1929, II, 76, 321—328; Chem. Zentr., 1929, i, 763—764).—Pure caseinogen is not attacked by streptococci unless a large quantity of unwashed cells are added. Caseinogen can also serve as a source of nitrogen. A. A. ELDRIDGE.

Influence of some metals on acetic acid fermentation. M. ROSENBLATT and M. MORDKOVITSCH (Biochem. Z., 1929, 209, 83—89, and Ukraine Chem. J., 1929, 4 [Tech.], 1—10).—Up to a certain concentration nickel, cobalt, iron, and manganese (as sulphates) stimulate the fermentation of alcohol to acetic acid by *B. Pasteurianum* and by *B. vini aceti*. The optimum concentration of metal in each case is about 0.000033%. At higher concentrations the metals have a paralysing effect the strength of which

varies very widely from metal to metal in the descending order nickel, cobalt, iron, manganese.

W. McCARTNEY.

Conversion of hexosediphosphate into lactate under the influence of *B. Delbrücki*. A. TYCHOVSKI and M. KOBEL (Biochem. Z., 1929, 209, 134—141).—From aqueous solutions of magnesium hexosediphosphate (but not from those of the sodium salt) by the action of large amounts of fresh cultures of *B. Delbrücki* or of the material prepared from them by dehydration with alcohol and ether *dl*-lactic acid is very rapidly produced in yields of 50—100%.

W. McCARTNEY.

Symbiosis among lactic acid organisms. H. LANDAU (Natuurwetensch. Tijds., 1929, 11, 115—117).—*Oidium lactis* has practically no influence on lactic acid bacteria, since milk develops acidity in presence of the latter at the same rate, whether the former is present or not.

S. I. LEVY.

Action of minute doses of sea-water on fermentation. C. RICHTER and M. FAGUET (Compt. rend., 1929, 189, 219—221).—The effect of varying doses of sea-water (Mediterranean) and of artificial sea-water (NaCl 28.90, MgSO₄ 2.80, MgCl₂ 2.35, CaSO₄ 0.90, KCl 0.80 g. per litre) on the fermentation of lactose by a lactic acid organism for 24 hrs. at 40° has been determined by measurements of the acidity produced. With decreasing doses of sea-water a decrease in the activity of the ferment occurs with 50% of sea-water (acidity 89; control experiment 100), then with 10⁻⁴% a slight increase (118) occurs; a second decrease occurs with doses of 10⁻⁶%, and finally a second slight increase (105) with minute doses of 10⁻¹⁰%. The same results are obtained with artificial sea-water and agree with earlier results obtained with various metallic salts.

J. W. BAKER.

Assimilation of nitrogen by pure cultures of *Clostridium Pasteurianum* and related organisms. E. MCCOY, W. M. HIGBY, and E. B. FRED (Zentr. Bakt. Par., 1928, II, 76, 314—320; Chem. Zentr., 1929, i, 762).—In Vinogradsky's nutrient solution for 15—20 days at 28°, the nitrogen assimilated per 100 c.c. was (max.): *C. acetobutylicum*, Weizmann, 1.06 mg., *C. Pasteurianum* 3.98 mg., *B. saccharobutylicus* 2.35 mg., *Plectridia* 2.75 mg. The ratio of sugar used to nitrogen fixed changes as growth proceeds.

A. A. ELDRIDGE.

Use of carbamide solutions as culture media. A. J. J. VANDE VELDE (Natuurwetensch. Tijds., 1929, 11, 118—122).—The decomposition of carbamide in solutions sterilised by heating has been examined; the formation of ammonium salts is reflected in the *p_n* value and results of titrations using various indicators. In media containing dipotassium hydrogen phosphate the effect of heating on the carbamide is not apparent.

S. I. LEVY.

Bacterial toxins. Tetanus toxin. S. HOSOYA and S. MIYATA (Compt. rend. Soc. Biol., 1928, 99, 773—776; Chem. Zentr., 1929, i, 1013).—The procedure described affords a product of antigenic character which no longer gives the biuret reaction. Tetanus toxin is not a protein. Nessler's reagent produces an orange-red precipitate.

A. A. ELDRIDGE.

Purification of *Bacillus botulinus* toxin. S. HOSOYA, G. J. STEFANOPOULOU, and S. MIYATA (Compt. rend. Soc. Biol., 1928, 99, 1465—1467; Chem. Zentr., 1929, i, 763).—The toxin, after precipitation with zinc chloride and liberation with ammonium sulphide, no longer gives a protein reaction, and is not precipitated by picric or picrolonic acid.

A. A. ELDRIDGE.

So-called specific dynamic action of foods. G. MANSFELD and Z. HORN (Biochem. Z., 1929, 209, 34—54).—The oxygen consumption of the bacillus of mouse-typhoid varies directly in proportion to the concentration of the food which the organism receives and there is no increase in the consumption when substances which it cannot consume are provided. The phenomena characteristic, in higher organisms, of the specific dynamic action of foods are observed in the case of the bacillus, the only difference between the higher and unicellular organisms being quantitative.

W. McCARTNEY.

Oligodynamic action of silver. R. WERNICKE and F. MODERN (Anal. Asoc. Quim. Argentina, 1928, 16, 158—169; cf. A., 1927, 992).—The bactericidal action of water which has been in contact with finely-divided silver under certain conditions is due to the presence of silver ions in a concentration of the order of 0.00005 g./litre. The silver may be removed and collected by passing the solution slowly over electrodes of special construction, and the bactericidal action is found to decrease proportionally as the silver is removed.

R. K. CALLOW.

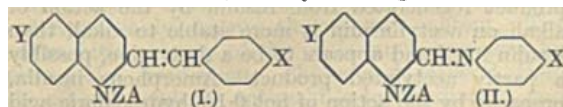
Disinfecting action of metallic salts. J. VIGNATI and P. SCHNABEL (Zentr. Bakt. Par., 1928, I, 109, 464—475, 475—481; Chem. Zentr., 1929, i, 763).—The disinfecting action of copper salts is not an adsorption phenomenon, but a coagulation process depending on interaction between protein or lipid molecules and copper ions. Bacterial action is revived by the action of sodium thiosulphate, which also neutralises the disinfecting action of silver, lead, or zinc salts and alcohol.

A. A. ELDRIDGE.

Disinfectant action of weak acids. H. FUST (Arch. exp. Path. Pharm., 1929, 142, 248—260).—A well-buffered lactic acid-lactate mixture of *p_H* 3.7 or 3.3 at physiological or lower concentrations has a definitely toxic action on *B. coli* and on the bacteria of the rat's tail; the *p_H* 3.3 mixture is superior to 65% alcohol if the tail is first washed with soap and water. The action appears to be due both to the hydrogen ions and to the undissociated lactic acid molecules. Lactic acid-lactate buffers are suggested as useful skin disinfectants.

J. H. BIRKINSHAW.

Trypanocidal action of some derivatives of anil- and styryl-quinoline. C. H. BROWNING, J. B. COHEN, S. ELLINGWORTH, and R. GULBRANSEN (Proc. Roy. Soc., 1929, B, 105, 99—111; cf. A., 1926, 1153; 1928, 1141).—The action of a large number of quinoline derivatives, mostly of the general formula



where Z is an alkyl group, A an anion, and X and Y are other substituent groups, has been tested in

respect of their curative action on rats infected with *T. brucei*. The anil compounds of formula II are in general without activity, but certain of the styryl derivatives are active, especially where X and Y represent an acylamino- and an amino- or alkylamino-group. The compounds with $X=NMe_2$ and $Y=NHAc$ and $X=NHAc$ and $Y=NH_2$ ($Z=Me$) were active when administered to infected rabbits. The active compounds were not particularly trypanocidal *in vitro*. The following compounds have been prepared: 7-dimethylamino-2-methylquinoline methiodide by the method previously described for the 6-isomeride; propionamidobenzaldehyde, m. p. 170–181°, by the action of propionic anhydride on *p*-aminobenzaldehyde; and 6-dimethylamino-2-styrylquinoline methochloride from the corresponding methiodide prepared by the interaction of benzaldehyde and 6-dimethylamino-2-methylquinoline methiodide.

W. O. KERMACK.

The Gram stain. A. ZEISSIG (Stain Tech., 1929, 4, 91–92).—A modification of the Gram stain in which an alcoholic solution of iodine is substituted for 95% alcohol as decolorising agent is advantageous in staining Gram-positive organisms in tissues and smears.

H. W. DUDLEY.

Differentiation of bacteria by means of a mixture of acid and basic dyes at different p_H values. A. V. TOLSTOUHOV (Stain Tech., 1929, 4, 81–89).—A mixture of methylene-blue and eosin-Y satisfactorily stains bacteria differentially from p_H 3 upwards. From p_H 3 to 0.8 a mixture of methylene-blue and acid-fuchsin is used. This mixture is used to study the chemical composition of different parts of the bacterial cell. Polar bodies in the typhoid group of organisms and in *B. diphtheriae* are stained differentially by it.

H. W. DUDLEY.

Mechanism of staining: physical theories. W. C. HOLMES (Stain Tech., 1929, 4, 75–80).—Adsorption is held to be the principal factor in biological staining.

H. W. DUDLEY.

Stain solubilities. IV. W. C. HOLMES (Stain Tech., 1929, 4, 73–74).—The solubilities, in water and 95% alcohol, of 28 dyes are tabulated.

H. W. DUDLEY.

Active substances of the heart. Heart hormone. D. IONESCO and A. T. BERNARD (Arch. Int. Physiol., 1928, 30, 267–279; Chem. Zentr., 1929, i, 1014).—Alcoholic extracts from various parts of the heart and skeletal muscle of the ox have a regulative effect on the frog's heart.

A. A. ELDRIDGE.

Insulin. K. FREUDENBERG, W. DIRSCHERL, and H. EYER (Naturwiss., 1929, 17, 603–604).—The slow inactivation of insulin by means of formaldehyde is partly reversible under the action of very dilute hydrochloric acid, and the inactivation is not due to the action of formaldehyde on amino-groups. The product regenerated from insulin by the action of alkali on acetylinsulin is more stable to alkali than insulin itself and appears to be a derivative, possibly a partly acetylated product. Amorphous insulin, prepared by the action of hot 0.1*N*-hydrochloric acid containing 1% of sodium chloride on technical insulin, and exhibiting 80% of the activity of crystalline

insulin, is also labile. The sulphur content of insulin increases with increasing purity, but the relationships disclosed between activity and the alkali-stable and alkali-labile sulphur indicate that whilst the protein which contains the effective group may be rich in stable and labile sulphur, the sulphur does not appear to form part of the active group. A relationship exists between optical and physiological activities. The absorption spectrum of crystalline insulin shows a strong band near 2700 Å. By the Debye-Scherrer method the crystals do not behave differently from amorphous insulin, the crystals thus resembling protein crystals. There is no certainty that the molecules comprising the crystal are all identical. With increasing purification the sulphur and the methyl content of insulin increases by equivalent amounts.

R. A. MORTON.

Orally effective compounds of insulin with bile acids. B. STUBER and K. LANG (Naturwiss., 1929, 17, 546).—In a weakly alkaline medium condensation products are formed between insulin and cholic or deoxycholic acids. Chollynsulin and deoxychollynsulin are physiologically active when administered orally or subcutaneously. Whilst the two methods of administration are equally effective, the dose must be large (200–300 units per dose) measured in terms of the initial material.

R. A. MORTON.

Effect of insulin on regeneration. Biological role of potassium and calcium. B. SCHAZILLO and M. KSENDZOWSKY (Pflüger's Arch., 1928, 220, 774–781; Chem. Zentr., 1929, i, 665).—Insulin stimulates the regeneration of bone. Calcium ions favour, and potassium ions retard, the formation of callus.

A. A. ELDRIDGE.

Inhibiting action of insulin on dextrose hyperglycaemia. G. SOLARINO (Boll. Soc. Ital. Biol. sper., 1928, 3, 108–111; Chem. Zentr., 1928, ii, 2481–2482).—The hyperglycaemia caused by insulin in variable degree is related to the hydrochloric acid content of the gastric juice and the more or less rapid degradation of the insulin. The effect of insulin in inhibiting hyperglycaemia is comparable with that of laevulose.

A. A. ELDRIDGE.

Antagonistic action of posterior lobe hormone and insulin. K. VELHAGEN, jun. (Arch. exp. Path. Pharm., 1929, 142, 127–138).—The substance of the posterior lobe of the pituitary which increases the blood-sugar and opposes the action of insulin is present both in *pars neuralis* and *pars intermedia*. Large amounts of the extract must be injected into rabbits to prevent insulin hypoglycaemia. Repeated injection does not inhibit the action of the insulin circulating in the body. The secondary hypoglycaemia which is frequently produced by administration of the posterior lobe is probably the result of increased insulin secretion; it does not occur in pancreas-diabetic animals. Insulin does not inhibit the action of the posterior lobe in increasing blood-pressure and stimulating the uterus.

J. H. BIRKINSHAW.

Relations of the pituitary gland to carbohydrate metabolism. A. PICKAT (Med. biol. Zhur., 1927, 3, 40–62).—Extirpation of the pituitary is followed by long-continued hypoglycaemia. Sub-

cutaneous injection of an extract of the posterior lobe of the pituitary, or puncture of the tuber cinereum, increases the blood-sugar in both normal and hypophysectomised dogs. **CHEMICAL ABSTRACTS.**

Testing of commercial ovarian preparations. M. KOCHMANN (Arch. exp. Path. Pharm., 1929, 143, 57—64; cf. this vol., 102).—A number of commercial preparations of ovarian hormone have been assayed by administering them to immature mice and observing the effect on the vaginal smear. Less precise determinations have also been made by observing their effects on the metabolism of castrated rats. **W. O. KERMAK.**

Internal secretion of the placenta. J. PAZOUREK (Rozh. chir. gynækol., 1928, 7, 115—121).—All the ovarian glands contain a common hormone; the action of the human hormone is identical with that of animals. The hormone is resistant to both low and high (193°) temperatures. and is unchanged by the digestive process. **CHEMICAL ABSTRACTS.**

Secretin. V. Preparation. L. TAKACS (Z. ges. exp. Med., 1928, 63, 553—556; Chem. Zentr., 1929, i, 1016).—A 10% aqueous solution of the substance obtained by the picrate method is filtered through a collodion ultra-filter at 1 atm. pressure, affording a colourless filtrate which gives no reaction with sulphosalicylic acid. The substance contains 9—10% N, but no phosphorus. **A. A. ELDRIDGE.**

Effect of secretin in the regulation of the alkali reserve of the blood. I. Experimental alkalosis. A. O. WOJNAR (Zhur. Exp. Biol. Med., 1928, 10, 414—442).—There is direct dependence between variations in alkalinity of, and the amount of secretin in, the pancreatic juice and the alkalinity of the blood. **CHEMICAL ABSTRACTS.**

Cod-liver oil and the antimony trichloride reaction for vitamin-A. P. B. HAWK (Science, 1929, 69, 200).—The antimony chloride reaction is not a trustworthy means of determining the vitamin-A content of a cod-liver oil. Samples of this oil exposed to the atmosphere gave a deeper blue coloration with the reagent than those kept in the dark to preserve the vitamin present. **L. S. THEOBALD.**

Effect of vitamin-A on hypercholesterolaemia. H. KIMURA (Acta Schol. Med. Univ. Imp. Kyoto, 1928, 11, 319—324).—The reduction of experimental hypercholesterolaemia in rabbits is not accelerated, but rather retarded, by addition of vitamin-A to the diet. Also feeding cod-liver oil did not influence the hypercholesterolaemia. **CHEMICAL ABSTRACTS.**

Water-soluble vitamins of group B. L. RANDOIN and R. LECOQ (Bull. Soc. Chim. biol., 1929, 11, 745—775).—A review. **J. H. BIRKINSHAW.**

Changes in blood constituents during avitaminosis. T. MUTO (Fukuoka Ikw.-Zasshi, 1927, 20, 1269—1279).—The blood-sugar, haemoglobin, fatty acids, cholesterol, and residual nitrogen are increased; the blood-phosphate is diminished. Acetone substances and lactic acid tend to increase. In rice-fed chickens the blood-acetaldehyde is increased. **CHEMICAL ABSTRACTS.**

Vitamin-C content of pasteurised milk. M. MIURA (Bull. Inst. Phys. Chem. Tokyo, 1929, 8, 502—505).—Autoclaved milk still retains a small quantity of vitamin-C, pasteurised milk retains a larger quantity, and raw milk contains still more of this vitamin. **B. W. ANDERSON.**

Sources of vitamin-C in India. R. C. WATTS (Indian Med. Gaz., 1929, 64, 79—85).—Experiments on feeding guinea-pigs with vegetable marrow, melon, pumpkin, and *Citrus medica* var. *acida* are described. **CHEMICAL ABSTRACTS.**

Vitamin-C. IV. Carbohydrate and nitrogen metabolism of experimental scurvy in guinea-pigs fed on an exclusive oat diet. K. TOMITA (Sei-I-Kwai Med. J., 1928, 47, No. 9, 6—7).—The blood-sugar and the urinary nitrogen increased. The glycogen content of the liver decreased just before death. Excretion of calcium, uric acid, and creatinine decreased, whilst that of creatine increased, with the development of scurvy. **CHEMICAL ABSTRACTS.**

Experimental scurvy. II. Carbohydrate metabolism of the animal fed on a vitamin-C diet. T. NAGAYAMA, H. MACHIDA, and Y. TAKEDA. **III. Nitrogen metabolism.** T. NAGAYAMA and N. SATO (J. Biochem. Japan, 1928, 10, 17—26, 27—44).—The carbohydrate metabolism is not appreciably disturbed during scurvy. Urinary creatine and ammonia increase, and the creatinine coefficient rises; uric acid excretion is unchanged. The creatine content of the muscle is normal. **CHEMICAL ABSTRACTS.**

Antiscorbutic potency of infusions of Japanese green tea. M. MIURA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 506—509).—When two successive infusions of green tea are made with water at 60—65°, decanting after several minutes at the ordinary temperature, two thirds of the vitamin-C contained in the tea is present in the first infusion and practically all the remainder in the second. Heating the tea with water at 70—75° for 5 min. destroys about 74% of its antiscorbutic activity. **B. W. ANDERSON.**

Evaluation of vitamin-D preparations. I. A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1929, 209, 290—303).—A method for evaluation of vitamin-D preparations depends on the determination of that amount of active substance (=1 antirachitic unit) which is just sufficient to protect young rats from rickets. Of the commercial preparations, 1 c.c. of "vigantol" contains 25,000, of "radiostol" 2000, and of "preformin," 800—1000 units.

P. W. CLUTTERBUCK.

Experimental rickets. II. Influence of ultra-violet irradiation on the antirachitic value of soya-bean oil. S. IZUME, Y. YOSHIMARU, and I. KOMATSUBARA (J. Biochem. Japan, 1928, 10, 177—182).—Oil extracted by pressure has the highest, and by alcohol the lowest, antirachitic value; petroleum affords an oil of intermediate value. Refining does not appreciably destroy the vitamin content. The antirachitic potency of the oil is much increased by ultra-violet irradiation. Phytosterol isolated from the oil was rendered antirachitic by irradiation, and exhibited the ergosterol absorption band in the ultra-violet. **CHEMICAL ABSTRACTS.**

Effect of growth-promoting substances of the character of vitamin-D on the yeast cell. H. LACROIX (Zentr. Bakt. Par., 1929, II, 76, 417—428; Chem. Zentr., 1929, i, 1118).—Large, but not small, inoculations grew in mineral nutrient free from amino-acid. The dead cells evidently liberate growth-promoting substances on autolysis; these substances can be withdrawn by adsorption on charcoal or fuller's earth. A. A. ELDRIDGE.

Action of "vigantol." H. BEHRENDT and J. BERBERICH (Münch. med. Woch., 1928, 75, 2134—2135; Chem. Zentr., 1929, i, 1019).—Administration to man of the usual doses of "vigantol" did not lead to a change in the blood-cholesterol value. In rabbits the value was increased. A. A. ELDRIDGE.

Epiphyses and liver extracts from rats after feeding with carotinoids. B. VON EULER, H. VON EULER, and P. KARRER (Biochem. Z., 1929, 209, 240—245).—Histological examination of the epiphyses of rats obtaining both carotinoid material and sufficient amounts of vitamin-D shows that, under this condition, bone formation is nevertheless deficient, although growth continues. In rats which receive more than the minimum necessary amount of carotin this accumulates in the liver. The results of previous experiments (cf. this vol., 358) are confirmed by the histological examination. W. MCCARTNEY.

Relation between water content and amount of photosynthesis. J. G. WOOD (Austral. J. Exp. Biol., 1929, 6, 127—131).—When a leaf (cherry laurel) is injected with water the rate of assimilation is low and remains low until nearly all the water of injection has disappeared from the intercellular spaces. The rate then rapidly assumes the normal value and remains at that value over a period represented by a change in water content of about 10% of the fresh weight of the leaf. P. W. CLUTTERBUCK.

Immediate effect of change of light on the rate of photosynthesis. T. T. LI (Ann. Bot., 1929, 43, 587—601).—Determinations by the bubble-counting method of photosynthetic activity in plants of the genera *Elodea*, *Myriophyllum*, *Potamogeton*, and *Ceratophyllum* when exposed to light of different colours, intensities, and available energies show that there is an initial inhibitory effect when the plant is changed from exposure to light of high available photosynthetic energy to light of low available photosynthetic energy and an initial accelerating effect when the reverse change takes place. It is concluded that these phenomena support the surface action theory of photosynthesis. W. MCCARTNEY.

Carbohydrate content of detached, partially-shaded leaves. R. GANE (Proc. Leeds Phil. Soc., 1929, 1, 497—505).—The effect of irradiation on detached leaves has been followed by determinations of the starch, sucrose, and reducing substance contents of the distal, median, and proximal portions of the leaves of *Plantago media* and *Scolopendrium vulgare*, the median portions only being shaded. Leaves of the former showed a marked increase in starch content during exposure to light, but leaves from which the main veins were removed formed little starch. *Scolopendrium* leaves continued to lose

starch during illumination, especially in the unshaded portions. Increases in the sucrose content and in the amounts of reducing substances occurred in both cases. The differences in the sucrose content found in the leaves appear to be associated with shading, but are not sufficient to explain the failure of starch to appear in the shaded portion. Carbohydrates can also move from illuminated to shaded regions in spite of a dislocation of the vein system. L. S. THEOBALD.

Nitrogen and carbohydrate distribution in organs of bearing apple spurs. A. E. MURNEER (Mo. Agric. Exp. Sta. Res. Bull., 1928, No. 119, 3—50).—Flowering is characterised by marked increase in all active forms of carbohydrates and nitrogen; a considerable part of the soluble carbohydrate is supplied by hemicellulose. Both carbohydrates and nitrogen appear to be reabsorbed from the dropping blossoms prior to abscission. Throughout the growing season the carbohydrate and nitrogen increasingly accumulate in the fruit, but the percentage of nitrogen does not necessarily increase. CHEMICAL ABSTRACTS.

Chemical relationship between scion and stock in *Citrus*. A. R. C. HAAS and F. F. HALMA (Plant Physiol., 1929, 4, 113—121).—Determinations of ash, and total and water-soluble calcium and magnesium, were made. CHEMICAL ABSTRACTS.

Angiosperm seeds and factors in germination. IV. Permeability to dyes and salts of the skin of fruits and seeds. A. NIETHAMMER (Biochem. Z., 1929, 209, 263—275).—A discussion of the penetration, changes of permeability, and ageing of seeds with reference to the mechanism of stimulation (cf. A, 1928, 1289). P. W. CLUTTERBUCK.

Transformation of acetaldehyde in higher plants. J. BODNAR and C. BERNAUER (Biochem. Z., 1929, 29, 458—470).—Pea meal added to acetaldehyde converted it into acetaldol and aldehyde resins, but neither acetic acid nor alcohol was formed; the meal after inactivation of its enzymes by heat still caused the same reaction. Pea meal is able to convert the nascent aldehyde arising from pyruvic acid into alcohol, but it is not decided whether this is by simple reduction or by a reaction of the Cannizzaro type. P. W. CLUTTERBUCK.

Iodine value of fatty acids from plant phosphatides. J. E. WEBSTER (Ohio J. Sci., 1929, 29, 39—42).—The following values refer, respectively, to acetone-insoluble phosphatides from wheat, maize, soya beans, and oats: N 0.99, 1.14, 0.70, 1.61%; P 1.26, 1.65, 0.495, 0.535%; iodine value (Hanus) 81.49, 65.30, 92.48, 88.80. CHEMICAL ABSTRACTS.

Concentration effect in *Nitella*. W. J. V. OSTERHOUT and E. S. HARRIS (J. Gen. Physiol., 1929, 12, 761—781).—The concentration effect due to the cell-wall tends to increase the values for the protoplasm, and a method for differentiation of the two effects is described, by means of which the chemical effect of the protoplasm is shown to be considerably greater than that of the cell-wall. No change of sign of the concentration effect in *Nitella* is found between p_H 5.0 and 9.5 if the c_H is small compared with that of other cations. P. G. MARSHALL.

Apparent storage of carbamide in mycotrophic plants. J. WEISSFLOG (Planta, Arch. wiss. Bot., 1927, 4, 358—372; Chem. Zentr., 1929, i, 762).—No accumulation of carbamide could be detected (cf. Weyland, Jahrb. wiss. Bot., 1912, 51).

A. A. ELDRIDGE.

Titanium in Cryptogams. G. BERTRAND and C. VORONCA-SPIRT (Compt. rend., 1929, 189, 73—75).—Titanium occurs to the extent of a few mg. per kg. in cryptogamic plants (ferns, algae, and fungi), although baker's yeast contained only 0.1 mg. per kg. and *Aspergillus niger* gave no definitely positive reaction (cf. this vol., 855).

J. GRANT.

Glucosides containing hydrogen cyanide. L. FLORIANI (Rev. Centr. Est. Farm. Biochim., 1928, 17, 343—357; Chem. Zentr., 1929, i, 761).—A discussion of behaviour on hydrolysis and of significance in plants.

A. A. ELDRIDGE.

Cyanogenetic glucosides in Australian plants. H. FINNEMORE and C. B. COX (J. Proc. Roy. Soc. N.S.W., 1928, 62, 369—378).—The isolation of sambunigrin (cf. Bourquelot and Danjou, A., 1905, i, 912) from *Acacia glaucescens* and *A. Cheelii* is described. The hydrogen cyanide content of the dry phyllodes of the former plant is 0.12—0.41%. Cyanogenetic glucosides have also been detected in the leaves of the following plants: *Euphorbia Drummondii*, Boiss. (in 11 of 113 examined), *Goodia lotifolia*, Salisb. (0.57% of hydrogen cyanide in air-dried leaves), *Poranthera microphylla* (0.051% of hydrogen cyanide), *P. corymbosa* (only faint reaction), *Eucalyptus corynocalyx* (0.179% of hydrogen cyanide). E. H. SHARPLES.

Absence of galactans from skeletal incrustation of cell-walls. E. SCHMIDT, M. ATTERER, and H. SCHNEGG (Cellulosechem., 1929, 10, 126—134).—Complex compounds of cellulose and hemicelluloses, known as skeleton substances, have been obtained from the cell walls of archegoniates and phanerogams by means of chlorine dioxide and sodium sulphite. The hemicelluloses were quantitatively separated from the cellulose residues by means of 5% sodium hydroxide and recovered from the latter by treatment with alcohol and acid. The hemicelluloses from the skeleton substances of spruce, flax-straw, and of a number of plants belonging to the gymnosperms, have been examined and found to contain no *d*-galactose; hence it is concluded that skeleton substances are free from this material, and it is presumed that they are formed from *d*-glucose and other carbohydrates. Sodium sulphite has no specific dissolution properties towards galactans and its action does not depend on the p_H of its solution. The hydrolysis of hemicelluloses by means of sulphuric, nitric, oxalic, and other acids, fermentation in the presence of nutritive solutions (buffered sugar solutions), the production and properties of hemicelluloses from the skeleton substances, and the fermentation of the hydrolysates prepared by the action of various acids on the hemicelluloses of various origin are described.

B. P. RIDGE.

Preparation of gentianose from gentian root without fermentation. M. BRIDEL and M. DESMAREST (Bull. Soc. Chim. biol., 1929, 11, 710—723).—

By cold percolation of dried powdered gentian root with 10 parts of 90% alcohol 96% of the gentianose is extracted. The resulting supersaturated solution deposits crystalline gentianose. An unstable complex more soluble than gentianose is probably present in the root.

J. H. BIRKINSHAW.

Grape pigments. II. Anthocyanins of Clinton grapes. R. J. ANDERSON and F. P. NABENHAUER. **III. Anthocyanins of Seibel grapes.** R. J. ANDERSON (N.Y. Agric. Exp. Sta. Tech. Bull., 1928, 146, 3—12, 13—21).—The pigment of Clinton grapes consists principally of a monoglucoside (hydrochloride, $C_{23}H_{25}O_{12}Cl$; picrate), affording on hydrolysis the anthocyanidin chloride, $C_{17}H_{15}O_7Cl$, which consists largely of delphinidin monomethyl ether, but contained some delphinidin dimethyl ether. The anthocyanin of Seibel grapes appears to be identical with cœnin.

CHEMICAL ABSTRACTS.

Banana. D. W. MAY (Porto Rico Agric. Exp. Sta. Rep., 1927, 7—8).—The dry matter of different varieties contained 1.8—12.2% K_2O . A high potash content is associated with freedom from disease.

CHEMICAL ABSTRACTS.

Pineapple. H. C. HENDRICKSEN (Porto Rico Agric. Exp. Sta. Rep., 1927, 19—24).—Moisture contents of various portions of leaves were determined. The p_H of the sap varied from 6 to 6.3. Young leaves contained 13%, and red, senescent leaves 30—40%, of carbohydrate; the average protein content was 6%. A high protein:carbohydrate ratio accompanied a low chlorophyll content, and a high reducing sugar content accompanied a high anthocyanin content. The normal leaves contain peroxidase, catalase, reductase, and diastase in greater amounts than do red or chlorotic leaves. The results of fertiliser experiments are recorded.

CHEMICAL ABSTRACTS.

Constituent of the bark of the peach. J. SHINODA and S. UYEDA (J. Pharm. Soc. Japan, 1929, 49, 97—98).—From the methyl-alcoholic extract of the bark of the peach, there has been isolated a compound, m. p. 248° (acetyl derivative, m. p. 194—195°; oxime, m. p. 233°), apparently identical with naringenin.

W. O. KERMACK.

Phytosterol of stinging nettle. I. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1929, 183, 74—77).—The sterol is isolated from the dry leaves of the nettle (*Urtica urens*) in 0.04% yield, and is shown to be sitosterol. Stigmasterol is not present.

H. BURTON.

Biological activity of sandy forest soil of the Hungarian lowlands. D. FEHER and R. BOKOR (Biochem. Z., 1929, 209, 471—488).—The bacterial flora of sandy forest soil is less than for heavier forest soils, but the soil respiration is greater, due to greater aeration. The number of nitrifying bacteria is higher in the sandy soil and the p_H approximates closely to 7.

P. W. CLUTTERBUCK.

Carpenter's form of the Haldane gas analysis apparatus. T. M. CARPENTER, E. L. FOX, and A. F. SEREQUE (J. Biol. Chem., 1929, 83, 211—230).—Technical modifications in the construction and use of the authors' apparatus (J. Metabol. Res., 1923, 4, 1) are described.

C. R. HARRINGTON.

Glass electrode apparatus for measuring p_H values of very small volumes of solution. D. A. MACINNES and M. DOLE (J. Gen. Physiol., 1929, 12, 805—811).—A glass electrode by means of which the p_H of about 0.14 c.c. of liquid can be determined is described; the error is shown to be not greater than 0.02 unit. With this apparatus it is shown that the penetration of brilliant-cresyl-blue (which poisons the hydrogen electrode) raises the p_H of the vacuolar sap of living cells of *Nitella*. P. G. MARSHALL.

Validity of the glass electrode in ammonium chloride buffers. S. E. HILL (J. Gen. Physiol., 1929, 12, 813—819).—The saturated potassium chloride in contact with the glass membrane is standardised against 0.05M-potassium hydrogen phthalate (p_H 3.97). The p_H values of a solution obtained by adding varying amounts of 0.5M-ammonium chloride to 0.5M-ammonia plus 0.5M-ammonium chloride could be accurately determined in this apparatus, the values (when plotted against the logarithm of the concentration of ammonia) falling on a straight line. A slight deviation occurs above p_H 8.6 when sodium chloride (0.5M in the original solution) is present and a table of corrections is given for values higher than 8.6. P. G. MARSHALL.

Quinhydrone electrode for measuring hydrogen-ion concentration in very small portions of tissue. N. OKUNEY (Biochem. Z., 1929, 210, 1—6; cf. A., 1928, 916).—An improvement on a previous modification of the Büllmann-Lund-Cullen micro-quinhydrone electrode is described. The platinum wire is replaced by a gilded platinum plate and a potassium chloride-agar mixture in the capillary point serves as bridge. This electrode may be used for buffer solutions or for small pieces of tissue.

J. H. BIRKINSHAW.

Effect of amino-acids on methods for the determination of sugar. Y. OKUDA and K. KATAI (Bul. Sci. Fak. Terkultura, 1929, 3, 182—186).—In Bang's method cysteine, cystine, and tryptophan behaved as dextrose; glycine, aspartic acid, tyrosine, alanine, leucine, and cleavage products of gelatin had little or no action. Cystine and cysteine influenced the results obtained by the methods of Folin and Wu, Benedict, Hagedorn, and Schaffer and Hartmann.

CHEMICAL ABSTRACTS.

Determination of lactic acid in animal fluids and tissues. S. TANAKA and M. ENDO (Biochem. Z., 1929, 210, 120—142).—An improvement in the von Fürth-Charnass technique for the determination of lactic acid consists in carrying out the oxidation with permanganate in an atmosphere of carbon dioxide. The hydrogen sulphite solution is also kept saturated with carbon dioxide. Further oxidation of the acetaldehyde is thus prevented. The method when applied to the determination of lactic acid in muscle, tissue, blood, urine, etc. is preceded by an ether extraction in the Kumagawa-Suto apparatus (A., 1903, ii, 702). The charcoal used for removing frothing substances must be thoroughly extracted with sodium carbonate solution. The improved method gives results accurate to within 1%.

J. H. BIRKINSHAW.

Detection of fats and their constituents. A. NIETHAMMER (Biochem. Z., 1929, 209, 447—457).—Examples are given of the use of Sudan III, of hydrolysis methods, of the setting form, and of the sublimation method for the detection of small amounts of fat.

P. W. CLUTTERBUCK.

Volumetric-micro-determination of cholesterol. A. HINRICHS and L. KLEMM (Biochem. Z., 1929, 210, 191—197).—The method of Szent-Gyorgyi (A., 1923, ii, 344) can be used to determine cholesterol volumetrically with an error not exceeding 7% on 2 c.c. of blood.

J. H. BIRKINSHAW.

Colorimetric determination of bile acids. R. GREGORY and T. A. PASCOE (J. Biol. Chem., 1929, 83, 35—42).—When a solution of bile acids in presence of sulphuric acid is heated with furfuraldehyde a blue colour is produced; in combination with a special source of monochromatic light, this is made the basis of a method for the determination of bile acids with an error of $\pm 5\%$. Bile acids are absent from normal human blood.

C. R. HARRINGTON.

Manometric measurement of peptide hydrolysis. H. A. KREBS and J. F. DONEGAN (Biochem. Z., 1929, 210, 7—23).—A method of measuring peptide hydrolysis depends on the fact that peptides are stronger acids than their amino-acid constituents. If the hydrolysis mixture contains hydrogen carbonate and is in contact with an atmosphere of carbon dioxide, the change in pressure produced gives a measure of the hydrolysis. The "constant of the vessel" may be measured directly, when all experiments must be carried out under exactly similar conditions, or may be calculated from the acid dissociation constants of the peptide and of the amino-acid and the first dissociation constant of carbonic acid. The method gives results within 1% and agrees well with the older methods.

J. H. BIRKINSHAW.

Solubility of lead salts in physiological salt solutions. L. C. MAXWELL and F. BISCHOFF (J. Pharm. Exp. Ther., 1929, 36, 279—293).—The solubility product law does not apply to the behaviour of lead orthophosphate, $Pb_3(PO_4)_2$, in solutions containing excess of phosphate probably because intermediate ions, solubility data for which are unknown, are formed. In a salt solution of the ionic strength of blood at p_H 7.35 and containing 4 mg. of phosphorus per 100 c.c. the solubility of lead orthophosphate is equivalent to 3.6×10^{-7} mol. of lead per litre. The solubility of lead carbonate in a salt solution of the ionic strength of blood containing hydrogen carbonate and under a carbon dioxide tension comparable with that of blood is equivalent to 1.0×10^{-6} mol. of lead per litre.

W. MCCARTNEY.

Micro-determination of phosphate. F. HOLTZ (Biochem. Z., 1929, 210, 252—260).—In a gravimetric micro-method for phosphate the substance is heated with sulphuric and nitric acids to destroy organic matter. After dilution with 25% ammonium nitrate solution containing nitric acid the mixture is precipitated hot with nitric acid ammonium molybdate-sulphate reagent. The precipitate is dried and weighed together with a porcelain filter crucible, dissolved out with alkali, and the tare weight of the crucible obtained.

J. H. BIRKINSHAW.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1929.

General, Physical, and Inorganic Chemistry.

Hydrogen spectra excited by electronic shock. S. VENCOV (Compt. rend., 1929, 189, 279—280; cf. this vol., 968).—Continuous and secondary spectra of hydrogen were obtained together in the neighbourhood of the ionisation potential of the hydrogen molecule (16.5 volts). Variations in gas pressure or in the accelerating field produced the strong Fulcher bands in the latter spectrum, whilst the former appeared as a homogeneous band. Further variations in conditions of excitation produced independent effects on the intensities of the two spectra. The appearance below 20 volts of the first Balmer lines indicates that ionisation of the hydrogen molecule at 16.5 volts is accompanied by dissociation. J. GRANT.

Separation of hydrogen lines in parallel and crossed electrical and magnetic fields. N. R. SEN (Z. Physik, 1929, 56, 673—683).—Mathematical. The theory of Dirac and Darwin is used to calculate the separation of the hydrogen lines in parallel and crossed electric and magnetic fields, small relativity effects being neglected. For parallel fields the same conclusion is reached as with the older quantum mechanics. For crossed fields the arrangement of the separated H_α lines and the possible switches are given. A. J. MEE.

Densities of hydrogen spectral lines as a function of the electronic velocity of excitation. C. J. BRASEFIELD (Physical Rev., 1929, [ii], 34, 431—437).—The densities of the principal lines of the singlet and triplet systems of molecular hydrogen, as well as H_α , H_β , and H_γ , were measured and plotted against electronic velocities for a range of 19—220 equivalent volts, at constant electron emission and gas pressure. The triplet lines approach a maximum density below 19 volts; the singlet lines show a maximum between 30 and 35 volts. The densities of H_α , H_β , and H_γ decrease rapidly below 30 volts, indicating that the number of dissociating collisions producing an excited atom must be very small at 19 volts. N. M. BLIGH.

Terms of the hydrogen molecule. G. H. DIEKE (Z. Physik, 1929, 55, 447—450).—Suggestions towards a complete theory of the origin of the various hydrogen terms are made. R. W. LUNT.

Structure of the band spectra of hydrogen and helium molecules. G. H. DIEKE (Nature, 1929, 123, 979).—The author's interpretation (cf. preceding abstract) of regularities in the spectrum of the hydrogen molecule was based on an incomplete

analogy with the helium band spectrum. The missing helium bands have now been observed, and the author's views are strengthened. The new bands consist of three groups, all belonging to the triplet system, one in the red, one near 535 m μ , and one near 495 m μ . A. A. ELDRIDGE.

Electron terms in the singlet systems of the fine line spectrum of hydrogen. W. WEIZEL (Z. Physik, 1929, 55, 483—501).—A complete analysis of the electron terms of the hydrogen molecule is described in which these are attributed to a photo-electron, whilst a second electron always remains in the lowest state; the ultra-violet bands, for example, are then symbolised thus: $A \leftarrow B$, $1, \sigma^{21} \Sigma - 1, \sigma 2_p \sigma^1 \Sigma$; $A \leftarrow C$, $1, \sigma^{21} \Sigma - 1, \sigma 2_p \pi^1 \Pi$. In this way it has been possible to evaluate all the electron terms. The ionisation potential is found to be 15.75 in agreement with experiment, 15.9 volts. The calculated value for the heat of dissociation $H_2^+ \rightarrow H + H^+$, for the first vibrational quantum, and for the nuclear spacing of H_2^+ are, respectively, 46.5 kg.-cal./mol., about 2100 cm.⁻¹, and about 1.06×10^{-8} cm. R. W. LUNT.

Doppler effect with homogeneous hydrogen canal rays. W. RIEZLER (Ann. Physik, 1929, [v], 2, 429—444).—The positive-ray stream contains H^+ , H_2^+ , and H_3^+ , but when a variable magnetic field is applied it is possible to determine the Doppler effect for homogeneous beams. The velocity calculated from the deflexion by means of an electric or a magnetic field agrees with that calculated from the Doppler effect, according to which the velocities observed are in the ratio 1:1:1 agreeing with H^+ , H_2^+ , and H_3^+ . The Doppler distribution for inhomogeneous positive rays observed by Kreff is in fair agreement with the superposed effects of all the homogeneous beams obtained by magnetic resolution. The intensity distribution of the Doppler effect for the complete stream is conditioned by processes occurring in the beam itself. R. A. MORTON.

New connexion between the absorption spectrum of hydrogen and the many-lined spectrum. O. W. RICHARDSON (Nature, 1929, 124, 408).—A number of band systems ending on Dieke and Hopfield's C level have been found; they all have initial states which are identical with one or other of the initial states of the bands ending on the 2^1S level, and they have the character of band sequences similar to those of the α , β , and other systems ending on 2^3S . They all have P' , Q , and R'

branches. The correctness of Hori's analysis of the Werner ($C \rightarrow A$) bands is confirmed. There are four, or probably five, 2-levels in the H_2 spectrum. A classification of a number of the more important levels is suggested. A. A. ELDRIDGE.

Band spectra of light molecules. I. Spectra of helium and hydrogen. W. WEIZEL (Z. Physik, 1929, 56, 727—739).—The characteristic features shown by the band spectra of light molecules are: (a) their approximate conformity to one or other of the two expressions deduced by Hund (A., 1926, 657), according to the rotational energy involved; (b) the complete decoupling of the spin, the l -decoupling attaining a very high degree; (c) the non-appearance of spin-multiplet structure, and (d) the rare appearance of intercombination between term systems of different multiplets. From this point of view the molecular spectra of hydrogen and helium are discussed, new terms being identified and previous interpretations corrected. The decoupling is dealt with in detail. An explanation is offered for the relative intensities of the Lyman and Werner bands of hydrogen and the interpretation of the former as singlet-singlet combinations is discussed.

J. W. SMITH.

Near infra-red spectra of helium and mercury. T. TAKAMINE and T. SUGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 131—137).—Using a method of heating a plate sensitised with neocyanine, and also by phosphoro-photography, the near infra-red spectra of helium and mercury were studied. With a strong-current Geissler tube as a source of light the helium line 2^3S-2^3P could be photographed with 5 min. exposure. The mercury arc spectrum showed a group of lines in the region $0.7-1 \mu$. The remarkable intensity of the two oxygen lines 0.846 and 0.777μ appearing as impurity is noted and its possible bearing in astrophysics is mentioned.

N. M. BLIGH.

Helium band spectrum. III. S. IMANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 139—149; cf. this vol., 616).—New measurements on the higher members of the helium $2^3\Sigma-m^3\pi I$ series bands in the ultra-violet region were made. Two new bands, $2s^1-8p^1$ and $2s^1-9p^1$, were found and analysed. Constants are calculated for these bands, and a Rydberg formula is suggested which expresses the electronic frequencies accurately, especially of the higher members. The convergence value of ω_0 , the vibrational constant for the p -states, is found to be $1627.2 \pm 0.2 \text{ cm}^{-1}$.

N. M. BLIGH.

Properties of a class of molecular terms, especially terms of the helium molecule. G. H. DIEKE (Z. Physik, 1929, 57, 71—105).—Mathematical. The rotational structure of the terms of a molecule is investigated. A calculation due to Hill and Van Vleck is used to follow the transition from stronger to weaker rotation or from weaker to stronger coupling. The results obtained are tested on the terms of the helium band spectrum. A. J. MEE.

Electron distribution in normal helium. H. BETHE (Z. Physik, 1929, 55, 431—436).—An exceptionally good agreement is to be found between the values of the energy terms and the eigenfunk-

tion of the normal helium atom calculated by the self-consistent field method of Hartree and by the analysis of Hylleras. R. W. LUNT.

Measurement of excitation [functions] of the helium spectrum. W. HANLE (Z. Physik, 1929, 56, 94—113).—The principle of the design of an apparatus for examining the spectrum of helium may be examined as a function of the velocity of the exciting electrons; this is discussed at length together with the errors involved in the procedure finally adopted. The gas pressure was adjusted to a value below that at which pressure effects become appreciable, and spectrograms were taken of the luminescence in the range $6678-3819 \text{ \AA}$, produced in a field-free space by electrons of velocity up to 450 volts. The curves for the intensity as a function of the electron velocity show the following characteristics: a well-defined maximum lying at or below about 100 volts; lines of the same spectral series have curves of the same type, characterised by the sharpness and position of the maximum; and the triplet lines exhibit a very much sharper maximum than do the singlet lines, the $2p-ms$ series having the sharpest maximum. R. W. LUNT.

Spectroscopic observations of the low-voltage nitrogen arc. H. HAMADA (Sci. Rep. Tohoku, 1929, 18, 155—164).—The distribution of spectra over the region $3800-7000 \text{ \AA}$ in the low-voltage nitrogen arc produced in a two-electrode hot-cathode tube has been studied. From the intensity distribution in the negative band system, it would appear that the greater is the voltage applied the greater is the probability of transition from the initial states at which the molecule has the greater vibrational quantum number. R. CUTHILL.

Excitation of the arc spectrum of nitrogen. O. S. DUFFENDACK and R. A. WOLFE (Physical Rev., 1929, [ii], 34, 409—420).—The complete arc spectrum of nitrogen was excited and measured in the region $8800-3400 \text{ \AA}$ with a low-voltage arc in a mixture of helium and nitrogen. The first step of the excitation process is probably the dissociation of nitrogen molecules into neutral atoms by impacts of the second kind with metastable helium atoms, and the second step the excitation of neutral nitrogen atoms by second impacts with metastable helium atoms. Wave-lengths, classifications, and a number of new lines are tabulated. N. M. BLIGH.

Classification of the arc spectra of nitrogen and carbon. S. B. INGRAM (Physical Rev., 1929, [ii], 34, 421—430).—The wave-lengths and approximate intensities of about 125 lines of the arc spectrum of carbon between 9000 and $20,000 \text{ \AA}$ were measured. About 90 of these lines are classified as combinations between terms in $C I$ and $N I$; new terms are fixed in both of these spectra and many identifications made by Fowler and Selwyn in $C I$ (cf. A., 1928, 450) and by Compton and Boyce (cf. this vol., 365) are confirmed. Using the data of Duffendack and Wolfe (cf. preceding abstract) a number of lines is classified in the visible spectrum of $N I$. The designations of the 2P and 2D terms found by Kiess (cf. A., 1925, ii, 911) at 5100 and 6800 \AA , respectively, are corrected by

assigning them to the $2s^2 2p^2 .3p$ configuration, basing them on the 1D term of N II. A complete term table of N I is given. N. M. BLIGH.

Additional series lines in the spectra of C II and N II. I. S. BOWEN (Physical Rev., 1929, [ii], 34, 534—536).—Several of the strong lines of C II were identified as combinations of the 4P term of the sp -configuration with the quadruplet terms observed by Fowler and Selwyn (cf. A., 1928, 1165). This fixes the term values $^4P_1=206810.7$, $^4P_2=206789.2$, $^4P_3=206760.6$. In N II the term value 1S term of the $s^2 p^2$ and the 1P term of the sp^3 configurations were fixed at 206,159 and 72,084, respectively, relative to Fowler and Freeman's term values (cf. A., 1927, 489). The 1S term combines with the 1D term of the same configuration to give the nebular line at 5754.8 Å. The relative term values are recorded for a number of terms, including those designated "a" by Fowler and Freeman, and these were shown to belong to the quintuplet system. N. M. BLIGH.

Nitrogen afterglow. E. J. B. WILLEY (Nature, 1929, 124, 443—444).—The decay of the afterglow is only partly a homogeneous reaction in clean glass vessels, the amount of divergence from homogeneity being determined by the purity of the nitrogen. The influence of the necessary traces of electronegative gas is confined to the surfaces. Under conditions of minimised wall decay no appreciable change in the order of the reaction takes place with time, and no apparent alteration occurs in the afterglow spectrum so far as 4000 Å. No simple relationship exists between the intensity of the glow and the concentration of chemically active nitrogen, except possibly under certain conditions determined by the state of the walls. Addition of small amounts of oxygen or nitric oxide to a stream of glowing nitrogen causes a large development of radiation in the blue and regions of shorter wave-lengths. The intensity of the green flame with nitric oxide (5%) is related to the concentration of chemically active nitrogen as is that of the luminosity of the nitrogen alone. The decay of a stream of luminous nitrogen can be varied by addition of photogens without affecting the amount of the chemically active species present. It therefore appears that atoms are concerned in both phenomena, and it is suggested that the chemical activity is probably due to 2.3-volt metastable atoms.

A. A. ELDRIDGE.

Rotational structure of the red bands of sodium. W. R. FREDRICKSON (Physical Rev., 1929, [ii], 34, 207—212).—Three bands of the red band system of sodium photographed at high dispersion were measured. Two strong series of lines run through the bands and these series are shown to be P and R branches, and the combination constants are evaluated. The final state values and those of the blue-green system agree closely and the constant for the upper state gives $I_0'=255.3 \times 10^{-40}$ g.-cm.² and $r_0'=3.52 \times 10^{-8}$ cm. The electronic transition is concluded to be of the $^1S \rightarrow ^1S$ type. N. M. BLIGH.

Ultra-violet spectrum of magnesium hydride. II. Many-lined γ -system. R. W. B. PEARSE (Proc. Roy. Soc., 1929, A, 125, 157—179; cf. this vol., 376).—The bands of the γ -system of magnesium

hydride have been measured in the region 2560—3240 Å. The distribution of band origins about the origin of the system is represented by the equation $v_0=35904.5+1138.4(n'+\frac{1}{2})-9.5(n'+\frac{1}{2})^2-1702.2(n''+\frac{1}{2})+34.2(n''+\frac{1}{2})^2$. The rotational structure has been analysed and the bands have been found to consist of a single R and P branch, with one line missing at the origin. The structure is characteristic of the $^1S \rightarrow ^1S$ type of transition, and the values for the vibrational constants show definitely that the two new S levels are quite distinct from the 2S level of the α - and β -systems. Using a rotational energy term of the form $F(j_k)=B_n j_k(j_k+1)-D_n[j_k(j_k+1)]^2$, the following values are calculated: $B_n'=4.3020-0.0492(n+\frac{1}{2})-0.0050(n+\frac{1}{2})^2$, $B_n''=6.3782-0.1854(n+\frac{1}{2})$, $D_n'=2.16 \times 10^{-4}$, $D_n''=3.45 \times 10^{-4}$, $I_0'=6.439 \times 10^{-40}$ g.-cm.², $I_0''=4.343 \times 10^{-40}$ g.-cm.², $r_0'=2.02 \times 10^{-8}$ cm., $r_0''=1.65 \times 10^{-8}$ cm. The observed values for the isotope effect, measured for the (0,2) and (0,1) bands, are in good agreement with those calculated on the assumption that the bands are emitted by the diatomic molecule, MgH, magnesium having isotopes of weights 24, 25, and 26.

L. L. BIRCHSHAW.

Optical excitation of phosphorus vapour. A. JAKOVLEV and A. TEREIN (Nature, 1929, 124, 337).—Fluorescence emitted in the region 3500—1900 Å. was observed in phosphorus vapour (0.1 mm.) at 600—700° illuminated by spark radiation Cd 2195, 2144 Å., Zn 2100, 2062 Å., or Al 1990, 1935 Å. The first vibration quantum and the dissociation energy of the normal P_2 molecule are estimated, respectively, to be 775 cm.⁻¹ and 6 volts.

A. A. ELDRIDGE.

Spark spectra of sulphur. L. BLOCH and E. BLOCH (Ann. Physique, 1929, [x], 12, 5—22).—A more detailed account of work already published (this vol., 225).

Arc spectrum of chlorine and its structure. C. C. KIESS and T. L. DE BRUIN (Bur. Stand. J. Res., 1929, 2, 1117—1136).—More than 200 lines between 4000 and 9900 Å. have been measured in the arc spectrum of chlorine excited by an uncondensed discharge in a Geissler tube at low pressure. Of these lines 62%, together with those observed by Turner in the Schumann region, have been classified as resulting from combinations between terms of the doublet and quadruplet systems. They arise mainly from the basic term 3P of the ion, the terms coming from 1S and 1D not being definitely established, owing to the faintness of the lines. From these, the distance separating 2P_2 from 3P_2 is 104,991 cm.⁻¹, giving 12.96 volts as the ionisation potential of neutral chlorine. C. J. SMITHELLS.

Arc spectrum of chlorine. K. MAJUMDAR (Proc. Roy. Soc., 1929, A, 125, 60—68).—From a consideration of the fact that in the arc spectra of a group of successive elements (e.g., aluminium, silicon . . . potassium) the wave-numbers of the strongest lines of the elements due to the transition $N \rightarrow N_2$ increase linearly with the atomic number (cf. Saha and Mazumdar, A., 1928, 1296), it is found that the group of chlorine lines due to the transition $4M_2 (N_1 \leftarrow N_2)$ should lie in the region 9300—

7700 Å. Therefore the group at 4700–4200 Å., identified by Laporte (A., 1928, 805) as being due to the transition $4M_2 (N_1 \leftarrow N_2)$, must be actually ascribed to $4M_2 (N \leftarrow O_2)$. With a view to discover these predicted infra-red lines the spectrum of chlorine has been photographed in the region 6400–8700 Å. The means taken to surmount the experimental difficulties are discussed. The new lines observed in the infra-red are identified as belonging to the transition $\text{---}N_2$ and are tabulated in the form of multiplets. The ionisation potential is calculated to be 13.1 volts. L. L. BIRCUMSHAW.

Spectrum of trebly-ionised argon. D. S. JOG (Nature, 1929, 124, 303).—The lines of trebly-ionised argon have been classified; all the quadruplet multiplets due to the transition $2M_2 (N_2 \leftarrow N)$ have been obtained. A. A. ELDRIDGE.

Number of excited atoms and the absorption spectrum of nickel vapour. A. T. WILLIAMS (Nature, 1929, 124, 373).—The equation $N'/N = e^{-E/RT}$, where N' is the number of excited atoms, N the total number of atoms, and E the energy, is modified to $N'/N = e^{-(E+\Delta E)/RT}$, since it is necessary to consider also the energy consumed in passing from one normal configuration to another: $(3d)^8(4s)^2 \rightarrow (3d)^9(4s) = \Delta E$. A. A. ELDRIDGE.

New zinc hydride bands in the ultra-violet. E. BENGTSSON and B. GRUNDSTROM (Z. Physik, 1929, 57, 1–10).—The new band system investigated extends from λ 2500 to 2000 Å., and five bands at 2092, 2152, 2240, 2332, and 2351 Å. are analysed. These bands have only simple P and R branches, the P -branch being always somewhat more intense. The term-differences of the initial and end states are obtained. They represent a $^1\Sigma'$ —electron switch of an ionised Zn^+H dipole. From these five bands it is possible to place a large number of bands in a level scheme. The dissociation energies of both electron states are calculated from the convergence limit to be $D' = 4.4$ and $D'' = 2.5$ volts. A. J. MEE.

Regularities in the arc spectrum of arsenic. K. R. RAO (Proc. Roy. Soc., 1929, A, 125, 238–246).—The spectrum of arsenic has been photographed between 8800 and 1370 Å., using as source the arc between metallic arsenic contained in poles of carbon or aluminium. No lines have been observed in the infra-red region. The arc in nitrogen was used for investigating the Schumann region down to 1650 Å. and below this region the arc in a vacuum between carbon poles containing arsenic and the spark between metallic arsenic in hydrogen. Several new lines have been measured which have led to the identification of combinations due to the electron transitions from the deepest $4p$ state to the higher $5s$, $4p'$, and $4d$ states. The resonance triplet corresponds with the combination $4p^4S\text{---}5s^4P$. L. L. BIRCUMSHAW.

Magnetic separation in the spectrum of ionised krypton. C. J. BAKKER and P. ZEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 565–577).—The magnetic separation of the Kr II spectrum has been investigated. The g -values of the terms arising from the coupling of the $5s$ and $5p$ electron have been fixed and it is shown that g -values with strong

“anomaly” appear. The g -sum rule has been confirmed. A comparison of the g -values of analogous terms in the spectra of Ne II , A II , and Kr II is given. R. A. MORTON.

First spectrum of krypton. W. F. MEGGERS, T. L. DE BRUIN, and C. J. HUMPHREYS (Bur. Stand. J. Res., 1929, 3, 129–162).—About 200 lines (3302.54 to 9751.77 Å.) characterising the spectrum of neutral krypton atoms have been photographed, and a list of estimated intensities and measured wave-lengths has been obtained. The main spectral terms, analogous to those in the related neon and argon spectra, have been identified and nearly all the Kr I lines classified in series of various types. From the combinations and series limits absolute terms are derived and the ionisation potential of 13.940 volts is deduced. The Kr I spectrum is closely analogous to Ne I and Ar I and good agreement with theory is obtained. The proposed substitution of the krypton line 5649.56 Å. for the cadmium line 6438.4696 Å. as a primary standard of wave-length is open to objection because the krypton line has relatively low intensity and involves a metastable level. The line 5870.92 Å. is in these respects preferable, but it cannot be recommended as a standard until it has been re-examined for hyperfine structure.

R. A. MORTON.

Extension of the Cd I-like isoelectronic sequence to Sb IV and Te V. R. C. GIBBS and (Miss) A. M. VIEWEG (Physical Rev., 1929, [ii], 34, 400–405).—The spectra of tin, antimony, and tellurium were photographed with a vacuum spectrograph. New Sn III lines, additional to those classified by Green and Loring (cf. A., 1928, 2), were identified, particularly second members of series. Sb IV lines were identified arising from transitions $5s5p\text{---}5s^2$, and from $5p^2$, $5s3d$, and $5s6s$ to $5s5p$; some second members were also found. The Cd I-like isoelectronic sequence was extended through Te V by the classification of lines resulting from transitions as in Sb IV .

N. M. BLIGH.

First spectrum of xenon. W. F. MEGGERS, T. L. DE BRUIN, and C. J. HUMPHREYS (Science, 1929, 69, 406; Chem. Abstr., 1929, 2655).—A preliminary notice of a new list of estimated intensities and measured wave-lengths for about 300 lines of the Xe I spectrum between 3442.7 and 9923.10 Å. Spectral terms accounting for most of the lines have been identified; the largest term, 1S_0 , represents the normal state of the neutral atom and has a value 97,835, from which an ionising potential of 12.078 volts is derived. L. S. THEOBALD.

Arc spectrum of platinum. J. J. LIVINGOOD (Physical Rev., 1929, [ii], 34, 185–198).—Eight new levels and 44 new combinations were found in Pt I , and 56 new lines were measured in the ultra-violet. Many levels were interpreted from an examination of the Zeeman effect and from the g -values. Low structures are d^9s , d^8s^2 , and d^{10} ; middle terms arise from d^9p and d^8sp ; high configurations are $d^9.s$, $d^8s.s$, with an indication of $d^8s.d$. Quintuplet terms appear in the middle and high sets. Evidence shows that the Russell-Saunders coupling has almost completely broken down. Similarity with the

theoretically analogous spectrum of Ni I is only approximate. The ionisation potentials calculated approximately are 8.9 for d^9s to d^9 and 9.7 volts for d^9s to d^8s .

N. M. BLIGH.

Mean life for the mercury spark spectrum.

L. R. MAXWELL (Physical Rev., 1929, [ii], 34, 199—206; cf. this vol., 112).—Mean life values found for the lines 3114 and 2572 of Hg IV were 9×10^{-7} and 8×10^{-7} sec., and for the lines 3090, 3312, and 4797 Å. of Hg III were 6×10^{-7} , 4×10^{-7} , and 4×10^{-7} sec., respectively. The prominent lines of Hg II have an estimated mean life of the order 10^{-8} sec. These results indicate that the greater the charge of the ion producing the line the longer is the mean life. Spark lines are produced by single electron collisions.

N. M. BLIGH.

Line absorption of mercury vapour for the line 2537 Å. H. KOPFERMANN and W. TIETZE (Z. Physik, 1929, 56, 604—616).—The total absorption of the 2537 Å. mercury resonance line by a layer of mercury vapour was measured by a photo-electric method at five different temperatures between -11° and 20° . The f -values for the line were calculated by the use of a formula connecting it with the product of the maximal absorption coefficient and the layer length. For the comparison of this f -value with that derived by other methods, e.g., measurement of the absorption of the pressure-widened lines and anomalous dispersion, it must be remembered that the 2537 Å. line has a complex structure, being made up of five lines at a distance of about 0.01 Å. from each other. The f -value is intermediate between those obtained for the extreme lines and is practically equal to one fifth of the total f -values. The normal life-period of the 3P_1 state of mercury calculated from five times the f -value is in good agreement with the life-value obtained by other methods.

A. J. MEE.

Efficiency of excitation by electron impact and anomalous scattering in mercury vapour. W. H. BRATTAIN (Physical Rev., 1929, [ii], 34, 474—485; cf. Messenger, A., 1927, 85; Maxwell, A., 1926, 989; Jones, A., 1928, 1168).—The efficiency of excitation by electron impact of the 6.67-volt resonance level in the mercury atom was studied as a function of the energy of the incident electrons. The electrons which have lost energy are separated out by a small retarding field and measured. The number of collisions is calculated from the experimental value of the mean free path. For the range 6.67—7.07 volts the maximum efficiency is 0.06 at 6.77 volts, falling to 0.04 at 7.0 volts. The number of electrons scattered elastically at large angles by mercury vapour as a function of their energy was measured for an energy range of 2—10 volts. Singularities were found corresponding with an increase in large angle scattering, the most prominent being at 4.9, 5.7, and 6.3 volts, and the less prominent at 9.6, 10.3, and 11.1 volts.

N. M. BLIGH.

Origin of long infra-red radiation of mercury. W. KROEBEL (Z. Physik, 1929, 56, 114—130).—In order to test the speculations of Franck and Grottrian as to the origin of the radiation from mercury vapour in the region 400—200 μ the conditions under which this radiation is emitted and absorbed have been

investigated. The method consisted in measuring the indications of a radio-micrometer on which was allowed to fall the total long wave radiation from a specially designed mercury arc lamp, the whole being contained in an atmosphere of dry air to avoid absorption by water vapour. Radiation of wave-length below 200 μ was removed by a series of filters, the final one being blackened cardboard, for which Rubens gives a transmissibility of 9% for $\lambda \cong 200 \mu$. It was found that the radiation $\lambda \cong 200 \mu$ was quenched by the addition of hydrogen to the arc source, but slightly increased by the addition of nitrogen; the radiation is absorbed by excited mercury vapour which is produced in the arc, and by mercury vapour excited by 4.9-volt electrons. It is therefore concluded, in agreement with the theory of Franck and Grottrian, that the radiation in question arises from a metastable excited Hg₂ molecule.

R. W. LUNT.

Relation between the intensities of multiplets of mercury and of neon and the energy of the exciting electrons. W. ENDE (Z. Physik, 1929, 56, 503—515).—The relative intensities of multiplets of mercury and of neon have been determined from spectrograms of the luminescence excited in these gases in an approximately field-free space by electrons of energy from 12 to 40 volts. The relative intensities of the components of the mercury triplet $2^3P-2^3S_1$, 5461, 4358, and 4047 Å. were 60 : 100 : $49 \pm 5\%$; the ratios were independent of the electron energy and almost independent of the strength of the electron beam. For the triplet $2^3P_2-3^3D$, 3663, 3655, 3650 Å. the ratios were 53 : 51 : 100, again independent of the electron energy. The measurements in neon were carried out at a constant pressure of 0.8 mm. and relate to the red and yellow groups of lines. The relative intensities differ widely from those observed by Dorgelo in the positive column.

R. W. LUNT.

Spark spectrum of thallium, Tl III. J. C. McLENNAN, A. B. McLAY, and M. F. CRAWFORD (Proc. Roy. Soc., 1929, A, 125, 50—53; cf. Carroll, A., 1926, 214).—The term structure of the second spark spectrum of thallium has been investigated, and the real F and G first members and members of each of the S , P , and D series higher than those already located by Carroll (*loc. cit.*) have been identified. The term values are based on the value zero for the state $^1S(\infty d^{10})$ reached at ionisation. The ionisation potential, computed from the value 240,600 cm.⁻¹ for $6s^2S_1$ term, is 29.7 volts. The wave-lengths assigned to Tl III, together with their wave-numbers, intensities, and series designations, are tabulated.

L. L. BIRCHUMSHAW.

Second spark spectrum of lead, Pb III. S. SMITH (Physical Rev., 1929, [ii], 34, 393—399; cf. this vol., 113, 227).—The multiplets $6^3P_{0,1,2}-8^3S_1$, $6^3P_{0,1,2}-7^3D_{1,2,3}$, $7^3P_{0,1,2}-7^3D_{1,2,3}$, and $6^3P_{0,1,2}-pp^3P_1$ arising from combinations between triplet terms of Pb III were found. Twenty-one lines arising from combinations between singlet terms and inter-combinations between singlet and triplet terms were identified. The pp^3D term is found in combination with $6^3P_{1,2}$, 6^1P_1 , $6^3F_{2,3}$, and 6^1F_3 . Seven new lines of Tl II are given, corresponding with some of the Pb III combinations.

N. M. BLIGH.

Band spectra. R. RUEDY (J. Phys. Radium, 1929, [vi], 10, 129—160).—A theoretical review based on Hund's theory slightly modified in regard to rotatory "doubling." The phenomenon is a general property of molecular electronic levels $i_e > 0$ and is not characteristic merely of symmetrical molecules. The relationships between the spectra of copper, silver, and gold atoms and the spectra of compounds of these metals disclose evidence of transitions between metastable states. The theory of the intensities of the bands of molecular oxygen is in agreement with experience concerning the vibration state. The selection rules for transitions between rotation levels (*P*, *Q*, and *R* branches) are not as strict as for atoms and depend on the speed of rotation and the nature (electric moment) of the molecule. R. A. MORTON.

Spectrum of the aurora borealis. J. KAPLAN (Science, 1929, 69, 296—297).—Two weak lines of wave-length 5176 and 5149 Å. in the auroral spectrum can be accounted for by assuming that collisions of the second kind take place between nitrogen atoms in the 2D -state and metastable nitrogen molecules in the A_0 and levels. L. S. THEOBALD.

Spectrum of sunlit aurora rays as compared with the spectrum of lower aurora in the earth's shadow. C. STÖRMER (Nature, 1929, 124, 263—264).

Form and structure of sparks. VI. T. TERADA, U. NAKAYA, and R. YAMAMOTO (Sci. Papers Inst. Phys. Chem. Res., 1929, 10, 271—290).—The effects of various volatile organic compounds on the form of long sparks in air has been investigated. The vapours of methyl iodide, ethyl iodide, chloroform, carbon tetrachloride, $\beta\beta$ -dichloropropane, and ethylene dichloride smooth out a zigzag spark; ethyl bromide has no effect. Alcohols, ether, and acetone cause branching of the spark and a gap in luminosity near the negative electrode. Benzene vapour is supposed to favour the formation of positive brush discharges. A transition stage in the type of spark is produced by benzoyl chloride and benzotrichloride—a smooth part of the spark near each electrode only. Halogen compounds in general, particularly those of chlorine, have the effect of smoothing zigzag sparks if their concentration exceeds a critical value depending on the ratio of the mass of the halogen atom to the mol. wt. of the compound. This effect is held to be due to enhanced ionisation near the electrodes favouring the formation of brush discharges. C. W. GIBBY.

Temperature and the Compton effect. G. E. M. JAUNCEY and H. BAUER (Physical Rev., 1929, [ii], 34, 387—392).—On Debye's theory the intensity of the unmodified X-rays scattered by crystals should increase with rise of temperature, and the ratio of modified to unmodified rays should decrease. This was investigated, using De Foe's method (*ibid.*, 1926, 27, 675). An aluminium absorbing sheet was transferred from the primary to the scattered beam and the ratio of the two ionisation currents was found at -140° , 25° , and 565° . X-Rays for the wave-length range 0.32—0.62 Å. were scattered by carbon at angles of 60° , 75° , and 90° , and by aluminium and copper at 90° and 130° . No effect of temperature on the ratio of modified to unmodified

rays was detected within the limits of experimental error. N. M. BLIGH.

Compton scattering and the new statistics. S. CHANDRASEKHAR (Proc. Roy. Soc., 1929, A, 125, 231—237).—Mathematical. The Compton scattering by an electron gas is considered on the Fermi-Dirac statistics. Equations are derived which indicate that the distribution of intensity of the radiation scattered by a degenerate electron gas follows a parabolic and not an exponential law. The theory predicts the peak of maximum intensity at a place where the Compton theory for a free-stationary electron predicts a line. Evidence is obtained that the Compton scattering of an electron gas should not be influenced by temperature or by the presence of a magnetic field. L. L. BIRCUMSHAW.

Reflexion and absorption of X-rays of large wave-length. M. A. VALOUCH (Compt. rend., 1929, 189, 283—285).—The reflecting powers of mirrors of different materials (lead and flint glasses, aluminium) have been measured as a function of the angle of incidence for the monochromatic $K\alpha$ carbon rays (44.9 Å.) produced at 320 volts. Prins' formula (A., 1928, 451) was applied to the experimental results, and the refractive indices and absorption coefficients were obtained. GRANT.

Continuous X-ray spectrum. C. ECKART (Physical Rev., 1929, [ii], 34, 167—175).—By the method of wave mechanics the quantum theory is shown to be capable of accounting for the various characteristics of the continuous X-ray spectrum. The theoretical principles are deduced from a schematic model, assuming that the target of an X-ray tube is a plane mirror which completely reflects the electron waves. N. M. BLIGH.

Resolution of the line $L\beta_2$ into its diagram components and the relative widths of some X-ray spectrum lines. S. K. ALLISON (Physical Rev., 1929, [ii], 34, 176—180).—The line $L\beta_2$ in iridium, thallium, and uranium was investigated using the double spectrometer. Theoretically the line should be double, its weaker component being designated $L\beta_{15}$. In iridium no separation was obtained owing to the width of $L\beta_2$; in thallium an incomplete resolution was obtained. In uranium practically complete separation, averaging 1.86 against a theoretical 1.94 Å., was found. Some experiments were made on the intrinsic widths of certain lines in the *L* series of thallium and lead. N. M. BLIGH.

K-X-ray absorption spectra of some chlorine compounds in aqueous solution. O. STELLING (Naturwiss., 1929, 17, 689).—The wave-length values for the *K*-absorption spectrum of chlorine are slightly different when solid sodium chloride, potassium chloride and chlorate are used. The results for nearly saturated solutions of chlorides differ, not only among themselves, but also from those of the solids. The values for potassium chlorate in solution and in the solid state are almost the same. R. A. MORTON.

Scattering of X-rays in mercury vapour. P. SCHERRER and A. STAGER (Helv. phys. Acta, 1928, 1,

518—533; Chem. Zentr., 1929, i, 1081).—The F -curve corresponds with that obtained for crystals.

A. A. ELDRIDGE.

Motion of an electric arc in a magnetic field under low gas pressure. R. TANBERG (Nature, 1929, 124, 371—372).

Use of series inductance in vacuum spark spectra. R. C. GIBBS, (MISS) A. M. VIEWEG, and C. W. GARTLEIN (Physical Rev., 1929, [ii], 34, 406—408).—An inductance was used in series with the spark gaps and condenser, as an aid to the identification of lines in the spark spectra of antimony and tin in the region below 2600 Å. The general effect is to strengthen lines arising from lower states of ionisation and to weaken those from higher states. Line identifications for the two elements are corrected.

N. M. BLIGH.

Electric arc in mixed gases. F. H. NEWMAN (Phil. Mag., 1929, [vii], 7, 1085—1091).—The author's third electrode method has been found to be inadequate for the starting of arcs in helium and neon atmospheres at pressures of 10^{-3} to 1 mm. This difficulty was eliminated by the fusing to the cathode of a small bead of borax, the effect of which is assumed to be a reduction in the cathode potential fall, which is then sufficient to ionise the molecules. With the arcs in the pure gases the characteristic radiations were absent, the arc core being white in colour with a surrounding column of yellow radiation showing only the D -lines. The Balmer lines were present with the CN bands. The effect of the addition of water vapour to either neon or helium was to enhance the Balmer lines and other lines of impurities while reducing considerably the spectra of the main gases.

A. E. MITCHELL.

New electroscope. B. F. J. SCHONLAND (Proc. Camb. Phil. Soc., 1929, 25, 340—343).—A new type of ionisation electroscope is described which combines a high voltage-sensitivity with a small capacity, and has a sensitivity for quantity of electricity of the same order as a combination of an ionisation chamber and a Compton electrometer.

J. W. SMITH.

Photo-electric threshold of a doubly-evaporated film. R. B. JONES (Physical Rev., 1929, [ii], 34, 227—232).—An investigation was made to determine what energy fraction is spent in separating the electron from the original atom, and what work is done to take the electron through the outer surface when light is incident on a metallic surface. The preparation of a platinum, nickel, and platinum-nickel film by evaporation, simultaneously and under the same conditions, is described. Threshold wavelengths found from saturation photo-electric currents obtained with monochromatic light of different wavelengths were Ni 3333, Pt 2804, Ni-Pt 3318 Å. Similar investigations with platinum and tungsten gave W 2338, Pt 2831, Pt-W 2804 Å. It is concluded that the threshold of the mixtures of two metals is the same as that of the constituent having the threshold of lower frequency.

N. M. BLIGH.

Photo-ionisation of the vapours of caesium and rubidium. E. O. LAWRENCE and N. E. EDLEFSEN (Physical Rev., 1929, [ii], 34, 233—242).—Light intensities and photo-ionisation were measured simul-

taneously by an improved form of Foote and Mohler's space-charge method (A., 1925, ii, 919), and an equation is given connecting the ionisation per unit light intensity and the frequency in the case of caesium and rubidium over the range 2200—3130 Å. The equation is in agreement with the relation that the effective collision capture cross-section of the ions for electrons varies inversely as the square of the energy of the electrons relative to the ions, or the Thomson recombination law, confirmed by Oppenheimer by wave mechanics (A., 1928, 456). Photo-ionisation by absorption of principal series lines in caesium was confirmed and was observed also in rubidium.

N. M. BLIGH.

Longitudinal distribution of photo-electrons. A. CARRELLI (Z. Physik, 1929, 56, 694—701).—Mathematical. The longitudinal distribution of photo-electrons is calculated by applying the new wave-mechanics with the theoretical treatment of Sommerfeld. The Sommerfeld expression is only a first approximation for the case when the wave-length is large compared with atomic dimensions, but the formula here derived applies without restriction of wave-length. The formula shows a dependence hitherto unknown on the atomic number of the substance.

A. J. MEE.

Effect of hydrogen on the thermionic emission from potassium. H. R. LAIRD (Physical Rev., 1929, [ii], 34, 463—473).—The thermionic currents at a given temperature were observed for a potassium surface successively cleaned by distillation and contaminated by hydrogen, and it was concluded that the large currents frequently observed from potassium are due to hydrogen contamination. A uniform field appeared to be an essential condition for the saturation of the thermionic currents at 150—185°, and probably to below 100°. The Richardson-type equation was obeyed over the range 150—210°. A value of approximately 1.3 volts for the thermionic work function ϕ was characteristic of the potassium surface after hydrogen contamination of a certain type (cf. Richardson and Young, A., 1925, ii, 343). This value was concluded to be due to a layer of KH on the potassium surface, and the emission being due to its decomposition was chemical rather than thermionic in origin. Values of ϕ of 0.26 volt were found at 100—110°. The conductivity of a thin layer of potassium on a pyrex insulating tube was greatly decreased by exposure to hydrogen.

N. M. BLIGH.

Distribution of electrons between the plate and grid of a three-electrode tube as determined by positive caesium ions. J. M. HYATT (Physical Rev., 1929, [ii], 34, 486—492).—Previous work was continued (cf. this vol., 228) using a plane-anode type of tube containing caesium vapour, the source of ions being a tungsten filament. The plate current and positive ion current emitted from the filament were observed for several negative grid potentials as the plate potential was varied; the number of electrons omitted from the caesium-covered grid per positive ion was calculated and found to increase uniformly from zero at 95 volts to 0.24 at 600 volts. An investigation of the ratio of the positive ion current

to the plate to the positive ion emission from the filament is described.

N. M. BLIGH.

Effect of light on the secondary electron emission of aluminium. E. FREY (Helv. phys. Acta, 1928, 1, 385—416; Chem. Zentr., 1929, i, 1084).—Illumination of non-outgassed aluminium plates with a quartz mercury lamp causes a diminution of secondary electron emission in a high vacuum.

A. A. ELDRIDGE.

Critical potentials of methane. E. PIETSCH and G. M. SCHWAB (Z. Physik, 1929, 55, 231—233).—The decomposition of methane by 15.4-volt electrons is discussed in relation to the recent work of Hogness and Kvalnes (this vol., 242), in which it was concluded that CH_3^+ ions were produced by electrons of this energy. It is shown that the authors' earlier results could be attributed either to direct decomposition of the methane molecule and the simultaneous but independent formation of CH_3^+ ions, or to a rapid secondary reaction between CH_3^+ ions and monatomic hydrogen adsorbed on the electron source.

R. W. LUNT.

Emission of electrons from metals on irradiation with X-rays. W. ESPE (Ann. Physik, 1929, [v], 2, 381—426).—The action of X-rays in liberating electrons from metals has been studied quantitatively in relation to the different variable factors. On the basis of Einstein's law of equivalence formulæ have been derived for the number of electrons set free when the X-rays strike the metal at 90° and at ϕ° , and it is found that the emission should increase as $1/\cos \phi$. For the rapid electrons this proportionality is strictly in accord with experiment, but for the slower secondary electrons the theoretical value is too low, the error amounting to 10% when ϕ is 50° . The error is less for roughened surfaces than for highly polished metal. Comparison of the strength of the electron emission for smooth and roughened surfaces shows that the emission of slow secondary electrons from a polished plate is at a minimum and increases with increasing roughness. The emission of rapid electrons decreases a little when a smooth plate is roughened. The electron emission increases with the atomic number of the metal irradiated, up to a point when the frequency of the radiation in use is exceeded by the excitation frequency of the metal. The relation between electron emission and the wave-length of the incident radiation has also been studied. The results disclose deviations from the Einstein law of equivalence which are accounted for by variable absorption of electrons by the metal. Since emission is proportional to the intensity of the exciting radiation, it is possible indirectly to determine the relation between intensity of X-rays and voltage applied to the tube. Electron emission E (for anticathodes of iron, nickel, and copper) varies as V^3 (V =voltage) minus a constant. Palladium charged with hydrogen shows no measurable increase in emission of slow or rapid electrons as compared with uncharged palladium.

R. A. MORTON.

Radii and collision probabilities of metastable neon and mercury atoms. M. W. ZEMANSKY (Physical Rev., 1929, [ii], 34, 213—226).—Theoretical. Assuming that metastable atoms either diffuse to the

walls of the container and give up their energy there, or are raised to a higher or lowered to the normal state by impact with other atoms, it is deduced that for large values of the time elapsing after the cut-off of the excitation the average number of metastable atoms per c.c. decays exponentially with the time.

N. M. BLIGH.

Analysis of electronic velocities by electrostatic means. A. L. HUGHES and V. ROJANSKY (Physical Rev., 1929, [ii], 34, 284—290).—Theoretical. From the equation of the electronic orbits it is shown that an analysis of electronic velocities should be possible by a radial electrostatic field as well as by the usual magnetic field. The plane of the receiving slit should be at an angle of $127^\circ 17'$ to the plane of the entrance slit. Expressions are found for the resolution at this angle, between two electrons with slightly different velocities, and for the departure from perfect re-focussing of two electrons with the same velocity.

N. M. BLIGH.

Distribution of mobilities of ions in moist air. J. ZELENY (Physical Rev., 1929, [ii], 34, 310—334).—A method which was used to measure the mobilities and distribution of the ions in air for various degrees of humidity is described, and a critical study of the effects of diffusion on the distribution of ions moving in an electric field was made; the results obtained were in fair agreement with theory. The mobilities of ions varied from 45% greater than the slowest for positive ions to 30% for negative ions. Groups of ions having different mobilities were not detected. Theoretical explanations of the distribution are discussed. The average mobility found for the negative ions was 2.00 and for positive ions 1.22 cm./sec. per volt/cm. for water contents of 3.2 and 2.7 mg. per litre of air, respectively.

N. M. BLIGH.

Longitudinal magnetic effect on beams of slow electrons. Periodic concentration and dilatation. J. THIBAUD (J. Phys. Radium, 1929, [vi], 10, 161—176).—See this vol., 231.

Quantum theory of electronic scattering by helium. N. F. MOTT (Proc. Camb. Phil. Soc., 1929, 25, 304—309).—The approximations introduced by Born (Z. Physik, 1926, 38, 803) in the calculation of the variation of electron scattering with angle in the case of hydrogen are discussed. Using the same approximations, similar calculations are made for the case of helium, the results being in good agreement with the measurements of Dymond and Watson (this vol., 368).

J. W. SMITH.

Dispersion electrons in the one-electron problem. J. HARGREAVES (Proc. Camb. Phil. Soc., 1929, 25, 323—330).—Mathematical. Dirac's relativity quantum mechanics is used to derive the Kramers-Heisenberg dispersion formula for an atom with one electron and the dipole moment to which is due the incoherent scattering. The formulæ obtained are similar to those obtained by Klein (Z. Physik, 1927, 41, 407) for the case of a central field, but are not limited to this case. This yields an expression for f (the number of dispersion electrons for any line of the optical spectrum) in terms of the solutions of the four wave equations of Dirac's theory. For any

state of the atom Σf is not equal to unity as deduced by London (cf. A., 1926, 1191) from the original simple wave equation of Schrödinger, but, owing to the relativistic treatment, differs from it by an amount of the order of 10^{-4} . J. W. SMITH.

Layers of caesium and nitrogen on tungsten. N. A. DE BRUYNE (Proc. Camb. Phil. Soc., 1929, 25, 347—354).—When a tungsten filament is heated in caesium vapour in the presence of a trace of nitrogen, the curve of emission against temperature shows two maxima, one being at the usual position observed in the presence of caesium, whilst the other occurs at a higher temperature. The minimum energy which the electrons must be given for this peak to appear lies between 4 and 9 volts, which is lower than the work of dissociation of the nitrogen molecule and much lower than its ionisation potential. Hence it is concluded that the effect must be due to excited atoms or molecules. As it seems impossible that an electro-negative element such as nitrogen could itself cause increased emission, it is suggested that the function of the activated nitrogen is to hold the caesium atoms to the surface to a temperature above that at which a caesium atom alone can adhere.

J. W. SMITH.

Ionisation of hydrogen by its own radiations. J. THOMSON (Phil. Mag., 1929, [vii], 7, 970—980).—The indications previously obtained (A., 1928, 1067) that hydrogen could be ionised by its own radiations have been confirmed, it having been found that the pure dry gas is ionised by radiations emitted by a point discharge within it. It is suggested that the ionisation is effected in stages, the molecules absorbing two or more energy quanta either from the radiations or by collisions with other active molecules. Some of the peculiar phenomena observed by Chattock and Tyndall (Phil. Mag., 1910, [vi], 19, 449) in their investigations of the pressure of the electrical wind are explained from a consideration of the ionising radiations emitted by the gas in the immediate vicinity of metallic points charged to high potentials.

A. E. MITCHELL.

Effective cross-section of the heavy inert gases with respect to electrons below 1 volt. C. RAMSAUER and R. KOLLATH (Naturwiss., 1929, 17, 671).—Preliminary. The curve effective cross-section/electron velocity in volts has been plotted for xenon, krypton, and argon for the region 0—2 volts, particular attention being given to the range 0.1—1.0 volt.

R. A. MORTON.

Ramsauer effect in argon. J. HOLTSMARK (Z. Physik, 1929, 55, 437—446).—The elastic scattering of electrons in argon has been evaluated by the method of Faxen and Hultsmark (*ibid.*, 1928, 52, 485) using the data of Hartree for the atomic field. It is shown that the Ramsauer curve for the effective target area as a function of the electron velocity may be considered as equivalent to the supposition of the target areas corresponding with zero, first, and second orders of the monochromatic ψ -waves by which a homogeneous electron beam may be represented.

R. W. LUNT.

Absorption coefficient for slow electrons in mercury vapour. R. B. BRODE (Proc. Roy. Soc.,

1929, A, 125, 134—142; cf. A., 1925, ii, 1020).—The absorption coefficient α in mercury vapour for electrons with energies of 0.5—400 volts has been determined, using a modification of Ramsauer's apparatus for measuring the effective cross-sectional area of a gas. By employing as the source of electrons a tungsten filament in the centre of a cylinder with a fine longitudinal slit in the side, a very fine beam of electrons could be produced. No indication of a Ramsauer effect, *i.e.*, small values of α for low-velocity electrons, was observed. The value of α was high at 0.5 volt and decreased rapidly with increasing velocity, a small change in the decrease being observed at about 5 volts. A minimum was reached at 20 volts and a maximum at 35 volts, followed by a regular decrease. Comparison with the results of previous investigators shows that Maxwell's measurements (A., 1926, 989) are on the whole in best agreement with the present values. Beuthe's recent work (A., 1928, 213) is criticised on the ground of inadequate experimental conditions.

L. L. BIRCUMSHAW.

Activation of oxygen by electron impact. R. H. DALTON (J. Amer. Chem. Soc., 1929, 51, 2366—2374).—Besides the critical potential of 7.9 volts, oxygen in presence of carbon also shows, more particularly between 0.2 and 0.4 mm., a critical potential of 10.6 volts. Oxygen excited by electron impact between these critical potentials reacts readily with carbon to yield mainly carbon dioxide. It is suggested that the critical potential of 10.6 volts may be due to carbon dioxide and not to oxygen (cf. A., 1927, 187).

S. K. TWEEDY.

Mass-ratio of proton and electron. R. FURTH (Naturwiss., 1929, 17, 688—689).—The fact that the numbers z and μ ($z = hc/e^2$, $\mu = m_P/m_E$, h being Planck's constant, m_P and m_E the respective masses of protons and electrons) are of the same order has been studied. Assuming the interconversion of radiation and matter $r_P + r_E = \lambda = c/v$ (r_P and r_E being the radii of protons and electrons), and equating energies $m_P c^2 + m_E c^2 = h\nu$; assuming a purely electrostatic origin of kinetic energy, $m_P c^2 = e^2/k r_P$ and $m_E c^2 = e^2/k r_E$, k being a numerical constant. The above equations lead to $\mu^2 + \mu(2 - kz) + 1 = 0$, and since z is great compared with 1, $\mu_1 = kz - 2$, $\mu_2 = 1/(kz - 2)$. Putting $k = 2$ and $z = 861.5$, $\mu = 1721$, whilst if evidence in favour of $k = 32/15$ is accepted $\mu = 1836$ as against the experimental value of 1846. Thus the ratio of m_P and m_E follows from general quantum theory considerations.

R. A. MORTON.

Electron counting tube. H. GEIGER and W. MULLER (Physikal. Z., 1929, 30, 489—493).—Experimental (cf. this vol., 114).

R. A. MORTON.

Investigation of natural H-rays with the tube electrometer. E. A. W. SCHMIDT and G. STETTER (Z. Physik, 1929, 55, 467—482).—By using the electrometer method of Ortner and Stetter the specific ionisation produced by beams of H-particles of approximately uniform velocity has been measured. Over a wide range of velocity it was found that the specific ionisation was one quarter of that produced by α -particles. Discrepancies between the electrometer and scintillation methods are discussed.

R. W. LUNT.

Gyro-magnetic effect and the magnetic deflexion of atomic rays from the viewpoint of the new theory of magnetism. K. HONDA (*Z. Physik*, 1929, **56**, 857—861; cf. *A.*, 1928, 454).—Assuming a nucleus of a ferro-magnetic atom to possess a magnetic moment but no appreciable moment of momentum, an explanation is given for the observed fact that the gyro-magnetic ratio is half that expected on the simple electron theory. This conception is also used to provide an explanation for experimental results on atomic rays obtained by experiments such as those of Gerlach and Stern (*Ann. Physik*, 1924, [iv], **74**, 673; 1925, **76**, 163).

J. SMITH.

At. wt. of helium. A. UPMARK (*Z. Physik*, 1929, **55**, 569—574).—The at. wt. of normal and ionised helium is discussed in the light of the author's electrostatic theory of atomic structure; the calculated values are 4.00106 and 4.00216, respectively, the latter being in agreement with Aston's mean value.

R. W. LUNT.

Isotope effect in spectra and precise atomic weights. W. F. GIAUQUE (*Nature*, 1929, **124**, 265).—A brief discussion.

A. A. ELDRIDGE.

Detection of the isotopes of lead by the band spectrum method. S. BLOOMENTHAL (*Science*, 1929, **69**, 229; cf. Grebe and Konen, *A.*, 1922, ii, 4).—A comparison of the band spectrum of ordinary lead (at. wt. 207.2 and containing the isotopes 208, 207, and 206) with that of uranium lead (at. wt. 206.1) gives results in agreement with theory on the basis of lead monoxide as the emitter of the spectra. The separation expected on theoretical grounds between the lines due to Pb^{208}O and Pb^{207}O near the head of γ 5678.3 is -0.37 wave number; that actually measured is -0.43 wave number. The negative sign indicates that the lines from the molecules of the lighter isotope are displaced towards lower frequencies with respect to those from the heavier isotope.

L. S. THEOBALD.

Approximate method of determining the high-velocity limits of continuous β -ray spectra. J. A. CHALMERS (*Proc. Camb. Phil. Soc.*, 1929, **25**, 331—339).—By observing the thickness of aluminium sheet at which a kink occurs in the absorption curve of β -rays from the disintegration products of thorium, measurements have been made of the high-velocity limits of the continuous β -ray spectra of these elements. The results are discussed theoretically and the possibility of further application of this simple electroscopic method is indicated. The absence of γ -rays from thorium-C, as in the case of radium-E' (Bastings, *A.*, 1925, ii, 9), is evidence against the supposed connexion between β - and γ -ray hardness; the softness of the β -rays from thorium-C' relative to the very hard γ -rays is also contrary to this idea.

J. W. SMITH.

Condensation of radioactive substances on solid surfaces. G. H. HENDERSON (*Proc. Camb. Phil. Soc.*, 1929, **25**, 344—346).—If a parallel beam of atoms of radon be allowed to impinge on a cooled copper disc, the latter on testing photographically is found not to show a spot representing the geometrical image, but to be fairly uniformly covered with active

deposit. This is explained by supposing that the atoms remain adsorbed on the surface only a short time and again fly off. In the case of polonium a deposit was also found spread over the disc, but with a greater density opposite the geometrical image of the source. Distributed over the disc, however, were intensely active aggregates of polonium (cf. Chamie, *A.*, 1927, 605, 1120, 1928, 103); aggregates of the same type were also found on attempting to secure polonium by recoil from radium-E.

J. W. SMITH.

Destructive action of α -rays on thin films of various substances. C. PAWLOWSKI (*J. Chim. phys.*, 1929, **26**, 374—378).—The action of α -rays on thin films of collodion, cellophane, and mica has been examined. The rays cause the conglomeration of water into drops in collodion and cellophane, producing opacity. Mica is thus the most suitable substance for covering the radioactive source in disintegration experiments.

J. A. V. BUTLER.

Ionising effect of α -rays in solid dielectrics. H. FOLMER (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 759—769).—An apparatus is described with which, in conjunction with a Wulf electrometer, attempts were made to obtain evidence of ionisation when polonium rays and intermittent polonium radiation falls on solid paraffin in an electric field. Ions formed would show a tendency to move relative to the field. Current measurements against time were made and the phenomena observed are discussed. Results are inconclusive, but there is some evidence of ionisation.

N. M. BLIGH.

Evaluation of radium preparations with the electron counting tube by the γ -ray method. H. NEUFELDT (*Physikal. Z.*, 1929, **30**, 494—495).—The method allows amounts of radium down to 10^{-6} mg. to be determined to within 10%. The sensitivity is 1000 times that of other methods. An automatic counting device is used.

R. A. MORTON.

Preparation of radium emanation. K. PETERS and K. WEIL (*Naturwiss.*, 1929, **17**, 690).—If the preparation of radium emanation is carried out under conditions permitting the γ -activity of the residue and the emanation to be determined during the progress of the separation, evidence is obtained of the existence of γ -radiation of about 1 minute life period arising from a volatile carrier. The material is condensed at -185° , and is apparently a gas. The work is being carried out on radium from other sources in order to ascertain if the particular material used contained an unusual constituent.

R. A. MORTON.

Use of radioactive recoil atoms for diffusion measurements. G. VON HEVESY and W. SEITH (*Z. Physik*, 1929, **56**, 790—801).—The emission of α -ray recoil atoms from a film of the chloride of thorium-B deposited on a surface of lead chloride diminishes on warming to temperatures between 160° and 270° . This change affords an accurate method of measuring velocities of diffusion in lead halides down to diffusion constants of 10^{-13} cm.² per day. The values obtained for the diffusion constants of lead ions in lead chloride and lead iodide are $D = 1.06 \times 10^7 e^{38120/RT}$ and $D = 3.43 \times 10^4 e^{30000/RT}$,

respectively. In the case of the iodide a value of the same order has been obtained by measurements of the decrease of α -ray activity. The transport number of the lead ion is calculated to be 10^{-5} . These values are in good agreement with the observations of Tubandt (Z. Elektrochem., 1928, 34, 482). The high value of the heat of relaxation of the lead ion (38120 g.-cal.) compared with that of the chlorine ion (11180 g.-cal.) explains the observation made by Tubandt that the conductivity in the solid state is due almost entirely to the chlorine ion.

J. W. SMITH.

[Radio]activity of lead obtained from the roof of Paris Observatory. A. SMITS and (Miss) C. H. MACGILLAVRY (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 610—613).—The observation of Maracineanu (A., 1925, ii, 348) that α -particles are emitted from lead, but only from the surface exposed to the sun's rays, has been confirmed with a sample cut from the roof of Paris Observatory two years previously. Lead is being subjected to solar radiation in sealed quartz vessels in order to establish whether the effect is due to irradiation or to atmospheric dust.

R. A. MORTON.

Calculation of radioactive decay constants by wave mechanics. T. SEIXL (Z. Physik, 1929, 56, 62—71).—The suggestions of Gamow, Gurney, and Condon have been elaborated into an exact analysis by means of which the decay constants of the three radioactive groups have been calculated; the values are in good agreement with experiment.

R. W. LUNT.

The differential equations of the treatment of radioactive α -particle emission in wave mechanics. T. SEIXL (Z. Physik, 1929, 56, 72—93).—Mathematical.

R. W. LUNT.

Reflexion of atoms from crystals. A. ELLETT, H. F. OLSON, and H. A. ZAHL (Physical Rev., 1929, [ii], 34, 493—501; cf. A., 1928, 566).—The specular reflexion of beams of cadmium atoms from clean cleavage surfaces of rock-salt was investigated, and an expression is given for the velocity of the reflected beam; the conditions for specular reflexion from a second crystal are considered. Results indicate that associated with motion of translation of uncharged atoms and molecules there is a wave phenomenon of the type postulated by de Broglie. N. M. BLIGH.

Wave-mechanics of an atom with a non-Coulomb central field. IV. Further results relating to terms of the optical spectrum. D. R. HARTREE (Proc. Camb. Phil. Soc., 1929, 25, 310—314; cf. A., 1928, 216, 933).—Mathematical.

J. W. SMITH.

Derivation of the dispersion formula according to the Dirac theory of the electron. K. NIKOLSKY (Z. Physik, 1929, 56, 709—712).—Mathematical. The form of the dispersion expression is the same as is obtained by the use of the older theory.

A. J. MEE.

Lattice energy of LiH and the normal potential of H⁻. R. S. BRADLEY (Phil. Mag., 1929, [vii], 7, 1081—1084).—Lithium hydride is assumed to have an ionic lattice and the lattice energy is determined from the force constants calculated by the method of

Lennard-Jones assuming that the repulsive exponents of Li⁺ and H⁻ are unchanged. The value 230.5 kg.-cal. so obtained leads to an internuclear distance of 2.18 Å., as compared with the experimental value 2.01 Å. found by Bijvoet (A., 1923, ii, 857). Calculations based on a thermodynamic cycle involving known thermochemical quantities give 245.2 kg.-cal. as the lattice energy, the discrepancy between the values being attributed to the uncertainties regarding the ionic radius of H⁻ and the repulsive exponent in the crystal. The heat of hydration of $\text{H}^+ + \text{F}^-$ is assumed to be the same as that of $\text{H}^+ + \text{F}^-$, whence the normal potential of H⁻ is found to be -1.70 volts, which value is used to calculate equilibrium concentrations of H⁻ aq., and it is shown that whilst the p_{H} of a solution may be about 14 the concentration of H⁻ is still of the order 10^{-14} to 10^{-15} , but may be increased by the aid of an oxidation-reduction system such as $\text{Fe}^{++} \rightarrow \text{Fe}^{+++} + e$.

A. E. MITCHELL.

Effect of retardation on the interaction of two electrons. G. BREIT (Physical Rev., 1929, [ii], 34, 553—573).

Potential thresholds and radioactive disintegration in quantum mechanics. E. H. KENNARD (Physikal. Z., 1929, 30, 495—497).—Theoretical.

R. A. MORTON.

Radioactive decomposition and relativity theory. C. MÖLLER (Z. Physik, 55, 451—466).—The quantum mechanical analysis of radioactive process by Gamow and Kudar is discussed from the point of view of relativity.

R. W. LUNT.

Rigid theory of diffusion of electrons in gases. H. BARTELS (Z. Physik, 1929, 55, 507—532).—A rigid theory of electron diffusion in rare gases has been derived by developing the analogy between this process and the optical theory of scattering; in contradistinction to Hertz' theory, it leads to integral equations. The application to the special case of diffusion through a finite layer of infinitely diluted gas is discussed in relation to the theory of Hertz, and it is shown that by careful choice of boundary conditions a valuable approximate solution may be obtained.

R. W. LUNT.

Wave function and velocity distribution in degenerate gases. W. LENZ (Z. Physik, 1929, 56, 778—789).—Mathematical.

J. W. SMITH.

Quantum theory and special relativity. M. S. VALLARTA (Nature, 1929, 124, 336).

Relationship between h , c , and e^2 . W. N. BOND (Nature, 1929, 124, 408—409).—A study of probability, and of the agreement of evidence, throws doubt on the validity of Eddington's relationship $ch/2\pi e^2 = 136$, and tends to confirm the equation $1.0968 \times 10^5 = (e^5/h^3)[2\pi^2/c(1+m/M)(e/m)]$.

A. A. ELDRIDGE.

Second-order wave equations of the spinning electron. G. TEMPLE (Proc. Roy. Soc., 1929, A, 125, 152—156).—Mathematical. The general theory of a system of second-order equations satisfied by a wave tensor of the first rank is given.

L. L. BIRCHMISHAW.

New quantum theory of the ideal monatomic gas and Avogadro's law. G. POLVANI (Nuovo

Cim., 1928, 5, 307—309; Chem. Zentr., 1929, i, 616—617).

Appearance of noble gases in vacuum tube discharges. D. DOOLEY (Nature, 1929, 124, 372).—No evidence for the production of noble gases from a magnesium nitride film on the electrodes was obtained (cf. Riding and Baly, A., 1925, ii, 925). The appearance of such gases, particularly helium, is probably due to diffusion from the atmosphere.

A. A. ELDRIDGE.

Turbulence in the sun's atmosphere. W. H. MCCREA (Nature, 1929, 124, 442—443).

Packing of atoms in alloys. A. WESTGREN and A. ALMÉN (Z. physikal. Chem., 1929, B, 5, 14—28).—The variation of the linear lattice dimensions with composition of the alloy has been investigated in the α -phases of the systems Ag—Al, Cu—Al, and Ni—Al, and in all cases the parameters are less than those calculated by Vegard's addition law from the parameters of the components. From calculations of the volume occupied per atom in the various phases of the above systems, and of the systems Cu—Zn, Ag—Zn, Ag—Cd, Cu—Mg, and Fe—W, it is shown that, in general, a contraction in atomic volume accompanies the formation of the intermediate phases. The atomic volumes in contiguous phases of any system differ only slightly, so that the curves of volumes drawn for a series of phase regions are almost continuous. The volume contraction is especially marked in nickel-aluminium alloys, and it is suggested that this depends on the fact that such alloys are formed by the union of an atom which is deficient in a nuclear electron with one of normal type. F. L. USHER.

Relation between colour and molecular structure in organic compounds. (SIR) C. V. RAMAN and S. BHAGAVANTAM (Indian J. Physics, 1929, 4, 57—78).—Existing theories of colour in relation to structure for organic compounds are reviewed, and a new generalisation is proposed to cover the facts supporting the various older theories. The theory is suggested by a comparison of the structure and physical properties of diamond and graphite. A general parallelism is shown to exist between the colour or light absorption and the degree of optical, electrical, and magnetic anisotropy of molecules from an examination of data on light absorption and scattering, electric and magnetic birefringence, magneocrystalline behaviour, and crystalline birefringence of carbon compounds. Structures and groups favouring colour development tend generally to enhance the degree of optical, electrical, and magnetic anisotropy of the molecule. A theoretical basis for the generalisation is given by the electron theory of dispersion and theories of the origin of optical anisotropy. The mechanism of light absorption is briefly discussed, with reference to electrical conductivity, and the special type of photoconductivity observed in illuminated crystals of high refractive index.

N. M. BLIGH.

Intensities in the harmonic band of hydrogen chloride. J. L. DUNHAM (Physical Rev., 1929, [ii], 34, 438—452).—The intensities of the first 9 lines of the negative branch of the first harmonic absorption

band of hydrogen chloride at 1.76μ were measured with a prism spectrograph, using a galvanometer and thermo-relay to observe thermopile voltages. The positive branch, not being resolvable, was measured as a whole. The integrated absorption coefficient of each line was calculated by Bourgin's methods (cf. A., 1928, 1076). A calculation of the intensity ratio of the band as a whole to that of the fundamental from the Schrödinger equation for an anharmonic oscillator shows satisfactory agreement with experiment. The relative intensities of the lines in a band are calculated from an analysis of the effect of rotation, in agreement with experiment. N. M. BLIGH.

Spectrophotometric study of micas. T. YOSHIMURA (Suppl. Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 1—4).—The extinction coefficients of various coloured micas for different wavelengths and different thicknesses of mica have been determined. The extinction coefficients of thinner layers were always greater than those of thicker layers, probably on account of the greater effect of reflexion in the former case. The colour is probably due to colloidal particles, as no characteristic absorption bands were found. C. W. GIBBY.

Rare earths associated with uraninites. J. K. MARSH (Phil. Mag., 1929, [vii], 7, 1005—1011).—An examination of six uraninites from different localities and of ages $205\text{--}900 \times 10^6$ years has shown that the proportion of rare earths associated with the uraninites is greatest in those of greatest age. There is, however, no relationship between the quantities of the different rare-earth metals associated in each uraninite, and it is suggested that the rare earths are intimate associates rather than real constituents of these. The occurrence of the rare earth is attributed to imperfections in the chemical or physical separations which occurred during magmatic segregation and the greater amount of the rare earths in the older minerals is attributed to greater magmatic turbulence and volcanic activity in the earlier geological times.

A. E. MITCHELL.

Absorption spectrum of praseodymium compounds in various term and aggregation conditions. R. BRUNETTI (Nuovo Cim., 1928, 5, 391—403; Chem. Zentr., 1929, i, 1307—1308).—The absorption spectrum of praseodymium compounds in dilute liquid and in solid solution consists of four bands in the visible region between 6000 and 4000 Å. The spectra of various compounds in equal small concentrations show only small differences. The absorption spectrum of the solutions and superimposed polarised multiplets of the crystal show the mean position of the characteristic radiations of the Pr^{III} ion.

A. A. ELDRIDGE.

Band spectrum of magnesium oxide. P. N. GHOSH, B. C. MOOKERJEE, and P. C. MAHANTI (Nature, 1929, 124, 303).—The spectrum contains eight groups of bands extending from 4372 to 5700 Å.; the 61 band heads have been arranged in the usual n' , n'' progression. The vibrational constants (cm^{-1}) of the molecule are: ω_0' 817.01, $\omega_0'x'$ 2.378, ω_0'' 773.85, $\omega_0''x''$ 2.86. The molecule is of the normal type with small change in the moment of inertia.

A. A. ELDRIDGE.

Spectra of mercury, cadmium, and zinc halides. K. WIELAND (Helv. phys. Acta, 1928, 1, 442—434; Chem. Zentr., 1929, i, 1081—1082).—The spectra of the three chlorides, bromides, and iodides were studied in the region 4000—2300 Å. The mercuric chloride spectrum between 2650 and 2380 Å. consists of nearly 100 bands. The isotope effect for chlorine and bromine was detected.

A. A. ELDRIDGE.

Parameters characterising partial polarisation of light emitted by fluorescence. P. SOLEILLET (Ann. Physique, 1929, [x], 12, 23—97).—A more detailed treatment of work already published (this vol., 120).

Duration of fluorescence of uranyl salts in the solid state and in solution. R. DELORME and F. PERRIN (J. Phys. Radium, 1929, [vi], 10, 177—186).—Uranyl salts excited by blue light emit intense green fluorescence, the intensity of which has been determined in relation to time by means of a phosphoscope and a photometric arrangement. The time τ , defined by $I = I_0 e^{-t/\tau}$, indicating the mean life period of the molecules in the excited state, has been determined at 20° and at -180°. For the solid uranyl salts the following values illustrate the results: sulphate (cryst.) $\tau \times 10^4$ sec. equals 2.5 at 20° and 3.5 at -180°; nitrate (cryst. 6H₂O) 6.1 and 8; chloride 1.54 and 3.6, respectively. The increased duration effected by cooling in liquid air is therefore relatively small. Dilute solutions of uranyl sulphate in pure sulphuric acid (viscosity 0.2) show fluorescence characterised by $\tau = 1.4 \times 10^{-4}$ sec. at 17°, the value decreasing with rise of temperature, with increasing concentration, or addition of water. Traces of added substances, e.g., hydrochloric acid, greatly reduce the value of τ . Solutions of uranyl metaphosphate in metaphosphoric acid show values of τ varying greatly with the viscosity, τ being 0.9×10^{-4} sec. for a solution twice as viscous as water, and 7×10^{-4} for a thick glassy solution. The results support the hypothesis that the luminescence is due to simple fluorescence of long duration, i.e., electronic activation followed by spontaneous deactivation.

R. A. MORTON.

Resonance-fluorescence phenomenon on the cyanogen spectrum. H. T. BYCK (Physical Rev., 1929, [ii], 34, 453—456).—Experiments were made to test Herzberg's view that the intensification of certain pairs of lines in the violet CN bands was due to the absorption of radiation of short wave-length from nitrogen bands in the far ultra-violet (cf. A., 1928, 813, 931; this vol., 489). Radiation from the nitrogen discharge was found to have no effect on the appearance or non-appearance of the doublets; the intensification was found to depend on the pressure under which the excitation of the CN spectrum occurs, and appears to result from collision with some higher-energy atomic or molecular species the formation of which is suppressed at higher pressures. Herzberg's explanation is not supported.

N. M. BLIGH.

Diffusion of photoluminescence by repeated absorption and radiation processes. G. A. GAMBURZEV (Z. Physik, 1929, 55, 533—545).—The changes resulting from diffusion of radiation on the increase

or decrease of the duration of luminescence of molecules are considered.

[Observation of] fluorescence. M. HAITINGER and V. REICH (Chem. Fabr., 1929, 379—380).—The exciting ultra-violet light falls vertically on to the surface of the liquid and the resulting fluorescence is observed laterally. The breadth of the fluorescence band at the surface is determined by the nature and concentration of the fluorescent substance and by the solvent used. The intensity of the fluorescence is increased by interposition of a water lens.

J. S. CARTER.

Raman effect. A. DADIEU and F. KOHLRAUSCH (Monatsh., 1929, 52, 220—240).—See this vol., 976.

Does the nitrogen nucleus conform with the Bose statistics? W. HEITLER and G. HERZBERG (Naturwiss., 1929, 17, 673—674).—The observations of Rasetti (this vol., 975) on the Raman effect with molecular nitrogen indicate that the nitrogen nucleus complies with the Bose statistics. Important theoretical significance concerning the quantum mechanics of the nucleus is attached to this fact, but the conclusions stand or fall with the correctness of the analysis of the Raman spectrum. R. A. MORTON.

Incoherent scattered radiation in diatomic molecules. F. RASETTI (Physical Rev., 1929, [ii], 34, 367—371).—Using a tube suitable for gases at 10—15 atm. pressure, the Raman spectra excited in hydrogen, nitrogen, oxygen, and nitric oxide by the mercury line 2536 Å. were photographed with a quartz spectrograph. Very complete results were obtained for hydrogen. The constants $B_0 = h/8\pi^2 I_0 c$, for zero rotation, and $\omega_{0/1}$, the frequency of transition from the zero to the first vibrational state, are found respectively to have the values 59.4 ± 0.03 and 4162.1 ± 0.3 for hydrogen, 1.992 ± 0.005 and 2330.7 ± 0.2 for nitrogen, and 1.436 ± 0.005 and 1554.7 ± 1.0 for oxygen. The spectra were in accordance with theoretical deductions (cf. this vol., 627, 975; Hill and Kemble, *ibid.*, 865).

N. M. BLIGH.

Fine structure of infra-red absorption in organic compounds and the Raman effect. R. B. BARNES (Nature, 1929, 124, 300—301).—The infra-red absorption bands of benzene, toluene, *o*-, *m*-, and *p*-xylene, ethylbenzene, butylbenzene, chlorobenzene, and bromobenzene have been studied. The benzene band at 3.25μ consists of three components at 3.231 , 3.253 , and 3.291μ , respectively. For toluene, intensity changes and new bands which combine to produce an apparent shift to 3.35μ are detailed. In *o*-xylene only one benzene vibration is possible, and it has been shifted by 0.007μ . In *m*-xylene only the band at 3.291μ occurs. In *p*-xylene the bands at 3.231 and 3.291μ occur. In the xylenes a group of strong, complex bands, apparently due to the two methyl groups, occurs in the region 3.3 — 3.5μ . Similar results were obtained with the other compounds. For each Raman line a corresponding infra-red band was found, but many of the infra-red bands have not been predicted by the observation of Raman lines.

A. A. ELDRIDGE.

Raman spectrum and fluorescence of benzene. C. V. SHAPIRO (Nature, 1929, 124, 372).—Since the

frequencies concerned in the Raman effect may be attributed to vibrational frequencies, or combinations of such frequencies, of the normal electronic state of the molecule, it is to be expected that these levels will appear as end states in the process of emission or fluorescence. This is confirmed for benzene. All the bands recorded by Riemann (A., 1926, 660) can be arranged in series according to the general equation $\nu = \nu_0 + n'a - n''_1b_1 - n''_2b_2 - n''_3b_3 - n''_4b_4$, where $\nu_0 = 37494$, $a = 921$, and the b levels (with corresponding Raman values in parentheses) are: b_1 998 (991), b_2 600 (605), b_3 855 (853), 1180 (1176).

A. A. ELDRIDGE.

Method for measuring the dielectric constants of conducting liquids. A. ASTIN (Physical Rev., 1929, [ii], 34, 300—309).—In view of the wide divergence of reported results, a modified resonance method for determining the dielectric constants of conducting liquids has been applied to dilute solutions of potassium chloride for various concentrations, and also to check values for sugar solutions. The dielectric constant of benzene determined by a method devised for non-conducting liquids and giving absolute values directly was 2.239 ± 0.005 at 25° ; the value for water by comparison is 79.5 ± 0.5 at 25° .

N. M. BLYTH.

Dielectric constants of imperfect conductors. R. T. LATTEY and O. GATTY (Phil. Mag., 1929, [vii], 7, 985—1004).—The corrections to be applied, for the inductance of the leads and the effects of leakage, in the determination of the capacity of a condenser are discussed and the results applied in the measurement of the dielectric constants of a number of liquids at different temperatures; the corrected values of the dielectric constants are compared with those obtained by other observers. In some cases there are wide discrepancies between the different values. For liquids of high dielectric constant the temperature coefficient of the dielectric constant is found to conform with Abegg's formula.

A. E. MITCHELL.

Dielectric constant of carbon dioxide as a function of its density. J. G. KIRKWOOD (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 56—58).—The dielectric constant, ϵ , of gaseous and liquid carbon dioxide under high pressures has been measured at various temperatures. With the gas at 35° , the molecular polarisation, as given by $(\epsilon - 1)V/(\epsilon + 2)$, where V is the molecular volume, rises continuously at first with increasing density, but just beyond the critical density there is a sharp discontinuity and the value begins to fall rapidly; at 100° the values are rather greater, but show a similar variation with density. The Clausius-Mosotti formula, as modified by Debye, on the other hand, would require the molecular polarisation to be independent of the temperature and density. This discrepancy is probably due to it being inadmissible to neglect the field due to neighbouring molecules when calculating the total polarising field at a point within a gas at high pressure when an external field is applied, and furthermore change in density has an effect on the structure of the molecules. At low densities the gas appears to contain at least two kinds of molecules; if one form had a permanent electric moment and were formed in increasing

amounts with rise in either density or temperature, the results obtained would be partly explained.

R. CUTHILL.

Dielectric constant of ethyl ether in the critical state. N. LITVINOV and V. LITVINOV (Z. Physik, 1929, 57, 134—144).—A resonance method is used for the determination of the dielectric constant of liquid ethyl ether at high temperatures, up to the critical temperature. The results are compared with the theoretical expectations from the work of Gans and Debye. Up to 180° there is agreement, but not in the neighbourhood of the critical point.

A. J. MEE.

Some applications of electric moments to electronic theories of valency. C. P. SMYTH (J. Amer. Chem. Soc., 1929, 51, 2380—2388).—Absence of an electric moment in the paraffins and also of any variation in the moments of the higher ketones and alkyl halides indicates absence of measurable alternate polarity in the hydrocarbon chain, or of inherent dissymmetry in the electronic linkings of alkyl radicals. No measurable polarity is transferred through more than two atoms in the chains. The ethylene double linking has no measurable polarity and appears to be comparatively rigid; polarity may arise when different radicals are attached on opposite sides of the linking. It is suggested that the directive influences and effects on chemical activity commonly attributed to differences in polarity may be due to differences in the energy levels occupied by the valency electrons, which may or may not give rise to measurable polarity.

S. K. TWEEDY.

Characteristic regularity in the molecular polarisation of some pure dipole substances. P. GROSS (Physikal. Z., 1929, 30, 504—506).—The molecular polarisation $P_m = (\epsilon - 1)M/(\epsilon + 2)d$ (ϵ being the dielectric constant, M the mol. wt., and d the density) for a given type of organic halogen derivative is a constant, independent of the particular halogen substituted. In some cases the constancy of P_m in a series is less clearly shown, but the deviations do not exceed the known errors in determining dielectric constants. The electron polarisation P_E , determined from the molecular refraction, increases whilst P_m decreases if the halogen derivatives from chlorine to iodine are compared. The total polarisation of the free molecule is approximately constant in some cases, but not in others.

R. A. MORTON.

Measurement of the magnetic rotation of gases and vapours. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1929, 189, 281—282).—The magnetic rotations of carbon dioxide, sulphur dioxide, carbon disulphide, ethylene, and ethyl chloride have been determined in an improved apparatus which enables measurements to be made at pressures up to 2—3 atm. The results are compared with those of other workers. In particular, the constant for gaseous carbon disulphide is two thirds that of the liquid, and the relatively large value obtained for acetylene is an example of the influence of the carbon triple linking.

J. GRANT.

Magnetic birefringence in liquids of the aliphatic series. M. RAMANADHAM (Indian J. Physics, 1929, 4, 15—38).—Apparatus is described by which, in conjunction with a Rayleigh compensator, the magnetic birefringence was observed and measured

for the first time for 30 liquids of the aliphatic series. Saturated compounds and their derivatives generally showed negative double refraction. Compounds containing the carbonyl group showed positive birefringence. Water was negatively birefringent. Values were found for $(n_p - n_s)/\lambda H^2$, the Cotton-Mouton constant, where $n_p - n_s$ is the difference of the two refractive indices, λ is the wave-length of the light employed, and H is the strength of the magnetic field. Some approximate calculations are given of magnetic anisotropy of organic molecules, obtained from birefringence data and the optical anisotropy of the molecules found from the work of Krishnan on light-scattering (A., 1928, 461). Aliphatic molecules are very feebly anisotropic compared with aromatic molecules.

N. M. BLIGH.

Anisotropy of the polarisation field in liquids.

K. S. KRISHNAN and S. R. RAO (Indian J. Physics, 1929, 4, 39—55).—It was supposed that the Lorentz expression for the polarisation field acting on any molecule in a refracting medium, due to the doublets induced in the surrounding ones, was applicable to liquid media consisting of optically anisotropic molecules only if the molecular distribution round the single molecule should be spherically symmetrical and if their orientations with respect to it should be entirely fortuitous. The validity of these two conditions is discussed on the basis of recent evidence on the fine structure of liquids by X-ray diffraction, and for highly asymmetric molecules the former condition is not found to be justified. The anisotropy of the polarisation field is evaluated for various liquids from X-ray data and shows good agreement with results calculated from measurements on light scattering. The influence of the molecular density is discussed. The anisotropy tends asymptotically to a maximum value determined by the asymmetry of the molecule, at high densities, and to zero at low densities, in agreement with theoretical considerations.

N. M. BLIGH.

Diamagnetism and wave mechanics. F. BITTER (Physikal. Z., 1929, 30, 497—504).—Mathematical.

R. A. MORTON.

Anomalous diamagnetism. C. V. RAMAN (Nature, 1929, 124, 412).—The assumption of the existence of closed electron orbits of dimensions larger than atomic in association with the crystal lattice of bismuth furnishes an explanation of the pronounced diamagnetic anisotropy, the large Hall effects, and the changes of electrical resistance exhibited by bismuth. Kapitza's results (this vol., 989) are also in accord with Ehrenfest's hypothesis.

A. A. ELDRIDGE.

Electrical spectrum of water with undamped oscillations in the wave-length range 3000—2200 mm. N. NOVOSILZEV (Ann. Physik, 1929, [v], 2, 515—536).—An apparatus is described whereby the refraction of undamped waves in the region 2—4 m. by liquids can be measured to within 0.15%. For water n^{17} has the following values: 8.996 at 3000—2800 mm., 9.003 at 2800—2600 mm., 9.0065 at 2600—2200 mm. No anomalous dispersion was detected in the region studied. The dielectric constant (n^{17})² is 81.02—81.07, in good agreement with other data.

R. A. MORTON.

Dispersion and absorption line width in the alkali vapours. S. A. KÖRFF (Physical Rev., 1929, [ii], 34, 457—462; cf. this vol., 635).—Measurements were made photographically at various vapour densities of the widths in absorption of the sodium-*D* lines, and of rubidium 4201 and 4215 Å. Stewart's line-width equation (Astrophys. J., 1926, 59, 30) was verified for higher series members for the first time. Photographic measurements of the refractivity of sodium vapour near the *D*-lines were made, using the interferometer-spectroscope method (cf. A., 1928, 1310), with increased accuracy over previous visual measurements. The dispersion conforms to the classical curve; the form of the dispersion to line width relation remains unchanged for higher series members. A short theoretical summary of dispersion and quantum modifications is given.

N. M. BLIGH.

Anomalous dispersion of lithium vapour. A. FILIPPOV (Naturwiss., 1929, 17, 689).—Preliminary. The anomalous dispersion in the region of the first 25 members of the principal series of lithium has been observed and measured interferometrically for 14 lines.

R. A. MORTON.

Anomalous dispersion of sodium vapour. A. FILIPPOV and V. PROKOFIEV (Z. Physik, 1929, 56, 458—476).—The anomalous dispersion associated with the doublets of the principal series of sodium has been measured in 16 out of 25 observed cases, using a fluor spar interferometer; from these measurements the transition probabilities in the principal series have been calculated. The values for the first four doublets agree with those calculated by wave mechanics.

R. W. LUNT.

Chemical combination as an electrostatic phenomenon. X. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 402—406; cf. this vol., 983).—The influence of atomic deformation on the energy associated with a binary compound is discussed with a view to derive the most probable configuration of the ions in the molecule. Types of molecule containing atoms bearing a different number of charges, e.g., water and ammonia, are considered, with special reference to molecules wherein the outlying ions exert considerable deformatory action on a polarisable central ion. The energy relationships of the water molecule are calculated and from the results the probable atomic orientation is deduced.

H. F. GILLBE.

Theory of complex compounds. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1927, No. 5, 118—156).—The "trans influence" is employed in explanation of the behaviour of complex compounds.

CHEMICAL ABSTRACTS.

Electronic interpretation of oxidation and reduction. W. A. NOYES (J. Amer. Chem. Soc., 1929, 51, 2391—2396).—Consideration of electronic oxidation mechanisms in the light of principles which have been used to reconcile the positive-negative valency theory of Noyes, Stieglitz, etc. with the theories of Lewis, Langmuir, and others leads to the formulation of three types of oxidation processes. (i) Oxidation by transfer of an electron from one atom to another (e.g., oxidation of sodium by chlorine; dissolution of aluminium in sodium hydroxide solu-

tion). (ii) Addition of a positive hydroxyl group to an unshared pair of electrons either of a negative ion or of an electrically neutral molecule, in the latter case with separation of a hydrogen ion and formation of a semipolar union (*e.g.*, oxidation by hydrogen peroxide of trimethylamine to its oxide). (iii) Separation of an electrically neutral semipolar oxygen atom (which may preserve its semipolarity in the new compound or may form a hydroxyl group), followed by its union with an unshared pair of electrons (*e.g.*, thermal conversion of potassium chlorate into perchlorate). S. K. TWEEDY.

New chemical theory and its thermodynamical consequences. A. GOSSELIN and M. GOSSELIN (J. Chim. phys., 1929, 26, 349—367).—A theory of chemical combination based on the conception that the molecules of gaseous elements, *e.g.*, H_2 , N_2 (doublets), and compound molecules remain intact in compounds. Thus ammonia is $HN-H_2$, methane H_2C-H_2 , hydroxylamine $NH-H_2O$. Three kinds of linkings are distinguished; polar (ionisable), steric (similar to Werner's co-ordination linking), and mixed. The formulæ of a large number of compounds on this basis are given. Heats of formation obtained from these formulæ by assuming that every linking has a constant value, independent of others present in the molecule, agree with the experimental values. J. A. V. BUTLER.

Surface tension of mercury in the presence of gas under varying pressures. S. G. COOK (Physical Rev., 1929, [ii], 34, 513—520).—Using a slight modification of Poindexter's apparatus (*cf.* A., 1927, 1132) the maximum surface tension was reached only when mercury vapour was present. For hydrogen, oxygen, air, and carbon dioxide the surface tension was investigated in relation to time of exposure to the gas and to gas pressure. For a given pressure as the gas is adsorbed, the tension falls to an equilibrium value, which rises, as the pressure is reduced, to a maximum depending on the nature of the gas. The maximum value for mercury-hydrogen was 441, and for mercury-mercury vapour 515 dynes/cm.

N. M. BLIGH.

Size of the molecules of fatty acids. F. J. HILL (Phil. Mag., 1929, [vii], 7, 940—946).—A combination of du Nouy's tensimeter and Ferguson's sphere method is used to replace Langmuir's balance method for determining the change in surface tension of water on the surface of which small quantities of fatty acids are spread. The acid is added to the water in ether solution of known concentration. The results of measurements from which are deduced the dimensions of the molecules of oleic, palmitic, and stearic acids are in fair agreement with those obtained by Langmuir, with discrepancies in the values for palmitic and stearic acids, the ratios of length to breadth being respectively 2.3 and 3.8, whilst Langmuir obtained 5.2 and 5.3. A. E. MITCHELL.

Scattering of X-radiation by two-dimensional gratings. W. LINNIK (Z. Physik, 55, 502—506).—The experimental difficulties which beset attempts to observe scattering from two-dimensional crystal gratings have been resolved by passing an X-ray beam through a number of thin sheets of the material under examination. These sheets are arranged so

that they all project on to the position they held in the crystal from which they were cut, and are spaced at irregular distances. Spectrograms are given for mica, gypsum, and calcite. R. W. LUNT.

X-Ray investigation of statistical anisotropy in crystal masses. W. E. SCHMID (Z. Physik, 1929, 56, 740—750).—The statistical anisotropy of crystal masses has been investigated by an X-ray method. The interpretation of the diagrams is discussed. J. W. SMITH.

Anomalous dispersion in the X-ray region. R. FORSTER (Helv. phys. Acta, 1928, 1, 18—46; Chem. Zentr., 1929, i, 969—970).—The refractive index of X-rays as a function of the wave-length between 0.5 and 2.3 Å. was studied for glass, silver, and copper. A. A. ELDRIDGE.

X-Ray investigation of some mixed crystal systems having monoxides as components. Systems $CoO-MgO$, $NiO-MgO$, and $CoO-NiO$. S. HOLGERSSON and A. KARLSSON (Z. anorg. Chem., 1929, 182, 255—271).—For the three systems investigated there exists complete miscibility, Vegard's law of the additivity of the linear dimensions of the interchangeable elements in the lattice being confirmed. H. F. GILLBE.

X-Ray investigation of iron and zinc alloys. A. ÔSAWA and Y. OGAWA (Sci. Rep. Tohoku, 1929, 18, 165—176).—X-Ray examination of iron-zinc alloys shows the existence of two compounds, Fe_3Zn_{10} and $FeZn_7$. The former has a cubic lattice with a parameter of 8.93 Å. and 52 atoms per unit cell, and the latter has a hexagonal closely-packed lattice of the magnesium type. Iron-zinc alloys are closely similar in their crystalline forms to silver-zinc, copper-zinc, and gold-zinc alloys. R. CUTHILL.

Crystal analysis of solid α -nitrogen. J. DE SMEDT, W. H. KEESOM, and H. H. MOOY (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 745—748; *cf.* A., 1926, 1082).—Carefully purified nitrogen was submitted at the temperature of liquid hydrogen to the $K\alpha$ radiations from copper. Analysis of the photographs obtained points to a quadratic crystal structure. N. M. BLIGH.

Crystal structure of solid nitrogen. L. VEGARD (Nature, 1929, 124, 267, 337, and Naturwiss., 1929, 17, 672; *cf.* this vol., 987).—The unit cubic cell, of side 5.65 Å., contains 8 atoms. The space-group is T^4 ; the distance between the two atoms of a molecule is 1.06 Å., and (the molecules being considered spherical) the minimum distance between the centres of the molecules is about 4.0 Å. A. A. ELDRIDGE.

Lattice structure of nickel. S. VALENTINER and G. BECKER (Naturwiss., 1929, 17, 639—640).—The statement of Bredig and Allolio (A., 1927, 502) that nickel sputtered in hydrogen exhibits a close-packed hexagonal lattice is not confirmed. The normal face-centred cubic lattice of edge 3.51 Å. is shown under all conditions investigated. R. A. MORTON.

X-Ray determination of structure of meta-silicates. B. E. WARREN (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 74—75).—Diopside has the lattice constants $a=9.71$, $b=8.89$, $c=5.24$ Å., and

$\beta=74^\circ 10'$. The space grouping is $2C_i-6$, the unit cell containing 4 mols. of $\text{CaMg}(\text{SiO}_3)_2$. The silicon atoms are each surrounded by four oxygen atoms, two of each four being held in common with neighbouring groups, so that the linked tetrahedra form chains parallel to the c axis of the crystal and held together by the calcium and magnesium atoms. Tremolite has the constants $a=9.7$, $b=17.8$, $c=5.26$ Å., and $\beta=74^\circ 48'$. The silicate chain consists of two diopside chains one above the other and separated by a reflexion plane, part of the intermediate oxygen being removed and the remainder shared between two tetrahedra, one in each chain. This new chain lies parallel to the c axis and there are 4 chains per unit cell. The calcium and magnesium atoms are on the 2-fold axis, the former in a group of 8 oxygen atoms and the latter in a group of 6. The 4 oxygen atoms which are outside the chains lie in the reflexion planes and are bound between magnesium atoms. The formula cannot be $\text{CaMg}(\text{SiO}_3)_4$; either there is isomorphous replacement by tervalent ions or else water is introduced, and the correct formula is $\text{H}_2\text{Ca}_2\text{Mg}_5(\text{SiO}_3)_8$. It is probable that in respect of structure diopside and tremolite are typical of the pyroxenes and amphiboles, respectively.

R. CUTHILL.

Crystal structure of tricalcium aluminate. F. A. STEELE and W. P. DAVEY (J. Amer. Chem. Soc., 1929, 51, 2283—2293).—X-Ray powder photographs show that tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, has a body-centred cubic structure, the unit cube having an edge of 7.624 Å. and containing 3 mols. The results indicate three possible structures for the substance, in none of which ionic groups occur. The structure is mixed ionic.

S. K. TWEEDY.

X-Ray study of minerals of the spinel group, and synthetically prepared substances of the spinel type. S. HOLGERSSON (Lunds Univ. Årsskr., [ii], Avd. 2, 23, 9; Kungl. Fysiogr. Sällskapet Handl., 1927, [iii], 38, No. 9, 1—112; Chem. Zentr., 1929, i, 372—373).—The following values (Å.) for the edge of the unit cube were obtained: spinel (Ceylon, red) 8.102 ± 0.003 , 8.099 ± 0.004 ; spinel (Aka, blue) 8.108 ± 0.002 ; chlorospinel (Achmatovsk) 8.103 ± 0.004 ; spinel (Amity, black) 8.126 ± 0.004 ; herynite (India) 8.120 ± 0.003 ; herynite (Ronsberg) 8.130 ± 0.004 ; gahnite (Falun) 8.085 ± 0.003 , 8.092 ± 0.003 ; kreittonite (Bodenmais) 8.115 ± 0.003 , 8.118 ± 0.003 ; magnesiaferrite 8.356 ± 0.004 ; magnetite (Dalarna) 8.400 ± 0.003 ; magnetite (Nordmarken) 8.412 ± 0.003 ; manganomagnetite (Silfberg) 8.408 ± 0.003 ; jacobsite (Silfberg) 8.402 ± 0.003 ; jacobsite (Jakobsberg) 8.424 ± 0.003 ; franklinite (New Jersey) 8.432 ± 0.003 ; chromite (Ural) 8.358 ± 0.003 , 8.355 ± 0.004 . The aluminates are thus differentiated from the ferrites; moreover, values of n are 1.716—1.80 and 2.35—2.42, respectively, chromite again occupying an intermediate position. The hardness is a function of the lattice dimensions. Synthetic substances possessed the following dimensions (Å.): MgAl_2O_4 8.090 ± 0.003 ; MnAl_2O_4 8.263 ± 0.007 ; ZnAl_2O_4 8.099 ± 0.003 ; CoAl_2O_4 8.059 ± 0.003 ; NiAl_2O_4 8.045 ± 0.005 ; CuAl_2O_4 8.072 ± 0.007 ; MgFe_2O_4 8.342 ± 0.005 ; MnFe_2O_4 8.572 ± 0.006 ; ZnFe_2O_4 8.403 ± 0.004 ; CoFe_2O_4 8.359 ± 0.005 ; FeFe_2O_4 .

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8.417; CuFe_2O_4 8.445 ± 0.002 ; CdFe_2O_4 8.731 ± 0.005 ; CoCr_2O_4 8.319 ± 0.003 ; ZnCr_2O_4 8.323 ± 0.004 ; MnCr_2O_4 8.487 ± 0.002 . The oxide Co_3O_4 is also of the spinel type, with a 8.110 ± 0.003 Å.; attempts to prepare Co_2O_3 afforded Co_3O_4 , whilst NiO was obtained instead of Ni_3O_4 or Ni_2O_3 . Siegenite and musenite gave the same lattice constant, 9.423 ± 0.003 Å.

A. A. ELDRIDGE.

Crystal structure of sesquioxides and compounds XYO_3 . W. H. ZACHARIASEN (Norske Videnskaps Akad., Mat. Nat. Kl., 1928, No. 4, 1—165; Chem. Zentr., 1929, i, 8—14).—Values of the parameter (r), α , c/a , and d , respectively, of oxides of the corundum type, ditrigonal-scalenohedral, space-group D_{3h}^{19} , with 2 mols. in the unit cell, are: Al_2O_3 5.13 ± 0.02 Å., $55^\circ 16' \pm 5'$, 1.366, 3.96; Ti_2O_3 5.42 ± 0.01 Å., $56^\circ 50' \pm 5'$, 1.317, 4.58; V_2O_3 5.45 ± 0.03 Å., $53^\circ 49' \pm 8'$, 1.413, 5.04; Cr_2O_3 5.35 ± 0.03 Å., $55^\circ 0' \pm 8'$, 1.374, 5.25; Fe_2O_3 5.42 ± 0.02 Å., $55^\circ 14' \pm 5'$, 1.367, 5.25; Ga_2O_3 5.31 ± 0.02 Å., $55^\circ 50' \pm 5'$, 1.347, 6.44; Rh_2O_3 5.45 ± 0.03 Å., $55^\circ 43' \pm 8'$, 1.351, 8.20. The average separation of metal and oxygen atoms, and the minimal separation of oxygen atoms, respectively, are: Al_2O_3 1.92, 2.495; Ti_2O_3 2.04, 2.68; V_2O_3 2.00, 2.56; Cr_2O_3 1.99, 2.57; Fe_2O_3 2.02, 2.545; Ga_2O_3 1.99, 2.59; Rh_2O_3 2.03, 2.66 Å. The following are the lattice constants of cubic, body-centred sesquioxides: Sc_2O_3 9.79 ± 0.03 , Mn_2O_3 9.41 ± 0.01 , Y_2O_3 10.60 ± 0.02 , In_2O_3 10.12 ± 0.03 , Sm_2O_3 10.85 ± 0.02 , Eu_2O_3 10.84 ± 0.02 , Gd_2O_3 10.79 ± 0.02 , Tb_2O_3 10.70 ± 0.02 , Dy_2O_3 10.63 ± 0.02 , Ho_2O_3 10.58 ± 0.02 , Er_2O_3 10.54 ± 0.02 , Tm_2O_3 10.52 ± 0.02 , Yb_2O_3 10.39 ± 0.02 , Lu_2O_3 10.37 ± 0.02 , Ti_2O_3 10.57 ± 0.03 Å., the calculated densities being 3.89, 5.00, 5.00, 7.07, 7.21, 7.30, 7.62, 7.81, 8.20, 8.36, 8.65, 8.77, 9.28, 9.42, 10.11. The unit cell contains 16 mols. R_2O_3 ; space-group (thallium oxide) T^5 . Lithium nitrate has r 5.74 ± 0.02 Å., α $48^\circ 3' \pm 10'$ and is isomorphous with sodium nitrate. Cadmium carbonate, isomorphous with calcite, has r 6.112 ± 0.006 Å., α $47^\circ 24' \pm 5'$. Rhombic lead, barium, and strontium carbonates are isomorphous with aragonite. Lead carbonate (cerussite) has a 5.14, b 8.45, c 6.10 Å., $a:b:c=0.609:1:0.723$; space-group V_h^{16} , with 4 mols. in the unit cell. Barium carbonate has a 5.29, b 8.88, c 6.41 (± 0.05) Å. Strontium carbonate has a 5.13, b 8.42, c 6.10 Å. Silver nitrate, rhombic-bisphenoidal, has $a:b:c=0.9430:1:1.3697$; a 6.97, b 7.34, c 10.14 Å., with 8 mols. in the unit cell; space-group V^1 , V^2 , V^3 , or V^4 . Rubidium nitrate, D_{2d} , D_3 , or C_{3v} , has r 4.36 Å., α 90° or r 7.37 Å., α $109^\circ 28'$, with 4 mols. in the unit cell; space-group probably C_{3v} . Potassium chlorate has $a:b:c=0.8331:1:1.2673$, β $109^\circ 42'$; a 4.64, b 5.58, c (calc.) 7.07 Å.; space-group C_{3v} . Potassium bromate, ditrigonal-pyramidal, has r 4.403 ± 0.005 Å., α $86^\circ 0' \pm 5'$, with 1 mol. in the unit cell; space-group C_{3v} ; atomic separations are recorded. Iodic acid is rhombic, a 5.53, b 5.92, c 7.75 Å., with 4 mols. in the unit cell; space-group V^1 , V^2 , V^3 , or V^4 . Sodium iodate, rhombic-bipyramidal, has $a:b:c=0.9046:1:1.2815$; a 5.75 ± 0.01 , b 6.37 ± 0.01 , c 4.05 ± 0.01 Å., with 2 mols. in the unit cell; space-group V_h^{19} . Cæsium iodate, apparently cubic, has a 4.662 ± 0.002 Å., with 1 mol.

in the unit cell. The compound SrZrO_3 is cubic, a 4.094 ± 0.003 Å., with 1 mol. in the unit cell. The compound CdTiO_3 , of the perovskite type, has a 3.75 ± 0.05 Å. Potassium nitrate has the aragonite structure: a 5.40 , b 9.14 , c 6.41 Å. Silver chlorate has a 8.475 ± 0.004 , c 7.90 ± 0.01 Å. The unit cell of silver bromate, space-group probably V'' , body-centred, contains 8 mols. The compounds MgTiO_3 and LiNbO_3 possess the ilmenite structure; the rhombohedral unit cell contains 2 mols. and has the dimensions, respectively, r 5.40 ± 0.02 Å., α $55^\circ 1'$; r 5.47 ± 0.03 Å., α $55^\circ 43'$. The above observations are examined theoretically, and the various crystal types are classified. A. A. ELDRIDGE.

X-Ray observations on cellulose. V. Lattice of cellulose hydrate. A. BURGENI and O. KRATKY (Z. physikal. Chem., 1929, B, 4, 401—430).—An experimental method is described for the determination of the lattice constants of cellulose hydrate with greater accuracy than has been possible hitherto. Films of higher orienting power than usual were prepared by converting cellulose xanthate into cellulose hydrate. The X-ray analysis attempts to estimate the statistical symmetry of the crystalline aggregates, the crystalline arrangement, i.e., the position of the translation lattice of the aggregates relative to the macroscopic form of the film, and the translation group of single crystals. It is assumed that as the statistical symmetry of the xanthate film is rhombic holohedral (anisotropic class 4), that of the hydrate film will be the same. This is proved by X-ray observations. As regards the crystalline arrangement, it may be described to a first approximation as a twin crystal with two mirror images, monoclinic in structure, one on each side of the plane of symmetry. The digonal axis coincides with the direction of extension. The plane A_0 makes an angle of between 0° and 15° with the plane of symmetry. The exact determination of the crystalline arrangement is also attempted. To a first approximation the following conclusions are reached with regard to the translation lattice. A_0 , A_3 , and A_4 are probably unique planes in the lattice. The angle between A_3 and A_4 is between 20° and 45° . The angle between A_0 and A_3 and A_4 is larger than 45° . The translation lattice has rhombic or monoclinic symmetry.

A. J. MEE.

Structure of the crystalline part of cellulose. III. H. MARK and G. VON SUSICH (Z. physikal. Chem., 1929, B, 4, 431—439).—Preparations of tunicin (animal cellulose) and β -cellulose can be obtained which give the ring thread structure with (101) parallel to the plane of symmetry, and the simple thread structure with [010] parallel to the direction of stretching. The X-ray diagrams of these substances agree with the monoclinic form of cellulose.

A. J. MEE.

Diffraction of X-rays in liquids and solutions. J. A. PRINS (Z. Physik, 1929, 56, 617—648).—The general theory of diffraction of X-rays is summed up and applied to concrete cases. The mathematical expressions of Zernike and Prins are used. In some cases it is sufficient to assume that the arrangement of molecules is purely a question of geometrical prob-

ability; in other cases it is necessary to take into account the kind of intermolecular forces which are brought into play. Strong diffraction beneath the principal maximum is connected with a tendency towards association. A consideration of the diffraction by monatomic and polyatomic molecules leads to the following conclusions. For monatomic molecules the whole diffraction pattern depends on the arrangement of the molecules. For polyatomic molecules for which the origin of diffraction is concentrated mainly in the neighbourhood of the centre, the principal maximum is favoured; above the principal maximum the inner structure predominates. For polyatomic molecules for which the origin of diffraction is concentrated more at the edge of the molecule, the diffraction pattern is strongly influenced by the inner structure where the principal maximum is to be expected. These results become unsatisfactory only if the molecules are strongly anisotropic and also if the anisotropic axes are correlated with those of neighbouring molecules. Solutions are also dealt with. The effect of the Coulomb force on the diffraction patterns of ionic solutions is investigated. Comparisons with experiment agree, at least qualitatively. An apparatus is described which enables photographs of the diffraction of X-rays at free liquid surfaces to be taken. A. J. MEE.

Crystallisation of gold from the liquid state. C. O. BANNISTER (Inst. Metals, Sept., 1929, Advance copy, 4 pp.).—Cupellation beads of pure gold solidify with the occurrence of "flashing," and the crystalline surface shows an irregular polygonal structure caused by solidification from the labile region. If traces of metals such as platinum, iridium, and ruthenium be present, or if the bead be touched with a gold wire, flashing is prevented, and solidification takes place in the metastable region by radial growth from centres, with velocities which are approximately equal in all directions. The phenomenon is illustrated photographically, and the formation of boundaries is discussed. W. HUME-ROTHERY.

Structure of Heusler's alloy. E. PERSSON (Z. Physik, 1929, 57, 115—133).—The crystal structure of copper-manganese-aluminium alloys was determined by the X-ray method. The β -phase which is responsible for the magnetism of the alloy has a space-centred cubic fundamental lattice, the aluminium atoms being situated at points forming a face-centred cubic superstructure. The manganese concentration must reach a definite limiting value before the alloy becomes magnetic. Experiments were carried out with a series of alloys with compositions corresponding with the formula $(\text{Cu}, \text{Mn})_3\text{Al}$, with varying manganese content. X-Ray diagrams were obtained for specimens in the ordinary state and after tempering at 210° for 15 days. The former consisted mainly of the β -phase, of which the parameters increased with increasing manganese content. With still greater manganese content some β -manganese was present with some aluminium in solid solution. The highest manganese content of the β -phase coincides with the highest magnetic effect. The tempered specimens showed the presence of the β -phase in two similar crystalline forms; one consisting of manganese-free

β -Cu-Al phase, and the other of a β -phase with maximum manganese content. The composition of the latter, or β' , phase corresponds with the formula Cu_2MnAl . Alloys containing the β' -phase are all ferro-magnetic. An X-ray analysis of Heusler bronzes of the composition Cu_2MnSn shows the presence of a phase of analogous structure to the β -Cu-Mn-Al phase. A. J. MEE.

Theory of isomorphous overgrowth in ionic crystals. I. N. STRANSKI (Z. physikal. Chem., 1929, 142, 453—467).—The method previously used (cf. A., 1928, 1178; Kossel, this vol., 18) is applied to find the conditions for the deposition on an ionic crystal of an overgrowth of a salt differing only in the charges carried by its ions. It is estimated that a supersaturation of 3% is necessary before sodium bromide is deposited on lead sulphide crystals. The conditions of formation of mixed crystals between salts having ions of different charges are discussed and an explanation is given of the separation of minute crystals of salts of doubly-charged ions.

J. A. V. BUTLER.

Isomorphous overgrowth in ionic crystals. I. N. STRANSKI and K. KUHELEV (Z. physikal. Chem., 1929, 142, 467—475).—The degree of supersaturation required for the deposition of sodium nitrate on crystals of calcite, siderite, and rhodochrosite and of sodium bromide on galena has been determined at different temperatures. Sodium bromide is deposited only below 50.7° as $\text{NaBr} \cdot 2\text{H}_2\text{O}$, since sufficient supersaturation for the deposition of NaBr above this temperature could not be obtained. The dependence of the degree of supersaturation on the temperature agrees with the theory (see preceding abstract).

J. A. V. BUTLER.

Hall effect in single metal crystal. P. I. WOLD (Science, 1929, 69, 72).—The Hall effect in a large single crystal of zinc of the close-packed hexagonal system is approximately 50% greater than in polycrystalline zinc (cf. *ibid.*, 1928, 68, 183).

L. S. THEOBALD.

Magnetic behaviour of some organic crystals. S. BHAGAVANTAM (Indian J. Physics, 1929, 4, 1—14).—A simple direct method is described by which, through the mechanical force on a crystal for different orientations in a magnetic field, the ratio of the principal magnetic susceptibilities was measured for iodoform, carbamide, succinic acid, azobenzene, *p*-nitrotoluene, and anthracene. The aliphatic compounds were in general feebly anisotropic and the aromatic highly anisotropic. The crystals form classes in which the axes of maximum optical moment and of maximum diamagnetic susceptibility coincide or are crossed respectively; they are similar chemically to those which, as liquids, exhibit negative and positive birefringence. The results are discussed in relation to chemical constitution and crystal structure. N. M. BLIGH.

Saturation of the electric and magnetic polarisation of gases in quantum mechanics. K. F. NIESSEN (Physical Rev., 1929, [ii], 34, 253—278).—An extension of the work of Van Vleck (A., 1928, 572). On the basis that the electric polarisation of a gas results from the effects of a change in the

spatial orientation of the rigid or permanent moment of the molecule, and of the inducing of an elastic polarisation or deformation of the molecule, a complete formula is derived, including a correction for rotation, in the cases respectively of gases of rigid molecules with a permanent electric moment and of gases of deformable molecules in a strong field. In the former the classical Langevin function is found to be valid. The divergence between Langevin's and Brillouin's function (J. Phys. Radium, 1927, 8, 74) is shown to be due to the non-commutativity of the magnetic moment or angular momentum matrices.

N. M. BLIGH.

Absence of change in magnetic susceptibility with crystallisation in strong magnetic fields. L. A. WELO (Physical Rev., 1929, [ii], 34, 296—299).—Lead, tin, bismuth, nickel chloride, and potassium ferricyanide were crystallised in strong magnetic fields and examined, against specimens similarly crystallised in absence of the field, for changes in the magnetic susceptibilities. The changes if any were of the order of 0.4—0.04%.

N. M. BLIGH.

Magnetisation diagram of single iron crystals. G. J. SIZOO (Z. Physik, 1929, 56, 649—670).—A number of determinations was carried out with single iron crystals of very pure iron. All mechanical strains were eliminated by a process of long heating. In order to obtain the magnetisation curve a magnetometric method was used. In many cases there were sudden changes of direction or discontinuities in the curve. Hysteresis was present without exception in all the crystals only in the region of low field strength. In the region above the last discontinuity in the curve the specimen is completely magnetised. At this point the hysteresis branch forms the continuation of the reversible part of the magnetising curve. The retentivity has the same general value as for ordinary polycrystalline iron.

A. J. MEE.

Intensity of magnetisation in iron-nickel-cobalt alloys. H. MASUMOTO (Sci. Rep. Tôhoku, 1929, 18, 195—229).—For the reversible iron-nickel alloys the magnetisation curves, obtained by plotting the magnetising field against the intensity of magnetisation, are similar in form to those for pure iron and nickel, but the irreversible alloys and those with hexagonal close-packed structure are magnetised much less readily. The iron-cobalt α and γ solid solutions and the nickel-cobalt γ solid solution are magnetised much more easily than the corresponding solid solutions with hexagonal closely-packed lattices. Irreversible ternary alloys and the H -solid solutions are very difficult to magnetise, but the reversible alloys are magnetised quite easily. R. CUTHILL.

Magnetisation diagram of single nickel crystals. G. J. SIZOO (Z. Physik, 1929, 57, 106—114).—A new method was used to obtain long wire-like crystals of nickel. The method used is also applicable to the preparation of nickel-iron alloys. The magnetisation diagrams of a number of these nickel crystals were obtained. Since the crystals were mechanically very soft, high values for the coercive force were obtained. In order to reduce this the specimens were heated for 24 hrs. at 900° .

The coercive force was thus reduced to 1–2 gauss. The characteristic magnetisation diagram was similar to that for iron (cf. this vol., 1133). Above a certain point there was no hysteresis. Below this point, however, hysteresis was present for all the crystals, and the curve showed one or more discontinuities. All the crystals showed a certain amount of retentivity.

A. J. MEE.

Law of paramagnetisation of a crystal and the law of the paramagnetic rotatory dispersion. J. BECQUEREL and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 578–589, Z. Physik, 1929, 57, 11–29, and J. Phys. Radium, 1929 [vi], 10, 283–293; cf. A., 1928, 823; this vol, 633).—Ladenburg's mathematical theory of paramagnetic rotatory dispersion (A., 1928, 348) has been verified experimentally for tysonite and parisite. Both substances appear to give a single paramagnetically active band only, and even if several bands exist they cannot be independent. The enormous paramagnetic rotation of tysonite is related to the presence of a band (or group of bands) near 2370 Å. greatly exceeding the visible bands in intensity. Tysonite contains a high percentage of cerium, only a little neodymium, and less praseodymium, and as the visible bands are due to the minor constituents, the intense ultra-violet band and the large rotation are ascribed to cerium⁺⁺⁺. The paramagnetic rotatory power of tysonite in the direction of the optical axis is given by $\rho = \rho_s \tanh \mu_B H / RT$, where H is the magnetic field strength, T the absolute temperature, and ρ_s , the saturation-rotation, is a function of rotatory dispersion and temperature, whilst μ_B is a magnetic moment which in this case is one Bohr magneton. This result is made clear by the demonstration that the paramagnetic rotatory power is due to a single element. The hyperbolic tangent indicates with certainty a reversal of the sense of the magnetic moment.

R. A. MORTON.

Law of the paramagnetic rotation of tysonite and tables of the paramagnetic rotatory power of some crystals. J. BECQUEREL and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 590–596; cf. preceding abstract).—The law of the hyperbolic tangent may not be general, as the value of one Bohr magneton for the moment may be a very special one, corresponding possibly with simplified conditions. Full data on paramagnetic rotation of tysonite, parisite, and bastnæsité are given.

R. A. MORTON.

Introduction to a theory of magneto-optical phenomena in crystals. J. BECQUEREL (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 749–758).—With the view of developing a general theory of the magneto-optics of crystals the ordinary and extraordinary spectra in uniaxial crystals are considered. Data and characteristics are reviewed and interpreted for the Zeeman effect in crystals; the rule for the asymmetries in the intensities of paramagnetic origin and its quantum treatment is discussed. The rare-earth crystals show fine distinct absorption bands, and in the Zeeman effect give doublets of abnormally large separation, and circularly polarised in two opposite senses, results not explained on the Lande

formula. An interpretation on the lines of a Paschen-Back effect due to an internal electric field is discussed.

N. M. BLIGH.

Anomalous magnetic properties at low temperatures: anhydrous ferrous chloride. H. R. WOLTJER and E. C. WIERSMA (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 735–738).—The specific magnetic susceptibility of anhydrous ferrous chloride was found to depend on the absolute temperature T according to the formula $\chi(T-0) = \text{const.}$, down to about 63° Abs. The formula is obeyed by many paramagnetic substances. The value of θ was found to be 20.4° Abs. Above 63° Abs. the susceptibility is independent of the intensity of the magnetic field. At the temperature of liquid hydrogen anomalies occur, the susceptibility becomes dependent on the intensity of the field, and the dependence on temperature is opposite to that at higher temperatures.

N. M. BLIGH.

Determination of the susceptibility of erbium sulphate at low temperatures. W. J. DE HAAS, E. C. WIERSMA, and W. H. CAPEL (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 739–744).—The susceptibility of erbium sulphate was determined for the range 290–14.3° Abs. to ascertain whether results previously found for gadolinium sulphate are specific or are general to the sulphates of all the rare earths. It appears that erbium does not follow the Curie law, but that θ has the value 1.9° Abs. in the formula $\chi(T+\theta) = \text{const.}$ The magnetisation plotted against field strength shows that the susceptibility is nearly independent of the field strength for liquid hydrogen temperatures, and no saturation was definitely observed.

N. M. BLIGH.

Magnetic susceptibility of praseodymium sulphate solutions. O. SPECCHIA (Nuovo Cim., 1928, 5, 432–440; Chem. Zentr., 1929, i, 1313).—The magnetic susceptibility of the salt $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is 18.625×10^{-6} ; the Bohr magneton number is 3.56, using the value 19900 for the magnetic moment of the Pr^{+++} ion.

A. A. ELDRIDGE.

Electrostriction in non-conducting liquids. B. BRUHAT and M. PAUTHENIER (J. Phys. Radium, 1929, [vi], 10, 209–218).—New expressions are derived for the adiabatic and isothermal electrostrictions of non-conducting liquids in terms of experimentally determinable quantities and independent of the Lorentz-Lorenz formula (cf. A., 1928, 695). The agreement between theory and experiment is good for carbon tetrachloride, approximate for benzene, and poor for carbon disulphide. The deviation in the last case is discussed in the light of several hypotheses, but is finally attributed to dissolved gases.

J. GRANT.

Dielectric breakdown in solids. P. BONING (Z. Physik, 1929, 56, 446–457).—Measurements of the dielectric strength of sylvine as a function of the thickness of the test specimen and of the temperature are described which are in good agreement with extensions of Semenov's theory.

R. W. LUNT.

Influence of rolling and recrystallisation on the structure of regular surface-centred metals.

VON GOLER and G. SACHS. III, IV, and V (Z. Physik, 1929, 56, 447—484, 485—494, 495—502).

Compressibility and pressure coefficient of resistance of zirconium and hafnium. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1928, 63, 347—350).—Expressions for the values at 30° and 75° are given.

CHEMICAL ABSTRACTS.

Has pure iron allotropic modifications? T. D. YENSEN (Science, 1928, 68, 376—377).—The amount of silicon required to prevent the change of α - to γ -iron decreases as the carbon content decreases, and assuming the absence of oxygen, the silicon content necessary to eliminate the change is zero at zero carbon content, indicating that pure iron exists only in one form. Equilibrium diagrams based on this view are in accord with experimental evidence.

L. S. THEOBALD.

Isodimorphism of sodium bromide and sodium chloride. Preparation of pure sodium bromide. A. V. RAKOVSKI and V. V. POLYANSKI (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 6, 5—9).—Sodium chloride and bromide exhibit isodimorphism of Roozeboom's fifth group. Sodium chloride and bromide can be separated by means of methyl alcohol.

CHEMICAL ABSTRACTS.

Thermodynamics and kinetics of the thermoelectric effect in crystals, especially the Bridgman effect. P. EHRENFEST and A. J. RUTGERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 698—706).—Theoretical.

Temperature dependence of electrical conductivity. W. V. HOUSTON (Physical Rev., 1929, [ii], 34, 279—283).—It is shown that the zero resistance of a pure metal at 0° Abs. can be explained by taking into account the restriction of the transition probabilities on account of the degeneration of the electron gas, using the Fermi statistics and Brillouin's equations of wave scattering as treated by Frenkel and Mirolubov (A., 1928, 933). A satisfactory law of temperature variation of resistance is also obtained.

N. M. BLIGH.

Dependence of ionic conductivity in crystals of salts on field strength. A. SMEKAL (Z. Physik, 1929, 56, 579—596).—The relationship between field strength and ionic conductivity in crystals is discussed. The normal case of inner transverse field for electrical transfer in pure crystals provided with "soluble" electrodes is a linear field distribution. The conditions for this normal case are stated. The differences which have been previously noticed in the results of experiments in non-homogeneous fields are due to the presence of electrolytic impurity conduction, which causes the conductivity of a crystal to exceed that of the pure crystal by a large amount. The crystals which have been used in most cases, i.e., quartz, calcite, and mica, belong to this class of substances. The increase in the "continued" conductivity of a crystal with increase in the field strength, first observed by Poole, also occurs with crystals with linear potential fall. This has been shown to be true for rock-salt. A method of finding the "true" ionic conductivity of crystals is outlined. Making use of a previously determined general temperature law of "continued" conductivity, it is possible to

find the "true" conductivity without knowing the field strength or the current, the latter being found indirectly from measurements of the "continued" conductivity and temperature with a vanishing field. The increase in the "continued" conductivity with the field strength is discussed theoretically. Two possibilities are given which lead to the same qualitative result.

A. J. MEE.

Dependence of electrical ionic conductivity of single crystals on field strength. F. QUITNER (Z. Physik, 1929, 56, 597—603).—The conductivity of rock-salt and sylvine crystals is investigated. The continued conductivity of natural rock-salt and the crystals of salt obtained after melting shows, after electrolytic purification of the crystals, an increase with increase of field strength. The temperature at which these experiments were carried out was 90°. Curves are given showing the specific conductivity of crystals from various sources as a function of the field strength. In the lower potential regions the increase in conductivity is large, but with higher field strengths there seems to be an exponential relationship between the conductivity and the field strength. There is a very marked difference between the increase in conductivity of natural crystals and those obtained by melting and cooling, and differences exist between crystals obtained by rapid and slow cooling. The increase in conductivity of natural crystals is greater than that of artificial crystals, which, however, possess a conductivity 10—1000 times as great. Natural sylvine crystals were investigated, and it was found that the conductivity is considerably greater than that of rock-salt, but the effect of alteration of the field strength was smaller. At high field strengths the distribution of the potential in the interior of the crystal is linear.

A. J. MEE.

Superconductivity of gallium. W. J. DE HAAS and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 733—734).—In a previous investigation (this vol., 496) a trace of indium as impurity was suspected. The experiments were repeated with spectroscopically pure gallium, using Keesom's new low-temperature cryostat (this vol., 1136). Previous conclusions on the superconductivity of gallium are confirmed.

N. M. BLIGH.

New superconductors. Resistance of alloys at the temperatures of liquid hydrogen and liquid helium. W. J. DE HAAS, E. VAN AUBEL, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 715—723).—Eutectic mixtures of the systems Sn—Bi, Sn—Zn, Sn—Cd, Ti—Au, Ti—Cd, Pb—Ag, Pb—Cd, Pb—Sb, and Pb—Bi were examined, and the influence of small admixtures of non-superconductors with superconductors was investigated. Values of the resistances are tabulated and plotted against temperatures in each case, and the displacement of the temperature interval of fall in resistance with respect to the thermal transition curve of the pure metal given first in each group is shown.

N. M. BLIGH.

A superconductor, consisting of two non-superconductors. W. J. DE HAAS, E. VAN AUBEL, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam 1929, 32, 724—730; cf. this vol., 652).—Previous

work was extended to a number of gold-bismuth alloys of varying composition. The resistances of each with respect to temperature were determined, and the results interpreted with the help of the m.-p. diagram for the system. It is concluded that the solid solution of about 4% of bismuth in gold becomes superconductive at 1.9° Abs. N. M. BLIGH.

Change of the electric resistance of pure hafnium and zirconium between 1.3° and 90° Abs. W. J. DE HAAS and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 707—709).—The specific resistance of hafnium was found to be 0.0000296. The ratio R/R_0 found for zirconium and hafnium is tabulated and plotted against temperature for the range 1.3—90° Abs. No minimum is found in the curves. There was no evidence of superconductivity. N. M. BLIGH.

Resistance of compounds of metals at the temperature of liquid hydrogen and liquid helium. W. J. DE HAAS, E. VAN AUBEL, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 731—732; cf. this vol., 496).—The resistances of the compounds of two metals, Sb_2Ti_7 , $AuPb_2$, and Cu_3Sn , were measured over a small range of very low temperatures. The first two compounds were found to become superconductive above the b. p. of helium 4.2° Abs. Cu_3Sn showed no superconductivity, as previously found in the case of Cu_3Sn . N. M. BLIGH.

Conductivities of solid lead chloride and lead iodide. W. SEITH (Z. Physik, 1929, 56, 802—808).—The variations with temperature of the conductivities of solid lead chloride and lead iodide may be expressed in the forms $x = 6.055e^{-10900/RT}$ and $x = 2.99 \times 10^{-2}e^{-10500/RT} + 2.69 \times 10^4e^{-27480/RT}$, respectively. In accordance with the views of Phipps, Lansing, and Cook (A., 1926, 231), this is interpreted as indicating that in the chloride only one ion takes part in the conduction, whilst with lead iodide both are mobile. This is in agreement with the observations of Tubandt (Z. Elektrochem., 1928, 34, 482). J. W. SMITH.

Thermoelectric phenomena and resistance in metallic single crystals. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1929, 63, 351—360).—The thermal $E.M.F.$ against copper of single crystals of zinc, cadmium, antimony, tin, and bismuth between 20° and 88° was measured, and the calculated thermal $E.M.F.$, Peltier heat, and difference of Thomson heat for rods of the same metal with different orientations are discussed. CHEMICAL ABSTRACTS.

Cause of the thermo-triboelectric anomaly of mercury. M. C. MONTU (Nuovo Cim., 1928, 5, 347—351; Chem. Zentr., 1929, i, 1421).

Sound propagation in gas mixtures. D. G. BOURGIN (Physical Rev., 1929, [ii], 34, 521—526).—Mainly mathematical. Previous results on a single gas and a mixture of two gases (cf. this vol., 637) are simplified and extended to a mixture of any number of gases. N. M. BLIGH.

Methods and apparatus used in the cryogenic laboratory. XXII. A cryostat for temperatures below 1° Abs. W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 710—714).—With

the object of diminishing as far as possible the pressure over a quantity of liquid helium large enough to allow measurements to be made in the space so cooled, two large-capacity vacuum pumps were arranged in parallel and connected to a cryostat filled with liquid helium through cryostats connected to the helium liquefier by vacuum siphon tubes. It was found possible to make measurements down to about 0.85° Abs. in a space of about 300 c.c., thus extending downwards by about 0.3° the range in which measurements can be made. N. M. BLIGH.

The null heat point and the heat of bodies. I. MAJDEL (Arh. Hemiju, 1929, 3, 93—105).—A body emits heat when the frequency of vibration of its atoms lies between 35 and 281×10^{12} /sec.: the temperature T_0 at which thermal vibrations cease, and at which the specific, atomic, and molecular heats are zero, although kinetic energy is still possessed by the atoms, is termed the null heat point. The functional relation between the actual specific atomic heat, μ , and the temperature is for solid elements given by $\mu = \gamma - \alpha/(t + \beta)$, where α is a constant (939.8) and β and γ are constant parameters characteristic for a given element. At low temperatures, $\mu = 0$ and $T_0 = \alpha/\gamma - \beta$. T_0 is shown to be a periodic function of the atomic number. It is proposed to abandon the use of the absolute zero temperature in physics, using in its place T_0 , which is a specific and characteristic constant of each element. The validity of this conception is supported by the periodicity of T_0 , γ , and β , by the agreement of a classification of the elements based on this principle with that of Goldschmidt, and by the derivation of Dulong and Petit's law from the above equations. R. TRUSZKOWSKI.

Heat of dissociation of diatomic hydride molecules. W. W. WATSON (Physical Rev., 1929, [ii], 34, 372—374).—Heats of dissociation for the hydrides of lithium, beryllium, magnesium, and calcium are given as found by extrapolation from vibrational band spectra data, and are compared with results from a conservation of energy formula. The apparent discrepancy between the values and those from the phenomenon of instability at high rotational speeds is discussed. This rotational distortion is attributed to an uncoupling action on the electronic angular momenta. N. M. BLIGH.

Ebullioscopic paradox. J. E. VERSCHAFFELT (J. Chim. phys., 1929, 26, 379—384).—Polemical with Berthoud, Briner, and Schidlof (this vol., 635).

J. A. V. BUTLER.

Joule-Thomson effect and heat capacity at constant pressure for air. O. C. BRIDGMAN (Physical Rev., 1929, [ii], 34, 527—533).—The constants for air in the equation of state (cf. A., 1927, 819) are evaluated, and the equation is used to compute μC_p at various temperatures and densities, and to calculate C_p for various pressures from accurate data at one atmosphere. The two sets of values of μ are plotted along isotherms against pressures. These values, the computed C_p data, and the Joule-Thomson inversion curve obtained from the equation of state are in good agreement with available experimental data. N. M. BLIGH.

Thermal conductivity of ice. S. ARZYBYSCHEW and L. PARFANOWITSCH (Z. Physik, 1929, 56, 441—445).—The thermal conductivity of ice at 0° has been redetermined, $55 \pm 0.8 \times 10^{-4}$ g.-cal. cm.⁻¹ sec.⁻¹; this value is approximately the same as the older determinations of Neumann and of Straneo, and the value of Forbes (0.0021) is therefore traversed.

R. W. LUNT.

Abnormally high heat production with the thorium mineral orangite. H. HERSZFINKEL (Naturwiss., 1929, 17, 673).—Poole's observation (Phil. Mag., 1912, 23, 183) that the heat emitted from orangite considerably exceeds that corresponding with the thorium content has been confirmed, the material from Arcendal giving 34 times and that from Langesund 30 times as much heat as the thorium present would require. Control experiments indicate that the heat evolution from mixtures of radioactive materials is additive.

R. A. MORTON.

Specific heat of tungsten between 90° and 2600° Abs. C. ZWIKKER and G. SCHMIDT (Physica, 1928, 8, 329—346; Chem. Zentr., 1929, i, 1313).—At 92° and 290° Abs. the atomic heat of tungsten is 3.48 and 5.88, respectively; at 2220° Abs. the value is 7.9. Another method gave 8.3₆ for 2500° Abs.

A. A. ELDRIDGE.

Variation of latent heat of vaporisation with temperature. V. KIREJEV (Z. anorg. Chem., 1929, 182, 177—181).—Mathematical. The function $L/RT - f(\theta) = K$, where L is the molecular heat of vaporisation and θ the reduced temperature, affords a simple means of investigation of the relationship between L and T . For various substances and for the temperature interval over which θ lies between 0.90 and 0_c, the approximation formula $K = (1.1 - 0)K_c/(1.1 - \theta_c)$ is valid.

H. F. GILLBE.

Fusion curves of some salt hydrates. G. TAMMANN (Z. anorg. Chem., 1929, 179, 186—192).—The curves obtained by Geller (Z. Krist., 1924, 60, 415) for sodium sulphate decahydrate and magnesium chloride hexahydrate are incorrect, as the method employed is unsatisfactory, especially at high temperatures and low pressures.

H. F. GILLBE.

Vapour pressures of piperidine and α -picoline. Application of Duhring's rule to compounds of the pyridine group. F. T. RILEY and K. C. BAILEY (Proc. Roy. Irish Acad., 1929, 38B, 450—453).—The b. p. of α -picoline and piperidine have been determined over a range of pressures between 760 and 6 mm., and those of pyridine, quinoline, and isoquinoline have been redetermined over the same range. When the b. p. of pyridine at a series of pressures are plotted against those of the other liquids straight lines are obtained, as is required by Duhring's rule.

C. W. GIBBY.

Entropy and specific heat of solid inorganic compounds. W. HERTZ (Z. anorg. Chem., 1929, 182, 189—191).—The quantity $Sc^{\frac{1}{2}}$, where S is the entropy and c the specific heat, is for all solid inorganic compounds containing the same number of atoms constant and equal to the value of $Sc^{\frac{1}{2}}$ for the elements multiplied by the number of atoms in the compound.

H. F. GILLBE.

Heat capacity of oxygen from 12° Abs. to its b. p. and its heat of vaporisation. Entropy from spectroscopic data. W. F. GIAUQUE and H. L. JOHNSTON (J. Amer. Chem. Soc., 1929, 51, 2300—2321).—The transition temperatures between the three solid forms of oxygen are 23.66° and 43.76° Abs.; the m. p. is 54.39° and the b. p. 90.13° Abs. The molal latent heats of transition at these four points are, respectively: 22.42, 177.6, 106.3, and 1628.8 g.-cal. The molal entropy of oxygen, corrected to the state of a perfect gas by means of Berthelot's equation, is 40.74 g.-cal./1° at the b. p., in substantial agreement with the value derived from spectral observations. The significance of this agreement is interpreted. The molal entropy at 298.1° Abs., calculated from spectroscopic data, is 49.03 g.-cal./1°. The Tetrode equation, suitably extended, leads to the accurate value, as is to be expected. The results show that the magnetons in solid oxygen at liquid hydrogen temperatures have little random distribution; they may be coupled into a sort of magneton crystal within the molecular lattice, and the strong paramagnetism of the oxygen may be due to destruction of these couplings by the applied magnetic field (Paschen-Back effect).

S. K. TWEEDY.

Limiting density of matter and energy. W. ANDERSON (Z. Physik, 1929, 56, 851—856).—Theoretical (cf. Stoner, Phil. Mag., 1929, [vii], 7, 63).

J. W. SMITH.

Zero volume of metal alkyls. W. HERZ (Z. anorg. Chem., 1929, 182, 173—176).—The zero volumes v_0 of a large number of metal alkyl compounds have been calculated from the refractive indices, and the results agree with those previously deduced. In each homologous series v_0 diminishes as the mol. wt. increases, whereas for corresponding compounds of different metals v_0 increases with increase of at. wt. of the metal; mercury is anomalous. The first law applies also to compounds containing mixed radicals; isomeric compounds usually exhibit but slight variations of v_0 .

H. F. GILLBE.

Molecular theory of friction. G. A. TOMLINSON (Phil. Mag., 1929, [vii], 7, 905—939).—The theory of dry solid friction is based on the assumed existence of molecular attractions and repulsions such that the repulsive force varies much more rapidly with the distance than does the attractive force and that its effective range is considerably less than the molecular dimensions. It follows that when two bodies move relatively one on the other and there is in consequence a continuous change in the molecules bearing the load, a loss of energy occurs which is manifest as friction. The force of friction is thus a statistical average of the repulsive forces between successive groups of molecules bearing the load between two bodies. Equations deduced for the coefficients of limiting and rolling friction indicate the characteristic properties of these factors. A number of experimental determinations of limiting and rolling friction are described the results of which are in fair agreement with the deductions from the theory. The theory indicates that, contrary to older ideas, there should be friction between bodies in normal contact, but the magnitude

of this is so small as not to be measurable by ordinary means.

A. E. MITCHELL.

Expansion of gases on mixing, especially at very low pressures. I. Its relation to the empirical calculation of the fugacities in gaseous mixtures. L. J. GILLESPIE (*Physical Rev.*, 1929, [ii], 34, 352—366).—The expansion of a gas in a mixture and the expansion of gases on mixing to form a mole of mixture from the pure gases at constant temperature and pressure are plotted as a function of the pressure for mixtures of ethylene and argon, ethylene and oxygen, nitrogen and hydrogen, and nitrogen and methane, and it is shown that these quantities do not vanish at zero pressure. A method is given for calculating the values for zero pressure from the equation of state for the mixture. The fugacity of a gas, or its pressure corrected for deviations from the ideal gas law, can be more accurately calculated when account is taken of data for expansion at zero pressure.

N. M. BLIGH.

Determination of the softening interval of glasses and the abnormal change of specific heat and volume over the interval. G. TAMMANN and A. KOHLHAAS (*Z. anorg. Chem.*, 1929, 182, 49—73).—By experiments with salicin, brucine, piperine, and various sugars and gums it has been shown that the temperature interval over which softening takes place has for its upper limit the lowest temperature at which thin threads may be drawn from the material, and for its lower that at which minute cracks appear in the surface when touched with a glass rod; these temperatures may be determined with ease to within $\pm 0.5^\circ$. At the lower limit the abnormal increase of specific heat commences and the volume isobars simultaneously exhibit a marked change of slope.

H. F. GILLBE.

Ceramic mixtures of high m. p. Systems kaolin-alumina-felspar and kaolin-zirconia-felspar. R. SCHWARZ and E. REIDT [with K. CHUDOKA] (*Z. anorg. Chem.*, 1929, 182, 1—18).—The softening points of mixtures of felspar and alumina, and of kaolin, alumina, and felspar, have been determined over a wide range of concentrations. The coefficients of linear expansion of certain mixtures have been determined, the results showing that increase of either the felspar or the alumina content of the three-component mixtures produces an increase of the coefficient of expansion. The resistance of the sintered mixtures to chemical action, measured by the loss of weight after heating with fusion mixture at 950° and treatment with hydrochloric acid, is roughly proportional to the porosity, and is a maximum when the ratio $\text{Al}_2\text{O}_3 : \text{SiO}_2$ is unity. The microscopic appearance of various specimens is described. Zirconia lowers the softening point of felspar in kaolin mixtures, and decreases the resistance to chemical action.

H. F. GILLBE.

Structure of gold-nickel alloys. W. HEIKE and H. KESSNER (*Z. anorg. Chem.*, 1929, 182, 272—280).—Hafner's view (*Diss.*, Freiberg-i.-S., 1927) of the mode of breakdown of gold-nickel mixed crystals appears in the light of microscopical investigation to be correct, in contradiction to Fraenkel and Stern's observations. Alloys rich in nickel undergo a far-

reaching change of structure when heated for a long period at 500 — 1000° . The most satisfactory etching solution for gold-nickel alloys is a hot solution of potassium sulphide.

H. F. GILLBE.

Stability of the hysteresis of iron-nickel alloys. G. GOSSELS (*Z. anorg. Chem.*, 1929, 182, 19—27).—The resistance isotherms of nickel-iron alloys containing up to 46% Ni have been determined from 0° to 900° . The maximum resistance is at 33.2% Ni, and has at 900° the value 132×10^{-6} ohm. Investigation of the stabilisation of alloys containing 9.6% Ni indicates that the resistance is unaltered by heating for several hours at 650 — 700° .

H. F. GILLBE.

Effect of pressure on the resistance of three series of alloys. P. W. BRIDGMAN (*Proc. Amer. Acad. Arts Sci.*, 1928, 63, 329—345).—The pressure and temperature coefficients of electrical resistance and the specific resistance at 30° have been determined for iron-cobalt, iron-nickel, and copper-nickel alloys. The results are discussed.

CHEMICAL ABSTRACTS

Dilatometric study of some univariant two-phase reactions. P. A. CHEVENARD, A. M. PORTEVIN, and X. F. WACHE (*Inst. Metals*, Sept., 1929, Advance copy, 29 pp.).—The changes taking place on the quenching and annealing of aluminium-rich aluminium-copper and aluminium-silicon alloys have been studied by dilatometric methods. The precipitation of silicon from solid solution in aluminium is accompanied by an expansion, an increase in hardness, and a decrease in the coefficient of expansion of the alloy. The precipitation of Al_2Cu from a super-saturated (quenched) solid solution by annealing above 175° causes an expansion, but ageing below 175° results in a contraction. It is concluded that most of the age-hardening of the aluminium-copper alloys at low temperatures cannot be due to the precipitation of Al_2Cu , but is the result of a reaction causing contraction; the nature of this is obscure, but is probably due to the combined influence of silicon and copper. The effect of the addition of copper to austenitic ferronickel alloys has been studied similarly. If sufficient copper be present two-phase alloys are formed, but the solubility increases with temperature, so that alloys can be obtained which are homogeneous on quenching, but precipitate a copper-rich constituent on annealing. These changes are in addition to the magnetic transformations, and the boundaries of the two-phase region in the equilibrium diagram have been determined for the iron-nickel-copper system.

W. HUME-ROTHERY.

X-Ray analysis of the iron-boron system. T. BJURSTROM and H. ARNFELT (*Z. physikal. Chem.*, 1929, B, 4, 469—474).—An X-ray analysis of iron-boron alloys, obtained by melting together technical ferroboron (19% boron) with iron, shows that within the range 0—19% B two phases, Fe_2B and FeB , occur. The first has a body-centred tetragonal lattice in agreement with the results of Wever. The lengths of the edges of the elementary parallelepipeds are $a_1=5.099$, $a_3=4.240$ Å. The unit cell contains four Fe_2B groups. The phase FeB has a rhombic lattice of which the parameters are $a_1=5.495$, $a_2=4.053$, $a_3=2.946$ Å. The elementary parallelepiped contains four FeB groups.

A. J. MEE.

X-Ray analysis of the copper-antimony and the silver-antimony systems. A. WESTGREN, G. HAGG, and S. ERIKSSON (*Z. physikal. Chem.*, 1929, B, 4, 453—468).—The observations are in agreement with the equilibrium diagram for the system obtained by Carpenter. Antimony can dissolve in copper up to a considerable concentration. The parameter of the copper lattice increases from 3.608 Å. for pure copper to 3.66 Å. for the alloy saturated with copper. At the ordinary temperature in the homogeneous region from 19 to 25 at.-% Sb there is a copper-antimony phase with hexagonal close packing, of which the lattice dimensions increase with increasing antimony concentration from $a_1=2.72$, $a_3=4.32$ Å., to $a_1=2.750$, $a_3=4.349$ Å. The Cu_2Sb phase has a simple tetragonal lattice with six atoms in the unit cell, of which the dimensions are $a_1=3.992$, $a_3=6.091$ Å. The alloy Cu_2Sb has obviously an analogous structure to Fe_2As . On this basis its structure can be calculated. The X-ray analysis of a series of silver-antimony alloys shows that the equilibrium diagram of Petrenko is incorrect. The maximum solubility of antimony in silver is about 5 at.-% Sb. The lattice parameter of the silver phase increases in the homogeneous region from 4.078 Å. for pure silver up to 4.113 Å. for the saturated phase. At the ordinary temperature between 10 and 16 at.-% Sb there is a phase with hexagonal close packing. The lattice dimensions increase with increasing antimony concentration from $a_1=2.921$, $a_3=4.775$ Å., up to $a_1=2.959$, $a_3=4.786$ Å. Between 20 and 25 at.-% Sb there is another intermediate phase which has a structure very similar to hexagonal close packing, but is really rhombic. The values for the parameters are: for 20%, $a_1=2.981$, $a_2=5.196$, $a_3=4.802$ Å.; for 25%, $a_1=2.988$, $a_2=5.239$, $a_3=4.842$ Å. A. J. MEE.

Determination of solubility of slightly soluble liquids in water and the solubilities of the dichloroethanes and dichloropropanes. P. GROSS (*J. Amer. Chem. Soc.*, 1929, 51, 2362—2366).—A saturated solution of the slightly soluble liquid is analysed by means of a liquid interferometer which has previously been calibrated against solutions of the liquid of known concentration. The following solubilities (g. per 100 g. of water at 25°) were determined: *s*-dichloroethane, 0.506; *as*-dichloroethane, 0.865; $\alpha\beta$ -dichloropropane, 0.280; $\alpha\gamma$ -dichloropropane, 0.273; carbon tetrachloride, 0.077 (provisional). S. K. TWEEDY.

Solubility of sodium and potassium hydroxides in methyl and ethyl alcohols. A. G. MURRAY (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 309).—Sodium or potassium hydroxide in excess was allowed to remain in contact with ethyl or methyl alcohol for a period of 3 weeks at about 28°. The clear supernatant liquid was decanted, diluted ten times, and titrated with *N*-sulphuric acid. The following solubilities (g. per 100 c.c.) are recorded: potassium hydroxide in ethyl alcohol 29, in methyl alcohol 40.3; sodium hydroxide in ethyl alcohol 13.6, in methyl alcohol 23.9. The densities and the solubilities expressed as percentages and normalities are also given. H. J. DOWDEN.

Influence of strong electrolytes on the solubility of potassium chlorate. J. HOLLUTA and F. PETER (*Z. physikal. Chem.*, 1929, 143, 119—134).—The solubility of potassium chlorate in water and in solutions of potassium chloride, nitrate, and sulphate, and sodium chloride and chlorate, has been measured at 25°, and at concentrations extending to the saturation point of the added salt. The solubility was raised by sodium chloride, and lowered by the remaining salts. The curves connecting the square root of the ionic strength with the reciprocal of the total molar concentration approximate to straight lines at low concentrations, except in the case of potassium nitrate, and from these curves the activity coefficients of potassium chlorate in the solutions were calculated. Calculation of the mean atomic radii by means of the Debye-Hückel expression lead to values considerably in excess of those calculated by Hückel, and of those arrived at by Goldschmidt from the results of crystal measurements, the differences being attributed partly to hydration. The solubility (η) of potassium chlorate in solutions of each of the salts (concentration = c) can be calculated by means of the expression $\eta = A + Bc$, A and B being constants the values of which are given. F. L. USHER.

Relation between sizes of ions and salting-out of quinol and quinone. K. LINDERSTRÖM-LANG (*Compt. rend. Trav. Lab. Carlsberg*, 1929, 17, No. 13, 1—6).—The effect of ammonium chloride and the alkylammonium chlorides on the solubility of benzoquinone and quinol in water at 18° can be represented fairly satisfactorily by the equation $\log(s_0/s) = kc$, where s is the solubility in a salt solution of concentration c , and s_0 is the solubility in pure water (cf. A., 1925, ii, 30). With quinol the value of the constant k decreases regularly with increase in the size of the salt cation, whilst with benzoquinone k scarcely varies at all. R. CUTHILL.

Theory of gas adsorption. A. MAGNUS (*Z. physikal. Chem.*, 1929, 142, 401—430; cf. A., 1927, 105).—A kinetic theory of the adsorption of gas molecules on surfaces is based on the assumption that the forces are purely electrostatic, due to either permanent or induced dipoles in the gaseous molecules. It is inferred that at very low pressures the amount adsorbed is proportional to the pressure, but this condition is rarely realised. By the use of Volmer's equation of state for the adsorbed substance, adsorption equations are obtained which are in good agreement with experiment. The dependence of the heat of adsorption on the gas pressure, predicted by the theory, corresponds qualitatively with that observed. J. A. V. BUTLER.

Heat of adsorption of oxygen and nitric oxide on charcoal. H. I. BULL and W. E. GARNER (*Nature*, 1929, 124, 409).—Repetition of the work of Garner and McKie (A., 1927, 1134), in which it is now shown that carbon is a relatively bad conductor in high vacua and that at low concentrations of oxygen the gas does not become uniformly distributed throughout the mass of the charcoal grains. For oxygen absorbed on charcoal the heat rises from 46 g.-cal. per mol. to 100 g.-cal. per mol., then falls to 65 g.-cal. per mol., and thereafter remains constant.

except for a curious type of alternation (cf. Marshall and Bramston-Cook, this vol., 999). For the same charcoal the maximum heat of absorption of nitric oxide occurs at higher surface concentrations than for oxygen, and alternation does not occur beyond the maximum. The presence of areas of different activities on the charcoal surface is indicated. The phenomena are probably due to incompleteness of the reaction between oxygen and carbon at low surface concentrations.

A. A. ELDRIDGE.

Adsorption phenomena in solutions. XVIII. Gas-free carbon as adsorbent. N. SCHILOV and K. TSCHMUTOV (Z. physikal. Chem., 1929, 143, 41—54).—In the adsorption of oxygen by gas-free carbon, carbon dioxide is always formed except at low pressures. Although oxygen, carbon dioxide, and hydrogen chloride are adsorbed by gas-free carbon, this material seems to be incapable of adsorbing potassium chloride from its aqueous solution. The primary stage of the adsorption is the formation of a film containing negatively charged ions, and the hydrolytic adsorption which follows has been studied by determination of the p_H changes.

H. F. GILLBE.

Adsorption of organic acids by charcoal. C. FROMAGEOT (Nature, 1929, 124, 412).—The author's results are correlated with those of Phelps and Peters (this vol., 1000).

A. A. ELDRIDGE.

Adsorption of fumaric and maleic acids by pure charcoals. H. J. PHELPS (J.C.S., 1929, 1724—1727; cf. Phelps and Peters, this vol., 1000).—The relation between the adsorption on pure charcoal and the ionisation of maleic and fumaric acids has been examined. The adsorption of both acids is zero at p_H 7, that of maleic acid rising steadily to p_H 1.5 (the most acid solution with which it was possible to work) with no indication of a maximum, whilst that of fumaric acid reaches a maximum at p_H 3.7. These results suggest that doubly-ionised molecules are not adsorbed in either case, and that the singly-ionised molecule of maleic acid is adsorbed, but to a smaller degree than the neutral molecule. These facts are consistent with the hypothesis that it is the oxygen of the un-ionised carboxyl group which holds the molecule on the charcoal surface, this attachment being effected probably by the presence of an electric charge, and, in the case of maleic acid, by the close proximity of the two carboxyl groups. Possibly also adsorption is hindered by the presence of the water sheath supposed to surround most ions.

C. A. SILBERRAD.

Adsorption hysteresis. A. R. URQUHART (J. Text. Inst., 1929, 20, 117—123r).—Previous work on adsorption hysteresis is reviewed and experimental results are described which show that the assumption of McGavack and Patrick (A., 1920, ii, 417), according to which hysteresis phenomena may be explained by the presence of residual traces of non-condensable gases in the material, is incapable of satisfying the conditions which obtain with cotton. That hysteresis in general cannot be so explained is proved experimentally by an investigation of the adsorption of water by silica gel in such circumstances that there could be no doubt about the removal of the last

traces of non-condensable gas. Two samples of the gel were used which gave different isotherms of the same general form, and definite hysteresis was observed in both cases.

B. P. RIDGE.

Adsorption by metallic hydroxides. VI. Adsorption of anions in relation to their coagulative action and their strength. VII. Adsorption isotherms and the mechanism of the adsorption of acids and bases by hydroxides. K. C. SEN (Z. anorg. Chem., 1929, 182, 118—128, 129—138).—Study of the adsorption of various acids, bases, and salts by ferric, aluminium, and chromic hydroxides shows the last-named to have the greatest adsorptive power. In all cases the adsorption follows a logarithmic law, but the quantity α adsorbed per unit weight of adsorbent is in certain cases dependent on the quantity of adsorbent used, the volume and concentration of the solution, and the physical nature of the hydroxide; with chromic hydroxide α varies also with time. For a fixed quantity of dissolved material α increases with increase of the quantity of adsorbent; heating decreases the adsorptive power. The adsorption of arsenious acid is irreversible only in the case of chromic hydroxide; different specimens of ferric and chromic hydroxides show different values of the adsorption constant. Arsenious acid and sodium arsenite are adsorbed to the same equivalent extent by aluminium hydroxide, but the acid is more readily adsorbed than the salt by chromic hydroxide. The adsorption of acids by the three hydroxides increases with the basicity of the acid, probably on account of complex formation. Citric acid, anomalously, is adsorbed by chromic hydroxide to a smaller extent than are oxalic and sulphuric acids. Other factors which influence the adsorption of acids, although to a smaller degree, are the strength and structure of the acid and the nature of the anion. Weiser's observations on the effect of neutral particles are confirmed. The second stage of the coagulation of a colloid by an electrolyte, viz., adsorption of ions by the neutralised particles, is a specific effect. The constant of the adsorption isotherms varies for each of the three hydroxides and even for different specimens of the same hydroxide. The mechanism of the adsorption process is ascribed to surface chemical activity, which is most in evidence when there is a tendency to salt formation between the adsorbent and material adsorbed. Chemical combination and adsorption are thus regarded as manifestations of the same forces.

H. F. GILLBE.

Adsorption of methylene-blue by lead sulphate. W. D. BANCROFT and C. E. BARNETT (Coll. Symp. Mon., 1928, 6, 73—76).—Lead sulphate crystals adsorb methylene-blue. For any concentration of dye, the amount adsorbed by a powdered solid is a function of the apparent p_H of the solution. The maximum adsorption of a dye by a crystal is not a measure of the total surface.

CHEMICAL ABSTRACTS.

Mechanism of the adsorption of water by cotton. A. R. URQUHART (J. Text. Inst., 1929, 20, 125—132r).—A theory is outlined which explains not only the hysteresis, but also most of the other hitherto unexplained phenomena observed with

cotton; it may also be applied to starch and to many elastic gels. It assumes that adsorption takes place in accordance with the number of free active hydroxyl groups on the micellar surfaces of the cellulose, and that absorption of water tends to restore the original orientation of the surface, so that the number of active groups increases. This increase is not so great as the original decrease which occurs when the cellulose is first formed in the cotton hair, since the amplitude of vibration of a molecule held to another by the attraction of one or more active groups will be less than that of a molecule with the active groups free, so that there is less tendency for a group to return to the surface than there was originally for it to leave it. Hence the adsorbing surface will be in a less active condition during adsorption than during desorption, and hysteresis will result.

B. P. RIDGE.

Two-phase theory of the absorption of water vapour by cotton cellulose. F. T. PEIRCE (J. Text. Inst., 1929, 20, 133—150r).—It is assumed that there are two distinct ways in which water molecules are held in the cellulose: (a) in which one water molecule is definitely associated with one hexose unit, as in a chemical compound, and (b) in which the water molecules fill the spaces available under attractive forces like those in a liquid. Mathematical treatment indicates how absorption isotherms and other experimental relations may be derived on the basis of the theory propounded.

B. P. RIDGE.

Absorption and adsorption of iodine by soils, and its elutriation. K. SCHARRER and J. SCHWABOLD (Z. anorg. Chem., 1929, 182, 193—206).—A variety of soils have been treated with iodine, iodides, iodates, and periodates, and considerable variation is found to exist in the quantities absorbed. By washing for many hours only a part of the iodine taken up is removed. Moor soils absorb greater quantities of iodine than do mineral soils, the quantities in the latter case being determined principally by the amount of colloidal material present. The quantity absorbed decreases in the order periodate, iodate, iodide, iodine following periodate in the case of mineral soils.

H. F. GILLBE.

Adsorption of sodium oleate at the air-water interface. M. E. LAING, J. W. MCBAIN, and E. W. HARRISON (Coll. Symp. Mon., 1928, 6, 63—72).—Contrary to the predictions of Gibbs' theorem, sodium oleate is positively adsorbed in the air-water interface. The adsorbed soap is in hydrolytic equilibrium with the solution, but its hydrolysis is completely suppressed by a small excess of alkali.

CHEMICAL ABSTRACTS.

Activity and adsorption of *p*-toluidine on the surface of its aqueous solution. J. W. MCBAIN, W. F. K. WYNNE-JONES, and F. H. POLLARD (Coll. Symp. Mon., 1928, 6, 57—62).—The partial pressure and activity of aqueous *p*-toluidine are proportional to the concentration. This supports the view that even in solutions far from saturated the surface is covered with a unimolecular film of solute, of which there is also an excess in the neighbourhood of the surface. Gibbs' thermodynamic treatment is insufficient.

CHEMICAL ABSTRACTS.

Interfacial tensions of water-*n*-butyl alcohol, water-*isobutyl* alcohol, and glycerol-*isobutyl* alcohol. K. SILBEREISEN (Z. physikal. Chem., 1929, 143, 157—166).—The interfacial tensions have been determined with a view to the use of these liquids in determining the pore diameter of ultra-filter membranes by Bechhold's method. A new apparatus making use of the capillary-rise method is described, and the interfacial tensions at temperatures from 1° to 37° are given.

F. L. USHER.

Relation between surface energy of liquids and saturation pressure. N. BARBULESCU (Bul. Soc. Stiinte Cluj, 1928, 4, 251—262; Chem. Zentr., 1929, i, 1427).—For non-associated liquids the surface tension is calculated from the molecular heat of vaporisation by a simplified method. For associated liquids a modified expression leads to good results with methyl alcohol, ethyl alcohol, and acetic acid.

A. A. ELDRIDGE.

Liquid-solid interface tension. M. LOEWENTHAL (Nature, 1929, 124, 301).—Experiments are described which demonstrate that the interfacial layer of mercury at the surface of a containing vessel is the seat of tension and potential energy.

A. A. ELDRIDGE.

Electrical relations at surfaces, spreading of liquids, thickness of surface films, and the drop-weight and ring methods for the determination of surface tension. W. D. HARKINS [with B. GINSBERG, D. M. GANS, and H. F. JORDAN] (Coll. Symp. Mon., 1928, 6, 17—40).—The behaviour of hexane emulsified in sodium oleate solution on passing a current through the liquid is discussed. Formulae for the spreading coefficient are developed and applied to the behaviour of films of benzene on water. Improvements in the ring method for determining surface tension are suggested.

CHEMICAL ABSTRACTS.

Internal pressures in adsorbed films. R. G. NUTTING (J. Wash. Acad. Sci., 1929, 19, 295—300).—An attempt is made to deduce energies of association and relations between internal and external pressures from weight-pressure and weight-temperature curves for dissolved or adsorbed vapours and gases. Expressions are deduced connecting the kinetic and cohesive pressures with concentration and temperature; these do not involve the use of an equation of state. Relations are also derived which connect surface tension with vapour pressure, and cohesive pressure in an adsorbed film with (i) vapour pressure and temperature, and (ii) osmotic pressure. The relations between adsorption and humidity and temperature are also discussed, the former with reference to silica (A., 1927, 509), and it is concluded that in the case of silica and water the inner layers are so compressed that the concentration is about 1.3, corresponding with an additional cohesive pressure of about 17,000 atm.

C. A. SILBERRAD.

Spreading of proteins. E. GORTER and F. GRENDL (Proc. K. Akad. Wetensch. Amsterdam 1929, 32, 770—771; cf. A., 1926, 790, 1094).—It has been found that various proteins have the same spreading-number, indicating that the surface occupied by 1 mg. of the substance is 1 sq. m. In aqueous

solution the molecules probably have their polar groups oriented towards the outer surface; when spread on an acid solution these groups are drawn to the surface and form a horizontal layer. The radius of the molecule is found to be 22.5 Å. and it appears that the spherical molecules are transformed into flat plates. Casein, hæmoglobin, and egg-albumin show the same transformation at the isoelectric point. The phenomenon is reversible.

N. M. BLIGH.

Preparation of dichroic gold-gelatin films. P. A. THIESSEN (Z. anorg. Chem., 1929, 182, 187—188).—In about 100 c.c. of a gold hydrosol, prepared by using sodium citrate as the reducing agent, 0.2 g. of gelatin is dissolved and the whole is evaporated to dryness. After washing free from electrolytes the material is dissolved in hot water, spread on a glass plate, and partly dried; it is then stretched to about double its length and dried, whereupon red and blue dichroism is clearly exhibited. H. F. GILLBE.

Ionic exchange peculiar to permutit. G. WIEGNER and K. W. MULLER (Z. Pflanz. Düng., 1929, 14A, 321—347).—In alcohol-water solution ionic exchange in permutits is reduced owing to the limited hydration of the ions. In aqueous sugar solutions the exchange of ions is but little affected. The dielectric properties of the dispersion medium cannot be correlated with altered ionic exchange as in the case of the alcohol-water mixtures. The capacity of these gels for ion exchange is largely influenced by their degree of dispersion. The molecules of sucrose and dextrose do not penetrate the fine framework of the gel because of their large diameters, and no regularised absorption is possible. The cations of methylene-blue undergo very little exchange with the permutit complex.

A. G. POLLARD.

Electrical method of measuring the concentration of suspensions. A. SLAWINSKI (J. Chim. phys., 1929, 26, 368—373).—Two glass tubes of the same size, with metal ends, are filled with the same suspension and one is placed vertical and one horizontal. The electrical conductivities are measured after the deposits have settled. Formulæ and tables are given for calculating the concentration. The method is more accurate than direct calculation from the conductivity (A., 1926, 1211) and is applicable to blood and to oil emulsions. J. A. V. BUTLER.

Dispersoid synthesis of gold by means of alkaline formaldehyde solutions. P. P. VON WEIMARN (Kolloid-Z., 1929, 48, 346—352).—A summary of several years' work on the synthesis of gold sols, the details of which have been published elsewhere (cf. this vol., 760). E. S. HEDGES.

Refractive indices of hydrosols. A. DUMANSKI and B. S. PUTSCHKOVSKI (Kolloid-Z., 1929, 48, 338—342).—The authors' formula for the refractive index of a hydrosol, $n = c_1^{n_1} n_2 / d_2 + n_1$, where n_1 and n_2 are respectively the refractive indices of the dispersion medium and of the disperse phase, c is the concentration, and d_2 the density of the disperse phase, agrees with the formula given by Wiegner (A., 1917, ii, 185). Data have been worked out for silicic

acid, stannic acid, molybdic acid, zinc hydroxide, casein, and dextrin. E. S. HEDGES.

Wo. Ostwald's "solid-phase rule" and the solubility of casein in sodium hydroxide. S. P. L. SØRENSEN and I. SLÁDEK (Compt. rend. Trav. Lab. Carlsberg, 1929, 17, No. 14, 1—35).—The fact that in the equilibrium between certain proteins and their saturated solutions in solutions of electrolytes the concentration of protein in the liquid phase is dependent on the ratio of the amount of solid to that of solvent can be explained by the assumption that the proteins are loose compounds of substances of differing solubilities just as satisfactorily as by Ostwald's "solid-phase rule" (A., 1927, 310). When casein is treated with an aqueous solution of sodium hydroxide and sodium chloride at 18°, the proportion which dissolves, Q , decreases with increase in the relative amount of solid, Z , and increases with increase in the hydrogen-ion activity, pa_H , of the solution. The concentration of casein in the solution at equilibrium, C , increases with increase in Z up to a point, after which it tends to fall again, probably owing to sodium hydroxide being bound by the solid phase. With a given salt concentration and value of Z , Q increases with increase in the concentration of sodium hydroxide, and the pa_H increases at the same time. For a fixed value of Z and pa_H , Q rises with the salt concentration, a result which, taken in conjunction with those of Linderstrøm-Lang and Kodama (A., 1925, ii, 1056), shows that the salt shifts the isoelectric point of casein towards the acid side. In general, the ratio of the amount of sodium hydroxide to that of casein is greater in the solution than in the solid phase. With a fixed concentration of alkali and a fixed value of Z , both Q and C rise continuously with the salt concentration up to about $2N$, beyond which they start to fall again; the pa_H decreases with increasing solubility. R. CUTHILL.

Structure viscosity of aqueous "solutions" of sulphonated oils. W. SCHINDLER and E. FLASCHNER (Kolloid-Z., 1929, 48, 328—338).—Measurements of the viscosity of aqueous solutions of sulphonated oils have been made by means of the overflow viscosimeter. Solutions of sulphonated castor oils exhibit considerable structure viscosity at p_H 7.8—8.0. In strongly alkaline solutions ($p_H > 10.0$) the phenomenon is less marked. The structure viscosity becomes observable at a definite concentration of solution. An emulsion of toluene with sulphonated castor oil and alkali has less structure viscosity than a solution of the sulphonated castor oil of the same concentration. Sulphonated train oil exhibits structure viscosity over a narrower range of hydrogen-ion concentration and in less intensity than sulphonated castor oil. E. S. HEDGES.

Dielectric polarisation of solutions of egg-albumin. (MLLE.) Y. GARREAU and N. MARINESCO (Compt. rend., 1929, 189, 331—333).—The ϵ - p_H curve at 20° for solutions of egg-albumin (fractionally precipitated by ammonium sulphate and purified by electro-dialysis) can be explained by the superposition of two opposite effects, namely, the amphoteric and hydrophilic effects for which ϵ is a minimum and maximum, respectively, at the isoelectric point, p_H

4.7 (cf. Marinesco, A., 1928, 1321). The presence in the sample of traces of adsorbed electrolytes may also modify the curve. J. GRANT.

Mechanism of gelatinisation. F. L. USHER (Proc. Roy. Soc., 1929, A, 125, 143—151).—Three possible types of mechanism for the gelation of sols are briefly discussed, and it is suggested that the behaviour of certain gelatinising lyophobic sols supports the theory which postulates a modification of the properties of the solvent in the vicinity of the disperse phase so as to produce a rigidity of the whole system, without necessitating any particular spacial arrangement of the solid units. From a consideration of the change in the disperse phase it is shown that, over a limited range of electrolyte concentration, collisions will result in the formation of linear aggregates rather than compact clusters, and if sufficiently close together these will tend to form a tangled network holding the liquid in its meshes. The above views are supported by microscopical observations on the formation of gels prepared from gamboge and cadmium sulphide by the addition of suitable concentrations of sodium chloride. A gel is regarded as an intermediate stage in the formation of a precipitate—a stage which, however, is realised only when the volume of the solid phase bears a large enough proportion to that of the liquid, and in the presence of a suitable electrolyte at a concentration lying between rather narrow limits. The suggested mechanism of gelatinisation is not applicable to turgescible substances, like gelatin or agar, or to gels formed in non-ionising liquids.

L. L. BIRCUMSHAW.

Swelling of gelatin in aqueous solutions of acids, bases, and salts and in mixtures of these. A. KÜNTZEL (Biochem. Z., 1929, 209, 326—437).—The swelling of gelatin in presence of electrolytes represents the result of "charge swelling," *i.e.*, the absorption of electrolytes and their charges, and of "peptisation swelling"; the former predominates in acid and alkaline solution and the latter in salt solutions. The former reaches a maximum for that concentration of electrolyte at which there is maximum adsorption. The amount of "charge swelling" is determined by the degree of adsorbability of both ions and is therefore small with neutral salts when both ions are approximately equally adsorbed and large with acids and bases. The union of gelatin with ions is regarded as one of adsorption and not of salt formation. According to their behaviour towards gelatin electrolytes can therefore be divided into cationophile (the cation is here more strongly adsorbed than the anion, *e.g.*, with acids, calcium chloride, etc.) and anionophile (the anion is more strongly adsorbed, *e.g.*, sodium hydroxide or chloride). Electrolytes of the same group show additive and of different groups antagonistic effects. If two antagonistic electrolytes added to gelatin are of such a kind that the protein adsorbs equal amounts of positive and negative charges, the gelatin is then in the isoelectric condition. This depends therefore on the concentration of the ions present and not merely on the concentration of hydrogen ions. The so-called second isoelectric point obtained with phosphate buffers corresponds

with a charge minimum and not with an inversion of charge. It is obtained only when the concentration of phosphate is greater than 0.005*M*. Peptisation occurring simultaneously with charge swelling causes a considerable increase of that effect. Different electrolytes have different peptising powers; the greater is the molar solubility the greater is the peptising power. The absolute amount of swelling is also affected by changes of dissolution swelling, *e.g.*, by increasing the time of the experiment and by changes of temperature, of ash and gelatose content, and of acid peptisation (cf. A., 1928, 237). P. W. CLUTTERBUCK.

Influence of volume in swelling. D. J. LLOYD (Kolloid-Z., 1929, 48, 342—345).—Measurements of the swelling of purified isoelectric gelatin in water, salt solutions, acids, and alkalis have been made. In pure water and in solutions of salts and acids the degree of swelling is independent of the volume, provided that no hydrolytic degradation of the gelatin occurs. In alkalis, a certain amount of hydrolysis always proceeds and the swelling therefore increases with greater volumes of swelling liquid. The influence of the volume of liquid on the swelling of commercial samples of gelatin is due to alteration of the relative concentration of electrolytes and degradation products present as impurities.

E. S. HEDGES.

Rôle of dielectric constants, polarisation, and dipole moments in colloid systems. V. Swelling of cellulose acetate in binary mixtures. I. I. SAKURADA (Kolloid-Z., 1929, 48, 353—361; cf. B., 1929, 713).—The swelling of acetone-soluble cellulose acetate in binary liquid mixtures of varying composition has been investigated by both volumetric and gravimetric analytical methods and has been compared with the polarisation curves of these mixtures. Weakly dipolar liquids, such as benzene, carbon tetrachloride, and carbon disulphide, do not cause swelling either singly or in pairs; the polarisation curves are linear and practically horizontal. As examples of mixtures of a non-polar with a dipolar liquid the following were examined: benzene with ethyl ether, toluene, chlorobenzene, nitrobenzene, chloroform, or ethyl acetate, and carbon tetrachloride with ethyl ether, ethyl acetate, or acetone. Certain mixtures (carbon tetrachloride with ethyl ether, ethyl acetate, or acetone) gave linear curves, but the majority of curves showed a bend. In these cases there was a correspondence between the swelling and polarisation curves, although in some instances (benzene with chloroform, carbon tetrachloride with ethyl acetate or acetone) the bends in the two curves are in opposite directions. The main result of the experiments is the establishment of a close relation between swelling and polarisation. E. S. HEDGES.

Effect of temperature on the coagulation of a colloidal solution of copper. E. F. BURTON and (Mrs.) B. R. DEACON (Coll. Symp. Mon., 1928, 6, 77—82).—When a colloidal solution of copper is heated in a copper tube a critical temperature above which coagulation takes place is observed.

CHEMICAL ABSTRACTS.

Coagulation of colloids by electrolytes. VI. Use of the glass electrode in the potentiometric

study of the coagulation process. A. J. RABINOVITSCH and V. A. KARGIN (*Z. physikal. Chem.*, 1929, 143, 21—40).—The properties of the Haber glass electrode have been studied in regard to its employment in the absolute determination of the p_H of solutions of weak acids. With change of the p_H of the solution the potential of the glass electrode exhibits a linear change which is, however, less than the change observed with the platinum electrode, and a further error is introduced by the difference of potential exhibited in solutions of the same p_H containing two acids of different dissociation constants. The errors may be eliminated by calibration of the electrode in buffer solutions of suitable p_H containing an acid having approximately the same dissociation constant as that of the acid to be investigated. With these precautions the glass electrode may be employed for the study of colloidal solutions. The end-point of a potentiometric acid-alkali titration obtained with the glass electrode agrees closely with that obtained when the platinum-hydrogen electrode is used, and p_H determinations correspond approximately with those calculated from conductivity data. Investigation of arsenious oxide sols with the aid of the glass electrode indicates the incorrectness of the view that at the conductimetric end-point of the titration all cations, irrespective of valency, are adsorbed to the same extent. For univalent cations the adsorption maximum is reached at considerably higher concentrations. If the curves showing the replacement of hydrogen ions by cations of various valency are assumed to be of approximately similar form to the adsorption isotherms for the corresponding cations, it is found that for cations of different valencies these curves are of different form, in contradiction to Freundlich's assumption. An abnormally high value has been established for the dissociation constant of the hydrogen sulphide adsorbed on the colloidal particles. H. F. GILLBE.

Inhibitive effect of starch on the velocity of coagulation of goethite sols by electrolytes. H. FREUNDLICH and B. S. GRENSFELDER (*Kolloid-Z.*, 1929, 48, 318—325).—The time-course of the coagulation by sodium sulphate of a goethite sol prepared from iron pentacarbonyl was followed by centrifuging the precipitate and titrating the remaining sol. Small amounts of starch have little effect on the rate of coagulation of the sol by sodium sulphate and sodium chloride, but larger amounts decrease the velocity greatly; still greater amounts of starch exert little further influence. The results suggest that a layer of starch of definite thickness is formed at the surface of the goethite particles and that protection reaches a maximum as soon as the layer is completed. The effect of the starch is irreversible, for subsequent dilution has little influence. The coagulation velocity of sols free from starch undergoes a steep rise over a small region of electrolyte concentration and reaches a constant value at a higher concentration of electrolyte. In presence of large amounts of starch, high concentrations of electrolytes give rise to a peptisation of the goethite sol. E. S. HEDGES.

Periodic precipitation in presence and absence of colloids. R. J. DOYLE and H. RYAN (*Proc. Roy.*

Irish Acad., 1929, 38B, 435—449).—Periodic precipitation of calcium phosphate occurs in the absence of colloids when capillary tubes containing calcium chloride solution are suspended with their open ends dipping in saturated sodium phosphate solution. The presence of glycerol or of a plug of gelatin in the tube reduces the speed of diffusion, but has no influence on the disposition of the rings. Experiments with lead nitrate and potassium iodide, also in the absence of gels, show that the distances of the bands from one another are in a geometrical progression (cf. Jabczyński, A., 1926, 473) and also proportional to the square root of the time. It is shown that the formation of the bands does not take place at the head of the diffusion wave, but behind it. Various suggested theories are discussed: that of Fischer (A., 1925, ii, 853) is the most satisfactory. The use of carrageen moss jelly for the preparation of Liesegang rings is described. C. W. GIBBY.

The Maxwell-Clausius relation without reference to Carnot's principle. V. KARPEN (*Compt. rend.*, 1929, 189, 359—360).—A reply to Verschaffelt (cf. this vol., 648), explaining in particular the term Kdv as representing the variation in intramolecular or kinetic energy. C. A. SILBERRAD.

Electrometric titration curves of dibasic acids. III. Substituted malonic acids. R. GANE and C. K. INGOLD (*J.C.S.*, 1929, 1691—1700).—The methods previously adopted (A., 1928, 846, 1083) have been applied to the determination of the distances (r) between the carboxyl groups of a series of alkylated malonic acids in order to examine the internal polar influences of the alkyl groups on the carboxyl groups, as these should in such a series constitute the main cause of disturbance in the spacial relations deduced from the valency deflexion hypothesis. The effects of solvation in augmenting, and of inductive electron attraction of the carboxyl groups in diminishing, the values of r are (as before) assumed to be nearly constant throughout the series, and practically eliminated by treating the results comparatively. The values obtained for $K_1 \times 10^4$, $K_2 \times 10^4$, and r are, respectively: malonic acid 17.7, 43.7, 1.54; methyl- 10.7, 34.3, 1.64; ethyl- 12.6, 28.1, 1.50; *n*-propyl- 10.7, 20.8, 1.47; isopropyl- 11.7, 15.9, 1.37; dimethyl- 8.27, 15.3, 1.45; diethyl- 62.3, 0.590, 0.71; di-*n*-propyl-malonic acid 86.7, 0.342, 0.64. The values of r are shown to be in accordance with expected results both as regards order and relative magnitude. The qualitative relations between the dissociation constants are also shown to be in accordance with those anticipated by the valency deflexion theory. C. A. SILBERRAD.

Idiomorphic crystals of cuprous oxide in copper. C. BLAZEY (*Inst. Metals*, Sept., 1929, Advance copy, 4 pp.).—The microstructure of a sample of copper containing 0.05% O showed small particles of cuprous oxide with well-developed crystal faces, in contrast to the usual rounded forms. The sample was found beneath the brick floor of a furnace, and must have melted with absorption of oxygen, and flowed between the furnace bricks, after which it was protected from surface oxidation, and remained for

nearly a year at a temperature which may have been more than 800°.

W. HUME-ROTHERY.

Hydrates of lithium chlorate. L. BERG (Z. anorg. Chem., 1929, 181, 131—136; cf. Kraus and Burgess, A., 1927, 627).—An investigation of the system lithium chlorate–water has furnished further evidence of the existence of the hydrate $3\text{LiClO}_3 \cdot \text{H}_2\text{O}$ (A., 1926, 1014).

J. S. CARTER.

Thermal analysis. Systems containing lead chloride or mercuric iodide as solvent. H. PELABON and (MME.) LANDE (Bull. Soc. chim., 1929, [iv], 45, 488—492).—Eutectic points have been observed in the following systems, at the temperatures and molecular compositions indicated: lead chloride–lead fluoride, 461.5°, 8.6% lead fluoride; lead chloride–litharge, 402°, 30% litharge; lead chloride–lead iodide, 338°; lead chloride–silver chloride, 291°, 61% silver chloride; lead chloride–cuprous chloride, 258°. The mean value of the cryoscopic constant of lead chloride is 464°. Cadmium iodide and mercuric iodide form a continuous series of mixed crystals. Mercuric iodide and mercurous iodide form a eutectic at 227°, containing 47.5 mol.-% of mercurous iodide. The curve could not be followed above a concentration of 70 mol.-% of mercurous iodide, on account of increasing decomposition of the latter above 290°.

C. W. GIBBY.

System sodium hydrogen carbonate–potassium hydrogen carbonate–water. N. E. OGLESBY (J. Amer. Chem. Soc., 1929, 51, 2352—2362).—Observations were made at 20°, 25°, and 30°, the sum of the partial pressures of the carbon dioxide and the water being maintained at 1 atm. The only solid phases found were sodium and potassium hydrogen carbonates. The solubility of the latter per 100 g. of water is 36.57 g. at 25° and 39.92 g. at 30°.

S. K. TWEEDY.

Ternary systems. VIII. Potassium carbonate, potassium sulphate, and water at 25°. A. E. HILL and S. MOSKOWITZ (J. Amer. Chem. Soc., 1929, 51, 2396—2398).—The solubility of the potassium sulphate is reduced to below 0.1% when the solution is still far from saturation with respect to carbonate, and to 0.03% at the saturation point. Solid solutions do not occur in the system.

S. K. TWEEDY.

System mercuric iodide, potassium iodide, and acetone. (MLLE.) M. PERNOT (Compt. rend., 1929, 189, 326—328).—Earlier experiments (this vol., 400) repeated at 20° give a curve with six instead of five branches; the results are said to be dependent on the method of preparation of the saturated solutions. The salt $\text{HgI}_2 \cdot \text{KI} \cdot 0.25\text{C}_2\text{H}_5\text{O}$ is indicated, but not $\text{HgI}_2 \cdot 2\text{KI}$ and $2\text{HgI}_2 \cdot 3\text{KI}$ (*loc. cit.*). J. GRANT.

Equilibria in the reduction, oxidation, and carburization of iron. VIII. System iron–oxygen. R. SCHENCK, T. DINGMANN, P. H. KIRSCHT, and H. WESSELKOCK (Z. anorg. Chem., 1929, 182, 97—117).—The oxidation of iron by carbon monoxide–carbon dioxide mixtures at 700°, 800°, and 1000° has been studied. Stable equilibrium between wüstite and oxoferrite is attained at these temperatures when the gaseous phase contains 40.3%, 35.1%, and

28.5% of carbon dioxide, respectively. The solubility of oxygen in the oxoferrite phase does not exceed 0.5% at 800° and 1000°, whilst the higher value, viz., 0.8%, observed at 700° is probably due to equilibrium not having been attained owing to the slowness of the reaction. Corrections have been made in the iron–oxygen diagrams previously given (Schenck and Dingmann, A., 1927, 1030). The question of the preparation of pure ferrous oxide is discussed; the stability of this compound is greatly increased by the presence of manganous or magnesium oxide. A state of stable equilibrium during the oxidation of iron by small quantities of carbon dioxide is reached much more readily in presence of small quantities (0.5—4.0%) of copper or nickel, whilst metastable phases are apparently not formed in appreciable quantity. The equilibrium is shifted somewhat towards the side of higher carbon dioxide percentages, and the oxygen content of the solid phase is considerably reduced, probably owing to the replacement by copper or nickel of the iron oxide in the mixed crystals.

H. F. GILLBE.

Heterogeneous equilibria in the gaseous phase in presence of appreciably volatile solids. K. JELLINEK (Z. physikal. Chem., 1929, 143, 69—78).—Mathematical. The equation of the reaction isochore of a heterogeneous gas equilibrium in presence of a solid of appreciable vapour pressure is discussed, particularly with reference to the relation between the calculated heat change and that observed calorimetrically.

H. F. GILLBE.

Thermodynamic consideration of certain reactions. I. BRICHTA (Arh. Hemiju, 1929, 3, 106—113).—The value of the Nernst theorem for the examination of certain reactions is pointed out, and the application of this theorem to a number of reactions, such as the synthesis of methane, of acetaldehyde, of methyl alcohol, etc. from carbon monoxide, hydrogen, and methane, is given.

R. TRUSZKOWSKI.

Heats of dissociation of the molecules CH, NH, OH, and HF. D. S. VILLARS (J. Amer. Chem. Soc., 1929, 51, 2374—2377).—By utilising principles discovered by Kuhn (A., 1926, 1192) and Mecke (A., 1927, 495) the above heats of dissociation are respectively calculated from band spectra data to be 82.0, 108.3, 138.0, and 172 kg.-cal.

S. K. TWEEDY.

Theoretical evaluation of the entropies of aqueous ions. W. M. LATIMER and C. KASPER (J. Amer. Chem. Soc., 1929, 51, 2293—2299).—The entropy change, ΔS , of the process: ion (g) = ion (aq.) is a function of e^2/r , where e is the ionic charge and r the radius of the ionic cavity in the water solution (Latimer and Buffington, A., 1926, 1102). Now ΔS is the sum of the entropy change, ΔS_1 , arising from the polarisability of the medium and of ΔS_2 due to the compressibility of the water arising from the electrostatic attraction of the water molecules. ΔS_1 cannot be calculated satisfactorily (Born's equation fails; Z. Physik, 1920, 1, 4) and in any case is very small compared with ΔS_2 , which is calculated thermodynamically, using Born's expression for ΔF_1 (F = free energy) for evaluating r , with the aid of Zwicky's relation between pressure, e , and r (A., 1926,

462). For large ions in water $\Delta S_2 = -22e^2/r$. In this way ΔS_2 (approximately ΔS) is calculated for alkali metals, thallium, silver, and barium. For large ions $\Delta S = 1.35 \times 10^{-4} \Delta F$, which is Latimer and Buffington's straight line relation. The electron affinities of chloride, bromide, and iodide ions, as calculated from the crystal lattice energies, lead to calculated values of ΔS which substantially agree with the experimental values. S. K. TWEEDY.

Calculation of heats of dilution of salts. J. B. GOEBEL (Z. physikal. Chem., 1929, 143, 167—171; cf. A., 1915, ii, 156).—The heat of dilution (U) of a salt solution can be calculated by means of a simple empirical formula $U = -13000(k_0' - k_0)(1 - 0.017t)(c_1 - c_2) + (209 + 4.5t)(\sqrt{c_1} - \sqrt{c_2})$, where k_0 is the equilibrium constant at 0° as determined by cryoscopic measurements, k_0' is an ideal equilibrium constant to which is assigned the value 0.265, c_1 and c_2 are respectively the initial and final concentrations, and t is the temperature. The heats of dilution of lithium, sodium, and potassium chlorides and of sodium and potassium nitrates are calculated for 33- and 50-fold dilutions over a temperature interval $0-26^\circ$, and compared with those measured by Naude (cf. A., 1928, 1097). The formula is also applied to the calculation of heats of dissociation.

F. L. USHER.

Reduction potential of selenious acid, free energy of aqueous selenic acid, and free energy of trichloride ion. E. F. IZARD (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 53—56).—The equilibrium constant for the reaction $X_2 + H_2SeO_3 + H_2O = H_2SeO_4 + 2HX$, where X is either chlorine or bromine, has the value 1.4×10^9 for the chlorine system and 0.88 for the bromine system, at 25° . From these figures the reduction potential of the reaction $H_2SeO_3 + H_2O = 3H^+ + HSeO_4^-$ is calculated to be -1.088 volts, which gives -107,710 g.-cal. for the free energy of $HSeO_4^-$.

The equilibrium constant of the reaction $Br_2 + Br^- = Br_3^-$ has been obtained by a distribution method, and that of the reaction $Cl_2 + Cl^- = Cl_3^-$ by determining the solubility of chlorine in aqueous solutions of sulphuric and hydrochloric acids and the chlorides of sodium, potassium, and barium at 25° . The equilibrium constant for the latter reaction has the value 0.010, which gives the figure of -28,637 g.-cal. for the free energy of the trichloride ion.

R. CUTHILL.

Electrical conductivity of ethyl alcohol and its aqueous solutions. M. CHANOT and G. CLUZET (Compt. rend. Soc. Biol., 1929, 99, 1999—2001; Chem. Zentr., 1929, i, 1661).—The electrical conductivity of absolute alcohol is smaller than that of distilled water; it increases on dilution, being maximal at 3% of alcohol. The simple ionisation $C_2H_5^+$, OH^- is impossible. A. A. ELDRIDGE.

Effect of adsorbed water on the electrical conductivity of powders. F. B. KENRICK and F. J. GIFFEN (Coll. Symp. Mon., 1928, 6, 53—56).

Surface conductance. D. R. BRIGGS (Coll. Symp. Mon., 1928, 6, 41—52).—In aqueous solutions of low specific conductivity present in the interstices of a diaphragm, the electrical conductance through

the interface phase is greater than that through an equal volume of liquid in bulk. A method for the determination of surface conductance of diaphragms is described. Salt solutions show definite valency and lyotropic effects.

CHEMICAL ABSTRACTS.

Capacity of certain saturated complex compounds for further combination. O. E. ZVJAGINSTSEV (J. Russ. Phys. Chem. Soc., 1929, 61, 515—519).—Measurements of the electrical conductivity of solutions of Wilm's salt, $(NH_4)_3[RhCl_6] \cdot NH_4NO_3$, indicate that this dissociates with the formation of five ions, viz., $3NH_4^+$, NO_3^- , and $[RhCl_6NH_4]^-$. This bivalent complex ion appears to act as a secondary complex-forming radical.

R. TRUSZKOWSKI.

Mechanism of ionic conduction in solid compounds [of the class of] "good conductors." A. SMEKAL (Z. physikal. Chem., 1929, B, 5, 60—80; cf. A., 1928, 1330; this vol., 871).—A theoretical discussion of the mechanism of electrical conduction in solid salts, of which the greater part has been previously abstracted. The large differences observed in the conduction by silver and sodium halides are due, not to different mechanisms, but to the relative importance of the contributions of the lattice ions and the "pore" ions to the total conductivity in the two cases. The mobile "pore" ions are identified with the "edge" ions of Blüh and Jost (cf. this vol. 32).

F. L. USHER.

Spectroscopic and chemical investigation of the phenomena at the boundary of an aqueous electrolyte and a gas space on the passage of a discharge. W. R. COUSINS (Z. physikal. Chem., 1929, B, 4, 440—452).—If in the electrolysis of sulphuric or phosphoric acid, sodium hydroxide, or silver nitrate, the anode is placed in the electrolyte and the cathode in the gaseous space above the liquid, which contains only water vapour corresponding with the saturation pressure of the electrolyte and its decomposition products brought about by the passage of the discharge, the light appearing in the gaseous layer at the surface of the liquid contains the spectra of the hydroxyl group and of atomic hydrogen. If the position of the electrodes is reversed, the anode being placed in the gas space, the spectrum of the singly-charged oxygen ion together with the weak spectrum of the uncharged oxygen atom is obtained. This has some bearing on the formation of persulphuric acid and Caro's acid observed by Haber and Klemenc in the electrolysis of concentrated sulphuric acid by this method. The probable explanation of the reaction is as follows. In the first case, with the cathode in the gaseous space, very little of these acids is obtained. In the second case, where the anode is outside, large quantities are formed. This may be due to the fact that in the former case there is very little oxidising action due to the hydroxyl group in the gaseous space, whilst in the latter there will be a very much greater oxidising effect owing to the presence of oxygen ions and atoms.

A. J. MEE.

Contact potential between [pieces of] the same metal. W. ENDE (Physikal. Z., 1929, 30, 477—480).—Contact potential differences between pieces of the same metal have been measured for brass, nickel, and platinum in air and in a vacuum (with

and without cooling by means of liquid air) the surface condition being varied with the object of finding conditions for minimum *P.D.* values. Satisfactory results (*P.D.* < 0.05 volt) are obtained when the surface layer of a hard metal is removed by sawing, turning, scraping, or treatment with a sand blast. Unsatisfactory results are given by washing, corrosion, and especially by treatment with all grades of emery paper. Reproducible contact potential differences below 0.05 volt could not be obtained with platinum.

R. A. MORTON.

Potential of carbohydrate solutions. (MLLE.) N. MAYER (Compt. rend., 1929, 189, 319—321).—The results obtained by Wurmser and Geloso (A., 1928, 846) for dextrose and laevulose apply also to lactose, galactose, mannose, xylose, arabinose, and dihydroxyacetone. Variations in concentration of xylose (0.1—2.5%) do not appreciably affect the potential.

J. GRANT.

Reduction potential of thiosulphate. J. SCHEFFER and F. BOHM (Z. Elektrochem., 1929, 35, 484—486).—The potential between a platinised platinum electrode and a solution containing thio-sulphate and tetrathionate ions and buffered with phosphate mixture at p_H 7 changes considerably on keeping the solution in an atmosphere of nitrogen. Values of the normal oxidation-reduction potential, varying from 0.346 to 0.405 volt referred to the normal hydrogen electrode were obtained by extrapolation from the observed potentials of platinum electrodes in solutions prepared from sodium thio-sulphate and potassium ferricyanide and buffered at p_H 7.

H. T. S. BRITTON.

Oxidation-reduction potentials of some vital stains. L. RAPKINE, A. P. STRUYK, and R. WURMSER (J. Chim. phys., 1929, 26, 340—348).—The oxidation potentials of cresol-blue, toluidine-blue, azure-blue I, Nile-blue, cresol-violet, Janus-green, neutral-red, and Unna's neutral-violet have been determined by electrometric titration with titanous chloride solutions over a range of p_H values. The potential corresponding with an equimolecular mixture of oxidant and reductant is plotted against p_H for each substance. The results show that these substances give sufficiently definite oxidation potentials for use in determining the potentials of living cells.

J. A. V. BUTLER.

Polarisation in standard cells. W. S. NIEDERHAUSER and G. S. HULETT (J. Amer. Chem. Soc., 1929, 51, 2327—2344).—Neutral saturated and unsaturated cadmium cells and zinc cells all behave similarly during the passage of current through the cell, the bulk of the polarisation occurring at the mercury electrode. On discharge, the greater polarisation occurs at the amalgam electrode. When polarisation is produced by large currents (1.7 milliamp., higher in presence of acid) a persistent recovery effect is observed at the mercury electrode, which markedly changes the subsequent behaviour of the cell during polarisation. This recovery effect disappears if the solid mercurous sulphate is removed; it is attributed to increase in the rates of dissolution and crystallisation at the surfaces of the sulphate crystals. The polarisation is diminished on addition

of acid and is always unaccompanied by any appreciable change in the resistance of the cell. A full discussion is given; the electrolytic actions at the mercury electrode of the standard cell appear not to be strictly reversible. The currents used when measuring cell potentials by the deflexion method are sufficient to produce polarisation, but the error introduced thereby is usually negligible.

S. K. TWEEDY.

Hysteresis in standard cells. W. E. NIEDERHAUSER and G. A. HULETT (J. Amer. Chem. Soc., 1929, 51, 2345—2351).—The hysteresis of the separate electrodes of the cadmium cell has been investigated experimentally for the sudden temperature drop from 35° to 25°. The magnitude of the hysteresis at the anode depends on the size of the cadmium sulphate crystals; it is practically zero when this size is very small. The effect is much more persistent at the cathode, but is completely absent when no solid mercurous sulphate is present. Hysteresis at the anode is explained by the rise in temperature producing a more concentrated, and therefore denser, cadmium sulphate solution, which descends to the amalgam surface; on cooling, the more concentrated solution can deposit its excess salt only on the crystals, and since it can reach these crystals only by slow upward diffusion a hysteresis effect occurs. When the crystals are large the diffusion distances are greater and the available surface is less, so the effect is prolonged. An analogous explanation, referred to mercurous sulphate, probably also holds for the cathode. Acid appears to diminish the hysteresis by decreasing the rates of crystallisation and dissolution at the crystal surfaces. Decrease in the magnitude of the hysteresis due to age is attributed to the crystals assuming a more perfect shape on keeping, with a consequent lowering in the rate of dissolution or crystallisation. The high *E.M.F.* of freshly-prepared cells is due, at least in part, to hysteresis consequent on the overheating of the cells during preparation. A method of avoiding this overheating is described; by this cells were made which show normal constant values within a few hours of assembling.

S. K. TWEEDY.

Flame speeds and their calculation. W. PAYMAN and R. V. WHEELER.—See B., 1929, 666.

Gaseous combustion at high pressures. XIII. Molecular heats of nitrogen, steam, and carbon dioxide at high temperatures. D. M. NEWITT (Proc. Roy. Soc., 1929, A, 125, 119—134; cf. A., 1928, 847).—Data accumulated during previous researches are analysed, with the object of obtaining a quantitative estimate of the energy distribution at the moment of maximum pressure in typical explosions at high pressures, and also of calculating the mean heat capacities of the various explosion products over a temperature range from 15° up to various definite points between 2600° and 3000°. Data derived from explosions at high initial pressures (1) of theoretical hydrogen-oxygen mixtures diluted with either argon or nitrogen and (2) of carbon monoxide-oxygen mixtures containing excess of the combustible gas are used to calculate the mean molecular heats of carbon dioxide, steam, and nitrogen. The method used to

calculate C_p for nitrogen depends on the assumption that C_p for the monatomic gas argon is independent of temperature. By exploding a series of $2\text{H}_2 + \text{O}_2$ mixtures diluted with argon or nitrogen in varying proportions, the compositions of pairs of mixtures which on explosion will attain the same mean maximum temperature may be found by interpolation. In this way values are obtained for the apparent mean molecular heats of nitrogen at the various temperatures, but in order to allow for the fact that the heat losses for the two mixtures are not the same, a second series of explosions of the nitrogen mixtures must be carried out at a different initial pressure. An equation is given from which the true C_p may be calculated. From this value and from a knowledge of the heat of combustion of hydrogen and the degree of dissociation of steam, the mean molecular heat of steam may be calculated. In the case of carbon dioxide, the results of a series of explosions of the mixture $2\text{CO} + \text{O}_2 + 4\text{CO}$ between initial pressures of 50 and 150 atm. are utilised. The results are discussed and compared with those obtained by previous investigators. The values for steam are by no means concordant. In the case of nitrogen, the values are in general higher than those found by Pier and Bjerrum and may be represented by $C_p = 4.87 + 0.000387T$ in place of $C_p = 4.85 + 0.000375T$.

L. L. BIRCUMSHAW.

Ignition of electrolytic gas. I. FARKAS, P. GOLDFINGER, and F. HABER (*Naturwiss.*, 1929, 17, 674; cf. this vol., 11, 278).—Earlier work on the suggested chain mechanism for the ignition of electrolytic gas has been confirmed and extended. Atomic oxygen or atomic hydrogen present in minute amount renders electrolytic gas immediately explosive. Further control experiments strengthen the case in favour of the chain mechanism. R. A. MORTON.

Rate of dissociation of nitrogen tetroxide.

A. R. OLSON and C. E. TEETER, jun. (*Nature*, 1929, 124, 444—445).—For nitrogen tetroxide containing 0.1% of air the velocity of sound is 192.6 m. per sec. at 25° and 565 mm., at a frequency of 51570 vibrations per sec., corresponding with a velocity coefficient 5630.

A. A. ELDRIDGE.

Unimolecular decomposition of some ethers in the gaseous state. J. V. S. GLASS and C. N. HINSHELWOOD (*J.C.S.*, 1929, 1804—1814).—The rates of decomposition of methyl ethyl, methyl propyl, and diisopropyl ethers in the gaseous state have been investigated (cf. A., 1927, 212, 630). The decomposition of methyl ethyl ether is mainly homogeneous, but partly heterogeneous at lower temperatures. The reaction is not a simple unimolecular one, acceleration by the products and intermediate formation of aldehyde causing the coefficient to increase for the first 25% of the reaction, but the times required for a given fraction to decompose are independent of the initial pressure. The heat of activation is 47,000 g.-cal. per mol. Methyl propyl ether decomposes, giving mainly carbon monoxide, methane, and ethane, not more than 10% giving carbon monoxide, hydrogen, and propane. The reaction is mainly homogeneous in an empty silica bulb, a 16-fold increase in the surface: volume ratio causing but little disturbance. The heat

of activation is 49,000 g.-cal. per mol. Diisopropyl ether can decompose in three ways: $\text{C}_3\text{H}_7\cdot\text{O}\cdot\text{C}_3\text{H}_7$ (a) $= \text{CO} + 3\text{CH}_4 + 0.5\text{C}_2\text{H}_4 + \text{C}$, a homogeneous unimolecular reaction, (b) $= 2\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2 + \text{H}_2\text{O}$, a surface reaction, (c) $= \text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 + \text{C}_3\text{H}_8$, probably homogeneous, accompanying (a) to a slight extent. The velocity of (a) is independent of pressure between 327 and 29 mm. With methyl ethyl ether and methyl propyl ether the presence of hydrogen raises the velocity coefficients, which diminish at low pressures.

C. W. GIBBY.

Hydration of ions and molecules. III. Velocities of hydration and dehydration. N. E. GAPON (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 375—380).—The velocity coefficient K_1 for the hydration of green chromic chloride remains constant at 0.0055 until 1 mol. of water has been added, when it suddenly falls to $K_2 = 0.00030$ and again remains constant until another molecule of water has been added. From the formula $L = SF(KT/2-m)e^{-W/RT}$ it is possible to calculate the number of mols. of water liberated on crystallisation of a particular salt when a crystallisation centre is present in the solution. In this equation L is the number of mols. striking the crystallising centre in unit time, i.e., the number of mols. which can be dehydrated, S is the number of mols. present in solution, F the area of the solid phase, K is Boltzmann's constant, m the mass of a molecule, and W the energy of dehydration which can be calculated from the observed velocities of crystallisation at different temperatures. From the values of W calculated from the results of Marc (A., 1909, ii, 798) and of Fischer the following values for m are calculated: potassium sulphate, 4; ammonium oxalate, 3; sodium oxalate, 3; sodium picrate, 3; potassium alum, 4; and ammonium alum, 3. The results are of the same order as those found by other workers by different methods. A. FREIMAN.

Mechanism of oxidative processes. XVII. Ratio of oxidation velocities of molecular oxygen and hydrogen peroxide. H. WIELAND and W. FRANKE (*Annalen*, 1929, 473, 289—300).—When a solution of potassium hexacyanocobaltate is shaken with oxygen, air, or a 3% oxygen-nitrogen mixture, diminishing amounts of oxygen are absorbed with decrease in oxygen concentration. The amounts of hydrogen peroxide produced decrease in the same order; almost the theoretical amount is obtained with pure oxygen. With the dilute oxygen mixtures, the peroxide formed takes part in the oxidation. Simultaneous oxidation with hydrogen peroxide and oxygen and determination of the amount of peroxide used shows that the reaction velocity for oxygen is about five times as great as for hydrogen peroxide. With benzoquinone (in an atmosphere of nitrogen) and methylene-blue as hydrogen acceptors oxidation of the cobaltate also occurs. Autoxidation of a cuprous chloride solution with oxygen at various p_{H} values (cf. A., 1924, ii, 35) shows that in strongly acid solution oxygen is consumed more rapidly than at p_{H} 2.3—7; the formation of hydrogen peroxide is detectable only in acid solution (cf. *loc. cit.*). The velocity of oxidation with peroxide decreases with increasing acidity, and oxidation is more rapid with

oxygen at all hydrogen-ion concentrations. The velocity of oxidation of ferrous sulphate with hydrogen peroxide at $p_H < 7$ is much greater than for autoxidation. Thus, at 5 and 4 oxidation is 2000—3000 times as great as with peroxide. In strongly acid solution autoxidation is extraordinarily slow (cf. A., 1928, 965), and the results show that intermediate formation of detectable amounts of hydrogen peroxide during autoxidation is excluded. H. BURTON.

Velocity of oxidation of hydrogen bromide by chromium trioxide in presence of chlorides, and the catalytic influence of the manganous ion. II. M. BOBTELSKY and A. ROSENBERG (Z. anorg. Chem., 1929, 182, 74—92).—At low concentrations all chlorides exert a retarding influence on the oxidation of hydrogen bromide by chromium trioxide, the optimum chloride concentration being about N . No specific action has been observed, even hydrogen chloride acting as an ordinary univalent chloride; the activity decreases as the valency of the cation increases. In highly concentrated solutions the retardation produced by the alkali chlorides is but slight, whereas that caused by zinc, cadmium, and mercuric chlorides is very great; other chlorides accelerate the reaction, their influence diminishing in the order nickel, magnesium, ferric iron, hydrogen, aluminium, chromic chromium. The only chlorides which tend to be attacked by the chromium trioxide are those of magnesium, ferric iron, and manganese, and there appears to be no relationship between this phenomenon and the catalysis of the oxidation process. The influence of the two neutral chlorides when present simultaneously is less than the sum of their separate influences. The catalytic influence of the manganese ion in dilute solution is exceptional, being greatly increased by the presence of neutral chlorides but nevertheless influenced by the nature of the neutral salt present; the order in which chlorides which have when alone a retarding action increase the activity is that in which they accelerate the reaction in concentrated solution. H. F. GILLBE.

Reaction velocity of iodine with sodium formate in presence of concentrated electrolytes. M. BOBTELSKY and D. KAPLAN [with (FRL.) C. DIESENHAUS] (Z. anorg. Chem., 1929, 182, 382—394).—The reaction between iodine and sodium formate is exceedingly sensitive to hydrogen ions, which at N concentration reduce the reaction velocity coefficient to less than 2% of its value in neutral solution. The influence of other cations is thus largely, if not entirely, governed by the extent to which the salt is hydrolysed. In general chlorides and sulphates at concentrations from N to $6N$ retard the reaction, the specific influence of the cations decreasing in the order aluminium, nickel, zinc, magnesium, calcium, strontium, barium, sodium, potassium; cobalt and manganese have approximately the same activity as nickel, and ammonium the same as sodium. At concentrations below about $3N$, cadmium salts accelerate the reaction, but at higher concentrations retardation is produced. The retarding influence of anions is relatively small, and for the halogens decreases with increase of at. wt., fluorine having a slight accelerative influence, whilst

the reaction velocity in presence of the sulphate, acetate, and perchlorate ions scarcely differs from that of the uncatalysed reaction. The presence at high concentrations of electrolytes which have a powerful retarding influence tends to arrest the retardation produced by the cation.

H. F. GILLBE.

Velocity of reaction between sodium hydroxide solution and carbon dioxide. S. MITSUKURI (Sci. Rep. Tôhoku, 1929, 18, 245—297).—The velocity of the reaction between carbon dioxide and aqueous solutions of sodium hydroxide of concentrations varying from N to about $9N$ has been investigated between 10° and 30° by observations on the absorption of gas from bubbles rising in a stationary solution and from bubbles stationary in a moving solution and the absorption at the surface of falling drops of solution and at the surface of stationary solutions in bulk. The results can be qualitatively accounted for by supposing the rate of absorption to depend on the rate of the chemical reaction at the interface and the rate of diffusion of alkali through a thin film of liquid at the interface, the thickness of which increases with increase in the viscosity of the solution. It is assumed that the chemical reaction is truly heterogeneous in character. In the absorption by the surface of solution in bulk, the rate of diffusion from the body of the solution is so rapid that the concentration of alkali on the lower side of the surface film, and therefore on the surface itself, is kept appreciably constant. If, however, the solution is stiffened with gelatin, diffusion is retarded, and the concentration of alkali in the surface falls gradually at first as absorption proceeds. R. CUTHILL.

Different reduction velocities of gold chloride by arsenious oxide, dissolved as glass or crystal. E. JENCKEL (Z. anorg. Chem., 1929, 182, 314—318).—Solutions of arsenious oxide prepared from the vitreous modification reduce gold chloride four to five times as rapidly as do solutions prepared from the crystalline form. Although the rate of dissolution in water of the vitreous oxide is much greater than that of the crystalline material, there is no appreciable difference in the velocity of deposition from supersaturated solutions. It is concluded that there exist anisotropic molecules which only slowly lose their anisotropic properties. H. F. GILLBE.

Esterification of formic acid in methyl alcohol. H. GOLDSCHMIDT and R. S. MELBYE (Z. physikal. Chem., 1929, 143, 139—156).—The rate of esterification of formic acid in methyl alcohol in the presence of hydrogen chloride, picric acid, trinitro-*m*-cresol, or trichlorobutyric acid as catalyst is proportional to the hydrogen-ion concentration of these substances in the respective solutions. Water exercises a powerful retarding influence on the esterification in the presence of hydrogen chloride. In the absence of any catalyst the reaction is bimolecular, and is very sensitive to traces of water or basic impurities. Addition of sodium formate causes a large diminution in the velocity up to a concentration of $0.025N$, above which it remains sensibly constant. It is concluded that the hydrogen ions arising from the dissociation of the formic acid play the same part in the esterification

as those furnished by the catalysts named above. The degree of dissociation of formic acid in methyl-alcoholic solution, obtained from the results of measurements of the alcoholysis constant, is given as $\alpha = (5.07 \times 10^{-9}/c)^{1/2}$, where c is the concentration of the acid. F. L. USHER.

Possibility of characterising kinetic processes in heterogeneous systems by a single stirring factor. W. HELLER (Z. physikal. Chem., 1929, **142**, 431—452).—The influence of temperature and rate of stirring on the velocity of dissolution of tin and cadmium in ferric chloride solutions and of magnesium in ammonium chloride solutions has been studied. The results can be expressed by equations of the type $k = (An + C_0)(t - \tau)$, where k is the velocity coefficient of the reaction, t the temperature, and n the rate of revolution of the stirrer. A , C_0 , and τ are constants, C_0 and τ being characteristic of the reaction and independent of the form of the apparatus, whilst A depends on both the reaction and the apparatus. The values of A in two different types of apparatus vary in the same proportion for different reactions, so that $A - A_0k$, where A_0 is the value in a "normal apparatus" and k is a constant which depends on the type of apparatus only. This constant can be found for a given type of apparatus, so that measurements may be referred to the "normal apparatus" only.

J. A. V. BUTLER.

Optical investigation of the passivity of metals. L. TRONSTAD (Nature, 1929, **124**, 373).—The oxide film on passive iron or nickel is not totally destroyed on activation, but becomes porous and spongy; on re-passivation the holes are refilled with oxide, and the film becomes thicker. A. A. ELDRIDGE.

Atmospheric corrosion of metals. J. C. HUDSON.—See B., 1929, 684.

Corrosion of steel in dilute acids. H. ENDO and K. NAKAWAGA.—See B., 1929, 751.

Homogeneous catalysis of a gaseous reaction. Kinetics of the catalytic decomposition of isopropyl ether. J. V. S. GLASS and C. N. HINSHELWOOD (J.C.S., 1929, 1815—1819).—The decomposition of gaseous isopropyl ether in accordance with the equation $C_3H_7 \cdot O \cdot C_3H_7 \rightarrow CH_3 \cdot CO \cdot CH_3 + C_3H_8$ is catalysed by isopropyl iodide, in virtue of the iodine produced by the decomposition of the latter.

The reaction is homogeneous, and the rate is proportional to the concentrations of ether and of isopropyl iodide. The heat of activation is $28,500 \pm 500$ g.-cal. per mol. C. W. GIBBY.

Air oxidation of hydrocarbons catalysed by nitrogen oxides. C. H. BIBB and H. J. LUCAS.—See B., 1929, 667.

Combination of hydrogen and oxygen on the surface of platinum. R. P. DONNELLY and C. N. HINSHELWOOD (J.C.S., 1929, 1727—1733).—The rate of combination of hydrogen and oxygen on the surface of platinum at ordinary pressures is independent of the hydrogen pressure, and increases with the oxygen pressure, the effect being the more marked the higher is the pressure. This differs from the behaviour observed at low pressures by Langmuir (A., 1922, ii, 629). It is concluded that in general, if

the law followed by a heterogeneous reaction changes with pressure; the centres on which reaction predominates also change with pressure. The presence of nitrogen or argon reduced the temperature to which the platinum could be heated without causing explosion; the presence of nitrogen peroxide reduced the rate. C. W. GIBBY.

Reduction of azoimide by hydrogen in presence of colloidal palladium. B. RICCA and F. PIRRONI (Gazzetta, 1929, **59**, 379—384).—The reducing action of molecular hydrogen on an alkaline solution of azoimide in presence of colloidal palladium is very slight, but in acid solution reduction takes place to completion with the formation of ammonia and hydrazine. The latter product is recognised after separation of the colloidal palladium by dialysis. The same result is obtained by the action of nascent hydrogen from zinc or iron and hydrochloric acid. The equation $HN_3 + 6H = NH_3 + N_2H_4$ is suggested (cf. Raschig, A., 1925, ii, 223). R. K. CALLOW.

Mechanism of the catalytic decomposition of hydrogen peroxide on colloidal silver. E. WIEGEL (Z. physikal. Chem., 1929, **143**, 81—93; cf. this vol., 643).—When a highly disperse Carey Lea silver sol prepared with alkaline dextrin is added gradually to excess of 5—10% hydrogen peroxide, the silver at first dissolves until a saturated (true) solution of $Ag \cdot O \cdot OH$ is produced. The quantity thus dissolved varies inversely with the concentration of alkali. After the saturation point has been reached further addition of the sol leads to deposition of silver from the solution on the particles introduced, with simultaneous liberation of oxygen. Evidence is given in support of the view that the dissolved silver hydrogen peroxide, when adsorbed at the silver interface, decomposes into hydrogen peroxide and silver peroxide, the latter then losing its oxygen. Since the metal is dissolved by hydrogen peroxide, so long as any of the latter remains this cycle is repeated, until the whole of the peroxide is decomposed. The process is accompanied by a large decrease in the total silver surface. F. L. USHER.

Topochemistry of contact catalysis. IV. Experimental proof of adlineation by topochemical reactions. E. PIETSCH, A. KOTOWSKI, and G. BEREND (Z. physikal. Chem., 1929, **B**, **5**, 1—13; cf. this vol., 519).—A number of topochemical changes occurring on the surfaces of various crystals, in which the reaction products contrast in colour with the attacked crystals, have been observed microscopically and photographed. Definite proof is obtained that the active centres of reaction are linear discontinuities in the surface (as assumed in the general theory of surface catalysis of Schwab and Pietsch), since in all cases the reaction is sharply localised at these parts before the entire surface becomes involved.

F. L. USHER.

Organic inhibitors in the acid corrosion of iron. J. C. WARNER.—See B., 1929, 751.

Decomposition of carbon monoxide in the silent electric discharge. III. R. W. LUNT and L. S. MUMFORD (J.C.S., 1929, 1711—1723; cf. A., 1925, ii, 1178; 1927, 531).—The velocity of

decomposition of carbon monoxide in the silent electric discharge is independent of the nature of the electrodes when the latter consist of mercury or dilute sulphuric acid. This is in agreement with the results of Berthelot (A., 1890, 691, 692), but not with those of Schutzenberger (A., 1890, 691, 692, 1358). With either kind of electrode carbon monoxide decomposes readily, even when very carefully dried. The brown solid produced during the discharge is not entirely polymerised malonic anhydride (cf. Ott, A., 1925, ii, 579; 1928, 720), but is probably a mixture containing carbon.

C. W. GIBBY.

Activation of sulphur. R. SCHWARZ and P. W. SCHENK (Z. anorg. Chem., 1929, 182, 145—158).—Activation of sulphur has been accomplished by the silent electric discharge. No increase of volume takes place and it is inferred that rupture of the molecule does not occur, and further, on account of the extremely short life of the active substance, that triatomic sulphur, analogous to ozone, is not produced. The activated sulphur shows an increased reactivity towards hydrogen and carbon monoxide.

H. F. GILLBE.

Structure of electro-deposited metals. F. FOERSTER and K. KLEMM.—See B., 1929, 685.

Production of electrolytic deposits of beryllium from molten electrolytes. H. FISCHER.—See B., 1929, 723.

Influence of the composition and temperature of the electrolyte in the preparation of beryllium by the Stock-Goldschmidt and Siemens & Halske methods. H. FISCHER.—See B., 1929, 723.

Preparation of beryllium by electrolysis. K. ILLIG, M. HOSENFELD, and H. FISCHER.—See B., 1929, 722.

Polarographic studies with the dropping mercury cathode. IV. Deposition of zinc from cyanide solutions. I. PINES (Coll. Czech. Chem. Comm., 1929, 1, 429—442; cf. this vol., 1015).—Zinc is deposited at the dropping mercury cathode from solutions of zinc cyanide in potassium cyanide when the mol. ratio of the two cyanides does not exceed 1:4; with more potassium cyanide only potassium is deposited. From solutions containing only a slight excess of potassium cyanide zinc is deposited at three different potentials, namely, -1.03 volt from Zn^{++} ions, -1.23 volt from the complex ions $\text{Zn}(\text{CN})_4^{--}$, and -1.4 volt from $\text{Zn}(\text{CN})_5^{--}$ ions. The equilibrium constant of $[\text{Zn}^{++}][\text{CN}]^4/[\text{Zn}(\text{CN})_4^{--}]$ is 10^{-16} and of $[\text{Zn}^{++}][\text{CN}]^5/[\text{Zn}(\text{CN})_5^{--}]$ 6.8×10^{-21} . The solubility product of zinc cyanide is 2.6×10^{-13} . Evidence is adduced which indicates that the deposition of zinc from double cyanide solutions is hindered by the slowness of dissociation of the complexes and not by the great complexity of the anions present.

A. R. POWELL.

Direct electrolytic preparation of some metal permanganates. G. RAPIN (Compt. rend., 1929, 189, 287—289).—Calcium and barium permanganates were obtained in solution by electrolysis of the hydroxide in an isolated porous vessel, with a block of silico-manganese as anode, and a platinum cathode immersed in distilled water. On electrolytic reduction

the former solution was decomposed with the formation of lime and oxides of manganese, whilst green, insoluble barium manganate was obtained from the latter.

J. GRANT.

Formation of perchlorate during electrolytic preparation of chlorate. II. A. V. PAMFILOV and O. S. FEDOROVA (J. Russ. Phys. Chem. Soc., 1929, 61, 363—367).—Owing to the disagreement found (A., 1928, 968) in the percentage yield values of the total products of the electrolysis as found by chemical analysis and gas analysis, the methods of analysis used are fully reviewed and discussed and possible sources of error are pointed out and eliminated; the total yields as found by gas analysis and chemical analysis agree very closely within the limits of experimental error (difference from -0.7% to $+0.6\%$). The authors conclude that the corresponding values of perchlorate as calculated by Spitalski, Sokolov, and Veintraub (J. Appl. Chem. Russia, 1924, [i], 1, 75) are too high.

A. FREIMAN.

Colloidal basic chromic chromate. Conditions for formation by cathodic reduction of chromic acid. S. TAKEGAMI (Bull. Chem. Soc. Japan, 1929, 4, 156—163).—During the electro-deposition of chromium from an aqueous solution of chromic acid there may be formed at the cathode a membrane of colloidal chromic chromate, permeable only to hydrogen ions. By the reduction of chromic acid solutions with alcohol it is shown that this can occur only if the ratio of ter- to sexa-valent chromium at the cathode is 1:0.5. When excess of alcohol is mixed with a solution of chromic acid at the ordinary temperature the mixture shows an increase in viscosity and a decrease in conductivity, and finally becomes coagulated. The ratio, $\text{Cr}^{\text{III}}:\text{Cr}^{\text{VI}}$, becomes steady at 1:0.4. Colloidal properties, as judged by viscosity measurements and ultramicroscopic observations, appear only when the ratio, $\text{Cr}^{\text{III}}:\text{Cr}^{\text{VI}}$, has reached the value 1:0.5. Dialysis yields a sol in which the ratio has risen to 1:0.2. This sol is positively charged, forming a gummy mass at the cathode, and is easily precipitated by bivalent anions. By concentration in a vacuum at 50° a sol containing 18 g. Cr per litre is obtained which has at 25° a specific conductivity of 9.4×10^{-4} and a relative viscosity of 330, and will if cooled to 20° slowly set to a gel which again becomes fluid on warming to the original temperature.

T. H. MORTON.

Photochemistry of the halogens. A. BERTHOUD (J. Chim. phys., 1929, 26, 333—339).—A reply to Plotnikov (this vol., 522).

J. A. V. BUTLER.

Photochemistry of silver iodide. LUPPO-CRAMER (Z. wiss. Phot., 1929, 27, 1—8).—When a film of silver iodide free from foreign substances such as desensitisers is exposed to diffuse light, subsequent exposure to more feeble light has a bleaching action. This is not, however, a manifestation of the Herschel effect, but is a solarisation occurring before the maximum possible blackening has been attained. A similar result is obtained even if 5% of the iodide is replaced by bromide, but not if 10% is replaced. There may also be a marked Schwarzschild effect, but this can be completely prevented by powerful iodine

acceptors, thus showing it to be an intermediate regression. Thallous iodide increases the sensitivity of silver iodide in much the same way as silver bromide, so that in either case the effect of the added substance is doubtless to be ascribed to its interfering with the crystal lattice. The effect of ripening on the sensitivity of silver iodide is probably a development phenomenon; the increase in size of grain consequent on ripening presumably reduces the protective action of the gelatin in respect of the separation of silver.

R. CUTHILL.

Photochemical reductions and oxidations from the electronic point of view. A. STEIGMANN (*Z. wiss. Phot.*, 1929, 27, 24—36).—The photochemical reduction of silver ions or other reducible groups can be effected either by transfer of electrons from another part of the molecule or by donation of electrons liberated along with hydrogen ions from gelatin or other reducing agent under the influence of light. If there is present a substance which has a greater affinity for electrons than the silver ion has, it will act as a desensitiser, whereas a substance which gives off electrons readily as well as takes them up readily will be a sensitiser. In general, in a ternary photochemical system consisting of a reducing agent or group and two oxidising agents, either of these last will be sensitised at the expense of the other being desensitised, depending on which has the stronger affinity for electrons. Neither has, however, its maximum theoretical effect, a sensitiser always having some desensitising action and *vice versa*. The difference in susceptibility to desensitisers between various emulsions is probably due to differences in activity of the ripening nuclei.

R. CUTHILL.

Photochemistry of the silver halides. VI. Analytical and photographic investigation of the silver halides. H. H. SCHMIDT and F. PRETSCHNER (*Z. wiss. Phot.*, 1929, 27, 36—47).—The disposition of the excess of silver in photographic emulsions before and after exposure is discussed. Before exposure, 75% of the silver above the amount corresponding with the halide is contained in the gelatin in a highly disperse state, and only 25% is in the grains of halide; 95% of the total quantity is not in the form of silver sulphide. Treatment with dichromate and sulphuric acid removes the whole of the highly disperse portion and most of the other portion too, and reduces the sensitivity. The effect on the sensitivity cannot, however, be explained on the assumption that the sensitivity centres are partly occluded within the grains, those on the surface being removed by the acid (cf. Kieser, B., 1929, 265), for the sensitivity is affected more in respect of chemical development than in respect of primary physical development. It seems probable that the chromic acid does not remove the silver completely but deposits some of it as dichromate, and that dichromate ions are also adsorbed, which would presumably alter the photographic properties of the emulsion. The effect of such substances as potassium iodide in laying bare the nuclei in exposed chloride and bromide emulsions treated with chromic acid (Lüppo-Cramer, "Grundlagen des Negativverfahrens," Halle, 1927, p. 533) has been observed with iodide emulsions as

well, and is readily explained by supposing that the anion of the salt displaces the dichromate ion from the sensitivity centres. The halogen produced on exposure in a chloride or bromide emulsion is free in the gelatin, whilst with a chloride emulsion the whole of the silver formed is adsorbed in the grains. Treatment with chromic acid removing 95%, without altering the threshold sensitivity to chemical development very much.

R. CUTHILL.

Action of ultra-violet light on certain inorganic compounds. E. MONTIGNIE (*Bull. Soc. chim.*, 1929, [iv], 45, 492—494).—After exposure to ultra-violet light the following potassium salts affect a photographic plate: chloride, bromide, sulphate, nitrate, chlorate, perchlorate, permanganate, chromate, dichromate, oxalate, and tartrate. Calcium fluoride and phosphate behave similarly, but ammonium chloride, ammonium phosphate, magnesium oxide, and magnesium sulphate showed no effect.

C. W. GIBBY.

Phototropy in inorganic compounds. E. L. RAO, K. VARAHALU, and M. V. NARASIMHASWAMI (*Nature*, 1929, 124, 303).—The phototropy of compounds of the formula $2\text{HgS}, \text{HgX}_2$ or $2\text{HgS}, \text{HgX}^{\text{II}}$ is due to dissociation into the simple salts by absorption of actinic energy; on preservation in the dark, recombination, with emission of radiant energy, takes place.

A. A. ELDRIDGE.

Photochemical methods of testing sources of ultra-violet radiation. F. C. HYMAS (*Quart. J. Pharm.*, 1929, 2, 281—291).—Three chemical methods of testing the emission of ultra-violet light, namely, the decompositions of carbon tetrachloride, of aqueous solutions of oxalic acid in the presence of uranyl sulphate, and of potassium iodide-starch solutions, have been compared. Failure to obtain concordant results with the first-named method was shown to be due to the fact that the reaction is most intense in the vapour phase. The potassium iodide-starch method has a temperature coefficient between 25° and 62° of -1.042 for 10°, and for periods less than 10 min. the amount of reaction is proportional to the energy absorbed. The rate of emission of the ultra-violet radiation decreases more rapidly when measured by the potassium iodide-starch method; this is attributed to the difference in the absorption spectra of the solutions employed and the deterioration of the quartz lamp due to the deposition of silica (cf. Pettersson, this vol., 377).

C. C. N. VASS.

Photochemical oxidation of ethyl alcohol by potassium dichromate. II. E. J. BOWEN and E. T. YARNOLD (*J.C.S.*, 1929, 1648—1655; cf. A., 1927, 1040).—The oxidation of ethyl alcohol by potassium dichromate under the influence of light of wave-lengths 4360, 4060, and 3666 Å. has been investigated with reference to the following factors: (1) Effect of neutral salts. Sodium sulphate had no effect on the photochemical rate; large quantities of calcium chloride affect the rate only slightly, but alter the concentration of alcohol which gives the maximum rate by the removal of water to form hydrated ions. (2) The order of the reaction with respect to alcohol in low concentrations. The quantum efficiency γ can be represented by the equation $\gamma = k_1 a + k_2 a^2$, a being

the percentage of alcohol by volume. It is concluded that the photoactive ions are dichromate ions solvated with one and two alcohol molecules. (3) The cause of the diminution of the rate at high alcohol concentrations. The quantum efficiency passes through a maximum at 85 vol.-% of alcohol, and then diminishes owing to the scattering of light by an amorphous precipitate, caused by the insolubility of basic chromium sulphates in concentrated aqueous alcohol. (4) The dependence of the rate on the concentrations of hydrogen ions and dichromate ions. This can be accounted for on the assumption that the ion HCr_2O_7^- is photochemically active. This hypothesis is supported by the results of experiments on the oxidation of glycerol by potassium dichromate, in which the quantum efficiency is proportional to the glycerol concentration when the latter is small, and at higher concentrations rises to a limiting value of 0.52, instead of to unity as for concentrated ethyl alcohol solutions. The photochemically active substance is a dichromate ion combined with one glycerol molecule. An approximate value has been determined for the second dissociation constant of dichromic acid in solutions of aqueous alcohol of various concentrations.

C. W. GIBBY.

Bromination of benzene in light. W. MEIDINGER (Z. physikal. Chem., 1929, B, 5, 29—59).—An attempt is made to explain the mechanism of a simple photochemical reaction in a liquid phase by means of the conceptions hitherto used for gaseous reactions, viz., atomic activation, chain reactions, and photochemical equilibrium. The factors influencing the bromination of benzene in light at low concentrations of bromine (1—2 mg./c.c.), using carbon tetrachloride as a diluting solvent, have been experimentally determined. It is found that either bromine can be substituted directly in the ring with formation of monobromobenzene, or the double linkings can be broken and benzene hexabromide formed. A reaction scheme based on the assumption that each quantum produces two bromine atoms and that the latter are the active agents in the bromination is suggested. An expression for the reaction velocity obtained in terms of experimentally measured quantities is in satisfactory agreement with the observations. The light reaction is independent of the bromine concentration and of the wave-length of the light used. No explanation can be offered for the fact that the temperature coefficient of the reaction decreases from 1.6 to 1.0 with decreasing concentration of benzene.

F. L. USHER.

Alkali aluminosilicates. I. Synthetic study of nepheline. E. GRUNER (Z. anorg. Chem., 1929, 182, 319—331).—The synthesis of nephelines by heating mica with sodium or potassium hydroxide and water for several hours has been studied. The lowest temperature at which nephelines are formed is about 200°, and at about 400° the reaction is first observed to proceed in the reverse direction. Other products, such as natrolite and other zeolitic minerals, are simultaneously formed in small quantities. Paragonite is more readily converted into sodium nepheline than is muscovite into potassium nepheline. In both cases preliminary ignition of the mica causes the appearance of an initial slow stage, in the synthesis

followed by a very rapid stage, whilst the end part of the reaction follows the same course as when the mica is not ignited. By the action of sodium hydroxide on kaolin at 800—1000° there results in addition to nepheline an aluminosilicate of the composition $2\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, which by treatment with water forms a nepheline monohydrate. H. F. GILLBE.

Composition of the cyanide complex radical of metals. I. Silver cyanide complex radical. K. MASAKI (Bull. Chem. Soc. Japan, 1929, 4, 190—193).—The addition of silver cyanide, chloride, thiocyanate, oxide, or chromate to excess of sodium cyanide and titration of the excess of cyanide with silver nitrate gives a molal ratio of combined cyanide to silver of 1:1. L. S. THEOBALD.

Silver iodidothiocyanate. A. C. VOURNASOS (Z. anorg. Chem., 1929, 182, 37—48).—The compound $\text{Na}_6[\text{AgI}(\text{CNS})_6]$ has been prepared by refluxing an acetone solution of silver iodide and sodium thiocyanate until a clear solution is produced, cooling, and allowing the solution to evaporate at about 20°. The resulting product, after recrystallisation from acetone and drying over sulphuric acid, forms colourless prismatic needles which are unaffected by light. Acetone solutions of the complex salt form with benzene, the paraffins, liquid terpenes, aldehydes, and nitriles clear solutions from which the complex may be obtained by evaporation; on addition of water, alcohols, fatty acids, or phenols to the acetone solution decomposition immediately ensues with precipitation of silver iodide. Addition of aliphatic mono-, di-, or tri-amines results in the gradual separation of crystalline complexes such as $[\text{AgI} \cdot 2\text{NH}_2\text{Me}]$, which are readily decomposed by water and show no tendency to ionisation in dilute acetone solution. By pouring an acetone solution of the complex salt into a large excess of 10% ammonia solution the complex $[\text{Ag}(\text{NH}_3)_2]\text{I} \cdot \text{H}_2\text{O}$ is produced, which is soluble in water without decomposition; sodium and potassium hydroxides cause complete decomposition of the complex. *Potassium silver iodidothiocyanate*, $\text{K}_6[\text{AgI}(\text{CNS})_6]$, and the *ammonium salt*, $(\text{NH}_4)_6[\text{AgI}(\text{CNS})_6]$, have also been prepared. A solution of the acid $\text{H}_6[\text{AgI}(\text{CNS})_6]$ is obtained by addition of concentrated hydrochloric acid to an acetone solution of the salt. H. F. GILLBE.

Decomposition of beryl and the preparation of beryllium salts suitable for electrolysis. K. ILLIG, M. HOSENFELD, and H. FISCHER.—See B., 1929, 722.

High-purity magnesium produced by sublimation. H. E. BAKKEN.—See B., 1929, 685.

Preparation of luminophores. L. VANINO and M. PREM (J. pr. Chem., 1929, [iii], 123, 85—88).—The views expressed by Breteau (A., 1916, ii, 100) with regard to the preparation of phosphorescent calcium sulphide are criticised. The addition of the phosphorogen to the ground-mass, after previous ignition of the latter, is not advantageous, immediate addition producing a far greater degree of phosphorescence. The use of sodium carbonate and chloride, as recommended by Verneuil (A., 1887, ii, 539), affords no improvement in phosphorescence, but the authors

consider that the flux contributes to the fusibility of the ground-mass, and to the ultimate phosphorescence (especially in the case of lithium salts). It is found that the use of lithium carbonate or sulphate as flux is much superior to employment of a mixture of sodium, potassium, and lithium sulphates. The advantageous replacement of bismuth by vanadium, recommended by Breteau (*loc. cit.*), is confirmed. Cerium salts in conjunction with bismuth yield a bright phosphorescence of warm violet colour, whilst replacement of cerium by uranium nitrate gives a duller tint; use of tungsten trioxide affords a greenish-yellow phosphorescence. A period of heating of 0.75 hr. is found to be sufficient (cf. Breteau, *loc. cit.*), and the after-glow is more efficient the greater is the velocity of cooling (cf. Breteau, *loc. cit.*). Certain mixtures exhibit phosphorescence which varies in intensity with the period of heating. The results for mixtures containing calcium oxide, barium oxide or carbonate, strontium oxide, carbonate, or thiosulphate, the colours produced, and the variation of the phosphorescence or luminescence with the time of heating, are given in tabular form. C. W. SHOPPEE.

Reducing action of metals on salts in liquid ammonia solution. Action of sodium on zinc cyanide. W. M. BURGESS and A. ROSE (J. Amer. Chem. Soc., 1929, 51, 2127—2131).—The formula NaZn_4 (Kraus and Kurtz, A., 1925, ii, 577) for the product of the above reaction is confirmed by quantitative analysis: $4\text{Zn}(\text{CN})_2 + 9\text{Na} = \text{NaZn}_4 + 8\text{NaCN}$. The compound reacts with dry oxygen in two stages: first sufficient oxygen to convert the sodium into monoxide is taken up rapidly and exothermically, and then the compound very slowly changes from black to white, apparently because of oxidation of the zinc. The second stage is so accelerated by moisture that the two stages become indistinguishable. The compound reacts with acid, yielding hydrogen equivalent to the total sodium and zinc present. Hydrogen is also formed when water acts on the compound; part of it is due to the direct decomposition of the water by the zinc. S. K. TWEEDY.

Cadmium and beryllium peroxides. T. R. PERKINS (J.C.S., 1929, 1687—1691).—Cadmium peroxides have been prepared by five different methods. (1) Cadmium hydroxide dissolved in concentrated ammonium nitrate solution reacts with hydrogen peroxide, giving a stable precipitate of $\text{Cd}_3\text{O}_7 \cdot x\text{H}_2\text{O}$. (2) Addition of alcoholic potassium hydroxide to an alcoholic solution of cadmium bromide containing "perhydrol" gave a precipitate of $\text{CdO}_{1.62}$. (3) The compound $\text{Cd}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$, a true peroxide, was obtained by adding a solution of cadmium hydroxide in ammonia to "perhydrol." (4) Addition of ethereal hydrogen peroxide to an ethereal solution of cadmium dimethyl gave the compound $3\text{CdO} \cdot 2\text{H}_2\text{O}_2$. (5) Passing ozone through a suspension of finely-divided cadmium oxide in chloroform gave small quantities of peroxide. The compounds $\text{Cd}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$ and $3\text{CdO} \cdot 2\text{H}_2\text{O}_2$ decompose unimolecularly. An attempted preparation of beryllium peroxide by method (4) was unsuccessful. C. W. GIBBY.

Ortho- and pyro-silicic acids. P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1929, 182, 343—

350).—By prolonged hydrolysis of ethyl orthosilicate with water at the ordinary temperature orthosilicic acid, $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, has been prepared, and by desiccation of this substance at 13° , pyrosilicic acid, $2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, has been obtained. H. F. GILLBE.

Germanium. XXX. Halogen substitution products of monogermane. L. M. DENNIS and P. R. JUDY (J. Amer. Chem. Soc., 1929, 51, 2321—2327; cf. A., 1928, 33).—*Monochloromonogermane*, GeH_3Cl , b. p. 28° , m. p. -52° , d_{-52}^{20} (liq.) 1.75, $\log p$ (vapour pressure in mm.) $= 7.961 - 1527.4/T$, obtained by the interaction of hydrogen chloride and monogermane in presence of anhydrous aluminium chloride, is somewhat unstable at the ordinary temperature: $2\text{GeH}_3\text{Cl} - \text{GeH}_4 - \text{Ge} + 2\text{HCl}$. *Dichloromonogermane*, GeH_2Cl_2 , b. p. 69.5° , m. p. -68° , d_{-68}^{20} (liq.) 1.90, $\log p = 7.969 - 1742.7/T$, was prepared similarly. Both substances are readily hydrolysed with evolution of hydrogen; the reactions with common reagents are recorded. *Monobromomonogermane*, b. p. 52° , m. p. -32° , d_{-32}^{20} 2.34, $\log p = 7.851 - 1614.7/T$, is a colourless liquid prepared analogously to the foregoing. *Dibromomonogermane*, b. p. 89° , m. p. -15° , d_{-15}^{20} 2.80, $\log p = 9.798 - 2461.9/T$, resembles the monobromoderivative. Evidence of the formation of the corresponding iodine compounds was obtained; these were, however, too unstable to be isolated.

S. K. TWEEDY.

Zirconium iodide. E. CHAUVENET and J. DAVIDOWICZ (Compt. rend., 1929, 189, 408—409).—Zirconyl iodide, $\text{ZrOI}_2 \cdot 8\text{H}_2\text{O}$, heated in a vacuum or in a current of dry hydrogen, decomposes simultaneously into zirconia, and either zirconium iodide, ZrI_4 , or (principally) hydrogen iodide. Iodozirconic acid, $\text{ZrI}_4 \cdot 2\text{HI}$, a brick-red crystalline powder which is decomposed by heat into its molecular constituents and by water into zirconyl iodide, is therefore formed. Zirconium iodide, which crystallises in white needles, is also decomposed by water, and may be distilled from a mixture of dry iodine and zirconium heated to redness in a vacuum, and any sublimed iodine subsequently removed in carbon disulphide. J. GRANT.

Action of the alkali carbonates on lead chloride. (MME.) N. DEMASSIEUX (Compt. rend., 1929, 189, 333—335).—Conductometric analysis of mixtures of solutions of lead chloride and of sodium carbonate at 17° show that lead chloridocarbonate, $(\text{PbCl})_2\text{CO}_3$, identical with phosgenite, is precipitated when the concentration is $0.5\text{Na}_2\text{CO}_3 + 1\text{PbCl}_2$, but is progressively transformed into lead carbonate on further addition of the alkali. Transformation is complete when the mixture is equimolecular, and the deposit thereafter consists of lead carbonate only. Some weeks are required to attain complete equilibrium.

J. GRANT.

Periodic structures from interacting gases. E. S. HEDGES (J.C.S., 1929, 1848—1849).—Regularly spaced bands of ammonium chloride may be obtained in narrow tubing connecting, through drying trains, solutions of ammonia and hydrochloric acid (cf. Koenig, A., 1920, ii, 594; Doyle and Ryan, this vol., 1144).

C. W. GIBBY.

Chemical reactions of dried substances. I. Ammonia and phosphorus pentoxide. L. HARRIS

and C. B. WOOSTER (J. Amer. Chem. Soc., 1929, 51, 2121—2126).—Pure sublimed phosphorus pentoxide absorbs rapidly appreciable quantities of intensively dried ammonia; the reaction product forms a protective film on the pentoxide.

S. K. TWEEDY.

Preparation of azoimide and its salts. W. HOTH and G. PYL (Z. angew. Chem., 1929, 42, 888—891).—Azoimide may be safely distilled from 5% acid solutions (made by mixing the requisite amounts of dilute sulphuric acid and crude sodium azide) at 40° under 40 mm. pressure. By collecting the distillate in well-cooled solutions of alkali hydroxide or in suspensions of alkaline-earth hydroxides the corresponding azide is readily obtained in a pure form. The excess of alkaline-earth hydroxide may be removed from the solution by passing a regulated stream of carbon dioxide through the liquid until the red colour of phenolphthalein is just discharged. Barium azide may be prepared by treating a 10% solution of sodium azide at 0° with the requisite quantity of a 27% solution of hydrofluosilicic acid and neutralising the liquor, after filtration, with barium hydroxide. For the preparation of potassium azide 80 g. of potassium are heated in a revolving tube furnace at 300° in a current of ammonia until absorption ceases, the ammonia is replaced by nitrogen, and the potassamide heated at 270—280° in a current of nitrous oxide. The resulting mass is dissolved in warm water and the azide recovered by crystallisation in almost quantitative yield. Barium azide in 30% yield may be prepared by slowly dropping ethyl nitrite into a well-stirred mixture of barium hydroxide and hydrazine hydrate. Lithium azide is obtained by double decomposition of an alcoholic solution of lithium chloride with sodium azide.

A. R. POWELL.

Preparation and properties of nitril chloride. H. J. SCHUMACHER and G. SPRENGER (Z. anorg. Chem., 1929, 182, 139—144).—Pure nitril chloride, NO_2Cl , has been prepared by treatment of gaseous nitrosyl chloride with ozone, cooling in liquid air, and removing the oxygen formed according to the equation $\text{NOCl} + \text{O}_3 \rightarrow \text{NO}_2\text{Cl} + \text{O}_2$. The product is at the ordinary temperature a colourless gas which condenses at -15° (1 atm.) to a colourless liquid of d_4^{20} 1.37 and f. p. -145° . The gas is non-associated at 100°. Unimolecular decomposition takes place with measurable velocity at 120°, the products being nitrogen peroxide and chlorine. The vapour-pressure curve has been determined from -15° to -80° ; the slight curvature of the $\log p-1/T$ curve is ascribed not to decomposition but to association, or, less probably, to the difference between the specific heats of the liquid and vapour. The calculated latent heat of vaporisation is 6140 g.-cal.

H. F. GILLBE.

Slow oxidation of phosphorus. I. Inhibition of the glow of phosphorus by phosphorous oxide. II. Oxidation products of phosphorus and phosphorous oxide. (MISS) C. O. MILLER (J.C.S., 1929, 1823—1829, 1829—1846; cf. A., 1928, 972).—I. Phosphorus trioxide prepared by the method of Thorpe and Tutton (J.C.S., 1890, 57, 545) can be freed completely from phosphorus by repeated exposure to light and distillation from the red phosphorus thus produced. Phosphorus trioxide inhibits the glow

of phosphorus; moisture and ozone destroy the inhibition and the trioxide. The inhibiting effect of oxygen is small compared with that of ethylene. The work of Schenck, Mihr, and Bantlien (A., 1906, ii, 326) on the vapour pressure of phosphorus trioxide is criticised.

II. Oxidation of phosphorus in moist air gives a solution containing hypophosphoric, phosphorous, and phosphoric acids. In dry air the product was a mixture of phosphorus tetroxide, phosphorus pentoxide, and small quantities of amorphous phosphorus and of a substance which on treating with water gave the reactions of hypophosphoric acid. No trioxide was found. Phosphorus tetroxide is oxidised in oxygen at 350—410°, but not appreciably at lower temperatures. The products of oxidation of phosphorus dissolved in phosphorus trioxide in the presence of a small quantity of moisture are essentially the same as those obtained in the absence of the trioxide. Oxidation of phosphorus-free phosphorus trioxide by ozonised oxygen at 25° gave a mixture of phosphorus tetroxide and phosphorus pentoxide; 1 mol. of ozone oxidised 2 mols. of P_4O_6 . When phosphorus was oxidised in the presence of phosphorus trioxide and a small amount of water vapour, 5 mols. of P_4O_6 were oxidised for every mol. of phosphorus (P_4) oxidised. The mechanism of the reaction between phosphorus and oxygen is discussed.

C. W. GIBBY.

Sulphur tetrafluoride. J. FISCHER and W. JAENCKNER (Z. angew. Chem., 1929, 42, 810—811).—Sulphur tetrafluoride has been prepared by heating at 120° a mixture of cobalt trifluoride and sulphur, diluted with powdered fluorspar, in a vacuum for 2 days, and condensing the gaseous product in a vessel surrounded by liquid air. By fractional distillation fairly pure sulphur tetrafluoride is obtained; the compound is a colourless gas, which condenses at -40° and 1 atm. pressure to a clear mobile liquid; the m. p. at 1.3 mm. pressure is -124° . The vapour-pressure curve of the liquid is expressed by the equation $\log p = -1132/T + 7.746$. The pure substance, as distinct from the crude material, does not attack dry glass and is stable towards paraffin oil, rubber, and sulphur. Mercury is immediately attacked, whilst the gas dissolves in water with decomposition, forming a clear solution.

H. F. GILLBE.

Interaction of carbon tetrabromide with sulphur and selenium. H. V. A. BRISCOE, J. B. PEEL, and J. R. ROWLANDS (J.C.S., 1929, 1766—1768).—Carbon tetrabromide reacts with sulphur to give sulphur monobromide, carbon disulphide, bromine, and carbon, and with selenium to form selenium monobromide, selenium tetrabromide, and a mixture of carbon and selenium. These observations are not in agreement with those of Barta (A., 1905, ii, 704; 1906, ii, 746).

C. W. GIBBY.

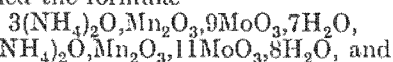
Hydrated chromic hydroxide free from electrolytic impurities. P. A. THIESSEN and B. KANDELAKY (Z. anorg. Chem., 1929, 182, 425—428).—By slowly dropping a solution of chromic ethoxide in ethyl alcohol into water a greyish-green chromic hydroxide hydrosol free from electrolytes may be obtained, and by permitting the concentration to

exceed a certain value (about 0.02% Cr_2O_3) the hydrogel is precipitated. After being freed from alcohol and carbon dioxide by heating, the sol has a concentration of about 0.015%, and possesses great stability. The colloidal particles have a weak positive charge, and the sensitivity of the sol towards electrolytes resembles that of metallic sols; the stability passes through a maximum on the gradual addition of sodium hydroxide solution. The hydrogel is greyish-green in colour and is easily peptised by hydrogen chloride or chromic chloride to a deep green sol.

H. F. GILLBE.

Reduction of permanganate by manganous salts. M. GELOSO and P. DUBOIS (*Compt. rend.*, 1929, 189, 296—298).—A study of the influence of time, temperature, concentration, and of the presence of calcium carbonate on this reaction has led to the conclusion that there is no formation of definite compounds, but a continuous variation in the degree of oxidation of the pseudo-dioxides formed. Calcium carbonate serves principally to neutralise the acid formed, whilst part of it is converted into insoluble manganese carbonate, and it also exerts a surface effect which is being further studied. J. GRANT.

Manganimolybdates. F. ZAMBONINI and V. CAGLIOTI (*Gazzetta*, 1929, 59, 400—460).—Evidence obtained from a re-examination of the products obtainable by the oxidation of mixtures of ammonium molybdate and manganic hydroxide points to the existence of compounds of the type $4\text{Mn}_2\text{O}_3 \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$ containing both bi- and quadri-valent manganese. Friedheim and Samelson's work (*A.*, 1900, ii, 547) has been repeated and a crystallographic examination of the products to which they assigned the formulae



$2(\text{NH}_4)_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 7\text{MoO}_3 \cdot 5\text{H}_2\text{O}$ showed that these are identical crystallographically, optically, and in density. Identity in chemical constitution was also proved, and the formula $4(\text{NH}_4)_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$ or $[\text{Mn}^{+++}(\text{Mo}_2\text{O}_7)_6](\text{NH}_4)_8 \cdot \text{Mn}^{++}\text{MoO}_4 \cdot 9\text{H}_2\text{O}$ is suggested. From this substance the compounds

$4\text{K}_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, $4\text{Rb}_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$ (both reddish-orange), $2(\text{NH}_4)_2\text{O} \cdot 2\text{Na}_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$, red, monoclinic, and the corresponding silver and barium compounds have been obtained by the action of the halides of the metals. A crystallographic examination has been made of most of these salts; the alkali manganimolybdates are isomorphous. It is suggested that Pechard's salt obtained by the action of potassium permanganate on the precipitate formed by mixing solutions of ammonium molybdate and manganous sulphate may be a mixture of the compounds $3[(\text{NH}_4)_2\text{K}_2\text{O} \cdot \text{MnO} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}]$ and $4[(\text{NH}_4)_2\text{K}_2\text{O} \cdot \text{Mn}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}]$ in the proportions 5 : 3. Ammonium nickelimolybdate prepared as purplish-black crystals by boiling ammonium molybdate with nickel sulphate and ammonium persulphate has the formula $4(\text{NH}_4)_2\text{O} \cdot \text{Ni}_2\text{O}_3 \cdot 13\text{MoO}_3 \cdot 9\text{H}_2\text{O}$ and is isomorphous with the alkali manganimolybdates. Spectroscopic evidence is adduced for the existence of quadrivalent manganese in these compounds, the

intensity of the band at $497\text{ m}\mu$ increasing with the change from Mn^{++} through Mn^{+++} to manganimolybdate solutions.

F. G. TRYHORN.

Formation of a manganese carbide decomposable by water from manganese oxide and methane at relatively low temperatures. F. FISCHER and F. BANGERT.—See B., 1929, 717.

Preparation and properties of an oxide of bromine. B. LEWIS and H. J. SCHUMACHER (*Z. anorg. Chem.*, 1929, 182, 182—186).—Bromine oxide, $(\text{Br}_2\text{O}_3)_n$, has been prepared by treatment of bromine with ozone at -5° to 10° in a closed vessel; the oxide deposits gradually on the walls of the vessel, the reaction being complete within 5—10 min. at the higher temperature. If the materials be impure or the temperature too high, the oxide fails to appear and the ozone decomposes explosively. Unless an excess of ozone be present the oxide decomposes into bromine and oxygen, but in presence of an excess of ozone slow decomposition takes place, the ozone being gradually and completely converted into bromine oxide and finally into oxygen; at -80° the oxide is stable for several days, even in absence of ozone. Two crystalline modifications of the new compound exist, the transition point being $-35^\circ \pm 3^\circ$. Bromine oxide dissolves in water, forming an acid solution containing neither free bromine nor bromine ions but capable of liberating iodine on addition of potassium iodide solution; titration shows the acid produced to have the formula $\text{H}_4\text{Br}_3\text{O}_8$. Evidence has been obtained of the existence of a second bromine oxide, which is gaseous at the ordinary temperature.

H. F. GILLBE.

Preparation of anhydrous hydrogen iodide. R. T. DILLON and W. G. YOUNG (*J. Amer. Chem. Soc.*, 1929, 51, 2389—2391).—Concentrated hydriodic acid is dehydrated by phosphorus pentoxide and the gaseous iodide bubbled through saturated calcium iodide solution in order to remove free iodine. The gas is then dried with phosphorus pentoxide and cooled to -30° . Light must be excluded, and the apparatus should be initially filled with nitrogen.

S. K. TWEEDY.

Action of carbonic acid under high pressures on iron. E. MÜLLER and H. HENECKA.—See B., 1929, 751.

Double sulphates and their components. VI. Rhodium double sulphates and their hydrates. F. KRAUSS and H. UMBACH (*Z. anorg. Chem.*, 1929, 182, 411—424).—Cæsium rhodium alum, $\text{CsRh}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, has been prepared by slow evaporation of a solution of the mixed sulphates at the ordinary temperature; it forms orange crystals having $d_x^{20} 2.23_8$, and lattice constant $a = 12.30 \text{ \AA}$. By desiccation at temperatures below 100° the yellow hexahydrate and the brown, sparingly soluble dihydrate, $d 2.72_6$ and 3.07_8 , respectively, are formed. If the dihydrate be heated above 100° decomposition ensues, but by heating with concentrated sulphuric acid the anhydrous salt is obtained as a rose-coloured powder which is but slightly soluble in water and has $d_x^{20} 3.2_6$. By evaporation on the water-bath of a solution of the alum a dark yellow powder of composition

$\text{CsRh}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is obtained. In cold dilute solution this does not liberate free sulphate ions, and it loses water continuously when heated. The complex rhodiosulphate ion breaks down gradually when the aqueous solution is heated. The dihydrated complex salt, obtained by heating the tetrahydrate at 165° , has d_4^{20} 3.4. The free acid, $\text{Rh}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 16\text{H}_2\text{O}$, is obtained as a yellow, crystalline powder by the slow evaporation of a concentrated solution of caesium rhodium alum to which 0.33 vol. of concentrated sulphuric acid has been added. H. F. GILLBE.

Osmium tetroxide. E. FRITZMANN (Z. anorg. Chem., 1929, 182, 34–36).—Polemical.

H. F. GILLBE.

Complex compounds of platinumous chloride with aminoacetal. L. TSCHUGAEV and B. ORELKIN (Z. anorg. Chem., 1929, 182, 28–34).—See A., 1913, i, 23.

H. F. GILLBE.

Oxidation of complex compounds of platinum.

II. Oxidation by persulphate and free oxygen. L. TSCHUGAEV and J. TSCHERNIAEV (Z. anorg. Chem., 1929, 182, 159–172; cf. A., 1926, 373).—By oxidation of Peyrone's salt with ammonium persulphate a black crystalline product of relatively high stability and composition and having the empirical formula $[\text{PtCl}_2\text{OH}(\text{NH}_3)_2]$ is obtained; the same substance is produced by the cautious reduction of the compound $[\text{PtCl}_2(\text{OH})_2(\text{NH}_3)_2]$ with zinc dust, or by heating at 100° a mixture of the compounds $[\text{PtCl}_2 \cdot (\text{NH}_3)_2]$ and $[\text{PtCl}_2(\text{OH})_2(\text{NH}_3)_2]$ with slightly acidified water. Oxidation of Peyrone's salt with ammonium persulphate in presence of potassium chloroplatinite results in the formation of a rather unstable complex containing one $[\text{PtCl}_4]^{2-}$ ion and two ions containing tervalent platinum. A very stable complex containing tervalent platinum is produced by the oxidation of ethylenediamine chloroplatinite with ammonium persulphate in presence of water and a little hydrochloric acid; this material is not decomposed by hot dilute acids nor by salt solutions containing free chlorine ions, and may readily be recrystallised from water: it has the formula $[\text{PtCl}_3 \text{ en}]$, and forms large red crystals. The co-ordination isomeride, $[\text{Pt en}_2]\text{PtCl}_6$, obtained by refluxing $[\text{Pt en}]\text{PtCl}_4$ with ethylenediamine and treatment of the product with potassium chloroplatinite, is red but easily differentiated from the red tervalent platinum compound. Oxidation of the green Magnus salt with ammonium persulphate yields a golden-yellow crystalline precipitate, $(\text{Pt} \cdot 4\text{NH}_3)_2(\text{SO}_4)(\text{PtCl}_4)_2(\text{OH})_2$ which is decomposed rapidly even by washing with water at the ordinary temperature; the dry substance oxidises alcohol to aldehyde, and forms with dry pyridine a bright red, amorphous substance which is fairly stable towards cold water. If nitric acid in presence of hydrogen peroxide be employed for the oxidation of Magnus' salt there results a similar unstable compound, which, however, possesses no oxidising properties: it is violet-red and of composition $(\text{Pt} \cdot 4\text{NH}_3 \cdot \text{NO}_3)(\text{PtCl}_4)$, and forms a red pyridine additive compound of probable composition $(\text{Pt} \cdot 4\text{NH}_3 \cdot \text{NO}_3 \cdot \text{C}_5\text{H}_5\text{N})(\text{PtCl}_4)$. The action of liquid ammonia on platinum trichloride is described.

H. F. GILLBE.

Recovery of platinum. G. J. HOUGH (Ind. Eng. Chem. [Anal.], 1929, 1, 162).—Alcoholic filtrates obtained in the determination of potassium by platinum chloride are treated with about 1 g. of ammonium chloride crystals to each 300 c.c. of filtrate and filtered after mixing and keeping. The filtrate, distilled to 0.25 of its volume, gives a distillate of 83–85% alcohol. The ammonium chloroplatinate and chloroplatinate residues are dissolved in hot water containing a few c.c. of hydrochloric acid (1:2), heated nearly to the b. p., and treated with magnesium powder in slight excess. After removal of the excess of magnesium with concentrated hydrochloric acid, the solution is boiled and the platinum-black collected, washed, and dissolved in aqua regia. Having been evaporated and redissolved three times with hydrochloric acid, the platinum chloride is finally taken up with hot water, acidified with a few drops of hydrochloric acid, and made up to standard volume.

H. J. DOWDEN.

Recommended specifications for analytical reagent chemicals. W. D. COLLINS, H. V. FARR, J. ROSIN, G. C. SPENCER, and E. WICHERS (Ind. Eng. Chem. [Anal.], 1929, 1, 171–174).—Specifications and methods of testing recommended by a Committee of the American Chemical Society are published for the following reagents: bromine, copper ammonium chloride, powdered and granulated cupric oxide, ether, potassium chromate, sodium potassium tartrate, silver sulphate, and two grades of zinc.

A. R. POWELL.

Limits of applicability of indicators in simple p_H determinations. J. EISENBRAND (Pharm. Ztg., 1929, 74, 989–992, 1009–1010).—The sources of error involved in these investigations are discussed in detail. The salt error occurring in buffered solutions is considered with reference to picric acid, bromothymol-blue, methyl-orange, and dimethyl-yellow, and the actual errors introduced, which vary with different indicators and also with the concentration of salt as well as with the nature of the salt, are calculated for various concentrations of sodium and potassium chloride from N to $5N$. For bromothymol-blue the error is small with high concentrations of salt and large with low concentrations (0.5–1*N*-potassium chloride), whereas for methyl-orange the converse is true. With unbuffered solutions the chief source of error is the degree of dissociation of the indicator, for which the following values are calculated: $\Delta p_H = 0.98, 1.43, \text{ and } 1.80$ for $K = 10^{-7}, 10^{-6}, \text{ and } 10^{-5}$, respectively. The limited applicability of indicators with very small dissociation constants and of neutralised indicator solutions is also discussed and it is concluded that no satisfactory method exists for measuring p_H by means of coloured indicators in unbuffered solutions. The effect of the indicator can be ignored only in those cases where the concentration is exceptionally low (10^{-14} mol. per litre). This may be accomplished by using fluorescent indicators such as fluorescein, umbelliferone, quinine, and naphthol in conjunction with the quartz lamp.

S. COFFEY.

Dilution method for the colorimetric determination of p_H in coloured solutions. F. C. THOMPSON and W. R. ATKIN (J. Soc. Leather Trades Chem.,

1929, 13, 297—299).—Portions of the solutions are diluted to 2, 4, 8, 16, and 32 times their original volume, respectively, the p_H values determined colorimetrically plotted against the logarithm of the concentration, and the p_H value of the original solution is determined by extrapolation. D. WOODROFFE.

Acid reaction and carbon dioxide content of conductivity water. R. J. BEST (Austral. J. Exp. Biol., 1929, 6, 107—110).—The carbon dioxide content of conductivity water of specific conductivity 0.3×10^{-6} to 0.75×10^{-6} mho is calculated and its p_H (calc.) is shown to agree fairly closely with that obtained by the indicator method.

P. W. CLUTTERBUCK.

Determination of halogen [in perchlorates] by Gasparini's method. II. K. HELLER [with F. HORA and K. WILLINGSHOFER] (Z. anal. Chem., 1929, 78, 127—131; cf. this vol., 528).—Perchlorates can be quantitatively reduced to chlorides by electrolysis in Gasparini's apparatus, a solution of titanous sulphate in concentrated sulphuric acid, together with silver and potassium nitrates, being used as electrolyte. Reduction is complete after 5—6 hrs., when a further quantity of silver nitrate is added, the solution rendered ammoniacal, filtered, the filtrate acidified with nitric acid, and the silver chloride weighed. Alternatively, the excess of silver in solution may be determined volumetrically by Volhard's method.

H. F. HARWOOD.

Argentometric studies. I. Potentiometric titration of iodides. O. TOMÍČEK (Coll. Czech. Chem. Comm., 1929, 1, 443—448).—The irregularities observed on the titration curve of potassium iodide near the equivalence point are shown to be due to the presence of bromide and not to adsorption of silver ions on silver iodide during the coagulation which takes place just before the equivalent point is reached. Even the purest samples of commercial potassium iodide contain about 0.5% of potassium bromide, so that for standardisation purposes iodide prepared by the action of a sulphite on pure resublimed iodine should be used.

A. R. POWELL.

Volumetric determination of alkali fluorides and silica. W. SIEGEL (Z. angew. Chem., 1929, 42, 856—857).—Silica, in the form of the freshly precipitated gel or as a carefully neutralised solution of alkali silicate, is added to the solution of alkali fluoride and the titration effected with 0.5*N*-hydrochloric acid, using methyl-red as indicator. The reaction is $6MF + SiO_2 + 4HCl = M_2SiF_6 + 4MCl + 2H_2O$. The presence of non-alkali metals is inadmissible. The silica content of silicate solutions may be determined by this method.

In alkaline solutions of alkali fluorides carbonate and silicate may be present, but not fluosilicate. To determine carbonate the solution is titrated with acid, after addition of calcium chloride, using phenolphthalein as indicator. The silica content is determined as described above. If solutions have an acid reaction hydrogen fluoride and fluosilicate may be present, but not silicate. The hydrogen fluoride content is determined after addition of calcium chloride by titration, using methyl-red, and the fluosilicate determined by continuing the titration, using phenol-

phthalein, the reaction being $M_2SiF_6 + 4MOH = 6MF + SiO_2 + 2H_2O$.

J. S. CARTER.

Determination of sulphuric acid in a mixture of sulphuric acid, acetic acid, and acetic anhydride. T. SOMIYA.—See B., 1929, 670.

Improvements in Deniges' colorimetric method for [the determination of] phosphorus and arsenic. E. TRUOG and A. H. MEYER (Ind. Eng. Chem. [Anal.], 1929, 1, 136—139).—Under certain conditions stannous chloride reduces ammonium molybdate to give a blue coloration in the absence of phosphate, whilst if the acidity is too high, the blue colour in the presence of phosphates may be repressed. To obviate these difficulties in conducting Deniges' test (cf. B., 1920, 781A), the reagents recommended are (A) 10*N*-sulphuric acid containing 2.5 g. of ammonium molybdate per 100 c.c. and (B) a solution of 25 g. of pure stannous chloride in 1000 c.c. of 10 vol.-% hydrochloric acid. The standard phosphate solution contains 0.25 p.p.m. of phosphorus (0.2195 g. of recrystallised potassium dihydrogen phosphate in 1000 c.c. of water is equivalent to 50 p.p.m. of phosphorus), 4 c.c. of solution (A), and 6 drops of (B) in 100 c.c. In conducting the test, the liquid after dilution should contain 4 c.c. of (A) and 6 drops of (B) per 100 c.c. At this concentration the colour develops immediately but fades in 10—12 min. The test is not vitiated by the presence of less than 700 p.p.m. of silica, nor by considerable amounts of aluminium, manganese, calcium, or magnesium salts. Ferric iron markedly influences the colour and should first be reduced. Arsenates may be determined in exactly the same way as phosphates, and if both are present the two may first be determined together and then the phosphate alone, after removal of arsenic by precipitation with hydrogen sulphide.

H. J. DOWDEN.

Iodometric determination of phosphorous acid. A. SCHWICKER (Z. anal. Chem., 1929, 78, 103—109; cf. A., 1919, ii, 77).—An excess of 0.1*N*-iodine is added to the phosphite solution, followed by 5—10 c.c. of *N*-ammonium borate. After 15 min. the solution is acidified with 2*N*-hydrochloric acid and the excess of iodine titrated with 0.1*N*-thiosulphate. In place of ammonium borate, *N*-ammonia, magnesia mixture, or *N*-potassium hydroxide may be used, but as all these require to be added drop by drop with avoidance of excess, they are less convenient. Phosphites may also be determined by addition of 0.1*N*-iodide-iodate solution to the solution of the phosphite, followed by the addition of hydrochloric acid and titration with thiosulphate, but in this case the reaction mixture must be kept for 2.5 hrs. before acidification. The above time may be reduced to 20 min. by working at 50°, but special precautions are then necessary to prevent loss of iodine. Both the above methods permit the determination of phosphites in presence of hypophosphites.

H. F. HARWOOD.

Colorimetric determination of phosphoric acid by Deniges' method. S. N. ROZANOV (Trans. Sci. Inst. Fertilisers, Moscow, 1928, No. 55, 139—158).—The optimal limits are 0.3—0.5 mg. P_2O_5 per litre; the quantity of aqua regia used is unimportant.

The maximum deviation, in comparison with the double precipitation method, was 1%.

CHEMICAL ABSTRACTS.

Volumetric determination of phosphoric acid. W. SMITH (*Quart. J. Pharm.*, 1929, 2, 238—241).—Solutions of phosphoric acid can be titrated directly by the employment of two indicators. Dimethylaminoazobenzene is used for the first titration, cresolphthalein for the second, and cresolphthalein with neutral calcium chloride solution at 70° for the third.

C. C. N. VASS.

Determination of neon in natural gases. N. P. PÉNTCHEV (*Compt. rend.*, 1929, 189, 322—324).—The density of the helium-neon mixture obtained after removal of argon, krypton, and xenon by coconut charcoal cooled in liquid air was determined (cf. A., 1928, 987), the procedure being controlled by spectral analysis. The results obtained with natural gas of known helium and argon content from a Bulgarian spring confirm the astrophysical theory of Moureu and Lepape.

J. GRANT.

Separation of calcium and magnesium by the oxalate method. Z. HERRMANN (*Z. anorg. Chem.*, 1929, 182, 395—410).—The supersaturation of solutions of magnesium oxalate and the mechanism of its precipitation have been studied and a theoretical explanation is derived. The induction period observed when ammonium oxalate solution is added to a solution containing magnesium ions is reduced by increase of concentration or of temperature. Smoluchovski's theory of the slow coagulation of colloidal solutions is applicable also to the precipitation of crystalline compounds.

H. F. GILLBE.

Effect of lead on the permanganate titration of antimony in white metal analyses. A. VASILIEV and H. STUTZER (*Z. anal. Chem.*, 1929, 78, 97—102).—Direct titration with permanganate of the solution obtained by treating a lead-antimony alloy with sulphuric acid, with subsequent additions of hydrochloric acid and water, shows only 98—99% of the total antimony present. Satisfactory results are obtained if the precipitated lead sulphate be subsequently dissolved in dilute hydrochloric acid and this solution also titrated; a deduction of 1% must be made from the total antimony figures. In the case of white metals containing tin and copper in addition to antimony and lead this correction is unnecessary, the figures then obtained being in good agreement with those yielded by the bromate method.

H. F. HARWOOD.

Electro-analytical determination of thallium as thallic oxide. A. JILEK and J. LUKAS (*Coll. Czech. Chem. Comm.*, 1929, 1, 417—428).—Electrolysis of thallic nitrate solutions containing hydrofluoric acid results in the deposition of a small amount of thallium on the cathode and the remainder as the compound, $Tl_2O_3 \cdot HF$, on the anode; addition of hydrogen peroxide converts all the thallium into the anodic compound, which, however, is not pure, containing only 84.44% instead of 85.73% Tl . For the determination of the metal the solution containing less than 0.25 g. of thallium as nitrate is treated with 1—2 g. of 40% hydrofluoric acid in a Classen platinum dish which serves as anode and electrolysed at 0.2

amp., using a rotating platinum disc cathode. After 1 hr. 1 c.c. of 30% hydrogen peroxide is added to dissolve the metal deposited on the cathode and electrolysis is continued for a further 1 hr.; this operation is repeated three times or until the electrolyte gives no test for thallium with sodium sulphide. The deposit is washed with water without interrupting the current, dried at 100°, and weighed; the weight multiplied by the empirical factor 0.8444 gives the weight of thallium present.

A. R. POWELL.

Determination of copper and nitrite in solutions of cuprammonium hydroxide. E. BUTTERWORTH and H. A. ELKIN.—See B., 1929, 717.

Determination of copper with 5:7-dibromo-8-hydroxyquinoline. L. W. HAASE (*Z. anal. Chem.*, 1929, 78, 113—124).—The above reagent is well adapted for the determination of small amounts of copper (0.5—20 mg. per litre) for which the colorimetric methods are unsuitable. The reagent is employed as a 0.5% solution in 5*N*-hydrochloric acid, and the solution under examination must not contain more than 0.7% of free hydrochloric acid or 5% of free acetic acid. The copper precipitate is dried for 1 hr. at 105°, and then for 2—3 hrs. at 140° before being weighed. The presence of large amounts of alkali salts has no influence on the accuracy of the results, but humus and similar substances must be destroyed by treatment with hydrochloric acid and hydrogen peroxide before precipitation of the copper. An improved method for the preparation of the reagent is recorded.

H. F. HARWOOD.

Quantitative oxidation with ceric sulphate. A. J. BERRY (*Analyst*, 1929, 54, 461—464).—The ceric sulphate solution (prepared from 25 g. of the nitrate treated with concentrated sulphuric acid and diluted to 500 c.c.) is standardised with a suitable reducing agent such as ferrous ammonium sulphate. Ferrocyanides are readily and quantitatively oxidised at the ordinary temperature, the end-point being found by means of diphenylamine sulphate. With tartrates 1 mol. of tartaric acid requires 3.51 atoms of available oxygen. In the case of thallic salts a solution of iodine in chloroform is converted quantitatively into iodine monochloride to furnish means for determining the end-point. To a few c.c. of a dilute solution of iodine in chloroform in a stoppered bottle are added about 50 c.c. of concentrated hydrochloric acid, and the solution of ceric sulphate is added until the violet colour disappears. A measured volume of the thallic salt solution is then added and the standard ceric sulphate run in until the chloroform is again colourless. The ceric sulphate is here standardised by oxidising a solution of potassium iodide of known concentration to iodine monochloride.

D. G. HEWER.

Determination of manganese by Volhard's method. F. J. WATSON.—See B., 1929, 753.

Potentiometric determination of iron and molybdenum [in presence of each other]. H. BRINTZINGER and W. SCHIEFERDECKER (*Z. anal. Chem.*, 1929, 78, 110—112).—The solution of the chlorides of the two metals containing 30 g. of calcium chloride and 25 c.c. of concentrated hydrochloric acid

in 100 c.c. is boiled for 5 min. in a stream of carbon dioxide, cooled to 90°, and titrated with 0.1*N*-chromous chloride. A sharp change in potential occurs when all the ferric iron has been reduced to ferrous and all sexavalent to quinquevalent molybdenum, and on continuing the titration a second break occurs when the quinquevalent molybdenum has been reduced to the trivalent state: from these data the amounts of each metal present can be calculated.

H. F. HARWOOD.

Detection of cobalt and nickel in presence of phosphates and identification of magnesium in presence of cobalt and nickel. R. ROSSI (*Annali Chim. Appl.*, 1929, 19, 255—260).—In the ordinary method of inorganic qualitative analysis, it is not the ammonium chloride but rather the ammonia, in excess and in the cold, which keeps the cobalt and nickel in solution in presence of phosphoric acid. Hence, after the subsequent boiling of the solution, these metals, particularly the cobalt, may be largely retained in the third group precipitate. A procedure is described which overcomes the difficulty thus presented and also prevents any possibility of error in the identification of magnesium.

T. H. POPE.

Volumetric determination of tin. H. WOLF and R. HEILINGOTTER (*Chem.-Ztg.*, 1929, 53, 683).—The most satisfactory reducing agent for the iodometric determination of tin is iron nails, reduction being effected in 1:1 hydrochloric acid at 90—95° on a boiling water-bath. Three nails 8—10 cm. long will reduce 0.1 g. of tin from the stannic to the stannous condition in 8 min. Directions are given for the determination of tin in antimony, copper, and lead alloys by this method.

A. R. POWELL.

Rapid analysis of bearing-metal alloys. J. F. ILTSCHENKO and R. M. STACHORSKI.—See B., 1929, 753.

Determination of tin and antimony in bearing-metal alloys. A. P. AFANASIEV.—See B., 1929, 753.

Preparation of antimony-free arsenious oxide and the determination of minute amounts of antimony in arsenious oxide. C. W. FOULK and P. G. HORTON (*J. Amer. Chem. Soc.*, 1929, 51, 2416—2419).—The impure arsenious oxide is converted into the chloride, which is then repeatedly extracted with concentrated hydrochloric acid, in which antimonious chloride is very soluble as compared with the arsenious compound. The remaining arsenious chloride is hydrolysed to the oxide, which is then purified by the usual methods. The procedure is applicable to the detection and the approximate determination of minute amounts of antimony in arsenious oxide.

S. K. TWEEDY.

Determination of bismuth [in ores]. G. J. HOUGH.—See B., 1929, 753.

Analytical chemistry of tantalum, niobium, and their mineral associates. XV. Separation of tantalum and niobium from titanium and zirconium. W. R. SCHÖELLER (*Analyst*, 1929, 54, 453—460).—Tantalum and niobium may be qualitatively separated from titanium and zirconium by the pyrosulphate and tannin method, whereby the mixed oxides (0.1—0.2 g.) are fused with 2—3 g. of

hydrogen sulphate, the mass is solidified in a thin layer round the sides of the silica crucible, and the hot reagent (1 g. of tannin dissolved in 90 c.c. of water and 10 c.c. of 1:1 sulphuric acid) added. After gentle heating the contents of the crucible are transferred to a beaker, boiled, left until clear, and the precipitate *A* is filtered off. The filtrate is boiled down with 5 c.c. of concentrated sulphuric acid, and treated with concentrated nitric acid, whereby the tannin is readily oxidised. After decolorisation and cooling, 50 c.c. of water are added, and titanium and zirconium identified. The precipitate *A* proves the presence of earth acids, and they are identified jointly by the tartaric hydrolysis method (this vol., 902) and separately by the tannin method (B., 1925, 974). The method has been worked out in a preliminary way as a quantitative test with satisfactory results. The salicylate process for the separation of titanium from tantalum, niobium, and zirconium is adversely criticised.

D. G. HEWER.

Electrode holder for arc spectrum analysis. L. L. QUILL and P. W. SELWOOD (*Ind. Eng. Chem. [Anal.]*, 1929, 1, 180).—The holder consists of two horizontal arms mounted on a rotatable fibre cylinder which can be adjusted vertically by means of a screw running through the main support and operated by a large vulcanised handle. The lower arm has also an independent vertical movement through a rack and pinion with two vulcanised handles to allow of frequent adjustment of the positive electrodes which are fixed in this arm. One pair of electrodes is made of iron and is used as a reference standard, whilst the other pair, of carbon, is used for the analysis. Either pair may be brought into the axis of collimation of the spectrograph by rotating the fibre cylinder.

A. R. POWELL.

Manipulation in intensive drying. H. B. BAKER (*J.C.S.*, 1929, 1661—1664).—The various precautions necessary to ensure success in experiments involving intensive drying are briefly summarised. The apparatus must be constructed of good Jena glass completely free from bubbles and thoroughly cleaned before being worked in the blowpipe flame. Preliminary drying of the apparatus is best effected by heating with a waving Bunsen flame while a current of air dried by phosphoric oxide is passed through both during the heating and subsequent cooling, and a bulb of pure phosphoric oxide must be sealed on to the apparatus. The only tap lubricant permissible is metaphosphoric acid protected from atmospheric moisture by purified vaseline, whilst for experiments involving hydrogen chloride and ammonia no lubricant may be employed, the taps being hand-polished with rouge and water. In all cases it is necessary to introduce phosphoric oxide into the hole in the barrel of the tap. The purity of the materials used must greatly exceed that required for at. wt. determinations.

J. W. BAKER.

Intensive drying of gaseous media. W. A. BONE (*J.C.S.*, 1929, 1664—1666).—Additional details (cf. preceding abstract) concerning the technique of intensive drying are summarised (cf. *J.C.S.*, 1906, 89, 652; A., 1926, 480). The possible limit of phosphoric oxide desiccation is reached in about 250 days,

the explosion vessels (of Jena red-line resistance glass) being externally heated to 150—200° once a fortnight. Sealing of the explosion vessels is effected with a blow-pipe flame of dried carbon monoxide and air to avoid any absorption of steam by the glass. With such precautions mixtures of dried carbon monoxide and oxygen can be subjected to repeated condenser discharges of 0.5 microfarad at 1000 volts without the slightest combustion occurring. J. W. BAKER.

Large metal Soxhlet extractor. L. R. BRYANT (Ind. Eng. Chem. [Anal.], 1929, 1, 139—140).—A sectional electrically-heated extractor constructed of copper has been used for the preparation of large quantities of fat-free material. The boiler, the extraction chamber, and the condenser system are separable, but are bolted together when in use. The material to be extracted is held in a linen bag supported by a copper frame, which rests on a perforated plate. Drainage taps and a level gauge are provided, and in order to obviate premature siphoning it is important that the internal diameters of the solvent vapour tube and the siphon tube should be in the ratio of 2.22 to 4.77 mm. H. J. DOWDEN.

Graduated wash bottles. E. R. CALEY (Ind. Eng. Chem. [Anal.], 1929, 1, 162).—To compensate for the loss in the washing of slightly soluble precipitates, graduated wash bottles are advocated. For hot washing media, the vessels may consist of large test-tubes, suitably calibrated and etched and provided with detachable wooden bases to act as stands. H. J. DOWDEN.

Modification of the Kjeldahl trap. G. H. W. LUCAS (Ind. Eng. Chem. [Anal.], 1929, 1, 140).—In the distillation of frothy liquids, the exit from the distillation vessel consists of a wide tube sealed through the side of a 500-c.c. Kjeldahl flask, the internal end being bent downwards. In the bottom of the flask is a hole, which is connected to the exit tube by a narrow inclined tube, so that froth entering the flask drains back slowly into the distillation vessel. The neck of the flask is constricted below the side limb in order to support a small glass funnel filled with glass wool, the replacement of which is effected through the mouth of the flask. H. J. DOWDEN.

New desiccator shapes and insertions. H. LIESEGANG (Chem. Fabr., 1929, 256—257).—A square-shaped desiccator with an internal arrangement similar to that in an egg-box is described. This insertion may be made of cardboard, metal, or porcelain and is removable. The new desiccators will hold more crucibles safely than the usual form; the internal compartments may also be used in the ordinary circular desiccator. A. R. POWELL.

Rapid-indicating continuous-reading vacuum and pressure gauges. H. G. ANDERSON (Ind. Eng. Chem., 1929, 21, 795—797).—The gauges described operate by recording the resistance of a piece of platinum ribbon supplied with a constant flow of heat. The temperature and consequently the resistance varies with the conductivity and therefore the pressure of the surrounding gases. They are capable of use at all pressures below atmospheric, but the sensitiveness increases with diminishing pressure. In

one type on which greater heat is used to give sensitiveness at higher pressures compensator bulbs for atmospheric fluctuations are necessary. For the other it is sufficient to set the zero under the conditions of measurement. The recording pointer comes to rest within 6 sec. C. IRWIN.

Differential pressure gauge. A. R. OLSON and L. L. HIRST (J. Amer. Chem. Soc., 1929, 51, 2378—2379).—An electrically controlled gauge which enables very slow reactions at any pressure to be studied is described. S. K. TWEEDY.

Platinum resistance thermometer. T. HSU (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 51—53).—The readings obtained at several temperatures with platinum resistance thermometers of two different types and filled with various gases have been compared. R. CUTHILL.

Apparatus for measuring the density of liquids by means of a hydrometer. P. FUCHS.—See B., 1929, 663.

Inexpensive pyrex conductivity cell. W. B. CAMPBELL (J. Amer. Chem. Soc., 1929, 51, 2419—2420).—The electrodes are narrow strips of thin platinum foil and are fused firmly on to the surface of the glass inside the cell. S. K. TWEEDY.

Conductivity of electrolytes. II. Improvements in the oscillator and detector. G. JONES and G. M. BOLLINGER (J. Amer. Chem. Soc., 1929, 51, 2407—2416; cf. A., 1928, 595).—Although when measuring conductivity it is desirable to use a low voltage across the bridge, and a modification of the oscillator previously described is given to enable suitable low and controllable voltages to be obtained, the sensitivity of the bridge is diminished thereby, and this is best surmounted by improving the amplifier. Transformer design for oscillating valve amplifiers is discussed. An improved amplifier is recommended, but when used it is necessary to place a "wave filter" across the telephones in order to diminish extraneous noises. The error produced by the mutual inductance between the oscillator and the detector and the oscillator and the bridge is also discussed. S. K. TWEEDY.

Three electrode lamps in electrochemical measurement. A. H. W. ATEN, (MISS) L. BOERLAGE, and D. CANNEGIETER (Chem. Weekblad, 1929, 26, 426—430).—Various circuits, in which valves are employed for magnifying alternating and direct currents, for rectifying, and as direct-current generators, are described. S. I. LEVY.

High-temperature technique and new fluorides. O. RUFF (Z. angew. Chem., 1929, 42, 807—810).—Modifications of the earlier apparatus (A., 1914, ii, 336) employed for the study of high-temperature reactions are described. Certain earlier work has been repeated, including determinations of the vapour-pressure curves of iron, cobalt, and nickel, and of the phase diagrams of the systems ZrO_2 -CaO and ZrO_2 -ThO₂ at temperatures above 2000°. Recent work on fluorides is summarised (cf. A., 1928, 854; this vol., 40, 160 527). H. F. GILLBE.

Fusion calorimeter. H. SACHSE (Z. physikal. Chem., 1929, 143, 94—96).—A modification of the

Bunsen ice calorimeter, in which the working substance is diphenyl ether, m. p. 26.55°, is described. When the volume change is determined by weighing mercury, 0.02 g.-cal. can be measured. The instrument is particularly suitable for the measurement of slow thermal effects. F. L. USHER.

Flow meter for gases. A. V. SIVOLOBOV (J. Chem. Ind. Moscow, 1928, 5, 1429—1431).—Riesenfeld's apparatus is improved.

CHEMICAL ABSTRACTS.

Bottle for accurate weighing of volatile liquid mixtures. Z. BLASZKOWSKA (Ind. Eng. Chem. [Anal.], 1929, 1, 170—171).—The bottle consists of a lower container of about 100 c.c. capacity joined to a smaller upper container of 50 c.c. capacity by means of a horizontal S-shaped neck and having a narrow, long side-tube sealed into its upper part. Both side-tube and upper vessel are provided with glass stoppers. In using the apparatus one liquid is introduced into the upper container, the whole is weighed, and the apparatus tilted to transfer the liquid to the lower container, a second liquid is then placed in the upper portion and, after weighing, transferred to the lower for mixing; this operation is repeated as often as necessary and finally the mixture is transferred to the reaction vessel through the side-tube. A. R. POWELL.

Volumenometer. A. W. FRANCIS and E. P. OXNARD (Ind. Eng. Chem. [Anal.], 1929, 1, 169—170).—For the determination of the volume or density of a powder or irregular solid which is soluble or porous a weighed quantity is placed into a thick-

walled, flat-bottomed, pyrex glass bulb, the neck of which is provided with a ground-glass collar and steel clamp which holds the collar in position above a leather or rubber washer on the top of the bulb. The cover is connected through capillary tubing with rubber joints to a pipette bulb of known volume slightly less than that of the bulb. The lower tube of the pipette is connected to a manometer about 2 m. long which is provided with two metre rules, the lower one being inverted, so that the zero points of the rules are opposite the graduation marks above and below the bulb of the pipette. A levelling bulb of 150—200 c.c. is connected by pressure tubing to the pipette below the lower graduation and readings are taken of the manometer when the mercury in the closed arm is at the lower and then at the higher graduation; the readings are repeated with the empty bulb. From the results obtained the volumes of air in the bulb with and without the sample can be calculated; the difference is the volume of the sample, which should be correct to 0.2 c.c. A. R. POWELL.

Modified Pauly receiver. J. B. BROWN (Ind. Eng. Chem. [Anal.], 1929, 1, 160).—In the base of a 250- or 500-c.c. pyrex suction flask are blown six depressions about 20 mm. in diameter and to each of these is sealed a piece of pyrex glass tubing 12 cm. long, 12 mm. in diameter, and with walls 2 mm. thick, the tubes sloping outwards on a line parallel to the side walls of the flasks. The adapter is made of ordinary glass, its lower end being at least 8 mm. outside diameter to prevent bubble formation and spattering. A. R. POWELL.

Geochemistry.

Formation of ozone in the highest layers of the atmosphere. W. ANDERSON (Physikal. Z., 1929, 30, 485—487).—Ozone in the upper layers of the atmosphere is not primarily formed by ultra-violet solar radiation nor does it arise from storms. Dobson's view that the connexion found between the amount of ozone and magnetic disturbance might suggest some action associated with the aurora borealis is criticised on the ground that the maximum ozone concentration occurs at heights between 30 and 50 km. from the earth, whilst the aurora occurs at 80—100 km. This view involves ozone formation at great heights and a gradual sinking of the molecules. The formation of ozone is assumed to be due to the absorption of corpuscular radiation, and by making simple assumptions it is shown that ozone formation should be very small below 30 km., maximal between 40 and 50 km., and again very small beyond 70 km. It is unlikely that the penetrating height radiation contributes materially to ozone formation.

R. A. MORTON.

Ground waters in Balakhani. A. KREMS (Azerbeid. Neft. Choz., 1928, No. 4, 34—37).—The chloride, carbonate, sulphate, lime, and magnesia contents of the water at various depths are recorded.

CHEMICAL ABSTRACTS.

Bodenbenderite, a new mineral of the Argentine. E. RIMANN (Bol. Acad. Nac. Ciencias, 1929, 31, 5—17).—Bodenbenderite has d 3.3—3.5, H 6.0—6.5, and fuses at 1000—1100° to a cloudy glass having d 2.8—3.0. It is of a clear red colour, with a glassy lustre, does not exhibit double refraction, and has $n > 1.77$. Finely-divided ferric oxide and minute bubbles of carbon dioxide are distributed throughout the crystals. After adjustment of the analysis for obvious impurities the chemical composition approximates to the formula $4MO.M'_2O_3.3M''O_2$, where $M = Mn, Fe'', Ca,$ and Mg , $M' = Al, Fe''',$ and Y , and $M'' = Si, Ti,$ and U . The chemical behaviour of the mineral indicates the presence of two components, viz., 1 mol. of similar composition to plazolite except that no water is present, and containing all the yttrium, magnesium, titanium, and uranium, and 3 mols., insoluble in hydrochloric acid, of vesuviana.

H. F. GILLBE.

Occurrence of beryllium. M. HOSENFELD.—See B., 1929, 722.

Crystallisation of basalts. C. N. FENNER (Amer. J. Sci., 1929, [v], 18, 225—253).—The theory that the crystallisation of a basaltic magma on cooling tends to give through differentiation a residue approx-

imating in composition to a granite or rhyolite is criticised. Numerous instances show that such a magma tends to become rich in iron through the separation of magnesia-rich pyroxenes, the iron finally appearing as magnetite. The intersertal intergrowths of quartz and felspar met with in many dolerites and adduced in support of the above theory are probably not due to differentiation by magmatic crystallisation but result from secondary reactions. The view is taken that several other processes co-operate with crystallisation in effecting differentiation, an important agency being gaseous transfer; the assumption usually made that basaltic magmas contain only insignificant amounts of gases and volatile substances is incorrect.

H. F. HARWOOD.

Pleochroic haloes in biotite. D. E. KERR-LAWSON (Univ. Toronto Stud., Geol. Ser., 1928, No. 27, 15—27).—A biotite from Murray Bay indicated no anomalies in the constants of the uranium series. The persistence of a marked concentric distribution of the darkening effect in the haloes is due to a terminal reversal effect by which, in the region of the range of a given set of α -particles, the develop-

ment of darkening due to other sets of α -particles is inhibited.

CHEMICAL ABSTRACTS.

Bromine content of Solikamsk carnallites. N. N. EFREMOV and A. A. VESELOVSKI (J. Chem. Ind. Moscow, 1928, 5, 1365—1369).—Solikamsk carnallite contains 0.17—0.30% Br, apparently chiefly as the compound $\text{KCl} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$. The estimated bromine content of the deposit is 22×10^6 tons.

CHEMICAL ABSTRACTS.

Diatomaceous earth. E. V. ROZHKOVA (Trans. Inst. Econ. Min. Met., Moscow, 1929, No. 42, 51—61).—Two deposits near Mt. Kamyshlov (Urals) contain, respectively, SiO_2 78.76, 75.59; TiO_2 0.27, 0.93; Al_2O_3 9.81, 10.57; Fe_2O_3 3.15, 3.74; CaO 0.69, 1.05; MgO 1.72, 1.46; K_2O 0.78, 0.56; Na_2O 0.27, 0.54; SO_2 0.11, 0.29; loss on ignition 4.70, 4.69%.

CHEMICAL ABSTRACTS.

Iron of Sumampa and other pseudometeorites. E. H. DUCLOUX (Rev. fac. cienc. quim. La Plata, 1928, 5, i, 77—81).—Analyses of a supposed meteorite, and two specimens proved not to be meteorites, are recorded.

CHEMICAL ABSTRACTS.

Organic Chemistry.

M. p. of normal paraffins. J. H. HILDEBRAND and A. WACHTER (J. Amer. Chem. Soc., 1929, 51, 2487—2488).—When the m. p. (lit.) of the normal paraffins from C_{19} to C_{38} are plotted against number of carbon atoms a smooth curve is obtained. No alternation exists and the data given by Levene, West, and van der Scheer (B., 1915, 634) for seven of the series appear to be high. Dicytyl has m. p. 70.2° (lit. $68\text{--}75^\circ$).

H. BURTON.

Synthesis of isomeric Δ^2 -butenes. W. G. YOUNG, R. T. DILLON, and H. J. LUCAS (J. Amer. Chem. Soc., 1929, 51, 2528—2534).— α -Hydroxy- α -methylbutyric acid, m. p. 72.5° (lit. $66\text{--}68^\circ$; all m. p. and b. p. are corr.) (improved method of preparation from methyl ethyl ketone given), on slow thermal decomposition affords α -ethylacrylic acid (11%), b. p. $76.5\text{--}83^\circ/12$ mm., m. p. -16° , angelic acid (I) (20%), b. p. $85.5\text{--}87.5^\circ/12\text{--}13$ mm., m. p. $45\text{--}45.5^\circ$, and tiglic acid (II) (20%), b. p. $95\text{--}96^\circ/11.5$ mm., m. p. $63.5\text{--}64^\circ$. Addition of hydrogen iodide to I in chloroform solution in the dark at 3° in presence of a small amount of molecular silver affords some tiglic acid hydriodide (III), m. p. $86.2\text{--}86.3^\circ$ (formed also by the addition of hydrogen iodide to II), as well as angelic acid hydriodide (IV), m. p. $57.9\text{--}58.5^\circ$. Treatment of III and IV with sodium carbonate solution at $15\text{--}50^\circ$ gives *trans*- Δ^2 -butene, b. p. $0.3\text{--}0.4^\circ/744$ mm. [dibromide (*meso*), b. p. $72.7\text{--}72.9^\circ/50$ mm., d_4^{20} 1.7829, n_D^{20} 1.5116], and *cis*- Δ^2 -butene, b. p. $2.95\text{--}3.05^\circ/746$ mm. [dibromide (*racemic*), b. p. $75.6\text{--}75.8^\circ/50$ mm., d_4^{20} 1.7916, n_D^{20} 1.5147], respectively (cf. Wislicenus and others, A., 1901, i, 2; Pfeiffer, A., 1904, ii, 525).

H. BURTON.

cycloPropane derivatives. N. VAN KEERSBILCK (Bull. Soc. chim. Belg., 1929, 38, 205—211).—The

preparation of δ -methyl- Δ^2 -pentadiene by way of α -chloro- δ -methyl- Δ^2 -pentene from cyclopropyldimethylcarbinol (Bruylants, A., 1909, i, 226; Kijner and Klawikordoff, A., 1911, i, 635; Bruylants and Dewael, A., 1928, 518) has led to the preparation of related hydrocarbons and derivatives for comparison. δ -Methyl- Δ^2 -pentadiene, b. p. $76\text{--}76.5^\circ/759$ mm., d_4^{20} 0.71814, n_D^{20} 1.45317, is prepared by the action of alcoholic potassium hydroxide on the monobromide derived from cyclopropyldimethylcarbinol. δ -Methyl- Δ^2 -penten- γ -ol, b. p. $121.6\text{--}122^\circ/757$ mm., d_4^{20} 0.83432, n_D^{20} 1.42946, is obtained by the interaction of ethyl crotonate and magnesium methyl bromide, and when warmed with a little concentrated sulphuric acid gives δ -methyl- Δ^2 -pentadiene, b. p. $75.6\text{--}76^\circ/760$ mm., d_4^{20} 0.71896, n_D^{20} 1.44655. When cyclopropyldimethylcarbinol is distilled with a little sulphuric acid it yields vinylcyclopropane, b. p. $69.5\text{--}70^\circ/751$ mm., d_4^{20} 0.74999, n_D^{20} 1.42524, accompanied by 2:5-dimethyltetrahydrofuran, b. p. $92\text{--}93^\circ$, d_4^{20} 0.8335. Dehydration of cyclopropyldiethylcarbinol yields γ -cyclopropyl- Δ^2 -pentene, b. p. $127.5\text{--}128^\circ/762.5$ mm. Dehydration of cyclopropylmethylethylcarbinol yields both β -cyclopropyl- Δ^2 - and - Δ^2 -pentenes, the products having b. p. $103.5\text{--}103.8^\circ$, d_4^{20} 0.7772, n_D^{20} 1.43901, and b. p. $105.5\text{--}106^\circ$, d_4^{20} 0.7804, n_D^{20} 1.44253.

R. K. CALLOW.

Additive properties of diacetylenic hydrocarbons. V. GRIGNARD and TCHOUFAKI (Rec. trav. chim., 1929, 48, 899—903).—See this vol., 448, 907.

Formation of liquid hydrocarbons from acetylene. I. Polymerisation of acetylene. F. FISCHER, F. BANGERT, and H. PICHLER.—See B., 1929, 703.

Promoter action with oxide catalysts for the decomposition of alcohols. H. ADKINS and P. E.

MILLINGTON (J. Amer. Chem. Soc., 1929, **51**, 2449—2460).—The percentage of ethylene in the products formed when alcohol is passed over a zinc oxide catalyst at 400° varies considerably when precipitated zinc oxide is used. Reproducible results are obtained when the oxide is prepared by ignition of zinc oxalate (standard catalyst). Addition of small amounts of various oxides, sodium hydroxide, and sulphuric acid to the standard catalyst shows that for ethyl, propyl, isopropyl, and butyl alcohols the effect of the added substance is never constant, but is specific for a given alcohol. With an iron oxide catalyst (from ferrous oxalate) and alcohol at 400°, only boric oxide increases the formation of ethylene and ethane at the expense of dehydrogenation; the amount of carbon dioxide produced is diminished by sulphuric acid, sodium hydroxide, and chromium oxide. With titanium oxide catalysts and alcohol at 400° added sodium hydroxide increases the amounts of ethane and hydrogen and diminishes the amounts of ethylene and methane. The ratio ethane : ethylene varies considerably using specimens of titanium oxide prepared by hydrolysis of ethyl and butyl orthotitanates; the amounts of methane and hydrogen produced are almost constant. Selective activation is possible, therefore, without addition of promoters or poisons. The results do not support Taylor's hypothesis (cf. A., 1927, 632) of the effect of acid and basic promoters on the ratio dehydration : dehydrogenation. H. BURTON.

Reactions of allyl alcohol over aluminium and zinc oxide catalysts. P. E. WESTON and H. ADKINS (J. Amer. Chem. Soc., 1929, **51**, 2430—2436).—When allyl alcohol is passed over aluminium oxide at 330° at 50 c.c. per hr. propaldehyde is formed; no acraldehyde results and only a small amount of hydrogen is produced. The change occurs presumably by intramolecular rearrangement of the alcohol (cf. Constable, A., 1927, 27). A marked lowering of activity of the catalyst is observed when 0.01 mol. of boric acid, sulphuric acid, chromic oxide, or sodium hydroxide is added. With zinc oxide catalysts at 330° both acraldehyde and propaldehyde are produced (cf. A., 1928, 968). A decrease in the rate of flow of the alcohol increases the percentage of acraldehyde in the products formed; an increase in the volume of catalysts (for constant flow) has the same effect. When the catalyst is prepared by igniting zinc oxalate the amount of acraldehyde produced is larger than with the catalyst obtained from zinc hydroxide. Addition of 0.01 mol. of boric, tungstic, or sulphuric acid, chromic oxide, or sodium hydroxide to the catalyst (from oxalate) causes selective activation, since, with a rate of flow of the alcohol of 50 c.c. per hr., an increase in the amount of aldehydes produced results (with the exception of sulphuric acid). In all the cases there is a decrease in the percentage of acraldehyde; this is again increased by decreasing the rate of flow of the alcohol. H. BURTON.

Relative configurations of *d*- β -octanol and its dextrorotatory halides. Interconversion of the optically active β -octanols by a new method. A. J. H. HOUSSA, J. KENYON, and H. PHILLIPS (J.C.S., 1929, 1700—1711).—*d*- or *l*- β -Octanol is con-

verted by the action of *dl*-*p*-toluenesulphonyl chloride and pyridine into *d*-, $[\alpha]_D^{25} + 24.16^\circ$, n_D^{25} 1.5071, and *l*-, $[\alpha]_D^{25} - 28.2^\circ$, n_D^{25} 1.5038, β -octyl *dl*-*p*-toluenesulphates, respectively, without change in configuration, the same esters being obtained by direct esterification of the alcohol with *p*-toluenesulphinic acid. These react with halogens (in aqueous or chloroform solution) thus: $C_7H_7 \cdot SO_2R + Cl_2 \rightarrow C_7H_7 \cdot SO_2Cl + RCl$, to yield, respectively, *l*- and *d*- β -chloro-octanes (the rotation values of which, compared with those of earlier investigators, are inexplicably low), a Walden inversion taking place, since, by the action of hypochlorous acid, which reacts in accordance with the similar scheme, $C_7H_7 \cdot SO_2R + HOCl \rightarrow C_7H_7 \cdot SO_2Cl + R \cdot OH$, they are converted, respectively, into *l*- and *d*- β -octanol. At the same time octenes and hence dihalogeno-octanes are formed as by-products. Oxidation of the *p*-toluenesulphates with potassium permanganate converts them into the corresponding *p*-toluenesulphonates, again without change in configuration. These, when boiled under reflux with an alcoholic solution of lithium chloride, yield the β -chloro-octanes of opposite sign, by a reaction exactly similar to that involved in the conversion of *d*- β -octyl *p*-toluenesulphonate into *l*- β -octyl acetate or benzoate by boiling with alcoholic potassium acetate or benzoate (Pickard and Kenyon, J.C.S., 1914, **105**, 830) and hence involving a change in configuration. Thus both methods point to the conclusion that *d*- β -octanol and its dextrorotatory halides have the same configuration. This is in agreement with the views of Pickard and Kenyon (*loc. cit.*), but not with those of Levene and Mikeska (A., 1924, i, 940), and both the validity of the assumptions and the experimental technique of these authors are criticised. The action of thionyl chloride on *d*- β -octanol yields *l*- β -chloro-octane of the same rotation ($[\alpha]_D^{25} - 31.0^\circ$) as that obtained in the presence of pyridine, which, therefore, does not affect the rotation. Mechanisms for these configuration changes based on the proved structure of *p*-toluenesulphates (Phillips, A., 1926, 159) are suggested and it is considered probable that the Walden inversion occurs whenever a group attached to an asymmetric carbon atom is replaced, unless a phenyl group is directly linked to the asymmetric atom or a carboxyl group is present in the molecule. J. W. BAKER.

[Aliphatic (open-chain) hydroterpenes.] S. SABETAY and J. BLEGER (Bull. Soc. chim., 1929, [iv], **45**, 497—498; cf. A., 1928, 1138).—Mainly a question of priority (cf. Longuinov and Margoliss, this vol., 538). The authors recommend restricting the use of the names tetrahydrogeraniol, dihydrocitronellol, and dihydrorhodinol to *dl*-, *d*-, and *l*- γ -dimethyloctanol, respectively. R. BRIGHTMAN.

Manufacture of γ -butylene glycol. I. G. FARBERIND. A.-G.—See B., 1929, 671.

Tetramethylene glycol and tetramethylene chlorohydrin. W. R. KIRNER and G. H. RICHTER (J. Amer. Chem. Soc., 1929, **51**, 2503—2506).—Fission of benzyl δ -hydroxybutyl ether (Bennett, A., 1925, i, 883) with hydrobromic acid (cf. Bennett and Hock, A., 1927, 355) affords tetramethylene glycol, b. p. 107—108°/4 mm., m. p. 19—19.5°, d_4^{20} 1.0171,

1-4467 [bisphenylcarbimide derivative, m. p. 179.5° (lit. 180—181°)], converted by treatment with thionyl chloride and pyridine at 55—80° into tetramethylene chlorohydrin, b. p. 84—85°/16 mm., d_4^{20} 1.0883, n_D^{20} 1.4518 [phenylcarbimide derivative, m. p. 54°; α -naphthylcarbimide derivative, m. p. 69—70° (lit. 66°)].
H. BURTON.

Crystalline acetin and diglycide. M. BATTEGAY, H. BUSER, and E. SCHLAGER (Bull. Soc. chim., 1929, [iv], 45, 494—497).—See this vol., 539.

Methionic [methanedisulphonic] acid. H. J. BACKER (Rec. trav. chim., 1929, 48, 949—952).—Treatment of methylene chloride (1 mol.) with potassium sulphite (2 mols.) and water at 150—160° affords about 85% of the theoretical amount of potassium methanedisulphonate. The free acid +2H₂O, m. p. 90.5° (thallous salt), is obtained by decomposition of the barium salt, prepared also by Schroeter's method (A., 1898, i, 614). The solubilities of the crystalline and anhydrous acid and salts in water at 25° are given.
H. BURTON.

Production of esters from acid amides. H. G. SMITH and IMPERIAL CHEM. INDUSTRIES, LTD.—See B., 1929, 671.

Acids of montan wax. D. HOLDE, W. BLEYBERG, and H. VORRER.—See B., 1929, 667.

Derivatives of homolævulic acid. R. LUKES (Coll. Czech. Chem. Comm., 1929, 1, 461—466).— γ -Acetoxy- γ -hexolactone, b. p. 135—136°/10 mm., d_4^{21} 1.1507, n_D^{21} 1.44731, is obtained by interaction of homolævulic [γ -ketohectic] acid and acetic anhydride in the presence of a little acetyl chloride, and when distilled under ordinary or reduced (200—250 mm.) pressure yields acetic acid and 5-keto-2-ethyl-4:5-di-hydrofuran, b. p. 75—76°/10 mm., d_4^{18} 1.0662, n_D^{18} 1.45835. The latter affords 5-keto-2-ethyl-2:5-di-hydrofuran, b. p. 99—101°/10 mm., d_4^{18} 1.0704, n_D^{18} 1.46467, when heated with trimethylamine at 100°, and yields homolævulanilide, m. p. 92°, with aniline.
A. I. VOGEL.

Manufacture of [alkoxy]aliphatic acids. H. DREYFUS.—See B., 1929, 671.

Polymerisation and ring formation. I. General theory of condensation polymerides. W. H. CAROTHERS. II. Poly-esters. W. H. CAROTHERS and J. A. ARVIN (J. Amer. Chem. Soc., 1929, 51, 2548—2559, 2560—2570).—I. Two types of linear polymerides, $[R]_n$, are recognised: (1) addition (*A*) polymerides (e.g., caoutchouc, polystyrene, polyoxymethylenes), where the polymeride has the same composition as the monomeric compound, and (2) condensation (*C*) polymerides (e.g., cellulose, hexaethylene glycol), where the monomeric compound differs from the structural unit (*R*) by H₂O (NH₃, HCl). Substances of the type $x \cdot R \cdot y$ are termed bifunctional (x and y are capable of interaction, forming z), and the change $x \cdot R \cdot y \rightarrow \cdot R \cdot z$ is a bifunctional reaction. The change $x \cdot R \cdot x + y \cdot R \cdot y \rightarrow \cdot z \cdot R \cdot z \cdot R \cdot$ is a bi-bifunctional reaction. Bifunctional reactions are intramolecular when five- or six-membered ring formation is possible and the monomeric ring compound, $R \diamond z$, results. If the monomeric ring substance is larger than six-membered

intermolecular change occurs and the products are of the type $[\cdot R \cdot z \cdot]_n$ or $x \cdot [\cdot R \cdot z \cdot]_{n-1} \cdot R \cdot y$. Various examples from the literature are discussed.

II. The bi-bifunctional reaction $R(CO_2H)_2 + R'(OH)_2 \rightarrow [CO \cdot R \cdot CO \cdot O \cdot R' \cdot O]$ (structural unit), where all the functional groups are involved, will give rise to polymerides when the number of atoms in the structural unit is seven or more. The following esters are described: ethylene malonate, succinate, m. p. 108°, adipate, m. p. 50°, and sebacate, m. p. 79°; trimethylene succinate, m. p. 52°, adipate, m. p. 45°, and sebacate, m. p. 56°; hexamethylene succinate, m. p. 57°, adipate, m. p. 56°, and sebacate, m. p. 67°; decamethylene succinate, m. p. 68°, adipate, m. p. 77°, and sebacate, m. p. 74°. The number of atoms in the structural unit varies from 7 to 22, and all the esters are highly polymerised. The lowest mol. wt. observed is 2300 (ethylene malonate), the highest 5000 (trimethylene sebacate). The esters are non-acidic and it is assumed that alcoholic hydroxyl groups are at each end of the complex molecule (excess of glycol is used in the preparations). Ethylene phthalate (prepared from the glycol and phthalic anhydride first at 190° and then at 300°/3 mm., similarly from the glycol and ethyl phthalate, and from the glycol and phthaloyl chloride in pyridine), trimethylene, hexamethylene, and decamethylene phthalates are also described. The mol. wt. of these esters varies from about 1500 to 5000. When a mixture of ethyl fumarate and ethylene glycol is heated at 190—230° (final pressure 4 mm.) in a current of nitrogen ethylene fumarate (mol. wt. determination not possible owing to insolubility) results. Ethylene maleate is obtained from the glycol and maleic anhydride first at 195—200° and then at 200—215°/vac. These preparations differ from those described by Vorländer (A., 1895, i, 17).
H. BURTON.

Determination of relationship of stereochemical structure existing between optical antipodes of different substances. J. TIMMERMANS (Rec. trav. chim., 1929, 48, 890—894).—*d*-Chloro- and *d*-bromo-succinic acids furnish a continuous series of mixed crystals, whilst *d*-chloro- and *l*-bromo-succinic acids afford a partial racemate. The stereochemical structures of both *d*-acids are therefore probably similar. The f.-p. curves of various closely related substances quoted in the literature are commented on.
H. BURTON.

Formation of *l*-malic acid from fumaric acid by *Aspergillus niger*. F. CHALLENGER and L. KLEIN (J.C.S., 1929, 1644—1647).—The fermentation of a 1% solution of potassium fumarate at 31—32° by cultures of *A. niger* which have been trained to grow in this medium produces *l*-malic acid which was isolated as such and identified by the formation of its di-*p*-nitrobenzyl ester, m. p. 125°. The formation of *l*-malic acid must arise from asymmetric addition of water to the double linking and not by the prior formation of *dl*-malic acid, since the latter becomes dextrorotatory after attack by *A. niger*. This view is in agreement with various biochemical observations which are summarised. Di-*p*-nitrobenzyl *dl*-malate has m. p. 109°.
J. W. BAKER.

Action of phosphorus pentachloride on ethyl tartrate. T. S. PATTERSON and A. R. TODD (J.C.S., 1929, 1768—1771).—Fractional distillation of the product obtained by the action of phosphorus pentachloride on ethyl tartrate yields dichloromaleic anhydride (I), ethyl chlorofumarate mixed with ethyl dichlorosuccinate (II), and ethyl hydrogen chlorofumarate (III). The initial product is probably ethyl β -chloromaleate, which is further chlorinated to ethyl dichlorosuccinate, and this is converted by loss of hydrogen chloride into ethyl chlorofumarate (II). The latter is then converted into ethyl chlorofumaryl chloride, which yields III on pouring into water, or it may become further chlorinated to give, ultimately, dichlorofumaryl chloride, from which I results. J. W. BAKER.

Production of acetaldehyde from acetylene. I. G. FARBENIND. A.-G.—See B., 1929, 708.

Condensation of acetaldehyde with methylmalonic ester. Methylations with methyl bromide. H. J. LUCAS and W. G. YOUNG (J. Amer. Chem. Soc., 1929, 51, 2535—2538).—Ethyl methylmalonate (I) and methylacetoacetate are conveniently prepared by passing methyl bromide into the hot alcoholic solution of ethyl sodio-malonate and -acetoacetate. Condensation of I with acetaldehyde in presence of acetic anhydride affords the ethyl ester, b. p. 100—106°/3—5 mm., d_4^{25} 1.0732, of γ -hydroxybutane- $\beta\beta$ -dicarboxylic acid [*diamide*, m. p. 209.5° (corr.; decomp.)]. H. BURTON.

Formation of cyclic acetals by the action of acetone and acetaldehyde on $\alpha\gamma$ -dihydroxycompounds. J. BOESEKEN (Rec. trav. chim., 1929, 48, 931—934).—An account of the formation of five- and six-membered isopropylidene and ethylidene ethers from $\alpha\gamma$ -glycols, glycerol, and related compounds (cf. Boeseken and van Loon, A., 1920, i, 837; Hill, Hibbert, and others, A., 1928, 1114, 1213; van Roon, this vol., 291). H. BURTON.

Acraldehyde, anti-oxidants, coloured hydrocarbons yielding dissociable peroxides (rubrene family) and hæmoglobin. C. MOUREU (Rec. trav. chim., 1929, 48, 826—837).—A resume of the author's work on the stabilisation of acraldehyde, anticycatalysts, the theory of anti-oxidation catalysis, and rubrene. The dissociation of rubrene peroxide appears to be analogous to the dissociation of oxyhæmoglobin. The respiratory function of hæmoglobin is, therefore, not necessarily a function of the iron present in the molecule. H. BURTON.

α -Bromo- and α -hydroxy-aldehydes. IV. α -Hydroxy-*n*-butaldehyde, α -hydroxyisobutaldehyde, and glycollaldehyde. R. DWORZAK and J. PIERRE (Monatsh., 1929, 52, 141—150; cf. A., 1927, 1055; this vol., 297).—Treatment of para-*n*-butaldehyde with bromine at -10° to -5° and subsequently with alcohol affords slightly impure α -bromo-*n*-butaldehyde ethylacetal, b. p. 76—81°/12 mm., which is hydrolysed by boiling with water to α -hydroxy-*n*-butaldehyde, b. p. 70—80°/14 mm. (*p*-nitrophenylhydrazone, m. p. 135°; *p*-nitrophenylosazone, m. p. 227°). The oil obtained by distillation crystallises after about two weeks. Similar bromination of para-

isobutaldehyde yields α -bromoisobutaldehyde ethylacetal together with a substance, $C_{12}H_{18}OBr_6$, m. p. 85.5°, the mol. wt. of which in benzene is low. Hydrolysis of the acetal furnishes α -hydroxyisobutaldehyde (*p*-nitrophenylhydrazone). Hydrolysis of bromoacetal and subsequent prolonged extraction of the partly neutralised reaction mixture with ether gives glycollaldehyde; this could not be isolated by distillation. The above hydroxyaldehydes are determined by Fehling's solution. The action of dilute alkali on glycollaldehyde appears to give products which are not analogous to those from lactaldehyde (cf. *loc. cit.*).

H. BURTON.

Ketonic transformation of aldehydes at high temperatures. I. S. DANILOV (J. Russ. Phys. Chem. Soc., 1929, 61, 723—725).—The transformation of di- and tri-substituted aldehydes into ketones at elevated temperatures in the presence of catalysts, such as mercury salts, aluminium oxide, zinc chloride, etc., is discussed. The possibility of the formation according to this mechanism of the ketones resulting from the destructive distillation of cellulose substances is suggested. Trimethylacetaldehyde, b. p. 74°, which is a product of wood distillation, was found to isomerise quantitatively into methyl isopropyl ketone, b. p. 93—94°, by the action of aluminium chloride at 350° in an atmosphere of carbon dioxide. Triphenylacetaldehyde with the same catalyst, at 320—340°/25 mm., gave triphenylethanone, m. p. 136°.

M. ZVEGINTZOV.

Conversion of sugars into furan or hydrofuran derivatives. E. VOTOCEK and S. MALACHTA (Coll. Czech. Chem. Comm., 1929, 1, 449—460).—Methyl 3-methoxy-5-methylfuran-2-carboxylate (I), m. p. 48°, prepared from 8-ketorhamnolactone, is converted by aqueous potassium hydroxide into 3-methoxy-5-methylfuran-2-carboxylic acid, m. p. 158—159° (potassium salt), which yields 3-methoxy-5-methylfuran, b. p. 124—125°, on dry distillation with lime. The ester I affords on prolonged exposure to the atmosphere or more rapidly in the presence of a little hydrochloric acid a relatively unstable, optically inactive yellow compound, $C_{15}H_{18}O_9$, m. p. 62°, which when warmed with 0.2*N*-potassium hydroxide or hydrochloric acid furnishes methyl 3-methoxy-5-methylfuran-2-carboxylate, m. p. 48°, and a compound, m. p. 70°.

A. I. VOGEL.

Structure of α -methylxyloside. F. P. PHELPS and C. B. PURVES (J. Amer. Chem. Soc., 1929, 51, 2443—2449, and Bur. Stand. J. Res., 1929, 3, 247—253).—Methylation of β -methylxyloside with methyl iodide and silver oxide affords trimethyl- β -methylxyloside (I), m. p. 51°, $[\alpha]_D^{20}$ -69.5° in chloroform. When methylation of xylose is carried out first with methyl sulphate and alkali and then with methyl iodide and silver oxide the yield of I is smaller and the product is optically impure (cf. Carruthers and Hirst, J.C.S., 1922, 121, 2299). Methyl iodide-silver oxide treatment of α -methylxyloside affords trimethyl- α -methylxyloside (II), n_D^{20} 1.4397, $[\alpha]_D^{20}$ $+121.5^\circ$ in chloroform, purified by distillation. Hydrolysis of I and II with 4% hydrochloric acid at 85° yields the same trimethyl- α -xylose, m. p. 91—92°, $[\alpha]_D^{20}$ $+64.5^\circ$ \rightarrow 17.7° in water. It is concluded that I and II

contain the same ring structure and are an α - and β -pair. H. BURTON.

Sugar oxidations and decompositions. III. Theory of sugar degradation. IV. Behaviour of dextrose in sulphuric acid solution. K. BERNHAUER (Biochem. Z., 1929, 210, 175—185, 186—180; cf. this vol., 543).—III. It is suggested that there are two main methods of degradation of dextrose: (1) Non-oxidative processes characterised by formation of C_3 chains preceded by a rearrangement into the labile furanose form and hence taking place chiefly in alkaline solution. This includes all processes giving rise to methylglyoxal, acetaldehyde, and products derived from them by simple oxidation and reduction, e.g., acetic acid. (2) Processes depending on a primary oxidation of the stable form of dextrose. This oxidation occurs most readily at the 1- and 5-carbon atoms (ends of the pyranose oxygen bridge) and at the 6-carbon atom, principally in acid solution.

IV. In sulphuric acid solution dextrose is much less easily oxidised by hydrogen peroxide and ferrous sulphate than in originally neutral solution. The dextrose appears to be present in a more stable form. Acetic acid is not produced. J. H. BIRKINSHAW.

Glucosides. II. Preparation of α -glucosides from β -glucosyl chlorides. W. J. HICKINBOTTOM (J.C.S., 1929, 1676—1687).—The conversion of 2-trichloroacetyl-3:4:6-triacetyl- (I) and 3:4:6-trichloroacetyl- (II) β -glucosyl chlorides, prepared by slight modification of Brigl's method (A., 1922, i, 225), into α -glucosides has been studied. Contrary to Brigl, I exhibits almost no mutarotation even in chloroform solution. In dry methyl alcohol, however, the rotation rapidly increases from $[\alpha]_D^{25} +2.5^\circ$ to $+92.5^\circ$ in 46.8 hrs. and then slowly falls to an equilibrium value, the solution acquiring an acid reaction. If, at the point of maximum rotation, the solution is shaken with silver oxide to remove the unchanged β -glucosyl chloride, α - (70%) and β -methylglucosides can be isolated. The formation of the β -glucoside cannot be ascribed in this case to the prior formation of the 1:2-anhydride, especially since the original β -glucosyl chloride is stable in the presence of silver chloride and silver oxide in dry benzene solution. Similar, but much slower, rotation changes occur in ethyl ($[\alpha]_D +7.0^\circ$ to $+44.5^\circ$ in 165 hrs.) and *n*-butyl ($[\alpha]_D +4^\circ$ to $+22.0^\circ$ in 193.5 hrs.) alcohols, although the change was not followed for a sufficient length of time to attain the maximum value. More rapid rotation changes of the same type occur with II; in methyl alcohol the rotation changes rapidly to $[\alpha]_D +160^\circ$ in 2 hrs., whilst in ethyl alcohol the maximum is reached in 9 hrs. Treatment with silver carbonate and subsequent deacetylation with anhydrous ammonia at the ordinary temperature again yields a mixture of α - and β -glucosides. The initial rise in rotation is determined partly by isomerisation to the α -glucosyl chloride and partly by reaction of the β -chloride with the alcohol to yield an α -glucoside. When equilibrium between the α - and β -glucosyl chlorides is attained the reaction with the solvent becomes predominant and causes the final fall in rotation. The predominant formation of α -glucosides

requires that the rate of replacement of halogen by the alkoxy-group should be rapid compared with the rate of isomerisation of the β -glucosyl chloride, and should be favoured by dilution of the reactants with an indifferent solvent. Isomerisation of I into the α -chloride occurs in acetone solution, but by the action of "active" silver oxide in methyl alcohol solution, the yield of α -methylglucoside never exceeds 70%. When an alcoholic solution of I or II is treated with silver nitrate and pyridine, however, the yield of α -glucoside is increased to 79.4 and 88—90%, respectively (cf. Schlubach and Schröter, A., 1928, 873). By the action of dry silver oxide on a suspension of II in a chloroform solution of phenol and subsequent deacetylation, α -phenylglucoside hydrate, m. p. 148—150°, $[\alpha]_D +143^\circ$, is obtained. J. W. BAKER.

Synthesis of glucosides. II. Preparation of some galactosides. A. ROBERTSON (J.C.S., 1929, 1820—1823).—Tetra-acetylgalactosidyl bromide (Fischer and Armstrong, A., 1902, i, 263) is obtained in good yield by addition of penta-acetylgalactose to a mixture of acetic anhydride and glacial acetic acid saturated at 0° with hydrogen bromide. It reacts with quinol in acetone in the presence of aqueous potassium hydroxide to give O-tetra-acetyl- β -p-hydroxyphenylgalactoside, m. p. 202—203°, which is deacetylated to β -p-hydroxyphenylgalactoside $+1.5H_2O$, m. p. 246—247°, $+2H_2O$, m. p. 246—247°, $[\alpha]_D -53.2^\circ$ in water. By similar methods are obtained O-tetra-acetyl- β -p-anisyl-, m. p. 104°, β -l-menthyl-, m. p. 100—101°, $[\alpha]_D^{25} -48.6^\circ$ in chloroform, and β -d-bornyl-, m. p. 140°, $[\alpha]_D^{25} +1.3^\circ$ in chloroform, -galactosides, from which by deacetylation are obtained, respectively, β -p-anisyl-, anhydrous, m. p. 161°, and $+H_2O$, $[\alpha]^{25} -40^\circ$ in water; β -l-menthyl-, $+2H_2O$, m. p. 40—41°, $[\alpha]_D^{25} -74.2^\circ$ in alcohol, $+0.5H_2O$, and β -d-bornyl-, $+H_2O$, m. p. 123°, $[\alpha]^{25} -6.5^\circ$ in alcohol, and anhydrous, m. p. 137—138°, -galactosides. J. W. BAKER.

Sugar anhydrides. A. PIETET and H. VOGEL (Rec. trav. chim., 1929, 48, 843—846).—When a concentrated, aqueous solution of trihexosan is exposed to ultra-violet light for 56 hrs. 60% conversion into hexahexosan (I) occurs; further irradiation of I appears to have no action. Amylase converts I into maltose, whilst acetyl bromide gives hepta-acetylmaltose. When I is hydrolysed with oxalic acid a mixture of dextrinose (II) (an iso-maltose; see Georg and Pietet, A., 1926, 823) and dextrinosan (III), $C_{12}H_{20}O_{10}$, m. p. 185—186°, $[\alpha] +150.7^\circ$, is obtained. A very dilute solution of III gives a reddish-brown coloration with iodine; III is not converted into II by boiling with water, whilst irradiation affords I. H. BURTON.

Polysaccharides. IV. Constitution of xylan. H. A. HAMPTON, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1929, 1739—1753).—Pure xylan, containing 10.7% of moisture, $[\alpha]_D^{25} -109.5^\circ$ (calculated as anhydrous material in 2.5% aqueous sodium hydroxide solution), isolated by extraction with boiling 12% aqueous sodium hydroxide from esparto cellulose, has definitely the composition $(C_5H_8O_4)_n$, and by hydrolysis with 3% nitric acid gives a 93% yield of crystalline xylose (cf. Heuser and Jayme, A.,

1923, i, 1061). Previous methods of methylation of xylan are shown to yield mixtures of hydrolysis products containing mono-, di-, and tri-methylxyloses. Pure *dimethylxylan* (I), m. p. 194–196° (slight decomp.), $[\alpha]_D^{25} - 92^\circ$ in chloroform, is obtained by two methylations of xylan with potassium hydroxide and methyl sulphate under prescribed conditions, proof that the methyl groups occupy the 2 and 3 positions being obtained from the following reactions. Hydrolysis of I with 1.2% methylalcoholic hydrogen chloride yields *dimethylmethylxyloside* (II), b. p. about 80°/0.04 mm., $n_D^{20} 1.4581$, $[\alpha]_D^{25} + 61.8^\circ$ in methyl alcohol, which is further methylated with methyl iodide and silver oxide to yield trimethylmethylxyloside; this is hydrolysed to 2 : 3 : 4-trimethylxylose (Carruthers and Hirst, J.C.S., 1922, 121, 2299) in 81% yield, slight losses arising from the formation of furan derivatives as by-products. Hydrolysis of II with 3% hydrochloric acid at 100° gives an 85% yield of 2 : 3-dimethylxylose, $n_D^{20} 1.4783$, $[\alpha]_D^{25} + 22.6^\circ$ in water, characterised as its *anilide*, m. p. 146°. By hydrolysis and subsequent oxidation with bromine II is converted into 2 : 3-dimethyl- γ -xylonolactone (III), b. p. about 115°/0.02 mm., $n_D^{20} 1.4640$, $[\alpha]_D^{25} + 97^\circ$ (initial value in water), characterised by conversion into the phenylhydrazide and *p*-bromophenylhydrazide, m. p. 150–151°, of 3 : 5-dimethylxylonic acid. Hydrolysis of III in aqueous solution is very slow, equilibrium being approached only after 400 hrs., and on complete methylation it is converted into 2 : 3 : 5-trimethyl- γ -xylonolactone, thus confirming its structure as a γ -lactone. Hence positions 4 and 5 of the original dimethylxylose from dimethylxylan must be unmethylated, the pyranose form of the sugar yielding a furanose type of lactone, and in xylan these two positions must be involved either in linking the β -xylose units or in ring formation. J. W. BAKER.

Starch. (SIR) J. C. IRVINE (Rec. trav. chim., 1929, 48, 813–816).—Polysaccharides derived from dextrose are divided into two classes. (1) Methylation (methyl sulphate and iodide) proceeds regularly until the methoxyl content is 37%; further methylation is effected indirectly by chlorination and subsequent treatment with sodium methoxide (e.g., starch, glycogen, tetra-amylose). (2) Methylation proceeds regularly, yielding the fully methylated derivative (e.g., cellulose, hexa-amylose). Hydrolysis of the fully methylated derivatives of both classes gives 2 : 3 : 6-trimethylglucose. This has a tendency to exist in 1 : 4- and 1 : 5-ring modifications, indicating that the parent substances may be structurally different. The oxygen ring in starch probably differs from that in cellulose. Starch and cellulose may be polymerides of isomeric anhydrides of α - and β -glucose (1 : 4- and 1 : 5-ring, respectively).

H. BURTON.

Dissolution and acetylation of starch. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1929, 4, 153–156).—Besides glycerol, starch is soluble to the extent of 10% in fused erythritol at 150–160°, less easily soluble in mannitol at 180–190°, and very slightly soluble in ethylene glycol at 190°. In methyl alcohol at 185° the starch neither swells nor dissolves.

Triacetyl starch is obtained by acetylation with acetic anhydride in glycerol solution. This product, which is more soluble, less viscous in solution, and has a lower specific rotation than that obtained by acetylation in zinc chloride solution (this vol., 175), has probably suffered some depolymerisation. Untreated potato starch, dissolved in glycerol containing zinc chloride at 160–170°, and acetylated by treatment with acetic anhydride at 70°, yielded a product $[\alpha]_D + 164^\circ$ in chloroform, M 4000–6000. Initial dissolution of the starch at a higher temperature gave a triacetyl compound which was further depolymerised, $[\alpha]_D + 146^\circ$, M 3200. The polysaccharides obtained in either case by deacetylation were non-reducing and gave a blue colour with iodine.

T. H. MORTON.

Lignin. III. Destructive distillation of lignin from corn cobs. M. PHILLIPS (J. Amer. Chem. Soc., 1929, 51, 2420–2426).—The lignins are obtained by the following methods: (a) heating the corn cobs with 2% sodium hydroxide solution under pressure and acidifying the alkaline liquors, (b) prolonged treatment with hydrochloric acid ($d_4^{20} 1.21$) at the ordinary temperature, and (c) prolonged treatment with 72% sulphuric acid at the ordinary temperature. Distillation of lignin *a* at 380–400° under ordinary pressure gives aqueous distillate (15.5% of dry, ash-free lignin), oil (17.7%), carbon residue (52.2% of lignin used), and gas (13.5% by difference). The aqueous distillate contains acetone (0.13%), methyl alcohol (1.9%), and acids (as acetic 0.05%; this small value is probably due to deacetylation during the alkali treatment), whilst the oil consists of acids (8.6%), phenols (84%), and hydrocarbons and neutral compounds (7.2%). Lignins *b* and *c* afford about the same amounts of aqueous distillates as *a*; these contain more acetone and acetic acid but less methyl alcohol (probably due to smaller methoxyl contents of *b* and *c*) than the distillate from *a*. About one half the amount of oil is formed, but the carbon residue increases.

H. BURTON.

Lignin colouring matters. F. PODBREZNIK (Bull. Inst. Pin, 1928, 233–236, 245–250; Chem. Zentr., 1929, i, 1212–1213).—A study of the colour reactions of lignin. The reaction with alcoholic phloroglucinol and hydrochloric acid is not merely a chemical reaction, but is concerned with selective adsorption. The behaviour of lignin obtained in different ways was examined A. A. ELDRIDGE.

[Preparation of] diamines and amino-alcohols. N. PUTCHIN (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 6, 10–21).—By the use of more concentrated sodium hydroxide solution and distillation of the liquid to dryness, nearly theoretical yields of diamines were obtained by Gabriel's method (A., 1888, 1292). The method is convenient for the preparation of primary hydroxyamines, e.g., of γ -hydroxypropylamine (90% yield) from γ -phthalimidopropyl bromide, and of ϵ -hydroxyamylamine, m. p. 26°, b. p. 221–222°, $d_4^{20} 0.9488$, $n_D^{20} 1.4618$ (chloroplatinate, m. p. 180°).

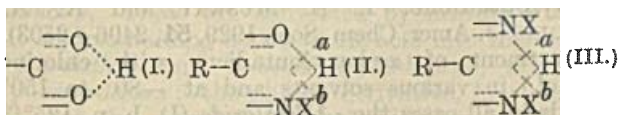
CHEMICAL ABSTRACTS.

Behaviour of isomeric *r*- α -bromopropionyl-norvalines and *r*-alanyl-norvalines towards

N-alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1929, 11, 119—125).—Treatment of *dl*-norvaline with *dl*- α -bromopropionyl bromide and 2*N*-sodium hydroxide solution affords two α -bromopropionylnorvalines, (A), m. p. 128.5—129.5° after sintering at 126°, and (B), m. p. 130.5—131.5° after sintering at 129°. Amination of A and B affords the corresponding inactive *alanyl*norvalines (I), m. p. 218—219° with darkening after sintering at 184°, and (II), m. p. 224—225° (decomp.), respectively. Fission of I and II does not occur with trypsin-kinase at p_H 8.4 and 37° or with *N*-sodium hydroxide at 37°. Erepsin (p_H 7.8) has no action on II, whilst I undergoes 25% hydrolysis. Partial hydrolysis of A and B occurs with *N*-sodium hydroxide; trypsin-kinase (p_H 7.8) has some action on A but practically none on B.

H. BURTON.

Constitution of sulphur and nitrogen compounds derived by substitution of the carboxyl group. G. ODDO (Rec. trav. chim., 1929, 48, 875—879).—On the basis of his tetragonal mesohydric form of the carboxyl group I (cf. A., 1907, ii, 15; 1922, ii, 367), the author discusses the constitution of various compounds obtained by substituting the ketonic or hydroxylic functions of the carboxyl group by :S or :SH, and by :NH or :NHR, both separately and together in the latter case. These compounds are considered to possess the usual formulæ only in their alkyl derivatives, the free substances having a mesohydric form, e.g., II, which, by fission in the directions (a) and (b) affords normal and *iso*-alkyl derivatives.



In support, the cases of amidines, hydrazines, and hydroxylamino-oximes, the mesohydrics III (X, X = H, NH₂, and OH, respectively) of which are symmetrical and can afford but one product by fission at (a) or (b), are instanced.

C. W. SHOPPEE.

Synthetic carbamide from ammonia and carbon dioxide. G. A. YAKOVKIN.—See B., 1929, 707.

Carbamide series: nitrocarbamide, nitrobiuret, and dicyanic acid. K. C. BLANCHARD (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 50—51).—Carbamide and monosubstituted carbamides may be used as a source of cyanic acid or carbylamines, respectively, for the preparation of mono- and *s*-disubstituted carbamides, the dry reactants being heated together at 160°, or boiled in aqueous solution. Aromatic and aliphatic secondary amines similarly give very poor yields of *as*-disubstituted carbamides. The introduction of a nitro-group decreases the stability, nitrocarbamide readily breaking down into cyanic acid and nitramide, and hence it acts as a nitrating agent in concentrated sulphuric acid solution. The decomposition is promoted by alkalis but hindered by mineral acids. In aqueous solution nitrocarbamide reacts with ammonia and amines to yield carbamide or its derivatives. In a similar manner nitrobiuret is a source of nascent dicyanic acid which,

in the absence of amines, forms allophanic acid and hence, ultimately, carbamide and carbon dioxide, whilst it reacts with amines to yield ω -substituted biuret derivatives. In moist alcohol nitrobiuret yields allophanic esters and ultimately carbamic esters, and in concentrated sulphuric acid the nitro-nitrogen is quantitatively evolved. By the application of these synthetic methods the following new compounds have been prepared but are not described: *s*-*di*-*n*-amyl-, *n*-amyl-, *as*-*di*-*n*-butyl-, (*picrate*), *as*-phenyl-*n*-propyl-, (*picrate*; *oxalate*), *as*-phenyl-*n*-butyl-carbamides; ω -*n*-propyl-, *n*-butyl-, benzyl-, α -naphthyl-, $\omega\omega'$ -dimethyl-, diethyl-, *di*-*n*-butyl-, phenylethyl-, and phenyl-*n*-propyl-biurets.

J. W. BAKER.

Preparation of ethyl phosphinoacetate. A. E. ARBUZOV and G. C. KAMAĬ (J. Russ. Phys. Chem. Soc., 1929, 61, 619—622).—Yields of ethyl phosphinoacetate reaching 95% are obtained by the interaction of sodium ethoxide, diethyl phosphate, and ethyl chloroacetate in absolute alcoholic solution. In other solvents, such as ether or light petroleum, the yields are considerably smaller (cf. A., 1914, i, 651).

R. TRUSZKOWSKI.

Syntheses with ethyl phosphinoacetate. A. E. ARBUZOV and A. I. RAZUMOV (J. Russ. Phys. Chem. Soc., 1929, 61, 623—628).—Ethyl sodiophosphinoacetate is condensed with methyl iodide to yield ethyl α -diethylphosphinopropionate, b. p. 127°/5 mm., and α -diethylphosphinopropionic acid, which could not be distilled without decomposition. These products gave on hydrolysis α -phosphinopropionic acid, m. p. 119—132°. Better yields of the phosphinopropionic ester are obtained using the potassium salt of ethyl phosphinoacetate in the above reaction, no diethylphosphinopropionic acid being obtained in this case. Ethyl benzyl-diethylphosphinoacetate, b. p. 180°/3 mm., and benzylphosphinoacetic acid, m. p. 137—145°, are prepared similarly.

R. TRUSZKOWSKI.

Organic additive compounds of calcium chloride and calcium iodide. F. R. GREENBAUM (J. Amer. Pharm. Assoc., 1929, 18, 784—789).—The following compounds have been prepared according to G.P. 306,804 (cf. B., 1918, 636A): calcium iodide additive products with carbamide, m. p. 95°, thiocarbamide, hexamethylenetetramine, m. p. 180°, urethane, thiosinamine, antipyrine, monoacetylthiocarbamide, monoacetylcarbamide, phenylcarbamide, and calcium chloride additive products with all the above (calcium chloride-urethane; calcium chloride-acetylcarbamide, m. p. 135—140°; calcium chloride-thiocarbamide, m. p. 175—177°). In the case of calcium chloride usually 4 mols. of the base enter into the additive combination and with calcium iodide 6 mols. The additive compounds are stable and less hygroscopic than either calcium chloride or iodide.

E. H. SHARPLES.

Acetoxymurcuric chloride. F. C. WHITMORE and G. J. LEUCK (J. Amer. Chem. Soc., 1929, 51, 2589—2590).—The salt, HgCl₂·Hg(OAc)₂, described by Donk (A., 1907, i, 819) is acetoxymurcuric chloride, HgCl₂·OAc. It is not possible to mercurate dimethylaniline, phenol, or *p*-cresol with this salt.

H. BURTON.

Manufacture of lead tetraethyl. H. W. DAUDT.
—See B., 1929, 709.

Nomenclature of organic compounds of complex function. A. M. PATTERSON (Rec. trav. chim., 1929, 48, 1012—1017).—Analysis of the nomenclature (literature) of 2557 compounds reveals an order of precedence of groups in fairly good agreement with the proposals previously made (A., 1918, i, 97).

H. BURTON.

Catalytic transference of hydrogen between organic compounds. S. AKABORI and T. SUZUKI (Proc. Imp. Acad. Tokyo, 1929, 5, 255—256; cf. Wieland, A., 1923, i, 167).—By treating a compound which is capable of splitting off hydrogen with one capable of easy reduction, in presence of an activating agent (palladium-black), transference of hydrogen takes place from the former to the latter. Cinnamic acid, oleic acid, eugenol, and coumarin when heated with tetrahydronaphthalene and palladium give good yields of hydrocinnamic acid, stearic acid, hydro-eugenol, and hydrocoumarin, respectively. A mixture of tetrahydroquinoline (1 mol.) and maleic acid (2 mols.) is converted quantitatively into quinoline and succinic acid. Piperidine is not reduced by maleic acid and palladium but gives an almost theoretical yield of pyridine with saffrole and palladium. Tetrahydroisoquinoline is, and tetrahydropapaverine is not, reduced by anethole and palladium; nicotine gives small quantities of nicotyrine with these reagents.

A. A. GOLDBERG.

Synthesis of isoamylcyclopentane. J. McA. HARRIS, jun. (J. Amer. Chem. Soc., 1929, 51, 2591).—Magnesium isoamyl bromide converts cyclopentanone into 1-isoamylcyclopentanol, b. p. 101°/17 mm., d_4^{20} 0.8848, n_D^{20} 1.4549, dehydrated by means of *p*-toluenesulphonic acid to 1-isoamyl- Δ^1 -cyclopentene, b. p. 168—170°/760 mm., d_4^{20} 0.8010, 1.4467. Catalytic reduction (platinum-black) of this affords isoamylcyclopentane, b. p. 168—170°/760 mm., d_4^{20} 0.7837, 1.4321.

H. BURTON.

Thermal reactions of pure organic substances under high hydrogen pressures. F. HOFMANN and K. LANG.—See B., 1929, 707.

3:4-Dichlorofluorobenzene. G. M. KRAAY (Rec. trav. chim., 1929, 48, 1055—1057).—Diazotisation of 3:4-dichloroaniline in a large excess of sulphuric acid and subsequent decomposition with boiling hydrofluoric acid (1 litre per mol. of base) affords a product which after removal of 3:4-dichlorophenol and fractionation has b. p. 170.9—171.4°/762.6 mm., and contains 90.6% of 3:4-dichlorofluorobenzene. The impurity present is probably *o*-dichlorobenzene.

H. BURTON.

2:5-Dichlorofluorobenzene and other aromatic fluoro-compounds. T. DE CRAUW (Rec. trav. chim., 1929, 48, 1061—1065).—Chlorination of *m*-fluoroacetanilide with 1 mol. of chlorine in acetic acid solution and hydrolysis of the mixture of products obtained with 38% hydrochloric acid affords 4-chloro-3-fluoroaniline (I), m. p. 61° (acetyl derivative, m. p. 146°), 2-chloro-5-fluoroaniline (II), m. p. 26° (acetyl derivative, m. p. 91°), and a small amount of 2:4-dichloro-5-fluoroaniline (III), m. p. 67° (acetyl derivative,

m. p. 126°, obtained also in 90% yield by dichlorination of *m*-fluoroacetanilide). Replacement of the amino-group with chlorine by the usual method gives 2:5-dichlorofluorobenzene, b. p. 168°/760 mm., m. p. 2°; similarly, II yields 3:4-dichlorofluorobenzene (cf. Kraay, preceding abstract) and III furnishes 2:4:5-trichlorofluorobenzene, m. p. 62°. When these chlorofluorobenzenes are treated with sodium methoxide the fluorine atom is replaced by the hydroxyl group, affording the appropriate di- or tri-chlorophenol.

H. BURTON.

Reaction between magnesium phenyl bromide and some amides of sulphonic, sulphinic, and sulphenic acids. H. GILMAN and C. C. VERNON (Rec. trav. chim., 1929, 48, 745—747).—Under ordinary conditions no reaction occurs between magnesium phenyl bromide and substituted amides of benzene-sulphonic, -sulphinic, and -sulphenic acids. Thus *p*-toluenesulphondiphenylamide in boiling anisole gives 62.5% of unchanged amide, a little diphenyl, and much tar; di-*p*-toluenesulphimide in toluene gives 63% of unchanged imide, a little diphenyl, and a small amount of a substance, m. p. 165°, whilst 88.8% of unchanged benzenesulphinanilide was recovered from its reaction in ether. Benzenesulphendiethylamide (Lecher and Holschneider, A., 1924, i, 728) in toluene at 70°, however, yields phenyl sulphide (69.4% yield calculated on the reacting sulphide) and diethylamine, 45.5% of the amide being recovered unchanged.

J. W. BAKER.

Conjugated systems. I. Chlorination of phenylbutadiene. I. E. MUSKAT and K. A. HUGGINS (J. Amer. Chem. Soc., 1929, 51, 2496—2503).—Treatment of α -phenylbutadiene with chlorine (1 mol.) in various solvents and at —80° to 150° affords in all cases the $\gamma\delta$ -dichloride (I), b. p. 125°/3 mm. (ozonolysis product benzaldehyde). Treatment of I with aqueous potassium hydroxide at 90° yields 8-chloro- α -phenylbutadiene (II), b. p. 115.5°/3.5 mm., m. p. 53°, obtained also when I is boiled for several hours. The action of silver oxide and water on I gives γ -phenyl- Δ^2 -butenoic acid, formed by oxidation of the corresponding intermediate aldehyde. Further chlorination of I in chloroform solution yields a mixture of stereoisomeric $\alpha\beta\gamma\delta$ -tetrachloro- α -phenylbutanes, b. p. 155—166°/7 mm., which on treatment with zinc dust (1 mol.) at the water-bath temperature furnishes I, and with 2 mols. gives α -phenylbutadiene. Treatment of II with chlorine (1 mol.) affords $\gamma\delta\delta$ -trichloro- α -phenyl- Δ^2 -butene, b. p. 140°/5 mm. (ozonolysis product benzaldehyde), chlorinated further to $\alpha\beta\gamma\delta\delta$ -pentachloro- α -phenylbutane, b. p. 162°/5 mm. Straus' results (A., 1909, i, 638) on the bromination of α -phenylbutadiene are confirmed.

H. BURTON.

Reactions and space formula of diphenyl. E. E. TURNER (Rec. trav. chim., 1929, 48, 821—825).—The theory of substitution in the diphenyl molecule is discussed. The different significance of physical and chemical experiments regarding the space formula of diphenyl is stressed.

H. BURTON.

Directive effects in the diphenyl and fluorene series. C. RUIZ (Anal. Assoc. Quím. Argentina, 1928, 16, 187—196; cf. this vol., 1063).—The course of

substitution in diphenyl and fluorene compounds is discussed from the point of view of Holleman's theory. In either series substitution takes place according to the usual rules in the less stable nucleus, containing an activating (*o*, *p*-directing) group. Under vigorous conditions the formation of a quinonoid conjugated system allows substitution in the second nucleus. Further support is given to the conception of fluorene as a 2 : 2'-substituted diphenyl. R. K. CALLOW.

Dicymyl [*s*-*pp*'-ditolyltetramethylethane]. E. BOEDTKER and R. KERLOV.—See this vol., 1071.

Phenylindenes. Extension of Wolff's reaction to the direct preparation of a hydrindene from the corresponding ketone. C. MOUREU, C. DUFRASSE, and P. GAGNON (Compt. rend., 1929, 189, 217—218).—By the reduction of $\gamma\gamma$ -diphenyl- α -hydrindone-phenylhydrazone (or semicarbazone) with alcoholic sodium ethoxide in a sealed tube at 200° (cf. Wolff, A., 1912, i, 988) a good yield of $\gamma\gamma$ -diphenylhydrindene is obtained. Best results are obtained by forming the sodium ethoxide *in situ*, the alcohol being introduced in a small separate tube and thus kept out of contact with the sodium until after the reaction tube is sealed. J. W. BAKER.

Synthesis of *meso*-alkyl and *meso*-aryl anthracene derivatives. VI. E. DE B. BARNETT and N. F. GOODWAY (J.C.S., 1929, 1754—1761).—9-Benzhydrylanthrene reacts with the appropriate Grignard reagent to yield 10-benzhydryl-9-methyl-, m. p. 216°, 10-benzhydryl-9-benzyl-, m. p. 181°, and 9-phenyl-10-benzhydryl-, m. p. 222°, -9 : 10-dihydro-anthranol-9. These are converted by heating with acetic acid containing hydrochloric acid into 10-benzhydryl-9-methyl- and 10-benzhydryl-9-benzyl-, m. p. 236°, -anthracenes: the phenyl derivative, however, could not be purified. 2-Methyl-9-anthrone (I), m. p. 103° (Limpricht, A., 1901, i, 145, gives m. p. 100°), generally gives only resinous products with the Grignard reagent, but a poor yield of 2 : 9-dimethyl-anthracene (II), m. p. 85°, and a good yield of 9-benzyl-2-methylanthracene (III), m. p. 139°, are similarly obtained. Treatment of II with bromine in carbon disulphide converts it into 9-bromomethyl-2-methyl-anthracene, m. p. 150° (decomp.), which is readily converted into the corresponding 9-piperidinomethyl-, m. p. 128°, and 9-anilinomethyl-, m. p. 159° (164° on remelting), derivatives, and by further action of bromine gives 10-bromo-9-bromomethyl-2-methylanthracene, m. p. 190°, which also yields the corresponding 9-piperidinomethyl-, m. p. 167°, and 9-anilinomethyl-, m. p. 144°, derivatives. Similar bromination of III yields 10-bromo-9-benzyl-2-methylanthracene, m. p. 164°. By the pyridine-acetic anhydride method I is converted into 2-methyl-9-anthranyl acetate, m. p. 143°, and by methylation with methyl *p*-toluenesulphonate into 2-methyl-9-anthranyl methyl ether, m. p. 77°. Reduction of 2-methylanthraquinone either by tin and hydrochloric acid (Padova, A., 1909, i, 655) or aluminium powder and concentrated sulphuric acid (G.P. 201,542) yields a mixture from which, after acetylation, 3-methyl-9-anthranyl acetate, m. p. 139°, may be separated by fractional crystallisation, and is hydrolysed to 3-methyl-9-anthrone, m. p. 101°. By reactions similar to those above this is

converted into 3 : 9-dimethylanthracene, m. p. 85° [9-bromo-derivative (not pure), m. p. 145° (decomp.)]; 10-bromo-9-bromomethyl-3-methylanthracene, m. p. 186° (9-piperidinomethyl derivative, m. p. 140°); 9-benzyl-3-methylanthracene, m. p. 101° (10-bromo-derivative, m. p. 139°). J. W. BAKER.

Sulphonation of phenanthrene. I. New monosulphonate. II. Disulphonation. L. F. FIESER (J. Amer. Chem. Soc., 1929, 51, 2460—2470, 2471—2486).—I. Sulphonation of phenanthrene with sulphuric acid (2 mols.) at 120—125° for 3 hrs. (cf. Werner and others, A., 1902, i, 437; Sandqvist, A., 1912, i, 843) gives optimum yields of phenanthrene-2-sulphonic acid (I) [25%; *p*-toluidine salt, m. p. 291° (corr.)], and -3-sulphonic acid (II) [27%; *p*-toluidine salt, m. p. 222° (corr.)]. Separation of I and II is best effected by conversion first into the mixed sodium salts, removal of I as the insoluble barium salt, and purification of II through the barium and potassium salts. The corresponding hydroxyphenanthrenes are readily obtained by fusion of the barium salts with potassium hydroxide at 290—325°. When sulphonation is carried out at 60° during 3 days, I (18%), II (18%), the 9-sulphonic acid (III) [13%; *p*-toluidine salt, m. p. 235° (corr.)], and phenanthrene-1-sulphonic acid (IV) [8%; *p*-toluidine salt, m. p. 267° (corr.)], potassium (V), barium, and ferrous salts; methyl ester, m. p. 102°] are obtained; these are separable by a process similar to that for I and II. The non-isolation of III and IV during sulphonation at 120° is probably because of their further sulphonation. Acetylation of the product obtained by alkali fusion of a residue from the sulphonation at 60° affords the acetate (VI), m. p. 135—136°, of 1-hydroxyphenanthrene (VII), m. p. 157° (corr.) [9 : 10-quinone, m. p. 227° (corr.)]. Oxidation of V and VI with chromic oxide in acetic acid solution gives potassium phenanthrene-9 : 10-quinone-1-sulphonate and 1-acetoxyphenanthrene-9 : 10-quinone, m. p. 201°, respectively. When VII is coupled with diazotised sulphanilic acid and the reaction product reduced with sodium hyposulphite 4-amino-1-hydroxyphenanthrene (hydrochloride; triacetyl derivative, m. p. 143°) results. Oxidation of this with chromic oxide and dilute sulphuric acid gives phenanthrene-1 : 4-quinone, m. p. 155° (corr.), converted by treatment with zinc dust in presence of acetic anhydride and sodium acetate into 1 : 4-diacetoxyphenanthrene, m. p. 137—138°. Oxidation of this with chromic oxide in acetic acid solution at 40° affords 1 : 4-diacetoxyphenanthrene-9 : 10-quinone, m. p. 184° (corr.).

II. Treatment of potassium phenanthrene-3-sulphonate with sulphuric acid at 125—130°, subsequent neutralisation of the reaction mixture with potassium hydroxide solution, and fusion of the dry, mixed potassium salts obtained with potassium hydroxide at 280—305° affords a mixture of dihydroxyphenanthrenes. Acetylation of this mixture followed by fractional crystallisation gives 3 : 6-, m. p. 124·5° (59%), 3 : 8-, m. p. 186° (corr.; 0·9%), and 2 : 6-diacetoxyphenanthrenes, m. p. 122—123° (10%). Similarly, potassium phenanthrene-2-sulphonate yields 2 : 6- (54%), 2 : 7-, m. p. 183·5° (corr.; 2·1%), and 2 : 8-diacetoxyphenanthrenes, m. p. 125° (1%). In both

cases substitution occurs in the 6-, 7-, and 8-positions. The following *dihydroxyphenanthrenes*, obtained by hydrolysis of the diacetates with alcoholic sodium hydroxide, are described: 2:6-, m. p. 239° (corr.; *dimethyl ether*, m. p. 87°); 2:7-, m. p. 265° (corr.; *dimethyl ether*, m. p. 167—168°); 2:8-, m. p. 205° (corr.); 3:6-, m. p. 225° (corr.; *dimethyl ether*, m. p. 105°); 3:8-, m. p. 253° (corr.; *dimethyl ether*, m. p. 117°). Oxidation of the diacetoxyphenanthrenes with chromic acid in acetic acid solution yields 2:6-, m. p. 220—221° (corr.); 2:7-, m. p. 244° (corr.); 2:8-, m. p. 223—224° (corr.); 3:6-, m. p. 232° (corr.), and 3:8-diacetoxyphenanthrene-9:10-quinones, m. p. 221—222° (corr.). 2:6- and 3:6-Dihydroxyphenanthrene-9:10-quinones are also described. Oxidation of 3:6-dimethoxyphenanthrene-9:10-quinone, m. p. 241° (corr.), with hydrogen peroxide in acetic acid solution at 60—90° affords a mixture of 5:5'-dimethoxydiphenic acid, m. p. 234° (corr.; obtained also from diazotised 2-amino-4-methoxybenzoic acid and cuprous hydroxide), and the lactone, m. p. 194° (corr.), of 2-hydroxy-5:5'-dimethoxydiphenyl-2'-carboxylic acid. Methylation of the lactone with methyl sulphate in alkaline solution gives 2:5:5'-trimethoxydiphenyl-2'-carboxylic acid, m. p. 147—148°, converted by treatment with cold sulphuric acid into 1:4:6-trimethoxyfluorenone, m. p. 157°. Treatment of the above diphenic acid with sulphuric acid at 50° yields 1:6-dimethoxyfluorenone-4-carboxylic acid, m. p. 303° (corr.), with elimination of carbon dioxide [*amide*, m. p. 268° (corr.)]. Application of Dimroth's boracetic anhydride test (A., 1926, 297) to a series of mono-, di-, and tri-hydroxyanthrene-9:10-quinones confirms the observation that a colour change is usually given only when a hydroxyl group is in the 1(8)-position. The 3:4-dihydroxy-derivative gives a colour change probably because of the formation of the $\begin{smallmatrix} \text{C} \\ \diagup \text{O} \end{smallmatrix} > \text{B} \cdot \text{OAc}$ grouping. Attempts to isolate the disulphonic acids formed during the monosulphonation of phenanthrene (this vol., 1171) failed. No 4- or 5-substituted derivative has been isolated during the investigations.

H. BURTON.

Phenylallylthiocarbamide as a solvent. V. P. SCHISCHOKIN (Ann. Inst. Anal. Phys.-Chim., Leningrad, 1928, 4, 195—224).—Phenylallylthiocarbamide forms compounds with chloroform, paraldehyde, trichloroacetic acid, and acetic anhydride, and probably with acetic acid, dibromobenzene, nitrobenzene, ethyl alcohol, methyl alcohol, allylthiocarbimide, benzene, toluene, and naphthalene, but not with aniline, *o*-nitroaniline, or diphenylamine. The heat of fusion of phenylallylthiocarbamide is computed to be 6400—6960 g.-cal. per mol. The internal pressure of phenylallylthiocarbamide must be near to that of aniline, and of allylthiocarbimide to that of nitrobenzene.

CHEMICAL ABSTRACTS.

Derivatives of 1:1'-dinaphthyl. A. CORBEL-LINI and E. DEBENEDETTI (Gazzetta, 1929, 59, 391—399).—Both the 2:2'- and 1:1'-positions have been assigned to the linking in di- α -naphthol (cf. Willstätter and Schuler, A., 1928, 408; Goldschmidt and Wessbecher, *ibid.*, 409; Zinke and Schöpfer, A., 1924, i, 1081). Further evidence has now been obtained for

the latter view. When naphthidine is diazotised in suspension in dilute sulphuric acid and the solution decomposed by heating after the addition of carbamide, a product is obtained which cannot be purified but yields when methylated with methyl sulphate 4:4'-dimethoxy-1:1'-dinaphthyl, m. p. 252°, identical with the methylation product of di- α -naphthol obtained by other methods. By Sandmeyer's reaction 4:4'-dichloro-1:1'-dinaphthol, m. p. 215—216°, and 4:4'-dibromo-1:1'-dinaphthyl, m. p. 217.5° (lit. 215°), are obtained from naphthidine. The formation of naphthacarbazole by the action of acid on the diamino-compound in the preparation of 2:2'-diamino-1:1'-dinaphthyl from $\beta\beta$ -azonaphthol is confirmed. By a Sandmeyer reaction 2:2'-diamino-1:1'-dinaphthyl yields 2:2'-dichloro-1:1'-dinaphthyl, m. p. 151—152°. Decomposition of the diazonium sulphate yields a substance, m. p. about 250—252°, of acid properties, and not the expected dinaphthol.

R. K. CALLOW.

Derivatives of 2:5-dibromonitrobenzene. L. C. RAIFORD and B. C. BREN (J. Amer. Chem. Soc., 1929, 51, 2539—2541).—Reduction of 2:5:2':5'-tetrabromooazobenzene, m. p. 247° (corresponding azoxy-derivative, m. p. 217°), with stannous chloride and hydrochloric acid gives a 42% yield of 2:5-dibromoaniline (I). The diazonium chloride (II), decomp. explosively above 117°, from I is reduced by stannous chloride and alcoholic hydrochloric acid to I, and when boiled with water does not yield a phenol. β -Naphthol and II yield a dye, $\text{C}_{16}\text{H}_{10}\text{ON}_2\text{Br}_2$, whilst with aniline the corresponding diazoaminobenzene, m. p. 185°, results. Rearrangement of this into the aminoazo-derivative is not possible. 4-Bromo-2-nitroanisole gives on alkaline reduction 5:5'-dibromo-2:2'-dimethoxy-azoxy- and -azo-benzenes, m. p. 121° and 238°, respectively. 5:5'-Dibromo-2:2'-dimethoxyhydrazobenzene, m. p. 120—121°, is converted by the usual method into 5:5'-dibromo-2:2'-dimethoxybenzidine, m. p. 168° (*dibenzoyl* derivative, m. p. 274°; dye from β -naphthol). 5:5'-Dibromo-2:2'-diethoxyhydrazobenzene has m. p. 171—172°. H. BURTON.

Formation of mixed azo-derivatives corresponding with alkylacetylacetones. G. FAVREL (Compt. rend., 1929, 189, 335—337).—The interaction of diazonium hydroxides and alkylacetylacetones under slightly modified conditions yields mixed azo-compounds which are the intermediate stages in the formation of monophenylhydrazones of α -diketones (A., 1901, i, 167). *p*-Chloroaniline is diazotised in hydrochloric acid and the solution treated with excess of sodium acetate and with precipitated calcium carbonate until only half an equivalent of acetic acid remains free. γ -Ethylacetylacetone in ethereal solution is then added. γ -*p*-Chlorobenzeneazo- γ -ethylacetylacetone, m. p. 34—35°, separates. The *p*-bromo-compound, m. p. 73—74°, *p*-nitro-compound, m. p. 76°, and γ -*p*-nitrobenzeneazo- γ -methylacetylacetone, m. p. 79°, are obtained similarly. When the azo-compounds are reduced, the aniline is obtained, and when warmed with water, acetic acid and the monophenylhydrazone of the diketone are formed.

R. K. CALLOW.

Addition reactions of azodicarboxylic esters. R. STOLLÉ and W. REICHERT (J. pr. Chem., 1929,

[ii], 123, 74—81; cf. A., 1924, i, 1002; 1925, i, 1469). —*p*-Cymene and methyl azodicarboxylate condense in the presence of concentrated sulphuric acid or of dry hydrogen chloride and a trace of iodine to yield methyl 2:5-dihydrazino-*p*-cymene-NN'N''N'''-tetra-carboxylate, m. p. 220°, reduced by acetic and hydriodic acids to 2:5-diamino-*p*-cymene; ethyl azodicarboxylate similarly affords the corresponding ethyl ester, m. p. 192°. Phenetole and methyl or ethyl azodicarboxylate furnish methyl and ethyl *p*-hydrazinophenetole-NN'-dicarboxylate, m. p. 135° and 81°, respectively, reduced by acetic and hydriodic acids to *p*-aminophenol; anisole yields methyl *p*-hydrazinobenzene-NN'-dicarboxylate, m. p. 99°. Indene condenses with methyl or ethyl azodicarboxylate in the presence of dry hydrogen chloride; the condensing agent also reacts with the indene, affording derivatives of 1-chlorohydrindene, which, since addition of azodicarboxylic esters to saturated compounds has not yet been observed, are considered to be methyl and ethyl 1-chloro-6- or -7-hydrazinohydrindene-NN'-dicarboxylate, m. p. 138° and 111°, respectively. Tetrahydronaphthalene condenses with methyl or ethyl azodicarboxylate when heated in a sealed tube, giving products which, by analogy with those obtained from toluene and bromobenzene (A., 1924, i, 881), are formulated as methyl and ethyl 3-hydrazino-6:7:8-tetrahydronaphthalene-NN'-dicarboxylate, m. p. 136° and 106°, respectively. C. W. SHOPPEE.

Thermal decomposition of azodibenzoyl and methyl azodicarboxylate. R. STOLLÉ and W. REICHERT (J. pr. Chem., 1929, [ii], 123, 82—84; cf. A., 1912, i, 225).—The thermal decomposition of azodibenzoyl in high-boiling media such as deca- and tetrahydronaphthalene and naphthalene has been investigated; 50% of the theoretical amount of nitrogen is evolved, with the production of diphenylfurodiazole and benzoic anhydride. The formation of these products is considered to be due to the intermediate production of "tetraazobenzoylhydrazine," CPhBz.N:N.CPhBz, which has been shown by Stollé and Benrath (A., 1904, i, 935) to yield them by thermal decomposition. A scheme to explain the formation of di- and tri-benzoylhydrazine, which have been found in small quantity by Stollé and Benrath (*loc. cit.*), by the action of water, is suggested.

Methyl azodicarboxylate is more stable than azodibenzoyl, and exhibits no decomposition when heated in decahydronaphthalene (188°); in tetrahydronaphthalene no decomposition occurs, but addition of the ester to the medium affords a compound of m. p. 136° (cf. preceding abstract). When heated in naphthalene (218°) for a long period, methyl azodicarboxylate evolves 65—70% of its nitrogen, giving, as the main decomposition products, carbon monoxide, and methyl carbonate and oxalate. C. W. SHOPPEE.

Amino-oxidation. XII. Hydrazyls. β -Benzoyl- α -diarylhydrazyls. S. GOLDSCHMIDT and J. BADER (Annalen, 1929, 473, 137—162).—Treatment of benzoylazo-*p*-bromobenzene with copper chloride in alcoholic solution affords benzoic acid, *p*-chlorobromobenzene, and β -benzoyl- α -di-*p*-bromophenylhydrazine, m. p. 235°, formed also by the action of

copper acetate on β -benzoyl-*p*-bromophenylhydrazine in boiling alcoholic solution. Similar treatment of β -benzoyl-*p*-anisylhydrazine, m. p. 139—140°, gives β -benzoyl- α -di-*p*-anisylhydrazine, m. p. 228°. β -Benzoyl- α -di-*p*-nitrophenylhydrazine has m. p. 276°. β -Benzoyl- α -diphenylhydrazine is obtained by the action of copper acetate on benzoylphenylhydrazine in alcoholic solution; in presence of benzenediazonium chloride or phenylhydrazine hydrochloride the yield is improved. The mechanism of the formation of β -benzoyl- α -diarylhydrazines from benzoylarylhydrazines is: $\text{NHR}\cdot\text{NHBz} \xrightarrow{\text{oxidation}} \text{NR}\cdot\text{NBz}$

$\text{Bz}\cdot\text{OH} + \text{NR}\cdot\text{NH} \xrightarrow{\text{oxidation}} [\text{NR}\cdot\text{N}]\text{X} \xrightarrow{\text{NHR}\cdot\text{NHBz}} \text{NR}\cdot\text{N}\cdot\text{NR}\cdot\text{NHBz} \longrightarrow \text{N}_2 + \text{NR}\cdot\text{NHBz}$ (cf. Tafel, A., 1892, i, 710; Gattermann, *ibid.*, 843). Mixed β -benzoyldiarylhydrazines are prepared by the action of copper acetate on an alcoholic solution of a benzoylarylhydrazine and arylhydrazine hydrochloride. Using phenylhydrazine hydrochloride and the appropriate β -benzoylarylhydrazine the following were prepared: β -benzoyl- α -phenyl- α -*p*-bromophenyl-, m. p. 198—199°; β -benzoyl- α -phenyl- α -*p*-anisyl- (readily oxidised in solution); β -benzoyl- α -phenyl- α -*p*-tolyl-, m. p. 171—172°, and β -benzoyl- α -phenyl- α -*p*-nitrophenyl-hydrazines, m. p. 172—173°. Oxidation of the above diarylhydrazines with potassium ferricyanide in presence of alcoholic sodium methoxide or occasionally with lead dioxide affords solutions of the corresponding tetrazans, which after purification are used to determine the equilibrium tetrazen-hydrazyl. At —80° to —50° the equilibrium point is reached much more slowly than at —18°. The equilibrium constant is smallest for the di-*p*-nitrophenyl derivative, and increases in the following order: di-*p*-nitrophenyl, phenyl-*p*-nitrophenyl, di-*p*-bromophenyl, phenyl-*p*-bromophenyl, diphenyl, phenyl-*p*-tolyl, di-*p*-tolyl, phenyl-*p*-anisyl, di-*p*-anisyl (wholly dissociated in acetone). The introduction of positive groups in the *para* positions causes an increase in the dissociation; negative groups cause a decrease. The heat of dissociation of the tetrazen N·N linking varies from 5500 to 10,500 g.-cal. for dibenzoyltetraphenyltetrazen in chloroform or toluene. For the series studied the values vary from 5200 to 18,100 g.-cal. (extremelimits), and an increased degree of dissociation corresponds with a decrease in the heat of dissociation.

H. BURTON.

Vapour-phase hydrolysis of chloro- and bromobenzene. L. CHALKLEY, jun. (J. Amer. Chem. Soc., 1929, 51, 2489—2495).—When chloro- or bromobenzene vapour mixed with steam is passed over silica gel at 500—600° under ordinary pressure varying amounts of phenol, hydrogen chloride, and diphenyl ether are produced. The amount of hydrolysis increases with decrease in the rate of flow of the reaction mixture. Poisoning of the catalyst occurs, but reactivation takes place when it is heated in air or oxygen. Other catalysts are titanium, zirconium, aluminium, thorium, and tungsten (blue) oxides. Kaolin has practically no action. Silica gel and titanium oxide are the most active catalysts used.

H. BURTON.

Trichloro- and higher chloro-phenols and their electrical conductivity in water. G. J. TIESSENS

(Rec. trav. chim., 1929, 48, 1066—1068).—2:3:6-*Trichlorophenol*, m. p. 58°, is obtained in about 15% yield when the corresponding diazonium salt is decomposed with a boiling solution of copper and sodium sulphates. The relative conductivities ($k \times 10^{10}$) of dilute aqueous solutions of the various chlorophenols used, at 25°, are: 2:4-dichloro-, 310; 2:3:4-trichloro-, m. p. 83.5°, 252; 3:4:5-trichloro-, m. p. 101°, 45; 2:3:6-trichloro-, 7360; 2:3:5-trichloro-, m. p. 62°, 500; 2:4:5-trichloro-, m. p. 68°, 430; 2:4:6-trichloro-, m. p. 69°, 3900; 2:3:4:5-tetrachloro-, m. p. 116°, 1100; 2:3:4:6-tetrachloro-, m. p. 70°, 42,000; 2:3:5:6-tetrachloro-, m. p. 115°, 33,000; pentachloro-, m. p. 144°, 55,000. The presence of chlorine atoms in the two *ortho* positions causes a marked increase in the acidity. The conversion of an amine into a phenol does not appear to depend on the basicity of the amine. Many of the above chlorophenols are new and details of their preparation are to be published later.

H. BURTON.

Synthesis in diphenyl ether series. I. Simple derivatives. C. M. SUTER (J. Amer. Chem. Soc., 1929, 51, 2581—2585).—Nitration of diphenyl ether with a mixture of nitric (d 1.52) and acetic acids in acetic anhydride solution at 25—30° gives an 86% yield of a mixture of the 2- and 4-nitro-derivatives. Separation of the 4-nitro-derivative by keeping the mixture at 0° is incomplete, but when the remaining mixture is reduced by zinc and calcium chloride in aqueous-alcoholic solution the resulting amines are readily separated owing to the insolubility of the 4-amino-sulphate in water. The original mixture of nitro-compounds contains 54% of the 4-derivative. 2-Acetamidodiphenyl ether has m. p. 81°. Bromination of 4-nitrodiphenyl ether in carbon tetrachloride solution affords the 4'-bromo-derivative, reduced by iron powder and alcoholic hydrochloric acid to 4-bromo-4'-aminodiphenyl ether, m. p. 109° (cf. Le Fevre, Saunders, and Turner, A., 1927, 660) [acetyl derivative, m. p. 162—163° (corr.), obtained also by bromination of 4-acetamidodiphenyl ether]. Bromination of diphenyl ether in carbon tetrachloride solution with an equimolecular quantity of bromine gives 47% of the 4-bromo-derivative, together with unchanged material, dibromo- and polybromo-(traces) compounds. 2-Cyano-, b. p. 188° (corr.)/14 mm., and 4-cyano-diphenyl ethers, b. p. 187—188° (corr.)/14 mm., m. p. 47°, are hydrolysed to the corresponding carboxylic acids.

H. BURTON.

Influence of structure on the breaking by heat of the carbon-oxygen linking in certain ethers. R. C. YOUNG (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 60—64).—By the action of ether on the molecular compound of triphenylmethyl chloride and aluminium chloride an 80—90% yield of triphenylmethane is obtained: $\text{CPh}_3\text{Cl} + \text{Et}_2\text{O} \longrightarrow \text{EtCl} + \text{CPh}_3\cdot\text{OEt} \longrightarrow \text{CHPh}_3 + \text{Me}\cdot\text{CHO}$, since the intermediate triphenylmethyl ethyl ether reacts with aluminium chloride in ether solution to yield triphenylmethane and in carbon disulphide to yield triphenylmethyl chloride. The latter reaction is proved to be represented by $2\text{CPh}_3\cdot\text{OEt} + 2\text{AlCl}_3 \longrightarrow \text{CPh}_3\text{Cl} + \text{CPh}_3\text{Cl}\cdot\text{AlCl}_3 + \text{Al}(\text{OEt})_2\text{Cl}$, decomposition of the product with ice

giving a quantitative yield of triphenylmethyl chloride. Similarly, the action of ether on the molecular compound of dichlorodiphenylmethane and aluminium chloride gives an 80% yield of benzophenone. By the action of the sodium derivatives of various alcohols on triphenylmethyl chloride a series of triphenylmethyl ethers has been prepared and their relative thermal stabilities have been compared, the temperatures of decomposition into triphenylmethane and an aldehyde or ketone being as follows: triphenylmethyl methyl ether, m. p. 81—81.8°, 262°; ethyl, m. p. 80.3—81.1°, 242°; *n*-propyl, m. p. 103.0—104.0°, 230°; isopropyl, m. p. 112.1—113.1°, 220°; *n*-butyl, 239°; sec.-butyl, 216°; isobutyl, 228°; isoamyl, 237°; benzyl, 226°; β -phenylethyl, m. p. 87.1—87.8°, 236°. The corresponding velocity coefficients for the reaction between the corresponding alcohol and *p*-nitrobenzoyl chloride are, respectively, 0.184, 0.085, 0.066, 0.074, 0.010, 0.0074, 0.031, 0.073, 0.017, and 0.040. Thus, in general, the greater is the reaction velocity the greater is the stability of the corresponding triphenylmethyl ether. Substitution of a methyl group in the *p*-position of the phenyl radicals decreases the thermal stability of the ether, tritolylmethyl ethyl ether decomposing at 224°. The lowering in the m. p. of these ethers caused by heating at 193° and 215° for 1 hr. is smaller the greater is the stability of the ether. Catalysts such as ferric chloride or aluminium oxide lower the decomposition temperature considerably. Interaction of sodium acetate or benzoate with triphenylmethyl chloride in acetic anhydride yields the corresponding acetate or benzoate, both of which are decomposed with ferric chloride to yield triphenylcarbinol. Thermal decomposition of the acetate (228°) yields triphenylmethylcarbinol, triphenylmethane, and acetic acid.

J. W. BAKER.

Ketones and acids containing the alkoxy-group. S. SABETAY (Bull. Soc. chim., 1929, [iv], 45, 534—540).—Improved yields of tetrahydro- β -naphthoxyacetone, b. p. 154—155°/5 mm., m. p. 37.5° (semicarbazone, m. p. 172°), are obtained from chloroacetone and *ar*-tetrahydro- β -naphthol in presence of porphyrised copper and 1 mol. of potassium hydroxide (cf. Thoms and Kross, A., 1927, 659). *p*-tert.-Butylphenoxyacetone, b. p. 131°/5 mm., n_D^{20} 1.5085 (semicarbazone, m. p. 164°), from *p*-tert.-butylphenol, m. p. 96°, and *p*-tolyl phenoxyethyl ketone, m. p. 73°, b. p. 181—184°/4 mm., are readily obtained by the same method, but sodium β -phenylethoxide does not condense with chloroacetone in this way or in presence of xylene or with the chloroacetal, $\text{CMe}(\text{OEt})_2\cdot\text{CH}_2\text{Cl}$. β -Phenylethoxyacetone, b. p. 120°/5 mm., n_D^{20} 1.5035, d_4^{25} 1.028, is obtained from magnesium methyl iodide and methyl β -phenylethoxyacetate, b. p. 133°/6 mm., 1.5025, d_4^{20} 1.085, prepared by converting β -phenylethyl chloroformate (A., 1928, 1130) into β -phenylethoxyacetone nitrile, b. p. 125—126°/5 mm., n_D^{20} 1.5105, d_4^{25} 1.046, and hydrolysing with hydrogen chloride in cold absolute methyl alcohol. β -Phenylethoxyacetic acid has m. p. 45—46°, b. p. 171°/6 mm., n_D^{20} 1.5211. *n*-Octyloxyacetone nitrile, b. p. 106°/5 mm., n_D^{20} 1.4308, d_4^{25} 0.8767, *n*-octyloxyacetic acid, m. p. 17°, b. p. 155—156°/7 mm., n_D^{20} 1.4433, d_4^{25} 0.9627 (isobutyl ester, b. p. 140°/5 mm., n_D^{20} 1.4312), and *n*-octyloxyacetone, b. p. 106°/6 mm.,

n_D^{25} 1.4325, d_4^{25} 0.8791, are similarly obtained from *n*-octyl chloroformate, b. p. 84—85°/5 mm., n_D^{25} 1.4418.

R. BRIGHTMAN.

Oxidation of *m*-xylorcinol. J. F. WALKER (Abstr. Theses Mass. Inst. Tech., 1929, No. 4, 58—60).—Oxidation of *m*-xylorcinol (I) (4:6-dihydroxy-*m*-xylene) with ferric chloride effects combination of two nuclei in the 5-position to yield first crystalline *dimetaxylorcinol* (II) (2:6:2':6'-tetrahydroxy-3:5:3':5'-tetramethyldiphenyl), m. p. 242—243° (slight decomp.) (tetra-acetate, m. p. 158°), which is converted by bromine in chloroform into a substance, $C_{16}H_{16}O_2Br_2$, m. p. 244—247° (decomp.). Further oxidation of I converts it into a green precipitate, possibly the *diphenyl ether*, $[C_6HMe_2(OH)_2 \cdot C_6Me_2(OH)_2]_2O$, charring above 250°. Bromination of I in chloroform solution converts it into the 5(?)*-bromo*-derivative, m. p. 119—120°, which readily loses hydrogen bromide when gently heated with a trace of sulphuric acid, forming a brilliant red melt, and is oxidised by ferric chloride in aqueous solution to give first a violet coloration and then a white precipitate from which a crystalline substance, charring above 265°, is isolated.

J. W. BAKER.

β -2:4:5-Trimethoxyphenylethylamine. M. JANSEN (Chem. Weekblad, 1929, 26, 421—422).—This compound, isomeric with mescaline, the 3:4:5-derivative, which has powerful physiological properties, has been prepared by condensing nitromethane and 2:4:5-trimethoxybenzaldehyde, and reducing the nitrostyrene. Its chemical behaviour is similar to that of mescaline.

S. I. LEVY.

Formation of rubrene from compounds not containing chlorine. J. ROBIN (Compt. rend., 1929, 189, 337—339).—Rubrene cannot be obtained from diphenylphenylacetylenylcarbinol by the action of heat alone or with dehydrating agents. When it is obtained by heating the carbinol in presence of hydrochloric acid, or the hydrochloride of the corresponding amine, the chloride is a possible intermediate stage. However, when the acetate, propionate, butyrate, or benzoate of the carbinol is heated, rubrene is obtained in successively less violent decompositions and in decreasing yield, accompanied by increasing amounts of a yellow hydrocarbon, m. p. 245°. The methyl or ethyl ether of the carbinol also yields rubrene when heated under carefully controlled conditions. The action of alcohol on the compound $C_{42}H_{29}Cl$ (Moureau, Dufraisse, and Robin, this vol., 922) yields a chlorine-free compound, m. p. 214—215°, which yields rubrene when heated. R. K. CALLOW.

Production of pinacols in the reaction between a carboxylic ester and a Grignard reagent. H. H. HATT (J.C.S., 1929, 1623—1632).—Attempts have been made to improve the small yields of benzpinacol previously obtained (A., 1927, 558) by interaction of methyl benzoate and magnesium phenyl bromide, by using larger quantities of magnesium and magnesium iodide. The production of pinacols in reactions of the foregoing type is assumed to be due to the reduction of the corresponding ketone, formed as an intermediate, by magnesium and magnesium iodide through the metal ketyl, $RR'CO \dots Mg$, or the

halogenomagnesium pinacolate, $[OMgI-CRR']_2$, (I) (cf. Gomberg and Bachmann, A., 1927, 245); when the above reaction was conducted in the presence of sufficient magnesium and magnesium iodide to give a theoretical yield of I (R and R' = Ph), no benzpinacol could be isolated. Similarly, the yield of the pinacol obtained from ethyl *o*-chlorobenzoate and magnesium phenyl bromide fell from 27 to 5%. Experiments indicated the primary production of I, which might immediately be converted into II (cf. Schlenk, A.,

1914, i, 396): $2RR'C \cdot OMgI \xrightarrow[\text{MgI}_2]{\text{Mg}} 2RR'C(MgI) \cdot OMgI$ (II); no evidence of the formation of II (R and R' = Ph) was obtained when benzophenone was shaken for long periods with excess of magnesium and magnesium iodide in ether-benzene solution. An ethereal solution of I (R and R' = Ph) showed no special reactivity toward methyl benzoate, magnesium phenyl bromide, or bromobenzene in the presence of magnesium and magnesium iodide. The optimum quantity of magnesium iodide is about 10% of theory, affording in the case of ethyl *o*-toluate and magnesium phenyl bromide a 45% yield of the corresponding pinacol. The effect of substituents in the benzene nuclei of the ester and of the Grignard reagent on the yield of pinacol has been studied under standard conditions. *o*-Substituted esters favour the production of pinacols; no pinacol is formed, however, if both ester and Grignard reagent contain *o*-substituents, although ethyl *o*-toluate and magnesium *o*-tolyl bromide in the absence of magnesium give a 66% yield of di-*o*-tolyl ketone, m. p. 70.5°, which reacts in ether-benzene solution with magnesium and magnesium iodide to form the iodomagnesium pinacolate, hydrolysis of which yields 25% of di-*o*-tolylcarbinol.

Ethyl α -naphthoate and magnesium phenyl bromide afford diphenyl- α -naphthylcarbinol (22%) and diphenyldi- α -naphthylpinacol, m. p. 199°; the latter appears to be the second form, m. p. 200°, described by Bachmann and Shankland (this vol., 316; cf. Cohen and Montagne, A., 1919, i, 210). Methyl *o*-anisate and magnesium phenyl bromide furnish a 52% yield of diphenyl-*o*-anisylcarbinol as the sole product. Ethyl *o*-bromobenzoate and magnesium phenyl bromide afford a 5% yield of *o*-bromotriphenylcarbinol, isolated as *o*-bromotriphenylchloromethane, and 9% of *s*-2:2'-dibromobenzpinacol, m. p. 166° (cf. Koopal, A., 1915, i, 693); in another experiment both the pinacol and *o*-bromotriphenylcarbinol were isolated, together with *o*-bromotriphenylmethane. Ethyl *o*-chlorobenzoate and magnesium phenyl bromide yield 27% of *s*-2:2'-dichlorobenzpinacol, α -form (III), m. p. 164° (decomp.), affording by rearrangement *o*-chlorophenyl 2:2':2'-trichlorotriphenylmethyl ketone, m. p. 139.5—140.5° [β -form (IV), m. p. 181°; cf. Koopal, loc. cit.], and 31% of *o*-chlorotriphenylcarbinol; treatment of III with hot alcoholic potassium hydroxide followed by reduction with zinc in the same medium gave *o*-chlorodiphenylcarbinol. Ethyl *o*-toluate and magnesium *p*-tolyl bromide afforded a 52% yield of di-*p*-tolyl-di-*o*-tolylpinacol, m. p. 174° (decomp.), reduced by zinc and alcoholic potassium hydroxide to *p*-tolyl-*o*-tolylcarbinol, m. p. 61—61.5°, and 6% of di-*p*-tolyl-*o*-tolylcarbinol isolated as di-*p*-tolyl-*o*-tolylchloromethane, m. p. 106°, together with

some di-*p*-tolyl. Ethyl *o*-toluate and magnesium phenyl bromide gave a 23% yield of diphenyl-*o*-tolylcarbinol and 40% of diphenyldi-*o*-tolylpinacol; the latter by treatment with boiling glacial acetic acid and iodine afforded *o*-toluoyldiphenyl-*o*-tolylmethane, m. p. 129°, hydrolysed by 10% alcoholic potassium hydroxide to *o*-toluic acid and diphenyl-*o*-tolylmethane; in a similar experiment a substance, $C_{28}H_{24}O$ (probably an isomeric *o*-toluoyldiphenyl-*o*-tolylmethane), m. p. 93.5–94.5° (compound, +1EtOH, m. p. 93.5–94.5°), was obtained, which passed into the isomeride, m. p. 129°, on keeping.

Reduction of *o*-chlorobenzophenone with zinc and glacial acetic acid at 50° affords both the pinacols III and IV; at 15° the yields are slightly improved. Reduction with magnesium and magnesium iodide in benzene at 15° yields III, IV, and a third substance (V), m. p. 180°, the yield of which is increased by raising the temperature of reduction. Magnesium phenyl bromide in benzene solution at 15° in an atmosphere of nitrogen partly converts IV into III; if the reaction is conducted under reflux, V is also obtained. It is suggested that the isomeric pinacols are *meso*- and racemic forms, and their production in the above reactions, and the transformation of one form into the other, are discussed. C. W. SHOPPEE.

Action of the halogen acids on acetylenic glycols. V. **Action of hydrogen iodide on tetraphenylbutinenediol.** J. SALKIND and A. KRUGLOV (J. Russ. Phys. Chem. Soc., 1929, 61, 803–814).—The products of reaction of hydrogen iodide and tetraphenylbutinenediol are not analogous to those with other aromatic glycols, since the cyclic iodo-oxide is obtained only with difficulty, and only hydrocarbons can be isolated, instead of di-iodo-derivatives. Dilute aqueous hydriodic acid and the glycol yield 3-iodo-2:2':5:5'-tetraphenyldihydrofuran, m. p. 139–140°, together with small quantities of $\alpha\delta\delta$ -tetraphenylbutatriene, m. p. 235°. If the hydriodic acid is more concentrated, this hydrocarbon is the main product, although a certain quantity of 1:10:10-triphenylbenzofulvene, m. p. 205–206°, is also obtained. With saturated solutions of hydrogen iodide in water or glacial acetic acid, the yield of 1:10:10-triphenylbenzofulvene is greatly increased, and traces of $\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -butadiene, m. p. 201–202°, are also obtained. M. ZVEGINTZOV.

Zymosterol. H. PENEAU and G. TANRET (J. Pharm. Chim., 1929, [viii], 10, 193–195).—See this vol., 809.

Mechanism of the azide rearrangement. G. POWELL (J. Amer. Chem. Soc., 1929, 51, 2436–2439).—An attempt has been made to obtain evidence of the intermediate formation of the univalent nitrogen postulate, $R\cdot CO\cdot N<$ (I), in the change $R\cdot CO\cdot N_3 \rightarrow I \rightarrow R\cdot NCO$. Benzoyl azide decomposes in boiling benzene solution in presence of triphenylmethyl to nitrogen and phenylcarbimide. No compound of the type $R\cdot CO\cdot NR'$ is formed, indicating the non-reactivity of I. Acid chlorides and potassium azide react in aqueous acetone, giving almost theoretical yields of the acid azides. *Dibenzylacetyl azide*, m. p. 52–53°, decomposes on keeping into *dibenzylmethylcarbimide* (ethyl *dibenzylmethylaminoformate*, m. p.

106–107°, and *phenyldibenzylmethylcarbamide*, m. p. 153–154°, are prepared by the action of alcohol and aniline, respectively). When methyl 2-phenylquinoline-4-carboxylate is treated with hydroxylamine in presence of methyl-alcoholic sodium methoxide 2-phenylquinolyl-4-formhydroxamic acid, m. p. 155–156° (decomp.) (copper and silver salts; benzoyl derivative, m. p. 150–151°, obtained by the action of benzoyl chloride on the sodium salt), results.

H. BURTON.

Structure of benzene. N. M. MAXIM (Bul. Soc. Chim. Romania, 1929, 11, 29–36).—The action of diethylamine on the three isomeric toluoyl chlorides gave *o*-toluidiethylamide, b. p. 160°/24 mm., d_4^{20} 0.998, 1.51951; *m*-toluidiethylamide, b. p. 160°/19 mm., d_4^{20} 0.996, n_D^{20} 1.52175; and *p*-toluidiethylamide, b. p. 163°/17 mm., d_4^{20} 0.990, n_D^{20} 1.52515. The exaltations of refraction and dispersion increase progressively in the order *o*, *m*, *p*, as observed by Auwers with other derivatives of the toluic acids, and a similar explanation to that of Auwers, based on the Kekulé benzene formula and conjugation, is accepted.

A. A. GOLDBERG.

cycloHexanone-2:6-dicarboxylic ester and the mechanism of the reducing action of zinc on halogen derivatives. M. I. USCHAKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 794–802).—The conditions of the formation of three-membered ring systems by the action of zinc dust on $\alpha\gamma$ -dihalogen derivatives are investigated. Ethyl pentane- $\alpha\alpha\alpha$ -tetracarboxylate is condensed by sodium in ethyl-alcoholic solution, giving, after hydrolysis, ethyl cyclohexanone-2:6-dicarboxylate, b. p. 165–165.5°/12 mm., m. p. 87.5–88°, d_4^{25} 1.1239, n_D^{25} 1.4692. Treatment of this with bromine yielded a yellow liquid 2:6-dibromo-derivative, which reacted vigorously when heated with zinc dust in toluene solution. On addition of water to the reaction mixture, zinc hydroxide was precipitated (indicating the presence of an organometallic zinc compound) and a 70% yield of ethyl cyclohexanone-2:6-dicarboxylate obtained, no ring closure in the 2:6-position having taken place. The mechanism of the reaction is discussed.

M. ZVEGINTZOV.

Action of phenylhydrazine on aromatic dithioacids. H. WUYTS [with T. JANSSENS] (Bull. Soc. chim. Belg., 1929, 38, 195–204).—The interaction of phenylhydrazine with aromatic dithioacids yields ultimately the phenylhydrazone of the corresponding aldehyde, the probable course of the reaction being: $R\cdot CS\cdot SH, NH_2\cdot NHPh \rightarrow R\cdot CS\cdot NH\cdot NHPh \rightarrow R\cdot CH\cdot N\cdot NHPh$. The intermediate stages may be isolated in some cases under appropriate conditions.

Dithioacids are prepared by the interaction of carbon disulphide with magnesium aryl halides. Dithio-benzoic acid and phenylhydrazine in ethereal solution yield a precipitate of the salt at –40°. When the solvent is removed and the residue heated to 100° the reaction goes to completion with the formation of hydrogen sulphide, sulphur, and benzaldehydephenylhydrazone. Similarly, dithio-*o*-toluic acid yields the salt, and then a mixture of *o*-toluthiophenylhydrazone, m. p. 116–118°, and *o*-tolualdehydephenylhydrazone, m. p. 105–106°. Dithio-*p*-toluic acid yields *p*-tolualdehydephenylhydrazone, m. p. 110–112°; the

salt or thiophenylhydrazide cannot be isolated. Dithio- α -naphthoic acid yields the salt, decomp. below 100°, the thiophenylhydrazide, m. p. 150–152°, and α -naphthaldehydethiophenylhydrazide, m. p. 79·5–80°.

R. K. CALLOW.

Reduction of cinnamaldehyde to β -phenylpropaldehyde with alcohols. P. E. WESTON and H. ADKINS (J. Amer. Chem. Soc., 1929, 51, 2589).—When a solution of cinnamaldehyde in methyl, ethyl, or propyl alcohol is passed over aluminium oxide at 330° β -phenylpropaldehyde is obtained (from about 60% of the cinnamaldehyde reacting), the alcohol being dehydrogenated to aldehyde (cf. A., 1928, 968, 991).

H. BURTON.

Reimer-Tiemann reaction with *m*-fluorophenol and the nitration of 4-fluoro-2-hydroxy- and 2-fluoro-4-hydroxy-benzaldehydes. H. H. HODGSON and J. NIXON (J.C.S., 1929, 1632–1639; cf. this vol., 559).—The influence of fluorine in the *m*-position on the Reimer-Tiemann reaction is similar to that of the other halogens; the ratio, *o*/*p*-hydroxyaldehyde is 0·87 and shows that the deactivation of the *p*-hydrogen atom is much greater than that produced by *m*-chlorine (*o*/*p* ratio 0·71); this is supported by the fact that, for nitration, 4-fluoro-3-bromo- and 4-fluoro-5-bromo-2-hydroxybenzaldehydes require more drastic treatment than the chloro-analogues. By the Reimer-Tiemann reaction, *m*-fluorophenol affords 4-fluoro-2-hydroxybenzaldehyde (I), m. p. 69° [sodium (bright yellow), iron, copper, and chromium derivatives; oxime, m. p. 125°; semicarbazone, m. p. 236°; *p*-nitrophenylhydrazide, m. p. 248°, cherry-red (the colours produced by alcoholic solutions of hydrazones and *p*-nitrophenylhydrazones with alcoholic potassium hydroxide are given immediately after the m. p.)], and 2-fluoro-4-hydroxybenzaldehyde (II), m. p. 171° [sodium (colourless), iron, copper, and chromium derivatives; benzoate, m. p. 63°; oxime, m. p. 151°; semicarbazone, m. p. 238°; *p*-nitrophenylhydrazide, m. p. 261°, bluish-red]. Mononitration of I yields 4-fluoro-5-nitro-2-hydroxybenzaldehyde, m. p. 120° [*phenylhydrazide*, m. p. 173° (decomp.), brownish-yellow; *p*-nitrophenylhydrazide, m. p. 340° (decomp.), bluish-red], which is volatile in steam, whilst dinitration affords 4-fluoro-3 : 5-dinitro-2-hydroxybenzaldehyde, m. p. 165° [*phenylhydrazide*, m. p. 221°; *p*-nitrophenylhydrazide, m. p. 254° (decomp.), bluish-red]. Mononitration of II furnishes 2-fluoro-5-nitro-4-hydroxybenzaldehyde, m. p. 126° [*phenylhydrazide*, m. p. 153°, red; *p*-nitrophenylhydrazide, m. p. 270° (decomp.), violet-red], readily volatile in steam, and dinitration gives 2-fluoro-3 : 5-dinitro-4-hydroxybenzaldehyde, m. p. 138° [*phenylhydrazide*, m. p. 212°, magenta; *p*-nitrophenylhydrazide, m. p. 260° (violent decomp.), cherry-red].

2-Bromo-3-fluorophenol, b. p. 123°/80 mm., f. p. below –20°, obtained from *m*-fluorophenol by disulphonation, bromination, and hydrolysis, by the Reimer-Tiemann reaction affords 3-bromo-4-fluoro-2-hydroxybenzaldehyde (III), f. p. below –20° [*phenylhydrazide*, m. p. 138°; *p*-nitrophenylhydrazide, m. p. 215°, ruby-red], and 3-bromo-2-fluoro-4-hydroxybenzaldehyde (IV), m. p. 106° [*phenylhydrazide*, m. p. 85°,

golden-yellow; *p*-nitrophenylhydrazide, m. p. 258° (decomp.), violet; oxime, m. p. 148°; semicarbazone, m. p. 210°]. Nitration of III in glacial acetic acid at 100° with nitric acid of *d* 1·5 furnishes 3-bromo-4-fluoro-5-nitro-2-hydroxybenzaldehyde, m. p. 151° [*phenylhydrazide*, m. p. 193°, brown; *p*-nitrophenylhydrazide, m. p. 270° (decomp.), ruby-red], also obtained by bromination of 4-fluoro-5-nitro-2-hydroxybenzaldehyde. By nitration of 5-bromo-4-fluoro-2-hydroxybenzaldehyde, m. p. 81° (*phenylhydrazide*, m. p. 166°; *p*-nitrophenylhydrazide, m. p. 242°, bluish-red), 5-bromo-4-fluoro-3-nitro-2-hydroxybenzaldehyde, m. p. 115° [sodium derivative (red); *phenylhydrazide*, m. p. 215°, golden-brown; *p*-nitrophenylhydrazide, m. p. 258° (decomp.), deep reddish-violet], is obtained. Nitration of IV under similar conditions to those employed with III, but at 30–40°, affords 3-bromo-2-fluoro-5-nitro-4-hydroxybenzaldehyde, m. p. 111° [*phenylhydrazide*, m. p. 166°, brownish-red becoming yellow; *p*-nitrophenylhydrazide, m. p. 256° (decomp.), purplish-red; semicarbazone, m. p. 230°], also obtained by bromination of the mononitration product of 2-fluoro-4-hydroxybenzaldehyde.

4-Fluoro-2-methoxybenzaldehyde, m. p. 53° (*p*-nitrophenylhydrazide, m. p. 213°, magenta; oxime, m. p. 128°; semicarbazone, m. p. 162°), from 4-fluoro-2-hydroxybenzaldehyde with methyl sulphate in the presence of anhydrous sodium carbonate in boiling xylene, by oxidation with alkaline potassium permanganate yields 4-fluoro-2-methoxybenzoic acid, m. p. 136°, readily demethylated by hydriodic acid, *d* 1·7, to 4-fluoro-2-hydroxybenzoic acid, m. p. 186°. The isomeric 2-fluoro-4-methoxybenzaldehyde, m. p. 47° (*phenylhydrazide*, m. p. 101°; *p*-nitrophenylhydrazide, m. p. 217°, ruby-red; oxime, m. p. 95°; semicarbazone, m. p. 228°), is obtained similarly and by oxidation affords 2-fluoro-4-methoxybenzoic acid, m. p. 192°, which could not be demethylated by hydriodic acid.

The bright yellow colour of the sodium derivatives of 4-halogeno-2-hydroxybenzaldehydes, the contrasting colourless sodium derivatives of 2-halogeno-4-hydroxybenzaldehydes, and the deeper colour of the copper and chromium derivatives of the former, are attributed to co-ordination, which may also account for the unexpected volatility in steam of 4-fluoro-5-nitro-2-hydroxybenzaldehyde, and for the liquid nature of 2-bromo-3-fluorophenol and of 3-bromo-4-fluoro-2-hydroxybenzaldehyde. The non-demethylation of 2-halogeno-4-methoxybenzoic acids and the greater reactivity of the isomeric 4-halogeno-2-methoxybenzoic acids are discussed and an explanation is suggested.

C. W. SHOPPEE.

Influence of substituents on the Reimer-Tiemann reaction. II. H. H. HODGSON and T. A. JENKINSON (J.C.S., 1929, 1639–1642; cf. this vol., 559).—The standardised reaction previously described has been conducted with other phenols and also with bromoform and iodoform. The following results for the *o*/*p* ratio are given: (a) with chloroform: phenol 0·6, *o*-cresol 0·48, *o*-chlorophenol 1·6, *o*-bromophenol 1·25, *o*-iodophenol 1·07; salicylic acid 0·06, *m*-cresol 0·46, *m*-chlorophenol 0·71, *m*-bromophenol 0·72, *m*-iodophenol 0·78; (b) with bromoform: phenol 0·44, *o*-cresol 0·37, *o*-chlorophenol 0·71, *o*-bromophenol

0.65, *o*-iodophenol 0.65; salicylic acid 0.05, *m*-cresol 0.85, *m*-chlorophenol 0.84, *m*-bromophenol 0.77, *m*-iodophenol 0.84. With iodoform, the *o/p* ratio for phenol and its *o*-halogeno-derivatives ranged from 0.2 to 0.3. These results are discussed on the basis of current electronic theories, and it is suggested that the variation observed by substitution of bromoform for chloroform may be explained by assuming that the cationoid reagent derived from the former has a greater specific volume than that derived from the latter. In general the presence of halogen leads to deactivation; thus 4-chloro- and 2:6-dichlorophenol give very small yields of aldehydes. Resorcinol monomethyl ether reacts very vigorously with production of much resin, and gives a much greater yield of 4-hydroxy-2-methoxybenzaldehyde than of 2-hydroxy-4-methoxybenzaldehyde (cf. Tiemann and Parrisius, A., 1881, i, 270). C. W. SHOPPEE.

Schiff bases from 5-chlorovanillin. R. M. HANN, G. S. JAMIESON, and E. E. REID (J. Amer. Chem. Soc., 1929, 51, 2586—2588).—The following Schiff's bases are described: 5-chloro-4-hydroxy-3-methoxybenzylidene-*o*-toluidine, m. p. 115° (all m. p. are corr.); -*m*-toluidine (picrate, m. p. 224°); -*p*-toluidine, m. p. 142° (picrate, m. p. 230°); -*m*-nitroaniline, m. p. 160° (picrate, m. p. 190°); -*p*-chloroaniline, m. p. 128° (picrate, m. p. 215°); -*cymidine*, m. p. 146—147°; -*p*-anisidine, m. p. 131° (picrate, m. p. 229—230°); -*benzidine*, m. p. 251—252° [picrate, m. p. 250—260° (decomp.)]; -*m*-aminobenzoic acid, m. p. 207° (picrate, m. p. 236°, +EtOH, m. p. 241°); -*p*-aminophenol, m. p. 150° [picrate, m. p. 224—225° (decomp.)]; -*o*-dianisidine, m. p. 188° (picrate, decomp. 225° with darkening). Condensation products are not obtained with *o*- and *p*-nitro-, 2:4-dichloro-, and trinitroanilines. 3-Nitro-*p*-toluidine and 5-chlorovanillin afford 5-chlorovanillylidenebis-3-nitro-*p*-toluidine, m. p. 125° (picrate, m. p. 148° not sharp). H. BURTON.

Nitrogen derivatives of 2-hydroxy-3-methoxybenzaldehyde and their metallic compounds. M. PICHON (Bull. Soc. chim., 1929, [iv], 45, 528—534).—2-Hydroxy-3-methoxybenzaldehyde (*o*-vanillin) in alcoholic solution with ammonia yields the hydramide ($C_8H_8O_2$)₃N₂, citron-yellow, m. p. 158°, hydrolysed by *N*-hydrochloric acid, and yielding in benzene solution a hydrochloride, $[C_8H_8O_2]_3N_2.HCl$, and a picrate, m. p. 188°. The following metallic salts of 2-hydroxy-3-methoxybenzylideneimine, $[NH:CH:C_6H_3(OMe)_2]_2M$, are obtained on adding the saturated metallic salt solution to an alcoholic solution of the aldehyde in presence of ammonia (1 mol.): cupric, m. p. 192°, nickel, m. p. 327°, cobaltous, m. p. 278°, and cobaltic, black, non-crystalline, $[NH:CH:C_6H_3(OMe)_2]_2Co$, m. p. 177°. Neither the ferrous nor ferric salts could be obtained in this way, or by the action of ammonia on the corresponding *o*-vanillin salt (Noelting, A., 1910, i, 176) as in the case of the cupric salt. 2-Hydroxy-3-methoxybenzylidenemethylimine, m. p. 77° (cupric salt, m. p. 207°; sodium salt), the cupric salt of 2-hydroxy-3-methoxybenzylidenedimethylidimide, $[(NMe_2)CH:C_6H_3(OMe)_2]_2Cu$, m. p. 236°, and 2-hydroxy-3-methoxybenzylidenebenzylimine, m. p. 61.5° (cupric salt, m. p. 211°), are similarly obtained. Analogous copper salts with aniline could not be

obtained. *o*-Veratraldehyde similarly yields a white hydramide, $[C_6H_3(OMe)_2CH]_3N_2$, m. p. 115° (hydrochloride). R. BRIGHTMAN.

Action of nitrosodimethylaniline on apiole. A. QUILICO and M. FRERI (Gazzetta, 1929, 59, 273—279; cf. A., 1928, 880).—Nitrosodimethylaniline acts slowly on parsley apiole at 90—100°, giving a mixture of azo- and azoxy-dimethylaniline with a substance, m. p. 90—100°, which has the properties of a Schiff's base, and probably has the structure $CH_2O_2 \cdot C_6H(OMe)_2 \cdot CH:CH \cdot CH:N \cdot C_6H_4 \cdot NMe_2$. This substance is hydrolysed by acids to dimethyl-*p*-phenylenediamine and apioleacetaldehyde, m. p. 140° (cf. Alessandri, A., 1915, i, 555), of which the *p*-nitrophenylhydrazone, m. p. 268°, and the oxime, m. p. 166° (cf. *loc. cit.*), are prepared. When dimethyl-*p*-phenylenediamine acts on apioleacetaldehyde in alcohol, the Schiff's base is regenerated.

The identification (A., 1928, 997) of the product from isoapiole with m. p. 228—229° as apiolealdehyde-*p*-nitrophenylhydrazone is confirmed by synthesis.

E. W. WIGNALL.

Anæsthetics. Acylaniline derivatives. W. H. HARTUNG and J. C. MUNCH (J. Amer. Chem. Soc., 1929, 51, 2570—2574).—Nitration of a series of aryl alkyl ketones and subsequent reduction of the *m*-nitro-derivatives obtained gives amino-ketones, $NH_2 \cdot C_6H_3R \cdot CO \cdot Alk$, the anæsthetic actions of which have been determined. For anæsthetic action *Alk* must be at least *Pr*^a; the isopropyl derivative is less active than the *n*-derivative. The following ketones are new: *m*-nitrovalerophenone, b. p. 145—150°/3 mm.; 3-nitro-*p*-tolyl propyl, m. p. 77.5° (semicarbazone, m. p. 215—216°); 3-nitro-*p*-tolyl isopropyl, m. p. 41°; 3-nitro-*p*-tolyl *n*-butyl, m. p. 48° (semicarbazone, m. p. 210°); 3-nitro-*p*-tolyl isobutyl, m. p. 54.5° (semicarbazone, m. p. 214°); *m*-aminovalerophenone, b. p. 160—163°/3 mm. (hydrochloride, m. p. 155.5—156°); 3-amino-*p*-tolyl ethyl, b. p. 190—195°/20 mm., m. p. 85.5—86° [acetyl derivative, m. p. 131.5°; hydrochloride, m. p. 204° (decomp.)]; 3-amino-*p*-tolyl propyl, m. p. 69° (acetyl derivative, m. p. 130.5°; hydrochloride, m. p. 168°); 3-amino-*p*-tolyl isopropyl, b. p. 150—153°/3 mm. (hydrochloride, m. p. 167.5°); 3-amino-*p*-tolyl *n*-butyl, m. p. 61° (acetyl derivative, m. p. 93—94°; hydrochloride, m. p. 91.5—93°); 3-amino-*p*-tolyl isobutyl, b. p. 165—170°/3 mm. (acetyl derivative, m. p. 117.5°; hydrochloride, m. p. 142.5°). H. BURTON.

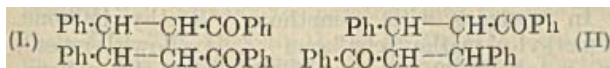
β-Phenylisobutyl methyl ketone and derivatives. Synthesis of α- and β-phenylisovaleric acids. A. HOFFMAN (J. Amer. Chem. Soc., 1929, 51, 2542—2547).—Mesityl oxide and benzene react in presence of anhydrous aluminium chloride, forming β-phenylisobutyl methyl ketone (I), b. p. 134°/22 mm., 252° (corr.)/760 mm., 0.972 (semicarbazone, m. p. 163—164°; oxime, b. p. 181°/27 mm., m. p. 52—54°; tetrabromo-derivative, m. p. 96—98°), which when heated with anhydrous zinc chloride gives, in addition to other products, a hydrocarbon (II), $C_{24}H_{28}$, b. p. 195°/18 mm., m. p. 130.5—131° (corr.). Nitration of II with boiling nitric acid (*d* 1.42) affords a trinitro-derivative, m. p. 180—184°; II is stable towards oxidising agents. Reduction of I with sodium and

alcohol yields β -phenylisobutylmethylcarbinol, b. p. 132—133°/17 mm., d_{25}^{25} 0.960, dehydrated by heating with zinc chloride to a hydrocarbon (probably δ -phenyl- δ -methyl- Δ^{β} -pentene), b. p. 96—98°/17 mm., d_{25}^{25} 0.889. Oxidation of I with sodium hypobromite gives β -phenylisovaleric acid (III), m. p. 58—58.5° (methyl ester, b. p. 120°/11 mm.; anilide, m. p. 122—123°; nitro-derivative, m. p. 169—172°), identical with the α -phenylisovaleric acid of Eykman (A., 1908, i, 794). Ethyl sodiophenylmalonate and isopropyl iodide react, yielding a mixture of ethyl phenylacetate and ethyl phenylisopropylmalonate. Hydrolysis of the mixture, distillation of the acids obtained, and removal of phenylacetic acid as the soluble silver salt afford α -phenylisovaleric acid, b. p. 159—160°/14 mm., m. p. 60° (anilide, m. p. 132—133°; silver salt). β -Phenylisopropyl chloride and ethyl sodiomalonate give mainly α -methylstyrene; a small amount of ethyl β -phenylisopropylmalonate is also formed. Hydrolysis of this and thermal decomposition of the resulting acid yields III.

H. BURTON.

Truxillic and truxinic ketones. II. Photochemistry of cinnamic acids, chalkones, and their derivatives. H. STOBBE and K. BREMER (J. pr. Chem., 1929, [ii], 123, 1—60).—The two dimerides previously obtained by Stobbe and Hensel (A., 1926, 1248) by irradiation of chalkone have been examined further, and the work has been extended to include *p*-methyl-, *p'*-methyl-, *pp'*-dimethyl-, *p*-methoxy-, *p'*-methyl-, *pp'*-dimethoxy-, methylene-3:4-dioxy-, β -methyl-, and *p'*-methoxy- α -methyl-chalkone.

Bischalkone A (I), m. p. 124° (truxinic ketone type), is non-volatile in steam, and affords a dioxime, m. p. 227°, and a disemicarbazone, m. p. 235—237°; it



is stable to hydrogen peroxide in glacial acetic acid solution and to cold alkaline permanganate, but with concentrated nitric acid yields benzoic acid and resinous products; it is unaffected by bromine. Rapid distillation furnishes traces of benzoic acid and chalkone, together with 4% of stilbene, the amount of the latter rising to 20% when the distillation is prolonged. By irradiation with sunlight or with a quartz-mercury lamp, either in the solid state or in solution, decomposition (probably depolymerisation) is caused with the production of brown resins; heating with sodium acetate and acetic anhydride effects no conversion into a furan derivative, whilst alcoholic potassium hydroxide, pyridine, and acetic acid are without action. Bischalkone B (II), m. p. 225—226° (truxillic ketone type), is also non-volatile in steam and stable to cold alkaline permanganate, but gives no oxime, and by heating with sodium acetate and acetic anhydride, or with a dilute acetic acid solution of semicarbazide hydrochloride containing potassium acetate, passes into bischalkone D, m. p. 195°. The dimeride B is not identical with the reduction product, m. p. 220—222°, of dibenzoyldiphenylbutadiene, described by Wislicenus and Lehmann (A., 1899, i, 59), which affords a dioxime, m. p. 230°, and by treatment with acetic anhydride and potassium

acetate yields a substance, $C_{30}H_{22}O$, m. p. 180—181°. The dimeride B is decomposed (probably depolymerised) to a small extent only by irradiation in the solid state or in chloroform solution; by distillation it gives 60% of chalkone and traces of stilbene, the latter resulting by decomposition, not of the dimeride B, but of monomeric chalkone, which has been shown to yield 8% of stilbene by distillation (cf. Stobbe and Hensel, *loc. cit.*), in addition to benzoic acid and resin. The dimeride B is unaffected by treatment with trichloroacetic acid in acetic acid solution, but by heating with sodium acetate and acetic anhydride it is converted into the stereoisomeride, bischalkone D, m. p. 195°. Irradiation of chalkone in solution affords the dimeride A only, irrespective of the wave-length of the light used; the yields obtained using acetic acid, chloroform, and ethyl alcohol are similar (30—35%), but are smaller in benzene. The atmospheric conditions (air, carbon dioxide, vacuum), and likewise the presence of hydrochloric acid or erythrosin, are without influence on the yield of dimeride A; the presence of chlorophyll, however, reduces the yield to about one third of the former value, and affords 1—1.5% of the dimeride B. In benzene solution containing a trace of iodine, chalkone, by irradiation with ultra-violet light from a quartz-mercury lamp, furnishes solely 7.5% of a third dimeride, bischalkone C, m. p. 178—179°, which was obtained only in one experiment; the dimeride C is stable to cold alkaline permanganate and to bromine. In all experiments, using solutions of phenyl styryl ketone, polymerisation occurs, whereas the analogously constituted cinnamic acids in solution always isomerise and never polymerise. Irradiation in the solid state or in suspension affords both the dimerides A and B, the relative yields depending on the wave-length of the light used. In general, the yield of the dimeride B decreases with decreasing wave-length, but the presence of hydrochloric acid or mercuric chloride, or the atmospheric condition, has no apparent effect. The production of the lower-melting truxinic ketone type (I) by irradiation in solution, and of the higher-melting truxillic ketone type (II) by irradiation in the solid state, are in agreement with the results obtained by Reimer (A., 1924, i, 642) on methyl benzylidenepyruvate. All attempts to obtain the dimeric ketone, m. p. 134°, prepared by Wieland (A., 1904, i, 432) by treatment of chalkone with acetic anhydride and concentrated sulphuric acid, were unsuccessful. The absorption spectra of chalkone, dihydrochalkone (which is stable to ultra-violet radiation), the three photo-dimerides A, B, C, and the dimeride D conform to the rule of Stobbe (Z. angew. Chem., 1926, 39, 673); the absorption curves of the dimerides lie between those of the monomeride and the saturated dihydro-compound, and exhibit a close formal resemblance to that of the latter.

In order to compare chalkones in which the keto-group is substituted with cinnamic acid derivatives in which the carboxyl group is modified (salts, esters, amide), *anti*-chalkoneoxime and the chalkone-semicarbazones have been examined. Exposure of *anti*-chalkoneoxime, m. p. 75°, obtained by Henrich's method (A., 1907, i, 324), to a quartz-mercury lamp produced a certain amount of discoloration but no

polymerisation. Chalkone- α -semicarbazone, m. p. 168° (cf. Heilbron and Wilson, J.C.S., 1912, 101, 1482; 1913, 103, 1504), by similar treatment yielded equal quantities of resin and unchanged product, but chalkone- γ -semicarbazone, m. p. 179—180° (cf. Heilbron and Wilson, *loc. cit.*), readily underwent a peculiar transformation to a yellow isomeride.

p'-Methylchalkone (α -form), m. p. 74—75° [oxime, m. p. 130—132°; hydroxylamino-oxime(?), m. p. 150—160°], was obtained by condensing benzaldehyde and *p*-methylacetophenone in alcoholic solution with 10% sodium hydroxide (cf. Weygand and Matthes, A., 1926, 1041). Irradiation of *p*'-methylchalkone in ethyl-alcoholic solution with sunlight affords a 45% yield of *bis-p*'-methylchalkone A, m. p. 114°, together with traces of *bis-p*'-methylchalkone B, m. p. 218°; use of the solid substance furnishes two other dimerides in equal proportion, *bis-p*'-methylchalkone C, m. p. 205°, and *bis-p*'-methylchalkone D, m. p. 243°. Ultra-violet light transforms the dimeride A into the dimeride B, and the yield of the latter increases with the use of shorter waves. By slow distillation, A yields traces of *p*'-methylchalkone and 10% of stilbene; since under the same conditions *p*'-methylchalkone affords but 2% of stilbene, the truxinic ketone structure (I) is assigned to the dimeride A. All four dimerides are stable to cold alkaline permanganate and to bromine; they yield no semicarbazones when heated with semicarbazide hydrochloride and potassium acetate in alcoholic solution, but under these conditions the dimeride A is partly converted into B, whilst D affords a fifth isomeride, *bis-p*'-methylchalkone E, m. p. 216°, a transformation also brought about by hot acetic anhydride. The five dimerides fall into two groups according to the colour produced with concentrated sulphuric acid; A and B yield a carmine-red, whilst C, D, and E give a yellow colour. Since B can be reconverted into A by acetic anhydride, it is considered to be a stereoisomeride of the dimeride A, whilst C, D, and E are stereoisomerides of the truxillic ketone type (II). The absorption spectra of the dimerides B, C, D, and E are identical and closely similar to those of A and dihydro-*p*'-methylchalkone; the absorption curves of all five dimerides lie between those of *p*'-methylchalkone and its dihydro-compound. The latter, m. p. 69°, was prepared by reduction of *p*'-methylchalkone with hydrogen and colloidal palladium in alcoholic solution; it is stable to light.

p-Methylchalkone (β -form), m. p. 96.5° (cf. Weygand, A., 1928, 180), was prepared by a slight modification of the method of Hanzlik and Bianchi (A., 1899, i, 890); by irradiation with sunlight the solid substance gives a 14% yield of a single dimeride, *bis-p*-methylchalkone, m. p. 198—200°; the yield falls to 2% with ultra-violet light, and no dimerisation occurs in solution with radiation of any wave-length. The dimeride is stable to cold alkaline permanganate and to bromine, and affords no semicarbazone; it is slowly depolymerised by ultra-violet rays of short wave-length. *p*-Methylchalkone yields an oxime, m. p. 134° (cf. Hanzlik and Bianchi, *loc. cit.*), which when irradiated with ultra-violet light in the solid state or in solution becomes greenish-yellow, the production of colour indicating fission to the monomeric ketone.

pp'-Dimethylchalkone, m. p. 127.5°, obtained from *p*-tolualdehyde and *p*-methylacetophenone by condensation with 10% sodium hydroxide in alcoholic solution (cf. Weygand and Matthes, *loc. cit.*), exhibited so great a tendency to resinification on irradiation, either in the solid state or in solution, that no polymeride could be isolated. This behaviour, anomalous compared with that of the foregoing monomethylchalkones, is not due to greater light absorption, since the absorption curves of chalkone, *p*'-methyl-, *p*-methyl-, and *pp*'-dimethyl-chalkone all lie close together and exhibit a close formal resemblance.

p-Methoxy-*p*'-methylchalkone, m. p. 94°, obtained in 45% yield by condensation of *p*-anisaldehyde and *p*-methylacetophenone, is rapidly and completely resinified by irradiation with sunlight or ultra-violet light in the solid state, but in ethyl-alcoholic solution a 2.5% yield of a substance, probably *bis-p*-methoxy-*p*'-methylchalkone, m. p. 208°, was isolated. *pp*'-Dimethoxychalkone, m. p. 101°, is rapidly and completely resinified by irradiation with ultra-violet light both in the solid state and in solution. The absorption curves of the foregoing disubstituted monomeric chalkones and of *p*-methoxychalkone (m. p. 76°) are extremely similar and in part coincident. Dihydro-*p*-methoxychalkone, m. p. 59°, could not be obtained by the method of Bargellini and Bini (A., 1911, i, 211), and was prepared using hydrogen with colloidal palladium and sodium protoalbinat in aqueous-alcoholic solution. Solid 3:4-methylenedioxychalkone, m. p. 122°, is largely unaffected by irradiation with sunlight or ultra-violet light, only traces of resin being produced; no polymerisation occurs in chloroform solution, but resinification increases (cf. Stobbe and Wilson, J.C.S., 1910, 97, 1724).

In contrast with *p*-methoxy-*p*'-methylchalkone, α -methyl-*p*'-methoxychalkone A (yellowish-green), m. p. about 30°, by irradiation with the quartz-mercury lamp as the solid or in solution affords a colourless isomeride, α -methyl-*p*'-methoxychalkone B, m. p. 64.5°, which decolorises permanganate and reacts with bromine.

The results are discussed in relation to other examples, previously reported; it appears that unsubstituted chalkone and all *p*- or *p*'-monosubstituted chalkones tend to photopolymerise, whilst *pp*'-disubstituted chalkones resist this process. The polymerisability of various arylideneacetophenones (chalkones) is compared with that of the corresponding arylideneacetic acids (cinnamic acids), but no general relation between light-sensitivity and constitution in the two series can be found. A comparison of existing data with results given above shows that chalkones with an α -substituted ethylene group, $\text{Ar}\cdot\text{CH}:\text{CR}\cdot\text{COAr}$, readily photo-isomerise when $\text{R}=\text{Me}$ or Ph , but that reaction is inhibited when $\text{R}=\text{Ac}$ or CO_2Et ; photopolymerisation never takes place. One example only of the effect of β -substitution has been investigated; β -methylchalkone (dypnone) alone, or in chloroform solution, is unaffected by ultra-violet light. A comparison with similarly constituted arylideneacetic acids shows that α - and β -substituents generally impede photopolymerisation, but certain exceptions are quoted. C. W. SHOPPEE.

Halogenated 3:9-dibenzoyl derivatives of perylene. Synthesis of *isoviolanthrone*. V. V. SCHARVIN and L. Z. SOBOROVSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 789—794).—Perylene, m. p. 265°, was obtained in 25% yield by the action of anhydrous phosphoric acid and phosphorus trichloride at 500° on β -dinaphthol. With *o*-chlorobenzoyl chloride in carbon disulphide solution, perylene gives, by the Friedel-Crafts reaction, 3:9-di-*o*-chlorobenzoylperylene (I) in 85% yield. By using the bromo- or iodo-benzoyl compounds, the corresponding bromo- and iodo-derivatives are obtained. All three compounds are deep red in colour, and do not melt at 320°. The internal condensation of I to *isoviolanthrone* is carried out either by heating at 170° with anhydrous aluminium chloride, or by boiling a mixture of the chloro-derivative with potassium hydroxide in quinoline. In both cases, on extraction with a solution of an alkaline hyposulphite, a deep violet precipitate of the vat dye is obtained, and on neutralising the alkaline mother-liquor, a precipitate of 3:9-di-*o*-hydroxybenzoylperylene is obtained as a by-product.

M. ZVEGINZOV.

Rotenone. I. Reduction products. F. B. LAForge and L. E. SMITH (J. Amer. Chem. Soc., 1929, 51, 2574—2581).—Reduction of rotenone with hydrogen (1 mol.) in presence of palladised barium sulphate and acetone or platinum oxide and ethyl acetate (cf. Kariyone, A., 1924, i, 251; Butenandt, A., 1928, 1017) gives a mixture of dihydrorotenone (I), m. p. 164° (lit. 216°), $[\alpha]_D^{25} -225.2^\circ$ in benzene [the oxime, m. p. 256—257° (decomp.)], obtained also by catalytic reduction of rotenoneoxime (Takei, A., 1928, 765) (benzenesulphonyl derivative, m. p. 143°), is converted by prolonged treatment with hydrochloric acid at the ordinary temperature into the *isoxime*, m. p. 270—273° (decomp.), and an *acid* (II), $C_{23}H_{24}O_6$, m. p. 209°, $[\alpha]_D^{25} +36.2^\circ$ in chloroform. Further reduction of I or II with hydrogen in presence of platinum oxide and ethyl acetate affords an *acid*, $C_{23}H_{26}O_6$, m. p. 215° (only in small amount from I). Reduction of rotenone with zinc dust and alcoholic potassium hydroxide yields a mixture of rotenol (III), m. p. 120° (lit. 115°), and derritol (IV), m. p. 164° (lit. 161°), $[\alpha]_D^{25} -62.2^\circ$ in chloroform (cf. Butenandt, *loc. cit.*); the use of 5% alkali gives mainly III, 20% alkali mainly IV. At the same time small amounts of a *substance*, m. p. 161°, are produced. Contrary to the statement of Butenandt, similar zinc dust reduction of I affords dihydrorotenol and dihydroderritol, m. p. 122°. *iso*Rotenone (Takei, *loc. cit.*) is converted by zinc dust and 15% alcoholic potassium hydroxide into a mixture of *isorotenol*, $C_{23}H_{24}O_6$, m. p. 133°, and *isoderritol*, m. p. 150°. Initial reduction of rotenone probably occurs at two centres and the production of derritol derivatives appears to be independent of the presence of a double linking, since *isorotenone* is probably a saturated (ring) compound.

H. BURTON.

[A constituent of] *Lactucarium germanicum*. K. H. BAUER and E. SCHUB (Arch. Pharm., 1929, 267, 413—424).—Lactucerin was isolated from the petroleum extract of the dried drug and attempts were made to purify it by crystallisation alternately from

alcohol and light petroleum, but it was impossible to effect complete purification. The product had m. p. 232°, $[\alpha]_D^{25} +39.08^\circ$ after nine crystallisations, M 460 (Rast). α -Lactuceryl, $C_{30}H_{48}OH$, was recrystallised eight times, when the m. p. and $[\alpha]_D^{25}$ gradually increased to 203° and $[\alpha]_D^{25} +78.44^\circ$, respectively (*benzoate*, m. p. 257°). β -Lactuceryl, m. p. 162°, $[\alpha]_D^{25} +53.81^\circ$, was isolated from the mother-liquor from α -lactuceryl (*benzoate*, m. p. 260°). Attempts to break down α -lactuceryl with nitric acid, chromic acid, hydrogen peroxide, mercuric acetate, hypochlorite, and copper oxide were abortive. Both lactuceryls afford *lactucene*, $C_{30}H_{48}$, m. p. 207°, when treated with phosphorus pentachloride, which gives propionic and other acids on ozonisation. The corresponding saturated hydrocarbon *lactucane* is obtained when lactucene is hydrogenated or when lactuceryl is reduced with hydriodic acid.

S. COFFEY.

Synthesis of some phenyl styryl ketones and related compounds. N. M. CULLINANE and D. PHILPOT (J.C.S., 1929, 1761—1765).—Phloracetophenone 4:6-dimethyl ether and 2:4-dimethoxybenzaldehyde (improved method of preparation described) condense in the presence of aqueous-alcoholic potassium hydroxide at 60° to give 2-hydroxy-4:6-dimethoxyphenyl 2:4-dimethoxystyryl ketone, m. p. 128° (cf. Kostanecki and Tambor, A., 1899, i, 891, who give m. p. 152°), which by bromination in chloroform solution at 0° and treatment of the crude bromination product (m. p. 230°) with hot 50% sodium hydroxide yields a compound, $C_{19}H_{17}O_6Br$, m. p. above 300°, which is probably 3:5:2':4'-tetramethoxy-4-bromobenzylidenecoumaran-2-one. The production of a coumaranone as opposed to a flavone (cf. von Auwers and Anschütz, A., 1921, i, 682) and its behaviour on bromination are analogous to the results previously described by Kostanecki and Tambor (*loc. cit.*) and by Tambor (A., 1912, i, 43).

Phloracetophenone trimethyl ether combines with salicylaldehyde under the conditions given above to yield 2:4:6-trimethoxyphenyl 2-hydroxystyryl ketone, m. p. 205.5°, converted by dry hydrogen chloride in glacial acetic acid solution into 2':4':6'-trimethoxyflavylium chloride, m. p. 162° (*ferrichloride*, m. p. 198°).

C. W. SHOPPEE.

Condensations of ketones with phenols. III. Condensation products of mesityl oxide and monohydroxybenzenes. J. B. NIEDERL [with N. AMBINDER, R. CASTY, D. W. C. KNOWLES, I. RAPPA-PORT, and W. SASCHEK] (J. Amer. Chem. Soc., 1929, 51, 2426—2430).—When a mixture of mesityl oxide (1 mol.) and a phenol (1 mol.) is treated with sulphuric acid (1 mol.) at 0° and kept at 15—20° for 1 week, substituted 2:4:4-trimethyl-2-chromanols or di-2:4:4-trimethyl-2-chromanyl ethers are obtained. Formation of the chromanol occurs either by direct addition of the oxide to the phenol, or by re-arrangement of an intermediate β -hydroxyphenylisobutyl methyl ketone, formed by interaction of the phenol with the additive compound from the oxide and sulphuric acid. The following substituted 2-chromanols are obtained from the appropriate phenol: 2:4:4-trimethyl-, m. p. 89° (*dimtro* derivative, m. p. 155°); 7-nitro-2:4:4-trimethyl-, m. p. 148°; 6-nitro-

2:4:4-trimethyl-, m. p. 132°; 2:4:4:8-tetramethyl-, m. p. 120°, and 2:4:4:7-tetramethyl-, m. p. 120° (from trinitro-*m*-cresol). Di-2:4:4:7-tetramethyl-, m. p. 58° (tetranitro-derivative, m. p. 145°); di-2:4:4:6-tetramethyl-, m. p. 57° (tetranitro-derivative, m. p. 167°); di-5-chloro-2:4:4:7-tetramethyl-, m. p. 71°; di-2:4:4:6:8-pentamethyl- (tetranitro-derivative, m. p. 155°); di-2:4:4:8-tetramethylisopropyl- (from carvacrol) (dinitro-derivative, m. p. 185°), and di-2:4:4:5-tetramethyl-8-isopropyl-2-chromanylethers, m. p. 136° (dinitro-derivative, m. p. 201°), are also described. Oxidation of the chromanols with chromic oxide in acetic acid solution affords substituted β -hydroxyphenylisovaleric acids.

H. BURTON.

Cyclic compounds containing aldehydic groups. I. G. FARBERIND. A.-G.—See B., 1929, 747.

Condensation products of the benzanthrone series [cyclic sulphur derivatives]. I. G. FARBERIND. A.-G.—See B., 1929, 748.

Anhydro-compounds derived from 2-nitro-3:4-dimethoxyphenylacetoneitrile and certain pseudo-bases. J. M. GULLAND and C. J. VIRDEN (J.C.S., 1929, 1791—1803).— β -3-Methoxyphenylethylamine, obtained from 3-methoxycinnamic acid (Chakravarti, Haworth, and Perkin, A., 1927, 1096) as described by Helfer (A., 1924, i, 1341), by treatment with anhydrous formic acid at 175° yields formyl- β -3-methoxyphenylethylamine, b. p. 216°/17 mm., converted by phosphorus oxychloride into 6-methoxy-3:4-dihydroisoquinoline, b. p. 155°/16 mm. [methiodide, (I), m. p. 199° (decomp.); periodide, $C_{11}H_{14}ON_3$, m. p. 82° (decomp.); periodide, $C_{11}H_{11}ON_5$, m. p. 82° (decomp.)]; treatment of I with potassium hydroxide affords 1-hydroxy-6-methoxy-2-methyltetrahydroisoquinoline (II), m. p. 102°. By reduction of I with zinc and hydrochloric acid is obtained 6-methoxy-2-methyltetrahydroisoquinoline (hydriodide, m. p. 173—174; picrate, m. p. 130—131°), and oxidation of the methochloride corresponding with I with alkaline potassium permanganate affords 6-methoxy-1-keto-2-methyltetrahydroisoquinoline, m. p. 50°. The preparation of β -3-methoxyphenylethylamine was also attempted as follows: condensation of 3-methoxybenzaldehyde and nitromethane using alcoholic sodium ethoxide at 0° gives the sodium salt of the *aci*-form of 3-methoxy- α -hydroxy- β -nitroethylbenzene (cf. A., 1902, i, 682), dehydrated by fused zinc chloride in hot glacial acetic acid to ω -nitro-3-methoxystyrene, dimorphic (α -form, needles, m. p. 91—92°; β -form, plates, m. p. 91—92°), also obtained directly from 3-methoxybenzaldehyde and nitromethane in the presence of methylamine hydrochloride and anhydrous sodium carbonate in alcoholic solution at 15°. Reduction of the nitro-compound with zinc and dilute acetic acid yields 3-methoxyphenylacetaldoxime, m. p. 91°; the method was abandoned on account of the poor yield (11%) obtained.

2-Nitrohomoveratrole, prepared by the method of Oberlin (A., 1926, 283) and also by methylation of 2-nitro-3-hydroxy-*p*-tolyl methyl ether, does not appear to condense with suitable pseudo-bases of the isoquinoline series, but by use of 2-nitro-3:4-dimethoxyphenylacetoneitrile, obtained by the inter-

action of 2-nitro-3:4-dimethoxybenzyl chloride and alcoholic potassium cyanide (cf. Kay and Pictet, J.C.S., 1913, 103, 953) along with 2-nitro-3:4-dimethoxyphenylacetamide, m. p. 151—153°, the following anhydro-compounds are obtained: II affords 1- α -cyano-2'-nitro-3':4'-dimethoxybenzyl-6-methoxy-2-methyltetrahydroisoquinoline (III), m. p. 95—96°; cotarnine yields anhydrocotarnine-2-nitro-3:4-dimethoxyphenylacetoneitrile (IV), m. p. 153° (decomp., gradually becoming red from 120°); and laudaline furnishes anhydrolaudaline-2-nitro-3:4-dimethoxyphenylacetoneitrile (V), m. p. 125—127°. Subsequent attempts to convert the anhydro-compounds III and V into aporphine bases were unsuccessful owing to ready hydrolysis by dilute acids to the components, a property shared by the base IV. It was also found impossible to effect reduction in alkaline media without causing fission of the molecule; thus with ammoniacal ferrous hydroxide, III yielded 2-amino-3:4-dimethoxyphenylacetoneitrile, m. p. 108° (acetyl derivative, m. p. 184°), also obtained by reducing similarly 2-nitro-3:4-dimethoxyphenylacetoneitrile, whilst this nitrile was obtained from III with hot alcoholic ammonium sulphide. In view of the synthesis of apomorphine dimethyl ether recently described by Avenarius and Pschorr (this vol., 457) the action of hydrochloric acid on III has been studied under a variety of conditions, but in every case fission of the molecule occurred. By combining hydrolysis and reduction in one reaction, the procedure adopted by Avenarius and Pschorr, a small quantity only of a base (probably 6-methoxy-2-methyltetrahydroisoquinoline), which could not be diazotised, was obtained.

The work of Avenarius and Pschorr has been repeated, but without success; formyl- β -phenylethylmethylamine, b. p. 183.5°/30 mm., now obtained in a state of purity, could not be isomerised by thionyl chloride to 1-hydroxy-2-methyltetrahydroisoquinoline, and isoquinoline methiodide was therefore used as starting material. As the results of a large number of condensations, following the method described by Avenarius and Pschorr, only 2-methyltetrahydroisoquinoline methiodide, m. p. 192° (corr.), was obtained. The assumed identity of the substance, m. p. 195°, described by Avenarius and Pschorr as *dl*-apomorphine dimethyl ether methiodide, with natural (laevorotatory) apomorphine dimethyl ether methiodide, m. p. 195° (corr.), $[\alpha]_D -42.03^\circ$ (Pschorr, Jaekel, and Fecht, A., 1903, i, 193), is criticised.

C. W. SHOPPEE.

Derivatives of 5-hydroxy-2-methylindole. C. D. NENITZESCU (Bul. Soc. Chim. Romania, 1929, 11, 37—43).—Condensation of benzoquinone with ethyl β -aminocrotonate, ethyl β -anilincrotonate, and ethyl glycineacetoacetate gave ethyl 5-hydroxy-2-methylindole-3-carboxylate, m. p. 205°, ethyl 5-hydroxy-1-phenyl-2-methylindole-3-carboxylate, m. p. 206°, and ethyl 5-hydroxy-2-methyl-1-carbethoxymethylindole-3-carboxylate, m. p. 148°, respectively. Methylation of ethyl 5-hydroxy-2-methylindole-3-carboxylate yielded ethyl 5-methoxy-2-methylindole-3-carboxylate, m. p. 161°, which, on alkaline hydrolysis, gave 5-methoxy-2-methylindole-3-carboxylic acid, melting at 208° to give 5-hydroxy-2-methylindole and carbon

dioxide. Condensation of 5-hydroxy-2-methylindole with ethyl orthoformate and with formic acid gave *tri-(5-methoxy-2-methyl-3-indolyl)methane*, m. p. 227°, and *(5-methoxy-2-methyl-3-indolyl)-(5-methoxy-2-methyl-3-indolylidene)methene hydrochloride*, m. p. 230° (decomp.), respectively. A. A. GOLDBERG.

3-Nitro-2-aminopyridine-5-sulphonic acid. DEUTS. GOLD- & SILBER-SCHNEIDENST.—See B., 1929, 737.

Hexamethylenetetramine phenylquinoline-carboxylate (atophanurotropin). L. VANINO and F. MUSSGÜT (Arch. Pharm., 1929, 267, 487—488).—The pure salt is obtained by allowing hexamethylenetetramine and phenylquinoline-4-carboxylic acid to react in warm alcoholic solution. Hexamethylenetetramine and thiocarbamide afford a well-defined compound, $2\text{CS}(\text{NH}_2)_2 \cdot (\text{CH}_2)_6\text{N}_4$, m. p. 176—177°, when concentrated solutions of the two components are mixed. S. COFFEY.

Organic [quinoline] bases from arylamines and acetylene. I. G. FARBERIND. A.-G.—See B., 1929, 747.

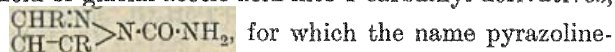
Tautomerism of 2:5-dithionpiperazine. S. ISHIKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 119—129).—2:5-Dithionpiperazine, darkening at 220—280°, may be prepared by a modification of the method of Gatewood and Johnson (A., 1927, 62) and also by heating 2:5-diketopiperazine with phosphorus pentasulphide. It dissolves in alkalis approximately as a dibasic acid. Colour reactions, e.g., with nitroprusside, indicate that it behaves as an enolic compound only in alkaline solution. The absorption spectrum of the solution in excess of dilute sodium hydroxide solution differs from those of solutions in ether, water, one equivalent of sodium hydroxide solution, or dilute acid. An attempt to isolate the enolic form by treatment with aniline was unsuccessful. 2:5-Dithion-1:4-dimethylpiperazine, darkening at 180°, m. p. 218°, is prepared by heating sarcosine anhydride with phosphorus pentasulphide. The action of hydrogen sulphide on α -aminoisobutyronitrile yields a substance, m. p. 156° (cf. Gatewood and Johnson, A., 1928, 745), but 2:5-dithion-3:3:6:6-tetramethylpiperazine, sintering at 160°, m. p. 188°, is formed by heating 2:5-diketo-3:3:6:6-tetramethylpiperazine with phosphorus pentasulphide. The fact that the 1:4-dimethyl and 3:3:6:6-tetramethyl derivatives are, respectively, sparingly and readily soluble in alkalis indicates that the mobile hydrogen atom is that of the imino-group, contrary to the assumption of Abderhalden and Schwab (A., 1926, 740). Absorption spectra of the two derivatives are given. R. K. CALLOW.

Pyrazolines. R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 541—545).—Yields of pyrazolines amounting to 80% are obtained when the condensation of the $\alpha\beta$ -ethylenic ketone with hydrazine hydrate is effected in methyl alcohol and the distillation is carried out in an atmosphere of nitrogen (cf. Auwers and Heimke, A., 1927, 1203). Hydrolysis of the distillation residues with 20% sulphuric acid yields a further small amount of pyrazoline and ketones not always identical with the original $\Delta^{\alpha\beta}$ -ketone. The

luminescence reported by Straus, Muffat, and Heitz (A., 1919, i, 41) has not been observed in pyrazolines prepared by the authors. The latter pyrazolines are stable to dilute mineral acids and on boiling afford only the salt of the original base, and the fission observed by Curtius and Wirsing (A., 1895, i, 248) appears to be peculiar to the first member of the series. No formation of gas was observed when the pyrazolines were heated in a sealed tube at 130° with 10% sodium hydroxide solution. Crystalline derivatives are obtained with benzenesulphonyl and *p*-bromobenzenesulphonyl chloride in pyridine, pyrazolines derived from alkylidenacetones, $\text{CHR}:\text{CHAc}$, giving one, those from alkyl-alkylidenacetones, $\text{CHR}:\text{CAc}:\text{CH}_2\text{R}'$, giving two isomeric derivatives (cf. this vol., 330). R. BRIGHTMAN.

Pyrazolines and their derivatives. R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 545—548).—3:5:5-Trimethylpyrazoline, b. p. 51—52°/11 mm., (benzenesulphonate, $\text{C}_6\text{H}_{11}\text{N}_2\text{SO}_3\text{Ph}$, m. p. 140—141°; *p*-bromobenzenesulphonate, m. p. 122°), 3-methyl-5-isopropylpyrazoline, b. p. 76—78°/11 mm. (benzenesulphonate, m. p. 114°; *p*-bromobenzenesulphonate, m. p. 134—135°), and 3-methyl-5-isobutylpyrazoline, b. p. 91—92°/10 mm. (benzenesulphonate, m. p. 115°; *p*-bromobenzenesulphonate, m. p. 148°), are described. The isobutylidene- and isoamylidene-acetone required were obtained from the corresponding ketols, methyl β -hydroxy- γ -methylbutyl ketone, b. p. 90°/16 mm. semicarbazone, m. p. 146—147°, and methyl β -hydroxy- δ -methylamyl ketone, b. p. 104°/17 mm. (semicarbazone, m. p. 141—142°), prepared by Grignard and Dubien's method (A., 1925, i, 111; cf. Pastureau and Zamenhoff, A., 1926, i, 272). R. BRIGHTMAN.

Action of potassium cyanate in acid medium on pyrazolines. Pyrazolinecarbamides. R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 549—552).—3:5-Dialkylpyrazolines are converted by potassium cyanate in dilute hydrochloric acid or glacial acetic acid into 1-carbamyl derivatives,



carbamides is proposed. These compounds are isomeric with the normal semicarbazones of the corresponding $\alpha\beta$ -unsaturated ketones and aldehydes. They yield crystalline picrates, are hydrolysed by hydrochloric acid (*d* 1:1) to the pyrazolines, and are converted by nitrous acid into the original ketone. 1-Carbamyl-3:5:5-trimethylpyrazoline, m. p. 129°, b. p. 140—141°/10 mm. (dibenzoyl derivative, m. p. 176°), 1-carbamyl 3-methyl-5-isopropylpyrazoline, m. p. 116—117°, b. p. 155—157°/11 mm. (dibenzoyl derivative, m. p. 141°), 1-carbamyl-3-methyl-5-isobutylpyrazoline, m. p. 110—111°, b. p. 162—168°/10 mm. (dibenzoyl derivative, m. p. 128—129°), and 1-carbamyl-4-methyl-5-ethylpyrazoline, m. p. 109—110°, b. p. 155—160°/11 mm., from 4-methyl-5-ethylpyrazoline, b. p. 65—70° (benzenesulphonate, m. p. 118°), are described (cf. A., 1925, i, 1185; Auwers and Heimke, A., 1927, 1203). R. BRIGHTMAN.

Constitution of "Scholtz' base." R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 553—555).—The base, m. p. 129°, b. p. 212—213° (decomp.), obtained by Scholtz (A., 1896, i, 343; cf.

Harries and Kaiser, A., 1899, i, 637) on heating the normal semicarbazone of mesityl oxide is 1-carbamyl-3 : 5 : 5-trimethylpyrazoline (picrate, m. p. 136—137°) (cf. preceding abstract). R. BRIGHTMAN.

1-Furyl-2-methylcyclopropane. N. KISHNER (J. Russ. Phys. Chem. Soc., 1929, 64, 781—788).—**5-Furyl-3-methylpyrazoline**, b. p. 127—128°/22 mm., d_4^{20} 1.1507, was prepared by the interaction of furfurylideneacetone, m. p. 37°, b. p. 105—106°/10 mm., and hydrazine in alcoholic solution. It was converted by phenylthiocarbimide into *phenyl-(5-furyl-3-methylpyrazolinyl)thiocarbamide*, which exists in two crystalline forms both having m. p. 135°, viz., unstable needles, and stable cubes or rhombohedra.

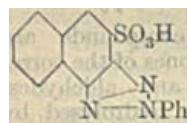
When 5-furyl-3-methylpyrazoline was gently warmed with potassium hydroxide and fragments of platinised porcelain, heat and nitrogen were evolved, 1-furyl-2-methylcyclopropane, b. p. 144.2°/743 mm. and 145.2°/758 mm., d_4^{20} 0.9522, n_D^{20} 1.4758, being formed. This is readily oxidised in air, responds to the furan pine-shaving test, and gives a crimson coloration with concentrated sulphuric acid in acetic anhydride solution. Bromine converts it into a *tetrabromide*, and potassium permanganate oxidises it to 2-methylcyclopropanecarboxylic acid, b. p. 98—99°/18 mm., 194°/742 mm. and 197—198°/768 mm., d_4^{20} 1.0480, n_D^{20} 1.4441 (calcium salt, +1.5H₂O; silver salt; amide, m. p. 99.5—100°). (See Marburg, A., 1897, i, 141.)

M. ZVEGINTZOV.

Condensation products of the benzodiazine [quinazoline] series. I. G. FARBENIND. A.-G.—See B., 1929, 747.

Dyes of the phenonaphthasafranine series. J. R. GEIGY.—See B., 1929, 674.

2-Phenyl- α -naphth-1 : 2 : 3-triazolemono-sulphonic acids. A. NERI (Gazzetta, 1929, 59, 384—391).—Sulphonation of 2-phenylnaphthtriazole (5 parts) by heating at 180° with concentrated sulphuric acid (1 part) yields the 4-sulphonic acid (annexed formula) [sodium (+1.5H₂O), potassium (+1.5H₂O), and barium (+5H₂O) salts].



The constitution of the acid is proved by the formation of 2-phenylnaphthtriazolequinone by oxidation with chromic acid and by its non-identity with the 5-sulphonic acid [sodium salt (+3H₂O)]. The latter is obtained from 1-aminonaphthalene-2-azobenzene-5-sulphonic acid [sodium salt (+1.5H₂O)] by dehydrogenation by the action of sodium dichromate and acetic acid in nitrobenzene. Sodium 2-aminonaphthalene-1-azobenzene-4-sulphonate (+H₂O) is similarly converted into 2-phenylnaphthtriazole-4-sulphonic acid (sodium salt, anhydrous), which is oxidised by chromic acid in acetic acid to yield 2-phenylnaphthtriazolequinone-4-sulphonic acid [sodium salt (+2.5H₂O)]; this yields with phenylhydrazine the *o*-hydroxy-4-azobenzene derivative [sodium salt (+3H₂O)].

R. K. CALLOW.

Porphyrin syntheses. XXIV. Syntheses of three pyrroporphyrins, a rhodoporphyrin, a pyrrosetioporphyrin, and a deuteroporphyrin. H. FISCHER and A. SCHORMÜLLER (Annalen, 1929,

473, 211—249).—Eight pyrrosetioporphyrins (tetramethyltriethylporphyrins) are theoretically capable of existence and these can give rise to twenty-four pyrroporphyrins (tetramethyldiethyl- β -carboxyethylporphyrins). Three of the last-named compounds have been synthesised by methods similar to those previously described (cf. A., 1928, 1384). Cryptopyrrolecarboxylic acid condenses with 2 : 4-dimethylpyrrolealdehyde in presence of alcoholic hydrobromic acid, forming (3 : 5-dimethylpyrryl)-(3 : 5-dimethyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide (I), m. p. 223° (decomp.) (free base, m. p. 172° after darkening at 145°). When I is heated with (5-bromo-3-methyl-4-ethylpyrryl)-(5-bromo-3-methyl-4-ethylpyrrolenyl)methene hydrobromide in presence of succinic acid about 15% of 1 : 4 : 5 : 8-tetramethyl-3 : 6-diethyl-7- β -carboxyethylporphyrin [termed *pyrroporphyrin* 6] (II) [methyl ester, m. p. 228° (*phyllin* derivative); copper salt, m. p. above 300°; *haemin* derivative] is obtained. Treatment of II with sulphuric acid at 100° affords the corresponding *rhodin* (copper salt), whilst treatment with pyridine and 10% sodium ethoxide solution at 180—190° and subsequent acidification gives the corresponding *chlorin*. Bromination of I with 1 mol. of bromine in hot acetic acid solution yields a *monobromo*-derivative, C₁₆H₂₀O₄N₂Br₂, m. p. 228—230°, which on esterification and subsequent treatment with ammonia furnishes the brominated *methene* ester, C₁₆H₂₅O₄N₂Br (?), m. p. 106°; with 3 mols. of bromine I gives the compound C₁₆H₁₉O₄N₂Br₃, not melted at 245°. When equimolecular quantities of I and (5-bromo-4-methyl-3-ethylpyrryl)-(5-bromo-4-methyl-3-ethylpyrrolenyl)methene are heated with methylsuccinic acid at 180—200°, 15% of 1 : 4 : 6 : 7-tetramethyl-2 : 3-diethyl-8- β -carboxyethylporphyrin [*pyrroporphyrin* 21] (III) [methyl ester, m. p. 218—219°; *haemin* derivative (IV); copper salt, m. p. about 300° after sintering at 270°; *rhodin*] results. Treatment of IV with acetic anhydride and stannic chloride, and subsequent removal of iron by treatment with acetic acid and hydrogen bromide at 40°, afford an *acetyl* derivative of III. 1 : 3 : 5 : 8-Tetramethyl-4 : 6-diethyl-7- β -carboxyethylporphyrin [*pyrroporphyrin* 18] (methyl ester, m. p. 248°) is prepared by heating (5-bromo-4-methyl-3-ethylpyrryl)-(5-bromo-3-methyl-4-ethylpyrrolenyl)methene hydrobromide with the methene from 2 : 4-dimethylpyrrolealdehyde and opsopyrrolecarboxylic acid and succinic acid at 180—200°. The three pyrroporphyrins described are designated *iso*-compounds, since the m. p. of the methyl esters differ from the m. p. of "analytical" pyrroporphyrin methyl ester; the absorption spectra of the porphyrins are identical.

Cryptopyrrolecarboxylic acid and 2 : 4-dimethyl-3-carbethoxypyrrole-5-aldehyde condense in presence of alcoholic hydrobromic acid, yielding (3 : 5-dimethyl-4-carbethoxypyrryl)-(3 : 5-dimethyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide (V), m. p. 205°, esterified by alcoholic hydrogen bromide to the *hydrobromide*, m. p. 169°, of the *methene* diester, m. p. 100°, and brominated first to a *perbromide*, C₁₆H₂₄O₄N₂Br₂, m. p. 203—206°, and subsequently to a *compound*, m. p. 219°. When a mixture of V, (5-bromo-4-methyl-3-

ethylpyrryl)-(5-bromo-4-methyl-3-ethylpyrrolenyl)-methene hydrobromide (VI), and succinic acid is heated rapidly over a free flame a small amount of the *monoethyl* ester, m. p. 290°, of *rhodoporphyrin* 21 (VII) (cf. this vol., 940) [*dimethyl* ester, m. p. 218° (*copper* salt, m. p. 239°; *hæmin*, m. p. 306°, and *phyllin* derivatives)] is obtained. Thermal decomposition of VII or decarboxylation by heating with methyl-alcoholic potassium hydroxide and pyridine at 180—190° in a sealed tube affords III.

Hydrobromic acid condensation of cryptopyrrole-aldehyde and 3-acetyl-2:4-dimethylpyrrole affords (3:5-dimethyl-4-ethylpyrryl)-(4-acetyl-3:5-dimethylpyrrolenyl)methene hydrobromide (VIII), m. p. 237° (decomp.) (free base, m. p. 159°), which on treatment with bromine in acetic acid solution at 40—50° gives a *perbromide*, $C_{17}H_{23}ON_2Br_3$, m. p. 202° (decomp.). Succinic acid fusion of VI and VIII yields 2—3% of 2-acetyl-1:4:6:7-tetramethyl-3:5:8-triethylporphin [*acetylpyrroætioporphyrin*], not melted at 290°. *Ethyl* 1:4:6:7-tetramethyl-3:5:8-triethylporphin-2-carboxylate, m. p. 264° (*methyl* ester, m. p. 262°), is obtained similarly from VI and (3:5-dimethyl-4-ethylpyrryl)-(3:5-dimethyl-4-carbethoxypyrrolenyl)methene hydrobromide, m. p. 203° (decomp.).

Succinic acid fusion of a mixture of VI and (3-methyl-5-bromomethylpyrryl)-(3-methyl-4-ethyl-5-bromomethylpyrrolenyl)methene hydrobromide gives 1:4:6:7-tetramethyl-2:3:8-triethylporphin [*pyrroætioporphyrin* 7] (*bromo*-derivative; *chlorin*, prepared by reduction of the *hæmin* derivative with sodium and amyl alcohol).

Opsopyrrolecarboxylic acid and dimethylpyrrole-aldehyde condense in presence of alcoholic hydrobromic acid, forming (3-methyl-4-β-carboxyethylpyrryl)-(3:5-dimethylpyrrolenyl)methene hydrobromide, m. p. 220—221° (decomp.), which when heated with (5-bromo-3-methyl-4-β-carboxyethylpyrryl)-(3-methyl-5-bromomethylpyrrolenyl)methene hydrobromide and succinic acid at 240° yields 1:4:5:8-tetramethyl-2:6-di-β-carboxydiethylporphin [*deuteroporphyrin* 5] [*dimethyl* ester, m. p. 300° (*copper* salt, m. p. 281°; *hæmin* derivative)]. Absorption spectra of most of the above porphyrins and their derivatives are given.

The absorption maxima of solutions of ætioporphyrin, meso- and proto-porphyrin esters in ethyl phthalate are displaced towards the red when the solution is warmed. At 200° the ætioporphyrin spectrum has the appearance of a rhodin spectrum; on cooling, it becomes normal again.

H. BURTON.

Chlorophyll. VII. Phæo- and phylloerythro-porphyrins. H. FISCHER and R. BAUMLER (Annalen, 1929, 474, 65—120).—Phæophorbide *a* (I), $C_{35}H_{38}O_6N_4$ (cf. Willstätter and Stoll, "Chlorophyllbuch," 282), decomp. 190—200° (block), phæophorbide *b* (II), decomp. 215—225° (block), and phæophytin do not contain an acetyl group. When II is heated with 70% sulphuric acid carbon dioxide (approximately 2 mols.) is eliminated; 1 mol. of carbon dioxide is eliminated when I or II is heated alone at 100—110°/vac. Esterification of I with diazomethane affords *methylphæophorbide a*, $C_{36}H_{38}O_6N_4$, decomp.

208° (block), whilst treatment of I with ferric acetate and sodium chloride or ferric chloride and sodium acetate in acetic acid gives an *iron* salt, $C_{35}H_{38}O_7N_4ClFe + Ac \cdot OH$. When I is heated with pyridine and methyl-alcoholic potassium hydroxide at 135—220° pyrroporphyrin is obtained; II is decomposed completely under these conditions, but at 155° small amounts of phyllo-, pyrro-, and verdoporphyrins result. In absence of pyridine at 150° I furnishes phyllo-, pyrro-, and rhodo-porphyrins (these and verdoporphyrin are obtained similarly from II), whilst at 200° rhodoporphyrin is the chief product. At 105° the hydrolysis products are chlorin (main) and rhodoporphyrin (small). Fission of I and II by boiling with methyl-alcoholic potassium hydroxide for a short time affords chlorin *e* and rhodin *g*, respectively. Both these last-named substances are formed in small amount by similar treatment of phæophytin (cf. Treibs and Wiedemann, A., 1928, 1383). Treatment of I with hydriodic acid in acetic acid at 100° gives *phæoporphyrin a*₆ (III), $C_{33 or 34}H_{36}O_6N_4$ (*iron*, *copper*, and *magnesium* complex salts), esterified by methyl-alcoholic hydrogen chloride to a *methyl* ester (IV), probably $C_{35}H_{37}O_5N_4$, m. p. 259° [*copper* salt, m. p. 228° (block) after sintering at 220°]. When esterification is carried out with diazomethane a *methyl* ester, $C_{31}H_{36}O_3N_4$, m. p. 243°, results. Hydrolysis of IV first with 15% and then with 3% hydrochloric acid yields β-*phæoporphyrin a*₄ (V), $C_{33}H_{35}O_4N_4$, whilst similar treatment of III gives β-*phæoporphyrin a*₃, $C_{30}H_{31}O_3N_4$. Fission of III with pyridine and methyl-alcoholic potassium hydroxide at 155° affords pyrro- and rhodo-porphyrins only. When phæophytin and ethyl chlorophyllide are treated with hydriodic and acetic acids III is also produced, but from the chlorophyllide two other substances (*methyl* esters, m. p. 228 and 239°, respectively) are also obtained. Treatment of III with acetic acid and pyridine gives *phæoporphyrin a*₄ (VI), $C_{32}H_{36}O_4N_4$ [*copper* and *iron* salts; *dimethyl* ester, m. p. 228° (not depressed by phylloerythrin ester)]. Alkaline fission of V and VI affords phyllo- in addition to pyrro- and rhodo-porphyrins. When phyllo- or rhodo-porphyrin is treated with hydriodic acid (*d* 1.96) in hot acetic acid solution pyrroporphyrin results (cf. Treibs and Wiedemann, *loc. cit.*).

Phylloerythrin (VII) (cf. Noack, this vol., 727) (*iron* salt) is esterified by methyl-alcoholic hydrogen chloride to a *methyl* ester, $C_{32}H_{36}O_3N_4$, m. p. 263°, and by diazomethane to a *methyl* ester, $C_{33}H_{36}O_6N_4$, m. p. 261°. The *copper* salt of VII is freed from metal by treatment with sulphuric acid, whereby a *porphyrin*, $C_{30}H_{36}O_3N_4$, results. Treatment of VII first with 15% and then with 3% hydrochloric acid furnishes β-*phylloerythro-porphyrin*, (?) $C_{31}H_{30}O_3N_4$, esterified by methyl-alcoholic hydrogen chloride to a *methyl* ester, $C_{32}H_{36}O_3N_4$, m. p. 246°. Treatment of VII with acetic acid and pyridine gives *phylloerythro-porphyrin* (VIII), $C_{34}H_{36}O_3N_4$. Alkaline fission of VII yields pyrro- and rhodo-porphyrins, whilst VIII affords phyllo- and rhodo-porphyrins. Crystallographic data (by STEINMETZ) and absorption spectra of a large number of the above compounds are recorded.

H. BURTON.

Ring formation from acetyloximes of aromatic α -hydroxyketones. H. LANDEMAN and S. ROMANOFF (J. pr. Chem., 1929, [ii], 122, 214—231).—Nitration of 2-hydroxyacetophenoneoxime by nitric acid (*d* 1.4) in acetic acid solution gave 5-nitro-2-hydroxyacetophenoneoxime, m. p. 231° (also obtained by oximation of the corresponding ketone), accompanied by (less) 3-nitro-2-hydroxyacetophenoneoxime, m. p. 182°. Nitration under similar conditions of 2-hydroxyacetophenoneacetyloxime afforded both 5-nitro-2-hydroxyacetophenoneacetyloxime, m. p. 167° (which passed, when heated at 175—185° in a vacuum, or when warmed with sodium carbonate solution, into 4-nitro-2-methylbenzisooxazole, m. p. 134°, b. p. 168—169°/13 mm.), and 3-nitro-2-hydroxyacetophenoneacetyloxime, m. p. 136—137° (also obtained by acetylation of the appropriate oxime, m. p. 182°, above).

Hydrolysis with hydrochloric acid of the oximes of m. p. 231° and 182° (above) gave, respectively, 5-nitro-2-hydroxyacetophenone, m. p. 111—112°, and 3-nitro-2-hydroxyacetophenone, m. p. 89—90°. The 5-nitro-ketone was reduced by stannous chloride and hydrochloric acid to the corresponding amine, m. p. 121—122°, which gave by oximation 5-amino-2-hydroxyacetophenoneoxime, m. p. 201—202°. The diacetyl derivative, m. p. 173—174°, of this compound, when heated in a vacuum at 180—190°, passed into 5-acetamido-3-methylisooxazole, m. p. 163°, b. p. 215°/13 mm.

Nitration of 3-methylbenzisooxazole by sulphuric acid and potassium nitrate yielded 5-nitro-3-methylbenzisooxazole along with some 4-nitro-3-acetamidophenol (from which O_N -diacetyl-4-nitro-2-aminophenol, m. p. 196°, was prepared); similarly during the nitration of 3:5-dimethylbenzisooxazole to 7-nitro-3:5-dimethylbenzisooxazole, some 2-nitro-3-acetamido-*p*-cresol, m. p. 250° (decomp.) (O_N -diacetyl derivative, m. p. 183°), was isolated. The production of these nitroaminophenols is taken as indicating the presence of alkylbenzisooxazoles in the *iso*-compounds.

The following compounds are also described: 5-nitro-3-acetamido-*p*-cresol, m. p. 143°; 3:5-dimethyl-4-aminobenzisooxazole (obtained by reduction of the nitro-derivative by sodium hyposulphite), m. p. 110°; 7-hydroxy-3:5-dimethylbenzisooxazole (by diazotisation of previous compound), m. p. 247°.

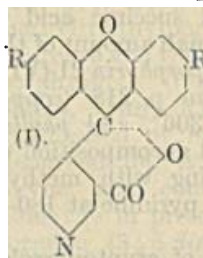
R. J. W. LE FEVRE.

Monoarylguanidines. II. **Benzoxazolylguanidine.** G. B. L. SMITH, J. H. KANE, and C. W. MASON (J. Amer. Chem. Soc., 1929, 51, 2522—2527).—*o*-Aminophenol and dicyanodiamidine react in presence of boiling alcoholic hydrochloric acid, forming the hydrochloride, m. p. 254—255°, of 2-guanidinobenzoxazole + H_2O , m. p. 182—184° [sulphate, m. p. 280—281°; nitrate, m. p. 219—220°; picrate, m. p. 247—248°; diacetyl derivative, m. p. 209—210°; methiodide (?), m. p. 192—194°]. Descriptions of the crystalline forms of the salts are given. Dicyanodiamidine is probably tautomeric: $NH:C(NH_2)\cdot NH\cdot CN \rightleftharpoons CN\cdot N:C(NH_2)_2$.

H. BURTON.

Dyes derived from cinchomeric acid. J. D. TEWARI (J.C.S., 1929, 1642—1644).—The following compounds were obtained by heating cinchomeric

acid with the appropriate amine or hydroxy-compound in the presence of stannic chloride or of concentrated sulphuric acid: *phenol*-, unmelted at 275°; *resorcinol*-, m. p. 200°; *phloroglucinol*-, m. p. 270°; *m*-diethylaminophenol-, m. p. 127°, and *m*-phenylenediamine-cinchomerein, m. p. 275°. The resulting dyes have the general formula I and resemble the corresponding dyes from quinolinic acid (Ghosh, J.C.S., 1919, 115, 1102) very closely in chemical and physical properties.



A. I. VOGEL.

Nicotine and its derivatives. II. Optical rotatory power and rotatory dispersion. T. M. LOWRY and W. V. LLOYD (J.C.S., 1929, 1771—1791).—Measurements at 20° of the optical rotatory power and also of the rotatory dispersion, over a wide range of wave-lengths, of nicotine, of nicotine in acetone, water, acetic and butyric acids, of nicotine butyrate and crotonate in acetone, and of the last-named in acetone, of the nicotine-zinc chloride double compound in water, and of nicotine dimethiodide in water have been made and the data employed to test the applicability of the one-term Drude equation. The characteristic frequencies deduced from the rotatory dispersions are compared with the observed maxima of selective absorption. It is suggested that nicotine forms a *pseudo*-base, and that the reversal in sign on salt formation is associated in nicotine with the saturation of a lone pair of electrons in the pyrrolidine nitrogen, and is dependent on the elimination of an incipient dative linking between the two rings.

The best values for the specific rotations of nicotine are $[\alpha]_D^{20} +169.3^\circ$, $[\alpha]_{589}^{20} +204.1^\circ$. A. I. VOGEL.

Sparteine. K. WINTERFELD (Arch. Pharm., 1929, 267, 433—455).—[With F. W. HOLSCHNEIDER.] *Dibromosparteine dicyanamide* (*chloroaurate*, m. p. 144—145°) and two isomeric *monobromosparteine cyanamides*, one monobasic, m. p. 89° (*chloroaurate*, m. p. 178°; *picrate*, m. p. 165°; *mercurichloride*, m. p. 117°), the other a dibasic oil (*chloroaurate*, m. p. 181° (decomp.); *picrate*, m. p. 176°), are produced when cyanogen bromide is allowed to react on sparteine directly. These compounds are also obtained along with sparteine hydrobromide when the reagents are mixed in moist ethereal solution, but in absolute ether a double compound of sparteine and cyanogen bromide is obtained. The two isomeric monobromosparteine cyanamides are obtained in varying amounts according to the conditions of experiment, the proportions of crystalline isomeride to liquid isomeride being 1:2 in ether, 2:1 in boiling benzene, whilst only the crystalline modification is produced in boiling cyclohexanol. Reduction of the crystalline form with tin and hydrochloric acid affords *sparteine cyanamide* (*chloroaurate*, m. p. 186—187°; *chlorostannate*), which gives a secondary base, $[\alpha]_D -16.3^\circ$ in chloroform, very stable towards alkaline permanganate solution, on treatment with 60—65% sulphuric acid (complex *chloroaurate*, m. p. 130—131°; *picrate*, m. p. 179°). This base affords an oily *monobenzoyl* derivative [*chloroplatinate*, decomp. 195°;

chloroaurate, m. p. 145° (decomp.), which on degradation by means of phosphorus pentabromide produces a base (*chloroplatinate*, m. p. 248—249°; *chloroaurate*, m. p. 178—179°) giving a pyrrole reaction. Under similar conditions, the liquid bromosparteine cyanamide affords a *sparteine cyanamide*, $[\alpha]_D -11.84^\circ$ in chloroform [*chloroaurate*, m. p. 172° (decomp.); *picrate*, m. p. 172—173° (decomp.); *chlorostannate*, m. p. 128°], and a liquid secondary base, $[\alpha]_D -16.5^\circ$ in chloroform [*chloroaurate*, m. p. 181—182° (decomp.); *picrate*, m. p. 178°; *chloroplatinate*; m. p. 257° (decomp.)], which gives a *benzoyl* derivative, $[\alpha]_D -13.6^\circ$ in chloroform [*chloroaurate*, m. p. 185° (decomp.); *chloroplatinate*, m. p. 248—249° (decomp.)]. Degradation of the latter with phosphorus pentabromide affords a bromo-compound (*chloroaurate*) produced by the partial fission of the ring and subsequent hydrolysis of a bromoimide, to which the formula $\text{NH}\cdot\text{Bz}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{Et}\cdot\text{CH}(\text{CH}_2\text{Br})\cdot\text{CH}_2\cdot\text{C}_7\text{H}_{15}\text{N}$ is ascribed. The latter gives a base, b. p. 160°, $[\alpha]_D -11.5^\circ$ in chloroform [*chlorostannate*, m. p. 160°; *chloroaurate*, m. p. 196—197° (decomp.); *chloroplatinate*, m. p. 255° (decomp.); *hydriodide*, m. p. 227°; *picrate*, m. p. 180°; *mercurichloride*; *methiodide*, m. p. 205°], which does not give the pyrrole reaction, on reduction with tin and hydrochloric acid. From these results it is concluded that sparteine is an alkylated α - or β -quinuclidine, which is confirmed by study of the degradation of α -methylquinuclidine.

[With C. VON RAUSCH.] Dehydrosparteine may be oxidised with potassium permanganate to an acid, which is readily esterified and the methyl (?) ester (cf. A., 1928, 906) affords a *benzoyl* derivative, m. p. 142—143° (decomp.). The latter is broken down by phosphorus pentabromide to the corresponding secondary cyclic amine, which gives a hydrocarbon and 2-methylpyrrolidine on oxidation with permanganate. Thus the second tertiary nitrogen atom in sparteine is situated in a pyrrolidine ring.

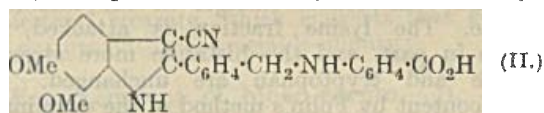
S. COFFEY.

Synthetical experiments on the aporphine alkaloids. VII. Attempted syntheses of apomorphine dimethyl ether. J. M. GULLAND, R. D. HAWORTH, C. J. VIRDEN, and (in part) R. K. CALLOW (J.C.S., 1929, 1666—1676).—Condensation of *m*-nitrobenzyl chloride and ethyl sodiomalonate in alcohol afforded a mixture of *ethyl di-(3-nitrobenzyl)malonate*, m. p. 112°, and *ethyl 3-nitrobenzylmalonate*, from which *3-nitrobenzylmalonic acid*, m. p. 171°, was obtained by partial hydrolysis with 30% potassium hydroxide solution. The latter on heating gave β -3-nitrophenylpropionic acid, m. p. 117—118°, converted by thionyl chloride and aqueous ammonia into the *amide*, m. p. 99°, then by sodium hypochlorite into β -3-nitrophenylethylamine hydrochloride, m. p. 207—209°, and finally by stannous chloride and hydrochloric acid into β -3-aminophenylethylamine dihydrochloride (I), m. p. 310° (decomp.). Condensation of the free base of I with 2-nitro-3:4-dimethoxyphenylacetyl chloride in benzene furnished 2'-nitro-3':4'-dimethoxyphenylaceto- β -3-(2'-nitro-3':4'-dimethoxyphenylacetamido)phenylethylamine, from which no basic material could be isolated after prolonged treatment with phosphorus pentachloride in chloroform.

β -Phenylethylamine 2-benzamidophenylglyoxylate,

m. p. 177—179° (decomp.) (from 2-benzamidophenylglyoxylic acid and β -phenylethylamine in ether), could not be converted into the amide by phosphorus pentachloride or phosphoric oxide; 2-benzamidophenylglyoxyl- β -phenylethylamine, m. p. 136.5—138°, was produced by interaction of the acid chloride of 2-benzamidophenylglyoxylic acid and β -phenylethylamine in benzene, but was unaffected by treatment with phosphorus pentachloride in chloroform for 1 month. α -Cyano-2-nitro-3:4-dimethoxystilbene, m. p. 125.5°, is obtained by condensation of 2-nitro-3:4-dimethoxyphenylacetonitrile and benzaldehyde in alcohol in the presence of sodium ethoxide or piperidine at 40—50°. α -Cyano-2-nitro-3:4-dimethoxy-2'-aldehydostilbene, m. p. 153° (*phenylhydrazone*, m. p. 179—180°), is similarly prepared (80% yield) from the nitrile and phthalaldehyde at 45°: it is unaffected by boiling with concentrated hydrochloric acid for 24 hrs., by stannous chloride or tin in a cold mixture of glacial acetic and hydrochloric acids, and by aqueous ammonia, is destroyed by zinc dust in hot dilute hydrochloric or acetic acid, and no crystalline product is obtained on heating with malonic acid and piperidine in pyridine solution.

When a mixture of *m*-aminobenzoic acid (1 mol.) and α -cyano-2-nitro-3:4-dimethoxy-2'-aldehydostilbene (1 mol.) is heated at 135° for 30 min. α -cyano-2-nitro-3:4-dimethoxy-2'-*m*-carboxyphenyliminomethylstilbene, m. p. 237° (decomp.), is obtained, and is converted by reduction with ferrous sulphate and ammonia in a hydrogen atmosphere into 2-(2'-*m*-carboxyanilinomethylphenyl)-3-cyano-6:7-dimethoxyindole (II) or the dihydro-derivative [*hydrochloride*, m. p. 307° (decomp.)], unaffected by concentrated hydro-



chloric acid and yielding the *tri*- and *hexa-hydrates*, m. p. 322°, of II on decomposition with aqueous sodium acetate. This substance is unsuitable for the synthesis of apomorphine dimethyl ether.

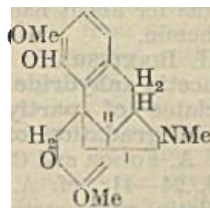
Piperonylidene-m- and *p*-aminobenzoic acids, m. p. 244—245° and 243°, respectively, are formed by heating piperonal with the acids at 160° for 30 min.

A. I. VOGEL.

Sinomenine and disinomenine. X. Synthesis of dimethylsinomenol. Sinomenolquinone. K. GOTO and H. SADZUKI (Bull. Chem. Soc. Japan, 1929, 4, 163—169).—The synthesis of 3:4:6:7-tetramethylphenanthrene and its identity with dimethylsinomenol (Kondo and Ochiai, this vol., 1088) has been confirmed. Sinomenol is considered to be 4:6-dihydroxy-3:7-dimethoxyphenanthrene. The reactions of sinomenine are reviewed and to it is assigned the annexed revised formula (cf. Goto, A., 1920, 1160).

When diacetylsinomenol is oxidised by chromic anhydride in acetic acid there is formed *diacetylsinomenolquinone*, m. p. 217—219° (*phenazine* compound, m. p.

256°), which on hydrolysis yields *sinomenol*-



quinone, m. p. 259—263° (*phenazine*, m. p. 272°). When dibenzoylsinomenolquinone (Goto, *loc. cit.*) is treated with alkyl sulphates in alkaline solution there are formed *sinomenolquinone diethyl ether*, m. p. 174° (*phenazine*, m. p. 188°), and *sinomenolquinone dimethyl ether*, m. p. 266° (*phenazine*, m. p. 184°).

T. H. MORTON.

Organic antimony compounds [arylstibinic acids]. I. G. FARBERIND. A.-G.—See B., 1929, 699.

Tin methyl derivatives. Action of zinc on tin trimethyl bromide. Tin trimethyl phenoxide. Decamethylstannobutane. C. A. KRAUS and A. M. NEAL (J. Amer. Chem. Soc., 1929, 51, 2403—2407).—Zinc and tin trimethyl bromide react in aqueous solution, giving mainly tin tetramethyl accompanied by tin trimethyl hydroxide and metallic tin. Sodium phenoxide in liquid ammonia solution converts tin trimethyl bromide into *phenoxytrimethylstannane*, $\text{SnMe}_3\cdot\text{OPh}$, b. p. 223—224°, which is stable in air but colours in sunlight, and reacts with the appropriate quantity of sodium as follows: $\text{SnMe}_3\cdot\text{OPh} + 2\text{Na} = \text{SnMe}_3\text{Na} + \text{NaOPh}$; $2\text{SnMe}_3\cdot\text{OPh} + 2\text{Na} = (\text{Me}_3\text{Sn})_2 + 2\text{NaOPh}$. *Decamethylstannobutane*, $\text{Me}_{10}\text{Sn}_4$, obtained by the interaction in liquid ammonia of disodium tetramethylstannoethane and tin trimethyl bromide, is a somewhat viscous, colourless liquid which readily oxidises to a white solid. S. K. TWEEDY.

Deaminocaseinogen. H. STEUDEL and R. SCHUMANN (Z. physiol. Chem., 1929, 183, 168—176).—Caseinogen was subjected to deamination by nitrous acid and the nitrogen loss in the various fractions obtained on hydrolysis investigated. Nitrous acid causes no considerable changes in the caseinogen molecule. The lysine fraction is attacked, the arginine in part, and the histidine more strongly. Tyrosine and tryptophan are unchanged. The cystine content by Folin's method of the deaminated molecule was about six times that of the original material. J. H. BIRKINSHAW.

Proteins. V. Benzoylproteins: benzoyl-ovalbumin and its hydrolysis. S. GOLDSCHMIDT and A. KINSKY (Z. physiol. Chem., 1929, 183, 244—260; cf. A., 1927, 581).—The hydrolysis of benzoyl-ovalbumin with alkali and acid was studied. Definite breaks in the time curve appear with *N*-sodium hydroxide (at 100°) at 6.5% and 12.5—13% hydrolysis. With sulphuric acid at 34° the benzoyl groups hydrolysed reach a steady maximum at 6.5%. At 100° the hydrolysis again reaches a maximum in a few hrs. and about 90% of the total nitrogen is present as amino-nitrogen. About 7% of the benzoyl complex remains unhydrolysed. ϵ -Benzoyl-lysine was isolated from this portion, showing that the ϵ -amino-group of lysine accounts for about half of the free amino-groups of egg-albumin.

J. H. BIRKINSHAW.

Degradation of gelatin with acetic anhydride. Isolation of acetylated associates of partly dehydrated polypeptides. IV. Degradation of proteins and their derivatives. A. FODOR and C. EPSTEIN (Biochem. Z., 1929, 210, 24—41; cf. A., 1928, 1387).—Degradation of gelatin with acetic anhydride under conditions in which hydrolysis is

excluded gives a value of 0.66 for the ratio amino-nitrogen/total nitrogen (*v*), but if the treatment with the reagent is repeated several times *v* approaches 0.5. This suggests a degradation of a tri- to a di-peptide of proline or hydroxyproline. From other considerations the proline group must occupy the central position in the chain between a glycine and an alanine group. The acetylated gelatin complexes represent associations of three tripeptide groups. Possible constitutions for these are considered.

J. H. BIRKINSHAW.

Denaturing of proteins. I. T. TADOKORO and K. YOSHIMURA. II. T. TADOKORO and S. WATANABE (J. Fac. Agric. Hokkaido, 1928, 25, 117—132, 133—149).—Rice oryzenin was denatured in solution by boiling and by freezing; soya-bean glycinin by boiling, freezing, superheated steam, gasoline, or benzene; soya beans by heating, boiling, freezing, and soaking in gasoline; salmon proteins by cooling, freezing, salting, and smoking. The resulting chemical and optical changes were followed.

CHEMICAL ABSTRACTS.

Nitrogen distribution of gelatin. F. S. DAFT (Compt. rend. Trav. Lab. Carlsberg, 1929, 17, No. 12, 1—17).—Contrary to the statements of other workers (Knaggs, A., 1923, i, 1143; Knaggs and Schryver, A., 1925, i, 90; Thornley, A., 1928, 81), preliminary treatment of gelatin with acid or alkali has no effect on the percentages of non-amino- and of diamino-nitrogen. The methods of determination of the different forms of nitrogen in proteins are discussed and certain modifications are described which, it is claimed, give comparable figures for nitrogen distribution. In particular, separation of amino-acids with phosphotungstic acid is carried out under strictly defined conditions of concentration and temperature, and the treatment of the fractions before determination by the nitrous acid or formaldehyde methods is described. R. K. CALLOW.

Determination of carboxyl groups in digestion products of proteins. I. A. SMORODINCEV, A. N. ADOVA, and S. S. TSCHULKOVA (Fermentforsch., 1929, 11, 37—44).—The method described by Felix and Müller (A., 1928, 535) gives best results when a 0.01% solution of alizarin-yellow is used as indicator and 0.5 c.c. of this is mixed with the alkali (10 c.c.). The total amount of carboxyl groups present is determined, whereas Willstätter and Waldschmidt-Leitz' method (A., 1922, ii, 169) gives values both for amino-acids and peptides. H. BURTON.

Determination of antimony in organic antimony compounds. S. GHOSH (Indian J. Med. Res., 1929, 16, 457—460).—The substance (0.05—0.07 g.) is digested with 2 g. of potassium sulphate and 3 c.c. of arsenic-free, concentrated sulphuric acid in a loosely-stoppered conical flask until colourless, diluted with 25 c.c. of distilled water, and boiled for 3—5 min. To the warm solution 3—4 c.c. of concentrated hydrochloric acid are added and the solution is rapidly cooled and diluted to 100 c.c.; 25 c.c. of this solution are made faintly alkaline to litmus by a 40% solution of sodium hydroxide, acidified with 5 c.c. of a 1% solution of tartaric acid, and again made alkaline with 10 c.c. of a 4% solution of sodium hydrogen carbonate.

After addition of 25—30 drops of a 1% starch solution, the antimony is determined by titration with 0.01*N*-iodine solution previously standardised against sodium antimony tartrate. By titration of the whole of the solution instead of an aliquot part, accurate results may be obtained with only 0.02 g. of substance.

J. W. BAKER.

Rapid determination of alcohol. W. L. O. WHALEY (Planter and Sugar Mfr., 1928, 81, 321—323).—Alcohol is satisfactorily determined by measurement, with the Juerst ebulliometer, of the lowering of b. p. of its aqueous solution.

CHEMICAL ABSTRACTS.

Influence of boric acid on oxidation of organic substances with which it forms complexes. I. General investigations based on methods used in sugar analysis. J. VOICU and (MILE.) V. DUMITRESCU (Bul. Soc. Chim. Romania, 1929, 11, 15—24).—Low results are obtained in the determination of reducing sugars by the usual methods when boric acid is present, the deficit increasing with increasing boric acid content. The formation of boric acid-tartrate complexes etc. as well as that of boric acid-sugar complexes is possible. Priority is claimed over Levy and Doisy (A., 1928, 741).

J. S. CARTER.

Biochemistry.

Storage of manganese and copper in the animal body; influence on hæmoglobin formation. R. W. TITUS and J. S. HUGHES (J. Biol. Chem., 1929, 83, 463—467).—Addition of small amounts of copper or manganese to a whole wheat-milk powder diet did not prevent the development of nutritional anaemia, but enabled the animals to utilise inorganic iron for the synthesis of hæmoglobin. C. R. HARRINGTON.

Physico-chemical properties of natural globin. G. ROCHE (Compt. rend., 1929, 189, 378—380).—The isoelectric point of globin, obtained from hæmoglobin by the method of Hill and Holden, has been determined by cataphoresis and by means of neutralisation curves, both methods giving a single value of p_H 7.5, whereas that of hæmoglobin is at p_H 6.8. It is suggested that this lowering of p_H is the natural result of combination with the acid hæmatin.

P. G. MARSHALL.

Change in oxyhæmin on drying. A. HAMSÍK (Z. physiol. Chem., 1929, 183, 269—272).—The reactivity of α -oxyhæmin preparations is lessened on drying, owing to anhydride formation. Probably α -oxyhæmin exists pure only in the moist state, but hæmins (especially formylhæmin) retain their reactivity on drying. J. H. BIRKINSHAW.

Peroxidase reaction. XXIV. Simultaneous application of the oxidase and peroxidase reactions on leucocytes. K. TOKUE (Tohoku J. Exp. Med., 1929, 12, 295—300).—Saturated aqueous benzidine (containing 2 drops of 3% hydrogen peroxide per 100 c.c.) is applied to an air-dried fresh blood smear for 2 min., followed by 1% aqueous eosin for 5—10 sec. After washing and examining, Winkler-Schultze oxidase reagent is added, the slide being washed and re-examined after 2 min.

CHEMICAL ABSTRACTS.

Immediate acid change in shed blood. R. E. HAVARD and P. T. KERRIDGE (Biochem. J., 1929, 23, 600—607).—There is a change in the hydrogen-ion concentration of blood, soon after being shed, of $-0.05 p_H$ at 38° and at 28°. It takes place within about 6 min. at 38° and 11 min. at 28°. It does not occur until after 1.5—2 hrs. at the ordinary temperature. The change is unaffected by sodium fluoride, anticoagulants, potassium cyanide, or thymol.

It takes place in laked blood and centrifuged laked blood, but not in plasma. S. S. ZILVA.

Blood-fat. I. Preparation and general characteristics. H. J. CHANNON and G. A. COLLINSON (Biochem. J., 1929, 23, 663—675).—Fat has been prepared from 12 samples of ox-blood at fasting level by precipitating the blood with 3 vols. of alcohol and by extracting with ether the protein residue and the residue obtained by evaporating the alcoholic filtrate. Of the fat present in blood 80% may be extracted in this way. The fat constants, phosphorus, and nitrogen of the samples have been determined. The amount of fatty acid present varies little from that required if the phosphorus of the fat be calculated as lecithin and the cholesteryl ester as cholesteryl stearate, which suggests that glycerides are not present in appreciable quantity.

S. S. ZILVA.

Water content of blood-serum. H. SPENCER (Amer. J. Dis. Children, 1929, 37, 546—552).—Of methods for determining sp. gr. of blood-serum, the falling-drop method is preferred.

CHEMICAL ABSTRACTS.

Tungstomolybdic acid as a precipitant for blood-proteins. S. R. BENEDICT and E. B. NEWTON (J. Biol. Chem., 1929, 83, 357—360).—A mixture of sodium molybdate and sodium tungstate is recommended as a substitute for the sodium tungstate employed in the Folin-Wu method for the precipitation of blood-proteins. Filtrates obtained with the aid of the new reagent show higher values for uric acid and ergothioneine. C. R. HARRINGTON.

Non-sugar reducing substances of blood and urine. I. Glutathione and ergothioneine in blood. S. R. BENEDICT and E. B. NEWTON (J. Biol. Chem., 1929, 83, 361—365).—Sheep blood was freed from proteins with tungstic acid, the filtrate was treated with silver lactate, and the precipitate separated and extracted with hydrochloric acid-sodium chloride solution; the residue was boiled with dilute hydrochloric acid and the filtrate, after treatment with zinc and platinum to remove traces of tungsten and silver, was treated with mercuric acetate. The solution obtained on recovery from the mercury precipitate was treated with mercuric sulphate, the

precipitate was decomposed, and the filtrate, after exact removal of sulphuric acid, concentrated and poured into excess of alcohol, yielding a precipitate of glutathione. The yield was 0.1 g. per litre of blood, and the product showed the high nitrogen and low sulphur content observed by Hunter and Eagles (A., 1927, 477, 478); it possessed a reducing action towards the Folin-Wu sugar reagent equivalent to one fifth of its weight of dextrose. Ergothioneine also shows a slight reducing action with this reagent.

C. R. HARINGTON.

New constituent of blood. E. W. ROCKWOOD, R. G. TURNER, and J. J. PFIFFNER (J. Biol. Chem., 1929, 83, 289—297).—Hydrolysis with sulphuric acid of a protein-free blood filtrate or muscle extract causes an increase in the apparent amount of ergothioneine as determined by the method of Benedict (this vol., 714); this increase is ascribed to the liberation of a new substance Z, figures for the concentration of which in various samples of blood and tissues are given.

C. R. HARINGTON.

Determination of carbamide in blood. S. L. LEIBOFF and B. S. KAHN (J. Biol. Chem., 1929, 83, 347—352).—The protein-free blood filtrate is heated at 150° for 10 min. in a special pressure tube with dilute sulphuric acid. Ammonia is determined directly in the resulting solution by Nessler's method.

C. R. HARINGTON.

Manometric determination of carbamide in blood and urine. D. D. VAN SLYKE (J. Biol. Chem., 1929, 83, 449—461).—Carbamide can be determined in diluted urine or in a protein-free blood filtrate by the use of the author's manometric apparatus (A., 1924, ii, 872), the reaction with hypobromite being employed. The error is about $\pm 4\%$ in the case of urine, and ± 2 mg. of nitrogen per 100 c.c. in blood.

C. R. HARINGTON.

Determination of acetone substances in blood and urine. D. D. VAN SLYKE (J. Biol. Chem., 1929, 83, 415—423).—The validity of the author's method (A., 1918, ii, 86) is confirmed, the criticisms of Smith (A., 1926, 1283) being answered on the ground that the latter author failed to make control determinations with pure β -hydroxybutyric acid.

C. R. HARINGTON.

Determination of sugar in blood and urine. P. J. CAMMIDGE and H. A. H. HOWARD (Brit. J. Urol., 1929, 1, 17—32).—A solution (I) is prepared by boiling arsenious oxide (4.948 g.) and sodium hydrogen carbonate (25 g.) with water (300 c.c.), and diluting the cold solution to 1 litre; a solution (II) is prepared by dissolving potassium citrate (81 g.), carbonate (70 g.), and oxalate (92 g.) in hot water (600 c.c.), adding a solution of copper sulphate pentahydrate (25 g.), in warm water (150 c.c.), and a solution of potassium iodate (3.2496 g.) in water (150 c.c.) which has been made alkaline with potassium carbonate and treated with potassium iodide (50 g.), the mixed solutions being diluted to 1000 c.c. For the determination of sugar in urine, 50 c.c. of II and 50 c.c. of water are boiled and treated with 5 c.c. of urine, 7.5 c.c. of 30% sulphuric acid are added to the cooled solution, and the mixture is immediately titrated with I, a blank determination being performed. The

preparation of solutions and the application of the method to the determination of sugar in blood deproteinised with tungstic acid are also described.

CHEMICAL ABSTRACTS.

Determination of blood-sugar. P. HORKHEIMER (Pharm. Ztg., 1929, 74, 546).—Micro-methods should replace macro-methods. That of Hagedorn and Jensen is better than the method of Kaufmann (Klin. Woch., 1927, No. 14; 1928, No. 5), which gives only approximate results, and more rapid than that of Glassmann and Zwilling (cf. this vol., 207). The blood sample is best taken by absorption in prepared filter-papers which are weighed on a torsion microbalance.

W. MCCARTNEY.

Carbohydrate metabolism. I. Micro-determination of dextrose. R. MIYAMA (Bull. Sci. Fak. Terkultura, Kjusu, 3, 122—131).—For the determination of blood-sugar Hagedorn's method is the most accurate. The results diminished in the order: Benedict, Folin-Wu, Hagedorn, Folin, Schaffer-Hartmann, Bang. All the results were affected by the addition of cystine; the addition of sodium sulphite gave high results in Folin and Wu's method and low results in Bang's method.

CHEMICAL ABSTRACTS.

Blood-sugar. J. C. BOCK (Wien. med. Woch., 1929, 79, 43—47; Chem. Zentr., 1929, i, 1364).—A study of the speed of reaction of the fasting human organism to administration of dextrose.

A. A. ELDRIDGE.

Influence of various substances on the sugar and ammonia content of blood. H. WANTOCH (Arch. exp. Path. Pharm., 1929, 143, 337—357).—The influence of administration of various acids, alkalis, salts, sugars, and of urea, "oxantin" (dihydroxyacetone), insulin, "synthalin," and liver as well as the effects of X-ray irradiation on the sugar and ammonia content of the blood in rabbits have been studied. Of the acids hydrochloric, sulphuric, and phosphoric, orally administered, the first produces no increase, the others, sometimes a slight increase in the ammonia content: all three always raise the blood-sugar. Oral administration of malic, citric, or β -hydroxybutyric acid causes sometimes very great increase in the ammonia content, sometimes, for reasons unknown, no increase, whilst oral or subcutaneous administration of the sodium salts of these acids produces no change. The organic acids also regularly cause hyperglycaemia. *N*-Sodium hydroxide solution or aqueous sodium carbonate solution, given orally, always causes the ammonia content to rise. Oral or subcutaneous administration of ammonium chloride or carbonate greatly increases both the ammonia and the sugar content and the administration of urea likewise causes distinct, and often great, increase in the ammonia content and distinct hyperglycaemia. Dextrose or oxantin when administered alone, orally or subcutaneously, has no effect on the ammonia content, but dextrose distinctly reduces the increase which follows administration of ammonium salts or urea. Lævulose acts like dextrose in this respect, but less powerfully. Insulin, subcutaneously injected, sometimes raises the ammonia content, but it has no definite effect on the increase occurring after the giving of urea. "Synth-

alin," given orally, does not increase the ammonia content, but appears to minimise the influence of previously-administered ammonium carbonate or urea. Raw or boiled liver has no effect on the ammonia content, but it likewise appears to have this minimising influence. Intense X-ray irradiation causes increase of the ammonia content. W. McCARTNEY.

Hæmatoporphyrin hæmolysis. H. KAWAI (J. Biochem. Japan, 1929, 10, 325—350).—When red corpuscles are hæmolysed by exposure to light in presence of hæmatoporphyrin no substance capable of producing hæmolysis is found. Hæmatoporphyrin hæmolysis is often observed in corpuscles with a high content of acid-soluble phosphoric acid, and is accompanied by decomposition of organic phosphoric acid. This, however, does not occur in the disintegration of the stroma. CHEMICAL ABSTRACTS.

Relationship between hæmolytic complement of guinea-pig serum and lipase. J. GORDON and A. WORMALL (Biochem. J., 1929, 23, 730—737).—The complement activities of various guinea-pig sera tend to run parallel with the esterase activities of these sera, although discrepancies occur. The destruction or inactivation of either of the two relatively heat-stable components of complement does not appreciably diminish the esterase or lipase activity of guinea-pig serum. The serum retains a distinct esterase power after the inactivation of the complement by heating it at 56% for 30 min. Protein preparations obtained by treating the serum with alcohol and ether at low temperatures possess no complete complement power, but retain a large part of the original esterase of the serum. The immune body essential for complement action has no influence on the esterase or lipase activity of guinea-pig serum when used in amounts sufficient to promote hæmolysis of ox red-cells. The esterase or lipase of guinea-pig serum does not take part in specific hæmolysis, nor can the action of hæmolytic complement be ascribed to a hydrolysis of the fatty substances of the red-cell envelope by lipolytic enzymes. S. S. ZILVA.

Electrometric determination of chlorides in whole blood and tissues. J. C. FORBES and H. IRVING (J. Biol. Chem., 1929, 83, 337—344).—Diluted blood or tissue extract is heated with dilute sulphuric acid and silver nitrate; after partial neutralisation with ammonia the excess of silver is titrated electrometrically with standard sodium chloride solution. C. R. HARRINGTON.

Determination of chloride in animal tissues. E. H. CALLOW (Biochem. J., 1929, 23, 648—653).—The chloride is completely extracted from the tissues by boiling with distilled water and is determined in the extract by a modification of Volhard's method. Christy and Robson's method for the determination of chloride in biological fluids (A., 1928, 564) is criticised. S. S. ZILVA.

Relation between cystine yield and total sulphur in various animal hairs. C. RIMINGTON (Biochem. J., 1929, 23, 726—729).—In all varieties except camel hair, the entire sulphur of the purified hair could be accounted for as cystine. Camel hair yields 94% of the total sulphur as cystine. S. S. ZILVA.

Quantity of cysteine in living tissue proteins and its biological significance. Y. OKUDA (Proc. Imp. Acad. Tokyo, 1929, 5, 246—248).—An iodometric method has been devised for the determination of cysteine and cystine in proteins, and the distribution of these two substances in various proteins contained in fresh muscle, liver, and egg has been studied. The proteins of physiologically active tissue contain most of their sulphur-containing amino-acids in the form of cysteine and very little in the form of cystine; with egg-protein and the keratins, the reverse is the case. The oxygen uptake of proteins containing either cysteine or cystine alone is very small; the presence of both cysteine and either cystine or glutathione is necessary for the rapid absorption of oxygen. A. A. GOLDBERG.

Chemical change in the drying by heat of fish muscle. I. S. YAMAMOTO and S. MASUDA (J. Imp. Fish Inst., Tokyo, 1926, 22, 53—55, 188—197).—During desiccation of fish muscle by heat the monoamino-acid nitrogen is generally gradually diminished, whilst the diamino-acid nitrogen tends to increase. Optimal conditions for drying are described. CHEMICAL ABSTRACTS.

Isolation of di-iodotyrosine from the thyroid. G. L. FOSTER (J. Biol. Chem., 1929, 83, 345—346).—The isolation of di-iodotyrosine and of thyroxine from the thyroid described by Harington and Randall (this vol., 839) has been repeated by a simplified procedure; 33% of the total iodine was obtained as di-iodotyrosine and 16% as thyroxine. C. R. HARRINGTON.

Distribution of various phosphoric acid fractions in different portions of the heart. A. C. WHITE (Z. physiol. Chem., 1929, 183, 184—190).—The various portions of ox-heart show differing water content; the left auricle has more dry matter than the right, and still higher values are found in the ventricle. The total phosphorus increases in the order right auricle, left auricle, right ventricle, left ventricle. The acid-soluble phosphoric acid is greater in the left auricle than in the right and still greater in the ventricles. The phosphatide-phosphorus is much lower in the auricle than in the ventricle, in the right auricle lower than in the left. J. H. BIRKINSHAW.

Choline in the placenta and its relation to labour. F. WREDE, E. STRACK, and E. BORNHOFFEN (Z. physiol. Chem., 1929, 183, 123—132).—Normally and abnormally born human placentas contained about 180 mg. of choline per kg. of fresh organ, the placenta of the cow 114 mg. per kg. J. H. BIRKINSHAW.

Protamine. I. R. HIROHATA (J. Biochem. Japan, 1929, 10, 251—258).—A protamine ("mugiline- β ") isolated from the sperm of *Mugil japonicus* probably contains no aromatic amino-acids, nor any basic amino-acids except arginine; large quantities of monoamino-acids soluble in ethyl or methyl alcohol are present. CHEMICAL ABSTRACTS.

Oxytocic substance of cerebrospinal fluid. H. B. VAN DYKE, P. BAILEY, and P. C. BUCY (J. Pharm. Exp. Ther., 1929, 36, 595—610).—The oxytocic action of the cerebrospinal fluid, as shown by

experiments on the isolated guinea-pig uterus is related to its calcium content. It is suggested that calcium may be responsible for the oxytocic action of normal cerebrospinal fluid and also for the melanophore-expanding action exhibited by normal cerebrospinal fluid and serum. W. O. KERMAK.

Excretion of lead. R. A. KEKHOE and F. THAMANN (J. Amer. Med. Assoc., 1929, 92, 1418—1421).—Lead in the faeces (mg. per g. of ash) and urine (mg. per litre) was found as follows: students 0.08, 0.08; workmen with slight, if any, exposure to lead, 0.10, 0.13; workmen with moderate or severe exposure, 0.65, 0.22. CHEMICAL ABSTRACTS.

Excretion of lead in urine. H. MILLET (J. Biol. Chem., 1929, 83, 265—268).—Figures are given for the urinary excretion of lead, the determinations being made electrometrically. Normal individuals and untreated cancer patients excrete daily about 0.09 mg. of lead; this amount is not increased by injections of colloidal lead phosphate. C. R. HARRINGTON.

Detection of ketonic substances in urine. B. SCHWENKE (Pharm. Ztg., 1929, 74, 992—994).—The iodoform reaction is more sensitive towards acetone than the nitroprusside reactions of Legal or Lange. The substance which gives the nitroprusside reaction is ethyl acetoacetate and not acetone, since urine, which gives the nitroprusside reaction and not the iodoform reaction in the cold, gives a positive iodoform reaction and a negative nitroprusside reaction after heating to 100° for ½ hr. The *p*-aminoacetophenone test is most sensitive for ethyl acetoacetate. S. COFFEY.

Determination of sugar in urine. W. G. EXTON, A. R. ROSE, and P. V. WELLS (Proc. 38th Ann. Mtg. Assoc. Life Ins. Med. Dir. Amer., 1928, 14, 436—441).—The urine (0.2 c.c.) is diluted to 10 c.c. with a reagent prepared by adding phenol (6 g.) and then sodium sulphite (5 g.) to 200 c.c. of 4% sodium hydroxide solution, diluting with water to about 500 c.c., adding sodium potassium tartrate (100 g.), and then a solution of 3:5-dinitro-2-hydroxybenzoic acid (7 g.) in water (300 c.c.), and diluting to 1000 c.c. The tube containing the mixture is immersed in boiling water for 5 min., cooled, placed in a scopometer with the green light filter in place, and the wedge reading at the extinction point is noted. The dextrose content is determined by reference to a chart. CHEMICAL ABSTRACTS.

Bergeim test for intestinal putrefaction. F. HOELZEL (J. Biol. Chem., 1929, 83, 331—332).—The presence of reducing substances in normal faeces renders the test of Bergeim (A., 1925, i, 99) for intestinal putrefaction valueless. C. R. HARRINGTON.

Sugar tolerance in arthritis. II. Arthritis of the menopause. B. H. ARCHER (Arch. Int. Med., 1929, 44, 238—243).—Of twenty typical cases of arthritis of the menopause 70% showed diminished sugar tolerance, whereas it had previously been shown that, in a parallel series of infectious cases, only 15% exhibited this phenomenon. The lowering of the sugar tolerance may be due either to the disease of the joints or to associated conditions. W. MCCARTNEY.

Acute yellow atrophy of the liver. Origin of carbamide in the body. I. M. RABINOWITCH (J. Biol. Chem., 1929, 83, 333—335).—A case of acute yellow atrophy showed great dilution of the (small amount of) urine, combined with complete absence of carbamide from the blood. The hypothesis that carbamide is formed exclusively in the liver is therefore supported. C. R. HARRINGTON.

Effect of muscular exercise in beri-beri. I. Gas and carbohydrate metabolism. R. INAWASHIRO and E. HAYASAKA. II. **Circulatory apparatus.** E. HAYASAKA and R. INAWASHIRO (Tohoku J. Exp. Med., 1928, 12, 1—28, 29—61).—The resynthesis of lactic acid is retarded; the decrease of oxygen consumption and respiratory volume to initial values is prolonged; acidosis and blood-sugar are increased. CHEMICAL ABSTRACTS.

Excretion of oxalic acid in phloridzin diabetes. G. VIALE, L. NAPOLIONI, and D. ROSSELLI (Compt. rend. Soc. Biol., 1929, 99, 2005—2006; Chem. Zentr., 1929, i, 1708).—Although oxalic acid is sometimes excreted by the phloridzinised dog in larger amounts than by the normal animal, no relation between oxaluria and glycosuria was detected. A. A. ELDRIDGE.

Effect of dextrose on alimentary galactosuria. O. WELTMANN (Wien. klin. Woch., 1929, 42, 8—10; Chem. Zentr., 1929, i, 1365).—On ingestion of 40 g. of galactose and 50—100 g. of dextrose the elimination of galactose is reduced (especially in disease of the liver) to a smaller extent than by ingestion of the galactose alone. A. A. ELDRIDGE.

Arterial hypertension. R. H. MAJOR (Amer. J. Med. Sci., 1929, 177, 188—194).—Few cases of hypertension (without diabetes) showed blood-sugar values greater than 120 mg. per 100 c.c., but 61% of cases of essential hypertension, and all cases of chronic nephritis with hypertension, showed abnormally high blood-guanidine values, the normal being 0.1 mg. (average), 0.2 mg. (max.) per 100 c.c. "Blood-guanidine" resembles guanidine, but the identity was not conclusively established. CHEMICAL ABSTRACTS.

Inflammation. III. **Carbohydrate metabolism in inflamed tissue during the initial stage.** F. BRIKKER and F. SUPONITZKI. IV. **Nitrogen exchange in the initial stage.** F. BRIKKER and I. LAZARIN. V. **Acetone substances in the blood of inflamed tissue.** F. BRIKKER (Zhur. exp. Biol. Med., 1928, 9, 285—290, 291—299, 300—403).—The venous blood of the inflamed (rabbit's) ear has an abnormally high dextrose and acetone-substance content and amylolytic index. The protein of the inflamed region undergoes increased catabolism. CHEMICAL ABSTRACTS.

Chemistry of increase of blood-pressure in nephritis. W. HÜLSE and K. FRANKE (Arch. exp. Path. Pharm., 1929, 143, 257—268).—In ordinary cases of hypertonic nephritis as well as in those in which there is no insufficiency in the action of the kidneys, the deproteinised blood-plasma contains considerably more amino-nitrogen after acid hydrolysis than does normal plasma. The material which gives rise to this extra amino-nitrogen is responsible for the

increase in blood-pressure in nephritis. Animal charcoal easily adsorbs the material and it is soluble in alcohol, ether, chloroform, acetone, and water. It gives positive ninhydrin, carbylamine, and iodoform reactions and negative phenyl reaction. It possibly belongs to the phosphatide group or to the group of compounds containing amino-nitrogen from which phosphatides are built up. W. McCARTNEY.

Effect of administration of amino-acids on the structure of plasma-protein. A. NITSCHKE (Z. exp. Med., 1929, 64, 111—119; Chem. Zentr., 1929, i, 1363—1364).—In pathological conditions of the kidneys administration of amino-acids caused a diminished elimination of protein; the albumin fraction is increased, whilst the fibrinogen and globulin fractions are diminished.

A. A. ELDRIDGE.

[Retention of] inorganic serum-sulphates, urea, and creatinine in cases of renal insufficiency. Effect of diuresis [and of chronic nephrosis] on serum-sulphates. E. G. WAKEFIELD (Arch. Int. Med., 1929, 44, 244—251).—In cases of renal insufficiency increase in the amount of urea or creatinine in the blood is usually accompanied by increase in the amount of inorganic serum-sulphate. No direct correlations can be traced, however, and patients showing no evidence of renal disease may have more inorganic sulphate in the serum than have normal healthy persons. Diuresis seems to lower the concentration of inorganic sulphates in serum. In cases of chronic nephrosis there may not be any retention of inorganic sulphates. W. McCARTNEY.

Chemical changes occurring in the body as a result of certain diseases. IV. Primary pneumonia in children. D. C. DARROW and A. F. HARTMANN (Amer. J. Dis. Children, 1929, 37, 323—334).—The plasma chloride, hydrogen carbonate, and total base are decreased; a low f.-p. depression and a high normal p_{H_2} value were observed.

CHEMICAL ABSTRACTS.

Calcium and phosphorus concentration in the intestinal contents of rats in relation to rickets. A. M. COURTNEY, F. F. TISDALL, and A. BROWN (Can. Med. Assoc. J., 1928, 19, 559—562).—The total calcium content of the cæcum of rats fed on McCollum's rachitogenic diet and kept inside was much higher than that of rats similarly fed and exposed to sunshine, although the calcium combined with phosphorus was practically the same in both groups.

CHEMICAL ABSTRACTS.

Carbohydrate metabolism of tumours. III. Rate of glycolysis of tumour tissue in the living animal. C. F. CORI and G. T. CORI (J. Cancer Res., 1929, 12, 301—313).—The tolerance limit of normal rats for intravenously injected sodium *D*-lactate was a rate of infusion of 95–5 mg. of lactic acid per 100 g. of body-weight per hr. Rats with tumours weighing 14–21% of the body-weight showed a marked increase in the blood-lactic acid. The decrease in lactic acid tolerance was approximately proportional to the size of the tumour. It is computed that the rate of lactic acid production by the tumour tissue in the living animal is 570–800 mg. of lactic acid per 100 g. of fresh tumour per hr. The rate of

glycolysis of the tumour *in vivo* depends on the blood-sugar concentration. At a normal blood-sugar level of the tumour-bearing animals the glycolysis corresponds with one half of the maximum possible glycolysis of the tumour. The intravenous dextrose tolerance of tumour-bearing rats is the same as that of normal rats.

CHEMICAL ABSTRACTS.

Actual reaction of urine and its relation to fatigue. M. S. RESNITSCHENKO (Biochem. Z., 1929, 210, 393—402).—A series of curves shows the variations of urinary acidity during various periods of muscular exercise. With severe work an increased acidity is usually obtained, but in athletes there is no increase and occasionally a decrease.

P. W. CLUTTERBUCK.

Absolute amount of hydrogen ions in urine on the march and in running. M. S. RESNITSCHENKO (Biochem. Z., 1929, 210, 403—413).—Work of medium intensity (10 km. march with pack) causes, in persons of average physique, an increased acidity of urine and in stronger persons first a decrease and subsequently an increase to normal acidity. More intense exercise but of shorter duration (700 m. run) increases the concentration and the absolute amount of the hydrogen ions of the urine.

P. W. CLUTTERBUCK.

Effect of "training" of muscle on its content of phosphorus compounds. D. FERDMANN and O. FEINSCHMIDT (Z. physiol. Chem., 1929, 183, 261—268).—"Training" of the leg muscle of the rabbit by electrical stimulation for 3–4 min. twice daily causes a considerable increase in the creatinephosphoric acid. On cessation of the training, the normal value is again attained after 4–6 days. No change is produced by training in the pyrophosphoric acid or the hexosephosphoric acid.

J. H. BIRKINSHAW.

Role of phosphorus in the metabolism of carbohydrate in muscle. E. AUBEL and T. CAHN (Bull. Soc. Chem. biol., 1929, 11, 903—928).—A review.

W. O. KERMAK.

Lactic acid metabolism of the surviving hind-limbs. A. BORNSTEIN and E. SCHMUTZLER (Pflüger's Archiv, 1929, 221, 395—399; Chem. Zentr., 1929, i, 1366).—The isolated hind-limbs of dogs were perfused with blood with addition of dextrose to a constant blood-dextrose content. The lactic acid remains constant or falls. Addition of insulin or alcohol to the perfusion liquid causes no change. Sodium cyanide increases the production of lactic acid, corresponding with the inhibition of oxidation. The disappearance of added lactic acid was studied.

A. A. ELDRIDGE.

Nerve metabolism. IV. Carbohydrate metabolism of resting mammalian nerve. E. G. HOLMES and R. W. GERARD (Biochem. J., 1929, 23, 738—747).—There is a rise of lactic acid and a corresponding fall in carbohydrates (i.e., "free sugars" and glycogen) in rabbit's nerves in nitrogen. In oxygen there is no disappearance of lactic acid, but a definite fall in the carbohydrates. About 60% of the resting metabolism of rabbit nerve may be maintained by the oxidation of these carbohydrates. The rate of lactic acid formation under asphyxial conditions is comparable with that of frog nerve and much less

than that of rabbit brain. No oxidation or resynthesis of lactic acid occurs on admitting oxygen to an asphyxiated nerve. The formation of lactic acid, even if concerned with hexosephosphate, does not involve breakdown of mono- or di-phosphate with liberation of free phosphate. A modification of the Van Slyke-Bissinger method for separation of carbohydrates from tissue extracts is described. S. S. ZILVA.

Brain metabolism. V. Role of phosphates in lactic acid production. C. A. ASHFORD and E. G. HOLMES (Biochem. J., 1929, 23, 748—759).—Inorganic phosphate is liberated from brain-tissue both anaerobically and aerobically and in the presence as well as in the absence of dextrose. No evidence of hexosephosphate synthesis has been found at any stage in the process of formation of lactic acid, although the tissue is capable to a small extent of performing this synthesis. Both phosphate liberation and lactic acid production from dextrose by brain-tissue are inhibited by sodium fluoride, but, whilst the former is affected only by a high fluoride concentration, the latter is sensitive to very high dilutions of the salt. There is no quantitative relationship between the amounts of phosphate and lactic acid which are prevented from appearing by fluoride. Lactic acid is freely formed from dextrose, even when all available phosphate is immobilised. The velocity of lactic acid formation from dextrose is not increased by the replacement of phosphate. Much less lactic acid is formed from glycogen than from dextrose. The process is inhibited by fluoride and by immobilising phosphate. It can be restored by replacing phosphate. Brain-tissue most probably forms lactic acid by one process which involves dextrose and is independent of phosphate and another which involves glycogen and is dependent on phosphate.

S. S. ZILVA.

Blood-sugar regulation, fat and carbohydrate metabolism. F. DEPISCH and R. HASENOHRL (Klin. Woch., 1929, 8, 202—204; Chem. Zentr., 1929, i, 1477).—In normal individuals, administration of fat (up to 50 g.) has no effect on the blood-sugar curve; in diabetes the curve is parallel to the hunger curve. Injection of adrenalin, however, causes in normal individuals a more marked increase of blood-sugar than in hunger-controls. Administration of fat moderates the action of administered or endogenous insulin.

A. A. ELDRIDGE.

Unsaponifiable fraction of liver-oils. V. Absorption of liquid paraffin from the alimentary tract in the rat and the pig. H. J. CHANNON and G. A. COLLINSON (Biochem. J., 1929, 23, 676—688).—The iodine value of the non-sterol fraction of the unsaponifiable fraction of the livers of rats which received liquid paraffin in their diet was 31 as against 119 for that from the control animals. A similar fall in the iodine value was observed in an experiment with pigs. The hydrocarbon was isolated from the liver of these animals which received it in their diet.

S. S. ZILVA.

Compounds of conjugated bile-acids with fatty acids and their importance in fat absorption.

II. Solubility and diffusibility. III. Surface

tension. F. VERZAR and A. KUTHY (Biochem. Z., 1929, 210, 265—280, 281—285; cf. this vol., 466).—II. Quantitative investigation of the dissolution of fatty acids in solutions of bile acids shows that at first molecular and then colloidal solutions arise. This is confirmed by nephelometric investigation and by diffusion experiments and ultrafiltration. Fatty acids diffuse along with bile acid, the diffusion of the latter being retarded by the union. The solutions may be precipitated by cations and positively-charged colloids. By means of bile acids 0.25% aqueous solutions of oleic, stearic, and palmitic acids may be prepared in which the greater part of the fatty acid is diffusible even at p_H 6.25. At higher concentrations the fat is more and more in colloidal solution.

III. Surface tension measurements with mixtures of higher fatty acids and conjugated bile acids are carried out by stalagmometer and platinum-ring methods. Changes of surface tension at varying p_H confirm the view that in neutral and faintly acid solution (up to p_H 6.25) water-soluble complexes of oleic, stearic, and palmitic acids with bile acids exist and are characterised by very low surface tension.

P. W. CLUTTERBUCK.

Production of ammonia by surviving kidney-tissue. A. PATEY and B. E. HOLMES (Biochem. J., 1929, 23, 760—766).—Washed kidney-tissue produces some ammonia under anaerobic conditions and more under aerobic conditions. In the presence of dextrose the aerobic ammonia production is brought down to the anaerobic level. The anaerobic production is not affected by dextrose. In the presence of glycine extra ammonia is formed. This occurs only in air and not anaerobically. Extra atmospheric oxygen is not, however, taken up by the tissue. The production of this extra ammonia is not inhibited by dextrose. Cyanide (0.02*M*) diminishes but does not entirely inhibit the aerobic ammonia formation by the tissue alone; on the other hand, the production of extra ammonia in the presence of glycine is inhibited by this reagent. Apparently three systems are involved in the ammonia production by kidney-tissue, one anaerobic and two aerobic.

S. S. ZILVA.

Kidney metabolism: ammonia and phosphate metabolism, sugar utilisation. P. GYORGY and W. KELLER (Biochem. Z., 1929, 210, 434—442).—The authors' previous work on the anaerobic glycolysis and respiration of cortical and medullary kidney-tissue of rats (A., 1928, 1396) is repeated and extended to phosphate and ammonia formation, using the kidney of both old and young animals. Phosphate formation in both kinds of tissue is greater in an atmosphere of nitrogen than in one of oxygen and, whereas with cortical tissue it is almost the same for young and old animals, with medullary tissue it is greater for the older animals. Both types of tissue placed in Ringer's solution gave large amounts of ammonia, the tissue of young animals giving larger amounts than that of older animals, and the cortical giving more than the medullary. That anaerobic glycolysis of the cortical tissue is small and of the medullary tissue is four to five times as great, whilst the reverse is true of the respiration, is confirmed.

P. W. CLUTTERBUCK.

Endogenous uric acid and hæmatopoiesis. J. KRAFFKA, jun. (J. Biol. Chem., 1929, 83, 409—414).—The uric acid excretion of a Dalmatian hound was doubled after loss of about one third of the total blood volume by hæmorrhage. The increased output of uric acid is ascribed to the breakdown of the nuclei of the erythroblasts during the period of active regeneration of red blood-corpuscles.

C. R. HARRINGTON.

Creatine-creatinine excretion during fasting. S. MORGULIS (J. Biol. Chem., 1929, 83, 299—310).—Experimental evidence is offered against the supposition (Howe and others, A., 1912, ii, 369; Palladin and Epelbaum, this vol., 345) that, in a fasting animal, increase of creatine excretion over that of creatinine necessarily indicates approaching death. Until inanition reaches an advanced stage, the creatinine coefficient remains unaltered. The experiments indicate a synthesis of creatine during fasting and a retention of creatine during re-feeding after a fasting period.

C. R. HARRINGTON.

Indican formation. I—III. Y. KISHI (Tohoku J. Exp. Med., 1928, 11, 504—544; 12, 75—80, 81—87).—The effect of fasting on the urinary indican of guinea-pigs and rabbits is described. Hyperindicanæmia in nephritis is attributed to increased formation, as well as retention, of indican. Indicanuria may be due partly to increased decomposition of body protein and partly to metabolic anomalies. Indican originates abacterially.

CHEMICAL ABSTRACTS.

Food value of legumes for albino rats. A. GALAMINI (Atti R. Accad. Lincei, 1929, [vi], 9, 809—812).—The urine of rats fed solely on raw beans changes to a neutral and then to an alkaline reaction, the animals losing weight and dying sooner than when fasting. A diet of cooked beans is more readily tolerated, although the animals still lose weight.

T. H. POPE.

Acid-base metabolism. Effects of administration of salt and of restriction of water. L. SCHOENTHAL (Amer. J. Dis. Children, 1929, 37, 244—251).—Changes observed in the blood-plasma and in the urine are recorded.

CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism in artificially fed infants. I. Influence of cod-liver oil and irradiated milk. A. L. DANIELS, G. STEARNS, and M. K. HUTTON (Amer. J. Dis. Children, 1929, 37, 296—310).—The following calcium:phosphorus retention ratios were observed after feeding the corresponding foods: pasteurised milk 0.5, boiled milk 1.2, pasteurised milk and cod-liver oil 0.8—1, boiled milk and cod-liver oil 1.2—1.48, milk with irradiated cod-liver oil 1.48, irradiated milk 2.0. The ratio for optimal development of infants less than 1 year old should be 2.

CHEMICAL ABSTRACTS.

Iodine in blood and gland secretions after administration of iodoproteins. G. BARKAN and W. LEISTNER (Arch. exp. Path. Pharm., 1929, 144, 83—104).—After the administration of an iodoprotein to rabbits, dogs, and men, the iodine present in the blood is not completely precipitable by silver ions, but is in part present as organically-bound iodine. This organic iodine differs from the inorganic iodide

in being more highly concentrated by the kidneys and in being absent from the saliva and gastric juice. After administration of potassium iodide all the iodine in the blood is precipitable by silver ions.

W. O. KERMAK.

Effect of secretions and vegetable poisons on the permeability of animal membranes. E. GELLHORN and H. GELLHORN (Pflüger's Archiv, 1928, 221, 247—263; Chem. Zentr., 1929, i, 1470).—The effect of *l*-adrenaline, thyroxine, insulin, pilocarpine, and atropine on the permeability of animal membranes towards dextrose was examined.

A. A. ELDRIDGE.

Influence of temperature on the permeability of animal membranes. E. GELLHORN and H. GELLHORN (Pflüger's Archiv, 1928, 221, 264—281; Chem. Zentr., 1929, i, 1470).

Permeability of animal membranes towards dyes. E. GELLHORN (Pflüger's Archiv, 1928, 221, 230—246; Chem. Zentr., 1929, i, 1469—1470).

Ionic permeability of the body surface of invertebrate sea animals as cause of the toxicity of sea-water of abnormal composition. A. BETHE (Pflüger's Archiv, 1928, 221, 344—362; Chem. Zentr., 1929, i, 1470—1471).

Effect of p_H on striated muscle. S. GOLDBERGER (Atti R. Accad. Lincei, 1929, [vi], 9, 812—816).—Experiments on the action of Ringer's solutions with various p_H values on frog's muscle by Trendelenburg's perfusion method are described.

T. H. POPE.

Influence of the external temperature on the glycogen and fat content of the liver, and the relations of the external temperature to changes in the thyroid gland and suprarenal capsule. T. NOSAKA (Folia endocrinol. Japon., 1928, 3, 1558—1580).

CHEMICAL ABSTRACTS.

Chemical and biological changes induced by X-rays in body tissue. M. T. BURROWS, L. H. JORSTAD, and E. C. ERNST (Radiol., 1928, 11, 370—377).—One effect is to remove lipid substances which are necessary for the growth of cancer cells.

CHEMICAL ABSTRACTS.

So-called water intoxication. H. MISAWA (Japan. J. Med. Sci., 1927, 1, 355—383).—Administration of water (amounting to one third of the body-weight) to rabbits caused a decrease of the dry blood-substance to 15%, a decrease of 23.5% in the serum-protein, a decrease of 20% in the blood-chlorine, -phosphorus, -sodium, -potassium, -calcium, and -magnesium, a slight decrease in the residual nitrogen and hæmoglobin, and an increase in the blood-sugar. The chlorine content of the liver was increased, and of other organs decreased. The urinary chlorine, sodium, calcium, phosphorus, and nitrogen were increased, the magnesium was unchanged, and the potassium decreased.

CHEMICAL ABSTRACTS.

Blood-calcium distribution in anaphylaxis in the guinea-pig. H. BROWN and S. G. RAMSDELL (J. Exp. Med., 1929, 49, 705—709).—The total calcium is unchanged; the membrane-diffusible fraction is greater than that for the animal similarly treated but not manifesting characteristic symptoms.

CHEMICAL ABSTRACTS.

Formation of complex compounds in the treatment of chronic lead and mercury poisoning. H. LUDWIG (Biochem. Z., 1929, 210, 353—392).—The affinity of the mercury ion for potassium iodide, sodium thiosulphate, and for the thiol group with complex formation is greater than that of the lead ion. With protein, however, lead sulphide is formed more readily than mercury sulphide. With serum formation of lead sulphide is less ready than that of mercury sulphide. The ammonium sulphide reaction with lead is inhibited by the presence of serum, but not of egg-albumin. Serum retains its inhibiting power after extraction with ether, but loses it after deproteinisation by either ammonium sulphate or trichloroacetic acid. In serum, lead is therefore partly in the form of complex ions. The affinity of lead for the hydroxyl group is much greater than that of mercury. The potassium iodide complex salts act as anions, precipitating proteins in acid solution, and displace the precipitation optimum of caseinogen to the alkaline side more strongly than potassium thiocyanate but less strongly than potassium ferro- and ferri-cyanide. The following heavy metals are arranged in order of strength of displacement of the caseinogen optimum to the acid side: $\text{Fe}^{+++} > \text{Hg}^{+} > \text{Hg}^{++} = \text{Cu} > \text{Fe} > \text{Ni} > \text{Co}$. In yeast fermentation experiments, mercuric nitrate is much more poisonous than lead nitrate. In cases of poisoning mercury is therefore brought into solution by potassium iodide more readily than lead, and, moreover, the mercury combined with protein amino-groups is set free by the iodide.

P. W. CLUTTERBUCK.

[Influence of administration of mixtures of] ammonium chloride and hexamethylenetetramine on the urine. E. C. WISE and F. W. HEYL (Arch. Int. Med., 1929, 44, 252—262).—Ammonium chloride (which yielded its maximum acidifying effect on the second day) in daily doses of 4.87 g. had a rapid acidifying effect on the urine of normal men and maintained the reaction at about p_{H} 5.5. Hexamethylenetetramine (given with the ammonium chloride) was found in the urine in concentrations which were much the same whether the daily dose was 2.43 or 6.82 g. The urinary concentrations of the tetramine are very much affected by the acidity. Other factors being equal, the concentrations of formaldehyde found in the urine were the higher the greater was the dose of the tetramine, and varied according to the times at which the urine samples were taken.

W. MCCARTNEY.

Hypoglycæmic action of allylisopropylbarbituric acid and adrenaline antagonism. G. FONTÈS and L. THIVOLLE (Compt. rend. Soc. biol., 1929, 99, 1977—1978; Chem. Zentr., 1929, i, 1708).—The injection of allylisopropylbarbituric acid causes hypoglycæmia; the hyperglycæmic action of adrenaline can be suppressed.

A. A. ELDRIDGE.

Action of certain alkaloids on leucocytes isolated from the organism. C. FORTI (Atti R. Accad. Lincei, 1929, [vi], 9, 800—806; cf. A., 1926, 968).—Before killing the cell, cocaine, novocaine, and tutocaine hydrochlorides cause arrest of its activity, which is, however, recoverable.

T. H. POPE.

Does *l*-ephedrine act more powerfully than *dl*-ephedrine (ephedrine)? H. KREITMAIR (Arch. exp. Path. Pharm., 1929, 143, 358—367).—Any difference in physiological activity between *l*-ephedrine and *dl*-ephedrine is so slight as to be undetectable by pharmacological methods available up to the present. The differences reported by other workers are due to differences in experimental methods and conditions and in the condition and reactions of the individual animals used.

W. MCCARTNEY.

Influence of the morphine derivative "laudan" on the metabolism following administration of various kinds of food. W. ARNOLDI (Arch. exp. Path. Pharm., 1929, 143, 283—309).—A special form of acidosis, characterised by lack of available alkali and reduced formation of ammonia, is caused by "laudan," especially when administration is long continued. The lack of alkali causes reduced formation or reduced excretion of keto-compounds and the amount of these in the urine is always lowered. "Laudan" also causes alterations in body-weight, in protein, carbohydrate, and fat metabolism, in the magnitude and extent of oxidative processes, in acid-base relationships, and in the functions of the kidneys and intestine. These alterations are more pronounced and more lasting in rats receiving food rich in protein than in those receiving food rich in carbohydrates, and sometimes the changes with the former food are the opposite of those with the latter. With food rich in carbohydrates the decrease in diuresis, the disturbance of the activity of the intestine, and the after-effects when administration of the drug ceases are smaller than with other food and the narcotic action seems to be more easily thrown off. The administration of single large doses of sugar rapidly counterbalances for lengthy periods the changes produced by "laudan."

W. MCCARTNEY.

Mechanism of pilocarpine hyperglycæmia. G. VIALE and L. NAPOLIONI (Compt. rend. Soc. Biol., 1929, 99, 2006; Chem. Zentr., 1929, i, 1708).—The effect is adrenaline hyperglycæmia; pilocarpine itself causes hypoglycæmia.

A. A. ELDRIDGE.

[Biological] evaluation of digitalis. A. STASIAK and B. ZBORAY (Arch. exp. Path. Pharm., 1929, 144, 283—296).

Active principle of camomile flowers. K. JUNKMANN and W. WIECHOWSKI (Arch. exp. Path. Pharm., 1929, 144, 1—7).—Tinctures and infusions of camomile flowers contain an active principle, apparently a glucoside, the pharmacological actions of which are described. It has an inhibitory effect on the mobility of the intestine.

W. O. KERMACK.

Adder venom. III, V, VII, VIII. C. KOBAYASHI (Osaka J. Med., 1928, 27, 779—786, 1405—1410, 1411—1418, 1725, 1730).—Subcutaneous injection of adder venom causes a gradual decrease in the amount of that substance in rabbit's blood which reacts with iodate. Other changes in the composition of the blood and urine were also observed. The venom does not pass through a collodion membrane. Separation of the active substance was attempted.

CHEMICAL ABSTRACTS.

Effect of cyanide on the respiration of animal tissues. M. DIXON and K. A. C. ELLIOTT (Biochem. J., 1929, 23, 812—830).—In most of the animal tissues studied, a cyanide concentration of 0.001*M* was sufficient to produce the maximum degree of inhibition, which varied in different tissues from 40% to 90%. The respiration of spleen is not affected by small amounts (0.001*M*) of cyanide. Negelein's statement that the respiration of yeast is almost completely inhibited by cyanide is confirmed; some samples of yeast show an incomplete (85%) inhibition. With liver small concentrations of pyrophosphate produce a slight acceleration, larger amounts an inhibition of the rate of respiration, the inhibitory effect of pyrophosphate being less than the corresponding effect of cyanide. With muscle pyrophosphate produces a greater inhibition than cyanide. It produces no effect on yeast. Whilst pyrophosphate inhibits the reduction of methylene-blue cyanide does not influence this reaction. The action of both cyanide and pyrophosphate on respiration is reversible.

S. S. ZILVA.

Amylases of cereal grains: oats. J. L. BAKER and H. F. E. HULTON (J.C.S., 1929, 1655—1660).—Amylase precipitated by alcohol from an extract prepared from ungerminated oats converts soluble potato starch almost completely into maltose, provided a sufficient quantity is employed. This result supports the view that starch is composed of condensed maltose units. When the conversion into maltose is incomplete, an alcohol-insoluble compound is formed closely resembling α -amylopectin. Ungerminated oat amylase has a solvent action on oat starch granules, producing dextrose. When the amylase from germinated oats acts on potato-starch paste it yields a dextrin insoluble in alcohol, a maltodextrin-like substance soluble in alcohol, and a sugar, apparently maltose. Similar results are also obtained with oat starch.

W. O. KERMAK.

Malt amylase. VI. Adsorption of amylase by blood-charcoal and kaolin at varying p_H with reference to its dextrinising and saccharifying powers. T. SABALITSCHKA and R. WEIDLICH (Biochem. Z., 1929, 210, 414—433).—Blood-charcoal readily adsorbs amylase at p_H 6.2—6.0, but more readily at p_H 3.2. Kaolin adsorbs amylase more strongly than blood-charcoal, the adsorption increasing considerably from p_H 6.2 to 4.5 and decreasing again at p_H 3. Merck's diastase is completely adsorbed under the experimental conditions by four times its weight of kaolin. With an absorption p_H between 6.2 and 4.5, no enzymic injury is apparent on subsequent buffering to the optimal p_H for amylolysis, whilst slight injury occurs with an absorption p_H of 4 and greater injury with p_H of 3, and with p_H 2.8 both dextrinising and saccharifying powers are destroyed. So long as the p_H of the adsorption medium does not cause injury, the two powers increase with increasing amounts of kaolin and with decreasing p_H .

P. W. CLUTTERBUCK.

[Biochemical factors in] heredity. II. H. VON EULER, S. STEFFENBURG, and H. HELLSTROM (Z. physiol. Chem., 1929, 183, 113—122; cf. this vol., 848).—The catalase content of *Brassica* runs

parallel with the number of chloroplasts. An attempt was made to determine the catalase value of a chloroplast. With further mutants of barley the catalase ratio k (normal)/ k (white) was 3.3 when germinated in the dark, 5.5 in the light. Two other strains gave ratios of 1.6 and 3.4, respectively.

J. H. BIRKINSHAW.

Kinetics of ester hydrolysis by enzymes. I. E. BAMANN and M. SCHMELLER (Z. physiol. Chem., 1929, 183, 149—167).—The action of hepatic lipases from man, ox, sheep, dog, and rabbit on methyl butyrate was studied. There were considerable variations in activity and in p_H optimum, which varied between 7 and 9. The relationship between the concentration of the substrate and the reaction constant for linear and unimolecular reactions and the affinity of the enzyme for the substrate was traced.

J. H. BIRKINSHAW.

Growth, development, and phosphatase activity of embryonic avian femora and limb-buds cultivated *in vitro*. H. B. FELL and R. ROBISON (Biochem. J., 1929, 23, 767—783).—The isolated femora of 5½- and 6-day fowl embryos were found to have a remarkable capacity for self-differentiation. During cultivation in a watch-glass the 5½-day femora increased to more than three times their original length, the gross anatomy remaining comparatively normal. During cultivation *in vitro* the isolated femora synthesised a phosphatase, the gross amount formed increasing with the age of the culture. The ratio of phosphatase to the dry weight of the femur increased during cultivation from zero to a maximum value and then declined. The increase corresponded with the progress of histological differentiation and the decline with degeneration. The maximum value of this ratio was higher than that found for normal embryonic femora. Undifferentiated 3-day embryonic limb-buds cultivated *in vitro* gave rise to small-celled cartilage only. Such explants after cultivation were completely devoid of phosphatase, thus confirming the view that the enzyme is formed by cartilage only if hypertrophic cells are present.

S. S. ZILVA.

Effect of emulsification on the peptic synthesis of protein. H. WASTENEYS and H. BORSOOK (Coll. Symp. Mon., 1928, 6, 155—172).—Benzaldehyde, benzoic acid, benzene, toluene, and chloroform accelerate peptic synthesis of protein; talc powder, barium sulphate, and kieselguhr have a slight, whilst oleic acid and olive oil have no, accelerative effect. Effective substances induce some protein synthesis even in absence of pepsin. The proteins synthesised vary in their rate of hydrolysis by hydrochloric acid and in their base-combining capacity.

CHEMICAL ABSTRACTS.

Comparison of enzymic degradation of proteins by successive alternating action of pepsin, trypsin-kinase, and erepsin. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1929, 11, 92—103).—When caseinogen is first acted on by pepsin—hydrochloric acid at p_H 1.8, then with erepsin at p_H 8, and finally with trypsin-kinase, degradation occurs during each successive action. If hydrolysis is carried out successively with trypsin-kinase and erepsin, then

pepsin has no further action. With fibrin, trypsin-kinase has no action after pepsin and erepsin, but pepsin causes hydrolysis after trypsin-kinase and erepsin; the total amount of fission is much greater in the last case. With edestin and gelatin more hydrolysis takes place with trypsin-kinase and erepsin than with pepsin and erepsin. The significance of the results is discussed. H. BURTON.

Action of cell enzymes on proteins and protein degradation products. E. ABDERHALDEN and O. HERRMANN (Fermentforsch., 1929, **11**, 78—85).—The enzyme preparation obtained by extraction of fat-free, dry liver (or kidney) powder with 87% glycerol generally hydrolyses di- and poly-peptides. The enzyme not adsorbed on aluminium hydroxide is capable of causing hydrolysis at p_H 8.4 as is the eluted (phosphate mixture) enzyme at the same hydrogen-ion concentration. The eluted enzyme has generally a more powerful action when elution is carried out at p_H 8.4 than at p_H 7.1. The eluted enzyme exerts optimum action on the peptides studied at p_H 7.1 and for the peptide derivatives at p_H 8.4. Hippuric acid is sometimes hydrolysed, sometimes unaffected. H. BURTON.

Influence of various alcohols in various concentrations on the rate of hydrolysis of proteins and polypeptides by proteases or the trypsin-kinase and erepsin complexes. E. ABDERHALDEN and F. REICH (Fermentforsch., 1929, **11**, 64—77).—The influence of a series of alcohols on the action of pepsin-hydrochloric acid on caseinogen, trypsin-kinase at p_H 8.4 on *dl*-leucylglycyl-*dl*-leucine, erepsin at p_H 7.8 on *dl*-leucylglycine, and the gastric, pancreatic, and intestinal juices of the dog on caseinogen at 37°, has been studied. At the concentrations studied only hexyl and *tert*-butyl alcohols, respectively, cause an increased action of trypsin-kinase and erepsin, respectively. The following alcohols exert only a retarding action: on erepsin, *n*- and *iso*-propyl, hexyl, *isobutyl*, and benzyl; on pepsin, methyl, ethyl, *n*-butyl, and *iso*amyl; on trypsin-kinase, *n*- and *tert*-butyl, *n*- and *iso*-amyl, benzyl. The following cause an acceleration in low concentration but retard at higher concentrations: on erepsin, methyl, *n*-butyl, *iso*amyl, ethyl (also on pancreatic and intestinal juices); on pepsin, *n*- and *iso*-propyl, *iso*- and *tert*-butyl, *n*-amyl, hexyl, and benzyl; on trypsin-kinase, methyl, ethyl, *n*- and *iso*-propyl, and *isobutyl*. *n*-Amyl, heptyl, and octyl alcohols and nicotine have no effect with erepsin, whilst caffeine has only an accelerating action. A temporary retardation is observed with nicotine on the gastric juice. H. BURTON.

Nature of proteases. III. Parallelism between the activities of pepsin preparations determined by the disappearance of the substrate and by the increase in carboxyl groups. A. N. ADOVA and I. A. SMORONINCEV (Z. physiol. Chem., 1929, **183**, 133—148).—Determination of the activity of various pepsin preparations by the rate of disappearance of the substrate (caseinogen and gelatin) gave the same results as the alcoholic titration of the carboxyl groups by Willstätter's method. All

the pepsin preparations attacked caseinogen more energetically than gelatin; the velocity coefficient of caseinogen digestion by strong preparations is about double that for weak ones. The velocity of digestion of caseinogen by all preparations and of gelatin digestion by strong preparations follows the Schütz-Borissov rule; for weak preparations on gelatin the equation is of zero order. J. H. BIRKINSHAW.

Caseinogen-splitting action of papain. M. SATO (Separate, 1928).—The quantity of caseinogen digested by papain during unit time is directly proportional to the concentration of papain so long as the equilibrium is not approached. The unimolecular velocity coefficient increases as the reaction proceeds. The temperature coefficient falls with rise of temperature; the optimal temperature is about 80°, and the optimal p_H 6.5. The action is arrested by *N*/75—*N*/125-sodium hydroxide. Acceleration by hydrogen cyanide is attributed to the undissociated molecules. CHEMICAL ABSTRACTS.

Effect of proteolytic enzymes on benzoyl- and deamino-derivatives of polypeptides. T. KAWAI (J. Biochem. Japan, 1929, **10**, 277—310).—Glycyl-*dl*-phenylalanine, *dl*-leucylglycine, glycyl-*l*-phenylalanine, and glycyl-*l*-leucine are split by erepsin but not by trypsin; benzoylglycylglycine is not hydrolysed by erepsin or trypsin, whilst the benzoyl derivatives of the other dipeptides are markedly hydrolysed by crude erepsin. Trypsin hydrolyses benzoyl-glycyl-*dl*- and -*l*-phenylalanine, -*dl*- and -*l*-leucylglycine, the hydrolysis of racemic compounds proceeding asymmetrically. Fission occurs at the peptide linking. Dipeptides not affected by trypsin are hydrolysed when the free amino-group is benzoylated. Tripeptides in which the amino-acid is combined with trypsin-resistant dipeptides are hydrolysed by trypsin. Benzoyldiglycylglycine is not split by trypsin. Deaminated dipeptides are not hydrolysed by erepsin. Deaminated polypeptides are generally resistant to erepsin, whilst some are hydrolysed by trypsin. CHEMICAL ABSTRACTS.

Problem of separation of erepsin and trypsin or trypsin-kinase complexes into fractions with specific action. E. ABDERHALDEN and A. SCHMITZ (Fermentforsch., 1929, **11**, 104—118).—An erepsin preparation (from fresh small intestine) hydrolyses *dl*-leucylglycine after 1 day, but does not after 5 days. During the same time the amount of fission with *dl*-leucylglycyl-*dl*-leucylglycine (I) increases (optimum p_H changes from 9.3 to 7.1); hydrolysis of the tetrapeptide occurs even after 17 days. The same preparation hydrolyses glycyl-*dl*-leucyl-*dl*-leucylglycine, m. p. 228° (from *chloroacetyl*-*dl*-leucyl-*dl*-leucylglycine), *dl*-dileucylglycylglycine (II), *dl*-leucyldiglycyl-*dl*-leucine, *diglycyl*-*dl*-leucyl-*dl*-leucine (III), m. p. 233° (from *chloroacetyl*glycyl-*dl*-leucyl-*dl*-leucine, m. p. 202°), and glycyl-*dl*-leucylglycyl-*dl*-leucine (IV). Another erepsin preparation has no action on *dl*-leucylglycine, II, or III, but hydrolyses glycyl-*dl*-leucine, glycyl-*l*-tyrosine, the four tripeptides obtainable from glycine and *dl*-leucine, I, and IV, at p_H 7.1 (optimum). H. BURTON.

Action of trypsin on conjugated bile-acids. A. VON BEZNAK (Biochem. Z., 1929, **210**, 261—264).—

Glycocholic and taurocholic acids are not attacked by trypsin.

P. W. CLUTTERBUCK.

Reaction of azine compounds with proteolytic enzymes. G. M. RICHARDSON and R. K. CANNAN (Biochem. J., 1929, 23, 624—632; cf. Marston, A., 1924, i, 350).—When pepsin solutions and gastric juice are precipitated by the addition of safranin or neutral-red the proteolytic activity is removed from solution. The supernatant liquors from trypsin precipitates, on the other hand, retain most of their activity. The addition of these dyes in very low concentrations does not retard the catalytic activity of either pepsin or trypsin. The optimum conditions of concentration and p_H for the complete removal of pepsin from solution by this means have been determined. The degree of removal of activity and the weight of precipitate both increase as the p_H rises above 1. These two factors are not, however, parallel, since the actual separation of insoluble matter is spread over a range of about four p_H units, whilst the precipitation of activity is localised about p_H 2. The precipitated enzyme can be regained from the precipitate by treatment with sodium hyposulphite and by extraction of the dye with benzene in the absence of oxygen. Trypsin can be recovered similarly at p_H 9. Observations on the purification of pepsin by means of the above precipitation method have been made. Marston's view that the azine nucleus reacts specifically with a protease, with the formation of a protease-azine complex, is not supported.

S. S. ZILVA.

Influence of hydrogen-ion concentration on the inactivation of urease by heavy metals. M. KITAGAWA (J. Biochem. Japan, 1929, 10, 197—205).—Inactivation of urease by zinc occurs in alkaline solution from p_H 6.0, whilst copper and mercury inhibit the action in either acid or alkaline solution. The effect is parallel to the influence of the p_H on the combination of protein with heavy metals. Iodine is much more injurious to urease than potassium iodide.

CHEMICAL ABSTRACTS.

Dried yeast. K. MYRBACK and H. VON EULER (Z. physiol. Chem., 1929, 183, 226—236).—Dried yeast under the best conditions has a fermenting power of 50—75% of that of fresh yeast. The fermentation curves of dried yeast in presence of toluene consist of two distinct portions. The fermentation proceeds normally until all the phosphate is esterified, when the rate of fermentation falls off, since the phosphatase is inactivated by toluene. The paralyzing action of toluene on the living cell is quite different and reversible. The initial velocity of dried yeast fermentation is at a maximum at 45—48°; it is zero at 52°.

J. H. BIRKINSHAW.

Fermentation and growth in dry yeast-cells. II. C. BARTEL, H. VON EULER, and K. MYRBACK (Z. physiol. Chem., 1929, 183, 237—243; cf. A., 1926, 1276).—The ratio of the total number of cells to the number of living cells of an active air-dried yeast which had lost only 35% of its fermenting power was 140,000 before and 11,500 after 48 hrs.' fermentation. Thus more than 99.95% of the total amount of fermentation is due to cells incapable of reproduction.

J. H. BIRKINSHAW.

Sugar combination and connected synthetic processes by yeast-cells. E. WERTHEIMER (Fermentforsch., 1929, 11, 22—36).—When a dextrose solution is added to a suspension of baker's yeast the sugar disappears from solution before fermentation begins. The combination is not due to adsorption and depends on the temperature. Thus, at 0—15° the coefficient is 2, at 15—35° it is 4—8. Combination is selective, since laevulose and sucrose behave similarly to dextrose, whilst galactose, lactose, maltose, and dihydroxyacetone are unaffected. It is found that part of the dextrose is converted into a polysaccharide insoluble in 60% potassium hydroxide solution. This polysaccharide is not glycogen, but when it is heated with a dilute acid solution fission occurs and glycogen appears to be formed. The same product is obtained from laevulose and sucrose, but not from galactose, lactose, maltose, dihydroxyacetone, glycerol, or acetaldehyde. Sodium fluoride arrests the synthesis, but 0.002*N*-potassium cyanide has no effect. Synthesis is best accomplished by an active yeast; macerated yeast-juice has no synthetic action. The yeast-cells must, therefore, first assimilate the sugar.

H. BURTON.

Fermentation of yeast at high gas pressures. R. LIESKE and E. HOFMANN (Biochem. Z., 1929, 210, 448—457).—Yeast fermentation is investigated in sealed steel vessels fitted with contrivances for measuring the pressure attained and for removing and measuring the gas produced. At the ordinary temperature, the fermentation ceases when the pressure of the carbon dioxide formed has risen to 38—40 atm., the amount of carbon dioxide formed then being 1 mol./litre and of alcohol 40 g./litre. If the vessel is initially placed under a pressure of an inert gas of 90 atm. the fermentation is not inhibited, but at 150 atm. there is considerable inhibition, and at 1000 atm. only about half of the alcohol and carbon dioxide are produced as at the ordinary pressure.

P. W. CLUTTERBUCK.

Role of phosphorus in fermentation. M. SCHOEN (Bull. Soc. Chim. biol., 1929, 11, 819—902).—A review.

W. O. KERMAK.

Salt effect on the induction period in fermentation by dried yeast. H. KATAGIRI and G. YAMAGISHI (Biochem. J., 1929, 23, 654—662).—The following is the order of potency of salts in prolonging the period of induction in the fermentation by dried yeast in the presence of 0.04*M*-phosphate: $\frac{1}{2}\text{Ca}^{++} > \text{Na}^{+} > \text{K}^{+} > \frac{1}{2}\text{Mg}^{++} > \text{NH}_4^{+}$ with chlorides and sulphates and $\text{I}^{-} > \text{Cl}^{-} > \frac{1}{2}\text{SO}_4^{--}$ with sodium and potassium salts. The acetate, lactate, succinate, and sulphate of ammonium were nearly as potent as acetaldehyde in reducing the period of induction, although they were less potent than hexosediphosphate. Ammonium ion produced a remarkable antagonistic action to that of sodium ion, and sulphate ion a slight antagonistic action to that of nitrate ion. A hyperbolic relation may exist between the induction period and the ratio of the concentrations of the two ions.

S. S. ZILVA.

Comparison of influence of various concentrations of alcohols on alcoholic fermentation. E. ABDERHALDEN (Fermentforsch., 1929, 11, 86—91).

—Fermentation of a 40% solution of dextrose in a phosphate mixture (25 c.c.) with fresh yeast (5 g.) at p_H 6 is accelerated by the addition of 0.05 c.c. of methyl or 0.01 and 0.05 c.c. of ethyl alcohol (in one case 0.025 c.c. caused a slight retardation). Very small amounts of *n*- and *tert*-butyl alcohols also cause acceleration, whilst *n*- and *iso*-propyl, and *isobutyl* alcohols effect a retardation. *n*- and *iso*-Amyl, hexyl, heptyl, and benzyl alcohols do not cause an acceleration. The results using dry yeast are qualitatively the same.

H. BURTON.

Mechanism of enzyme action. III. Relation between enzyme action and adsorption. IV. Enzymic processes in germinating barley. F. F. NORD and J. WEICHERTZ (Z. physiol. Chem., 1929, 183, 191—217, 218—225; cf. A., 1928, 1284).—III. The action of ethylene, acetylene, and amylene on yeast-cells was found to take place in three successive phases: external narcosis, increase in permeability, internal narcosis. The adsorptives became physically attached to the lyophilic colloid elements of maceration juice and could exercise an inhibiting and also a protective action. The inhibition is independent of the precipitating action of the narcotic. Both the increase in cell permeability and the narcosis of the enzymes inside the living cell can be separated from the harmful phase of narcosis.

IV. The enzymic processes in germinating barley are influenced by ethylene and acetylene. This is shown in the increased rate of diastatic and proteolytic degradation and the increase in the yield of green malt. Ethyl acetate was formed in green malt when air was excluded.

J. H. BIRKINSHAW.

Desmolytic formation of methylglyoxal by yeast. C. NEUBERG and M. KOBEL (Biochem. Z., 1929, 210, 466—488).—The formation of methylglyoxal and hexosemonophosphate and the separation of free phosphate from magnesium hexosediphosphate under the action of plasmolysis juice of fresh top yeast, the residue of plasmolysed top yeast, washed dried bottom yeast, the washings of the same dried yeast, and untreated dried yeast are investigated quantitatively. With the plasmolysis juice an 85.4% yield of methylglyoxal was obtained. The monophosphate in all cases had a high rotation and low reducing power and was probably a mixture of hexose- and trehalose-monophosphate. With untreated dried yeast small amounts of pyruvic acid and acetaldehyde were also obtained.

P. W. CLUTTERBUCK.

Sterols from yeast. H. WIELAND and M. ASANO (Annalen, 1929, 473, 300—313).—Benzoylation of a sterol mixture (greater part of ergosterol removed) from yeast with benzoyl chloride and pyridine and subsequent fractionation of the benzoates produced affords in addition to ergosteryl benzoate, m. p. 168—170° (lit. 162—168°), $[\alpha]_D^{25} - 71.5^\circ$ (all rotatory powers are in chloroform) (cf. Bills and Honeywell, this vol., 104), benzoates of four other sterols, three of which are new. The sterols, obtained by hydrolysis of the benzoates with 3% alcoholic potassium hydroxide, are: zymosterol (I), $C_{27}H_{45}OH$ (cf. Smedley-Maelean, A., 1928, 329), m. p. 108—110°, $[\alpha]_D + 47.3^\circ$ [benzoate, m. p. 126—128° (turbid),

138° (clear), $[\alpha]_D^{25} + 36.4^\circ$; acetate, m. p. 104—106° (cf. *loc. cit.*)], which contains two double linkings; *fecosterol* (II), $C_{27}H_{46}O$ (one double linking), m. p. 161—163°, $[\alpha]_D^{25} + 42.1^\circ$ (benzoate, m. p. 144—146°; $[\alpha]_D^{25} + 34.7^\circ$; acetate, m. p. 159—161°); *ascosterol* (III), $C_{27}H_{46}O$, m. p. 141—142°, $[\alpha]_D^{25} + 45^\circ$ (benzoate, m. p. 130—131°, $[\alpha]_D + 37^\circ$), and *neosterol* (IV), probably $C_{27}H_{44}O$, m. p. 164—165°, $[\alpha]_D^{25} - 105^\circ$ (benzoate, m. p. 173—175°, $[\alpha]_D - 50.6^\circ$; acetate, m. p. 173—174°). The colour reactions of ergosterol and IV are identical, as are those of II and III. The colour reactions of I differ from those of II and III.

H. BURTON.

Determination of micro-organisms in suspension. R. J. WILLIAMS, E. D. MCALISTER, and R. R. ROEHM (J. Biol. Chem., 1929, 83, 315—320).—The density of a suspension of yeast or other micro-organisms can be determined by observing the effect of interposition of a cell containing the suspension between a small electric light and a thermo-couple connected with a galvanometer. C. R. HARRINGTON.

Methods of studying the surfaces of living cells, with special reference to the relation between the surface properties and the phagocytosis of bacteria. S. MUDD, M. LUCKE, M. MCCUTCHEON, and M. STRUMIA (Coll. Symp. Mon., 1928, 6, 131—138).—A study of bacteria treated with normal and immune sera leads to an expression of the mechanism of the action of opsonins and bacteriotropins in physico-chemical terms.

CHEMICAL ABSTRACTS.

Butyric acid fermentation of calcium lactate. V. N. SHAPOSHNIKOV and I. P. ZAKHAROV (Trans. Sci. Chem.-Pharm. Inst. Moscow, 1927, No. 18, 7—25).—The acids produced by fermentation of calcium lactate with a mixed culture consisted of butyric, acetic, and succinic, with small amounts of formic, valeric, and hexoic acids. Only small amounts of ethyl and propyl alcohols were produced.

CHEMICAL ABSTRACTS.

Metabolism of *Vibrio cholerae* in aerobic and anaerobic culture. J. HIRSCH (Z. Hyg. Infekt.-Krankh., 1928, 109, 387—409; Chem. Zentr., 1929, i, 1360).—The aerophilic behaviour of *Vibrio cholerae* in amino-acid or peptone solutions free from carbohydrate is attributed to the substrate; the bacillus grows under strictly anaerobic conditions on carbohydrates, which are preferred to amino-acids as a source of energy. The significance of amino-acid or peptone for growth in saccharine medium lies chiefly in its being a source of nitrogen. The anoxybiotic decomposition of dextrose by *V. cholerae* proceeds in two independent ways: $C_6H_{12}O_6 = 2CH_3 \cdot CH(OH) \cdot CO_2H$, and $C_6H_{12}O_6 + H_2O = 2H \cdot CO_2H + CH_3 \cdot CO_2H + CH_3 \cdot CH_2 \cdot OH$.

A. A. ELDRIDGE.

Oxidation-reduction equilibria in biological systems. II. Potentials of aerobic cultures of *Bacillus typhosus*. C. B. COULTER and M. L. ISAACS (J. Exp. Med., 1929, 49, 711—725).

Precipitable substances of bacilli of the salmonella group. J. FÜRTH and K. LANDSTEINER (J. Exp. Med., 1929, 49, 727—743).—Specific precipitable substances rich in carbohydrates, containing very little protein and small quantities of a material apparently of fatty nature, have been

prepared from the main serological types of the typhoid-paratyphoid groups. Pronounced chemical differences have not been observed.

CHEMICAL ABSTRACTS.

"Soluble specific substance" derived from gum arabic. M. HEIDELBERGER, O. T. AVERY, and W. F. GOEBEL (J. Exp. Med., 1929, 49, 847—857).—Partial acid hydrolysis of gum arabic affords a specific carbohydrate comparable in precipitating activity for types II and III antipneumococcus serum with the bacterial soluble specific substances themselves. Hydrolysis affords galactose and two or more complex sugar acids, one of which appears to be a disaccharide acid comparable with those of bacterial origin.

CHEMICAL ABSTRACTS.

Fractionation of diphtheria antitoxic plasmas. P. J. MOLONEY and E. M. TAYLOR (Coll. Symp. Mon., 1928, 6, 109—114).—The antitoxin was precipitated with alcohol, tannin, and Biebrich-scarlet at various p_H values, and its stability with respect to p_H and alcohol was determined.

CHEMICAL ABSTRACTS.

Influence of boric acid on *Micrococcus ureae* and urease in presence of dextrose: J. VOICU (Bul. Soc. Chim. Romania, 1929, 11, 25—28).—The inhibitory effect of boric acid on the hydrolysis of urea by urease and by a species of *M. ureae* is considerably diminished by the presence of dextrose.

A. A. GOLDBERG.

Presence of adrenaline in the suprarenals in the human and bovine foetus. S. SAITO (Tohoku J. Exp. Med., 1929, 12, 251—262).—The suprarenals of the bovine foetus (4—8 months) contain proportionally as much adrenaline as the adult glands. Values (mg. per g. of gland) for the human foetus are: 12 weeks, 0; 5 months, 0.82 (Folin); 0.02 (biological); full-term, 2.45 (Folin), 0 (biological).

CHEMICAL ABSTRACTS.

Determination of adrenaline in organs by means of the spectrophotometer. I. Adrenaline content of the adrenals. H. HANDOVSKY and A. REUSS (Arch. exp. Path. Pharm., 1929, 144, 105—122).—Details are given of the spectrophotometric determination of adrenaline in alcoholic extracts of the adrenal medulla. The results agree well with those obtained by the biological blood-pressure method.

W. O. KERMACK.

Influence of adrenaline on formation of sugar. II. Mobilisation of muscle-glycogen by adrenaline. E. GEIGER and E. SCHMIDT (Arch. exp. Path. Pharm., 1929, 143, 321—328; cf. A., 1928, 1160).—In fasting phloridzinised dogs a first injection of adrenaline leads to increase in the amount of blood-lactic acid, but there is no increase following a second injection. The administration of adrenaline leads to conversion of the muscle-glycogen into lactic acid which, passing into the blood stream and thence into the liver, is there reconverted into glycogen and immediately, as a result of phloridzin, excreted as extra sugar. The first adrenaline injection causes decomposition of all the muscle-glycogen. In animals from which the liver has been removed no reconversion of the blood-lactic acid, and consequently no excretion of extra sugar, can occur.

W. MCCARTNEY.

Carbohydrate metabolism. VI. Antagonistic action of pituitrin and adrenaline on carbohydrate metabolism with special reference to gaseous exchange, inorganic blood-phosphate, and blood-sugar. C. G. LAMBIE and F. A. REDHEAD (Biochem. J., 1929, 23, 608—623).—In the human subject pituitrin frequently causes a transient fall in metabolism followed by a rise. Sometimes only a rise is observed. In small doses it causes a slight fall in the inorganic phosphate of the blood. It apparently inhibits the slight rise in metabolism which occurs after the administration of insulin, but the changes produced by either insulin or pituitrin are not sufficiently marked to be of much significance. Pituitrin delays and reduces the rise in metabolism and the fall in blood-sugar following the intravenous administration of dextrose or dihydroxyacetone. In small doses sufficient to prevent the fall in blood-sugar resulting from the administration of insulin it did not prevent the fall in inorganic blood-phosphate. In rabbits large doses of pituitrin cause a transitory rise in the inorganic blood-phosphate and for a short period inhibit the fall in inorganic phosphate resulting from administration of dextrose or dihydroxyacetone. A dose of pituitrin which just suffices to prevent the fall in inorganic phosphate following administration of dextrose may fail to overcome the fall due to dihydroxyacetone. In animals rendered hypoglycaemic as a result of insulin administration pituitrin causes the blood-sugar and inorganic blood-phosphate to return to the normal level or even to exceed it. Adrenaline administered alone causes a marked and rapid rise in metabolism which is not solely dependent on the rise in blood-sugar. It does not inhibit the rise in metabolism following intravenous administration of dextrose. Adrenaline administered in large doses to hypoglycaemic animals causes a rise in inorganic blood-phosphate.

S. S. ZILVA.

Hormones of the anterior pituitary lobe. L. F. HEWITT (Biochem. J., 1929, 23, 718—725).—Preparations are described of filtered alkaline extracts of this gland which promoted growth, unfiltered alkaline extracts which promoted growth and inhibited oestrus, and acid extracts treated with kaolin which produced precocious sexual maturity and caused ripening of Graafian follicles in the rat. When the animals which had been treated with the growth-promoting extracts were no longer injected a rapid fall in weight ensued.

S. S. ZILVA.

Glycosuria and insulin. G. FRICKE (Z. ges. exp. Med., 1929, 64, 81—94; Chem. Zentr., 1929, i, 1363).—By simultaneous administration of dextrose and insulin to the normal dog the dextrose threshold of the kidneys is diminished. In the pancreas-diabetic dog the renal elimination of sugar is increased by the action of insulin with diminishing blood-sugar.

A. A. ELDRIDGE.

Study of sugar regulation by the insulin tolerance test. M. SENDRAIL (Compt. rend. Soc. Biol., 1929, 99, 1901—1903; Chem. Zentr., 1929, i, 1708).

Behaviour of liver-glycogen after oral administration of yeast. A. BICKEL and G. NIGMANN (Biochem. Z., 1929, 210, 443—447).—Administration of

dried yeast to dogs which had been largely freed from liver-glycogen by starving increased the liver-glycogen considerably. This action is not due to organic nutrients in the yeast, but to thermolabile substances in the yeast which act similarly to insulin, causing decrease of blood-sugar and increase of liver-glycogen.

P. W. CLUTTERBUCK.

Secretin. II. T. NISHIKAWA (Sei-I-Kwai Med. J., 1928, 47, No. 10).—Hydrochloric acid, but not aqueous or saline, extracts of the bovine duodenum contain activated secretin. Atropine inhibits the action of choline or histamine on pancreatic secretin.

CHEMICAL ABSTRACTS.

Preparation of the female sexual hormone from urine in pregnancy. S. VESHNJAKOV and A. LIPSCHUTZ (Biochem. Z., 1929, 210, 348—352).—A method of preparation is described which gave 4800 mouse units per litre of urine, the unit after purification weighing 0.01 mg.

P. W. CLUTTERBUCK.

Absorption spectrum of vitamin-A. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1929, 23, 633).—Dehydroergosterol, which is devoid of growth-promoting properties and does not give the blue colour reaction with arsenic or antimony trichloride, shows a selective absorption in the ultra-violet region at about 320—328 μ . The absorption is therefore not specific for vitamin-A (cf. Takahashi and others, A., 1925, i, 1365; Morton and Heilbron, A., 1928, 1058). The peroxide of dehydroergosterol is also biologically inactive.

S. S. ZILVA.

Nature of the vitamin-A constituent of green leaves. D. L. COLLISON, E. M. HUME, I. SMEDLEY-MACLEAN, and H. H. SMITH (Biochem. J., 1929, 23, 634—647; cf. Euler and others, this vol., 358, 610; Duliere, Morton, and Drummond, Chem. and Ind., 1929, 48, 518; Moore, Lancet, 1929, i, 499).—The unsaponifiable material from green cabbage contains at least ten times as much vitamin-A as that from white cabbage. The vitamin-A of green spinach and cabbage leaves and of carrots is present in the most highly-unsaturated fraction of the unsaponifiable matter and remains associated with the carotin. It was not diminished in specimens of carotin and crystals of higher m. p. and therefore of presumably greater purity (active dose 0.002—0.005 mg.). The carotin from cabbage softened at 174° and melted at 178°, that from spinach at 163—164°, and that from carrots at 164—169°. Since the observations of Drummond and co-workers (who found carotin inactive) were made on a fat-free diet, it is suggested that either the presence of fat or of something in the unsaponifiable fraction of the fat is possibly necessary for the utilisation of carotin.

S. S. ZILVA.

Vitamin-A and carotin. Association of vitamin-A activity with carotin in the carrot root. T. MOORE (Biochem. J., 1929, 23, 803—811).—By using a basal diet containing vitamin-D it was found that daily doses of 100 mg. of fresh carrot sufficed to cure xerophthalmia and restore good growth in rats deprived of vitamin-A. Carrot-fat from which much of the carotin had been removed was found active in a dose of 0.4 mg. daily. Carotin

(m. p. 174° in air) was found even after many recrystallisations to be active in doses of 0.01 mg. A possible explanation of the divergent results of others may lie in unsuspected differences in biological technique.

S. S. ZILVA.

Assay of vitamin-A. J. C. DRUMMOND and R. A. MORTON (Biochem. J., 1929, 23, 785—802).—A comparative study of the assay of vitamin-A in cod-liver oils by the biological, colorimetric, and spectroscopic (intensity of absorption band at 328 μ) methods is described. Even with the use of large number of rats, quantitative differences in vitamin-A potency of less than 100% could not be detected by the biological method. The relative values of the potency of the oils obtained by the three methods were in agreement. The results of the colorimetric and spectrographic methods were very concordant.

S. S. ZILVA.

Biological and colorimetric assay of vitamin-A in fish oils. E. R. NORRIS and I. S. DANIELSON (J. Biol. Chem., 1929, 83, 469—475).—The intensity of colour produced by treatment of fish oils with antimony trichloride is approximately proportional to the amount of oil employed only at very low concentrations. By working at such low concentrations, colorimetric results in good agreement with those of biological determinations are obtained.

C. R. HARRINGTON.

Analytical remarks on vitamin-A. S. H. BERTRAM (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 664—668).—A "daylight" lamp is recommended for tintometer readings with the blue colour produced by the interaction of antimony trichloride and vitamin-A. Turbidity is often caused by basic substances such as amines or by traces of soaps, and can be avoided by adding a negligibly small volume of acetic anhydride after adding the trichloride solution. The blue colour is not quite specific and is thought to arise from the condensation of vitamin-A with impurities (perhaps aldehydic) or with itself. The reaction is probably due to a definite group, which may be present in oxycholesterol. This compound does not prevent xerophthalmia. The carotinoids in general give blue colours with antimony trichloride, indicating that conjugated double linkings are necessary. Vitamin-A and carotin can be brominated in light petroleum (the products no longer giving blue colours) and debrominated with zinc dust and acetic acid, the resulting products again giving blue colours. The colour reaction with phloroglucinol in alcohol and a few drops of hydrochloric acid is given by vitamin-A preparations, but not by carotin. Of the fats studied by the author only those containing vaccenic acid contain vitamin-A. If, as there is some evidence, oleic acid is the parent substance of cholesterol, a genetic relationship between vaccenic acid and vitamin-A seems possible. All estimates of the vitamin-A content of foods, oils, etc. based on the colorimetric method must be accepted with the utmost reserve unless the presence of bixin and carotinoids has been excluded. An extract of green cabbage leaves gave the blue colour and the phloroglucinol reaction and also showed growth-promoting and antixerophthalmic properties.

R. A. MORTON.

Antimony trichloride colour test for vitamin-A. N. EVERS (Quart. J. Pharm., 1929, 2, 227—237).—Solutions of antimony trichloride obtained from different sources after recrystallisation from anhydrous chloroform and not more than 1 month old give lower but more consistent results than those prepared from samples of antimony chloride which have been merely washed with chloroform or kept for more than 1 month. Since the colorimetric readings obtained are not proportional to the concentration of the oil in the reaction mixture, the quantity of oil used is an important factor, especially with highly active fats, e.g., ox-liver fat; such errors are minimised by the addition of an inactive oil (arachis oil) so that the concentration of oil in the reaction mixture is about 2%. The natural colouring matter of ox-liver fat affects the determinations. C. C. N. VASS.

Effect of p_H on thermolability of vitamin-B of yeast. R. R. WILLIAMS, R. E. WATERMAN, and S. GURIN (J. Biol. Chem., 1929, 83, 321—330).—Vitamin- B_1 in brewer's yeast is not completely destroyed by autoclaving for 6 hrs. at 15 lb. pressure unless the yeast be first rendered alkaline; the vitamin- B_1 of the relatively alkaline baker's yeast is destroyed by such treatment. In no case could complete removal of vitamin- B_1 be achieved without considerable simultaneous loss of vitamin- B_2 .

C. R. HARRINGTON.

Sparing action of fat on vitamin- B_1 . H. M. EVANS and S. LEPKOVSKY (J. Biol. Chem., 1929, 83, 269—287).—Growing rats on a diet of very low fat content, but receiving supposedly adequate amounts of the various vitamins, showed marked improvement if the diet were supplemented either with fat (free from vitamin- B_1) or with an extra amount of a substance rich in vitamin- B_1 ; it thus appears that fat exercises a sparing action on this vitamin.

C. R. HARRINGTON.

Second thermolabile water-soluble accessory factor necessary for the nutrition of the rat. V. READER (Biochem. J., 1929, 23, 689—694).—Rats which grow satisfactorily on a basal diet supplemented with marmite failed to grow when this untreated yeast extract was replaced by one which had been previously subjected to alkaline hydrolysis (p_H 9) for 1 hr. at 120°, even when vitamin- B_1 (the treated marmite contained vitamin- B_2) was supplied in the form of Peters' extract. This failure to grow is due to the destruction of a factor B_3 in the marmite in the process of hydrolysis. Vitamin- B_3 is more thermolabile than vitamin- B_1 . Extraction with ether removed the vitamin- B_3 activity of marmite, but no active substance could be recovered from the ethereal extract. S. S. ZILVA.

Vitamin-B. R. A. PETERS (Nature, 1929, 124, 411).—The factor discovered by Reader (preceding abstract) differs from that discovered by Hunt (A., 1928, 1405) and from Williams and Waterman's (A., 1928, 1058) thermolabile factor. At least five B-factors have now been described.

A. A. ELDRIDGE.

Distribution of vitamins-B and -C in young plants. C. KUCERA (Compt. rend. Soc. Biol., 1928, 99, 971—972; Chem. Zentr., 1929, i, 1705).—Whilst

vitamin-C is present in all parts of the young plant, vitamin-B is present only in the seed.

A. A. ELDRIDGE.

Action of vitamins and surface activity. III. Parallelism between the changes of antiscorbutic action and the surface activity of cabbage juice. N. E. SCHEPILEVSKAJA (Biochem. Z., 1929, 210, 334—347).—The parallelism between changes of surface activity and vitamin action of cabbage juice as described by Hahn (A., 1925, ii, 664; 1926, 760) does not exist. P. W. CLUTTERBUCK.

Vitamin-D in ergot of rye. E. MELLANBY, E. SURE, and D. C. HARRISON (Biochem. J., 1929, 23, 710—717).—Ergot of rye is a powerful stimulus to calcification of bone. The factor responsible for this action is soluble in alcohol and ether, is present in the unsaponifiable fraction, and possesses the properties of vitamin-D. Rye germ, not affected by the ergot fungus, contains a small quantity of calcifying substance which can be extracted by light petroleum. The irradiation of unground ergot grains by strong sunlight produces no increase and the irradiation by the mercury-vapour lamp only a slight increase in the calcifying activity of ergot, although there is abundant ergosterol present. S. S. ZILVA.

Nature of the rickets-producing factor in cereals. L. MIRVISH (Nature, 1929, 124, 410—411).—Oatmeal contains a substance which, when injected into rabbits, lowers the blood-calcium, the character of the effect being the same as that produced by extracts of bovine ovaries. Hence rickets is not purely a condition of vitamin deficiency.

A. A. ELDRIDGE.

Existence of a further factor necessary for growth of the rat. K. H. COWARD, K. M. KEY, and B. G. E. MORGAN (Biochem. J., 1929, 23, 695—709).—Rats often cease to grow on a diet satisfactory in calorific value, salt content, digestibility, and content of recognised vitamins when "vitamin-free casein" (Glaxo) is used. Resumption of growth takes place when this casein is replaced by "light white casein" (B.D.H.) or by the addition of certain substances such as fresh milk, lettuce, fresh and dried grass, ox-muscle, liver, or wheat embryo. Less rapid growth is brought about by water-cress and milk which has been boiled for 15 min. Butter and etiolated wheat shoots show little activity in this respect. Heat impairs the power of "light white casein" to cause growth. Treatment with cold alcohol, ether, or 2% acetic acid does not damage this property of the casein. Extraction with boiling alcohol and ether gives slightly active extracts and leaves definitely impaired casein. Boiling alcohol (90%) and ether yield extracts of definite activity from wheat embryo. S. S. ZILVA.

Avitaminosis and hæmatopoietic function. I. Vitamin-A deficiency. II. Vitamin-B deficiency. III. Vitamin-E deficiency. B. SURE, M. C. KIK, and D. J. WALKER (J. Biol. Chem., 1929, 83, 375—385, 387—400, 401—408).—I. In the early stages of vitamin-A deficiency there is a slight reduction in the number of red corpuscles and in the amount of hæmoglobin in the blood; in the later

stages the effect of inanition in causing a concentration of the blood is predominant.

II. The blood-picture in vitamin-B deficiency is in general similar to that observed in deficiency of vitamin-A, with, in addition, marked reduction of the serum-proteins in the anæmic stage.

III. Vitamin-E has no effect on the hæmatopoietic function. Neither ferric citrate nor the ash of lettuce was capable of relieving sterility in females on diets deficient in vitamin-E. C. R. HARRINGTON.

Behaviour of nitrogenous compounds during germination. R. BONNET (Compt. rend., 1929, 189, 373—375).—Seeds of *Lupinus luteus* and *Ervum lens* were grown in the dark in distilled water at 20° for 15 days and the various nitrogen fractions determined at different stages. Before germination the bulk of the nitrogen is in the form of protein (85%), which breaks down during germination, giving rise to ammonia etc. and amino-acids (largely asparagine, the formation of which corresponds with that of urea in the animal kingdom). Urea and allantoic acid are waste materials in the plant and nitrates do not appear to play any part in nitrogen metabolism during germination. P. G. MARSHALL.

Transformation (particularly saponification) of the reserve fat of seeds during germination. J. LEMARCHANDS (Compt. rend., 1929, 189, 375—377).—Ungerminated seeds constitute a neutral medium in which mineral salts occur in very small amount, whereas germinating seeds constitute an acid medium consisting chiefly of acid phosphates (produced by hydrolysis of an organic phosphorus compound) together with some free phosphoric acid, sulphates, and chlorides, and free fatty acids. The cytoplasm of sunflower seed has no lipolytic activity, but that of the castor seed has a powerful action which is promoted most effectively by the acid phosphates of calcium and magnesium.

The mol. wt. of the fatty acids of sunflower-seed oil remains constant at about 292 in the initial stages of germination and rises to about 353 in the final stages. Saponification of the fats therefore takes place before utilisation of the fatty acids, the latter process beginning with the unsaturated acids. Aldehydes, produced by oxidation of the fatty acids, have only a transitory existence. P. G. MARSHALL.

Formation of xanthophyll, carotin, and chlorophyll in barley germinated in light and in darkness. H. VON EULER and H. HELLSTRÖM (Z. physiol. Chem., 1929, 183, 177—183; cf. this vol., 848).—The chlorophyll, xanthophyll, and carotin content of germinating barley shoots was determined. The germination was allowed to proceed in the dark for 9 days; some of the shoots were then exposed to light. The xanthophyll content increased at a steady rate until the 9th day; the rate then diminished in both cases but much more in the etiolated shoots. The chlorophyll and carotin corresponded closely; both were practically absent from plants germinated in the dark. J. H. BIRKINSHAW.

Quantitative changes in chloroplast pigments in the peel of bananas during ripening. H. VON LOESECKE (J. Amer. Chem. Soc., 1929, 51, 2439—

2443).—Determinations of the amounts of chlorophyll ($a+b$), xanthophyll, and carotin present in the green and yellow skins of a variety of *Musa sapientum* show that the chlorophyll content decreases to zero as a linear function of time during the change from green to yellow, whilst the amount of yellow pigment (xanthophyll+carotin) remains unchanged. The amount of xanthophyll is always greater than that of carotin, but the ratio changes during ripening. H. BURTON.

Zinc content of vegetable foods. G. BERTRAND and B. BENZON (Ann. Inst. Pasteur, 1929, 43, 386—393).—See this vol., 362.

Variation of colour of plants during desiccation. Glucoside of *Lathræa clandestina*, L., is aucubin. M. BRIDEL (J. Pharm. Chim., 1929, [viii], 10, 97—110).—See this vol., 857.

"Minjak pelandjau," the exudation from the wood of *Pentaspadon Motleyi*, Hook. P. VAN ROMBURGH and A. G. VAN VEEN (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 692—697).—The exudation consists mainly of a crystalline acid, $C_{24}H_{36}O_3$, m. p. 25—26°, n_D^{20} 1.5225, d_4^{25} 1.005, having five ethylenic linkings, one hydroxyl group, and a ring system. Oxidation with potassium permanganate gave azelaic and suberic acids. Propaldehyde, hexoic acid or one of its isomerides, oxalic acid, and azelaic acid were obtained by the ozonisation of the methyl ester and subsequent decomposition of the ozonide. N. M. BLYTH.

Spike disease of sandal (*Santalum album*). IV. **Chemical composition of healthy and spiked sandal stems.** D. A. R. RAO and M. SREENIVASAYA (J. Indian Inst. Sci., 1929, 11A, 241—243).—The diseased stems of *Santalum album* have usually a low content of ash, calcium, and potassium, and a high content of nitrogen, phosphorus, and starch as compared with healthy stems. W. O. KERMACK.

Micro-determination of calcium. P. L. KIRK and C. L. A. SCHMIDT (J. Biol. Chem., 1929, 83, 311—314).—A special filter is described for the separation of minute amounts of calcium oxalate which makes possible a simplification of the method of Kramer and Tisdall (A., 1921, ii, 595) for the determination of calcium. C. R. HARRINGTON.

[Iodine determination.] G. PFEIFFER (Biochem. Z., 1929, 210, 231—233).—The modifications in the author's method proposed by Glimm and Isenbruch (this vol., 838) are unnecessary. J. H. BIRKINSHAW.

Manometric determination of amino-nitrogen. D. D. VAN SLYKE (J. Biol. Chem., 1929, 83, 425—447).—The solution is introduced into the apparatus of Van Slyke and Neill (A., 1924, ii, 872) and treated with sodium nitrite and acetic acid; the liberated gases are transferred to an absorption pipette containing alkaline permanganate, and the liberated nitrogen is returned to the apparatus and determined manometrically. The method is capable of determining 0.0005 mg. of amino-nitrogen and can therefore be applied directly to a protein-free blood filtrate, the carbamide being either determined separately or destroyed with urease. C. R. HARRINGTON.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1929.

General, Physical, and Inorganic Chemistry.

Method for obtaining simplified spectra. B. DE LA ROCHE (Bull. Soc. chim., 1929, [iv], 45, 706—707).—Electrodes of purified carbon with a gap of about 25 mm. are placed horizontally in the flame of a Méker burner so that the whole gap is in the flame. A condenser of 0.01—0.02 mf. capacity with a self-induction of 0.02—0.05 Henry in the circuit is discharged across the electrodes, a solution of the salt to be examined being simultaneously atomised and passed into the flame. The spectrum shows only the principal lines and "raies ultimes"; the spectrum of the surrounding gas disappears entirely.

C. A. SILBERRAD.

Absorption of the H_α line. T. TAKAMINE and T. SUGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 193—197).—The intensity distribution in the reversed H_α line has been investigated by a method similar to that of Ladenburg and Loria (Verh. Deut. physikal. Ges., 1908, 10, 858). The "black" and "white" stages described by Wood (A., 1926, 1069) were observed also when a strongly condensed discharge was passed through hydrogen. Only when the "black" stage was obtained in the absorption tube was the core of the H_α line quite black.

J. W. SMITH.

Spectrum of H_2 bands analogous to the ortho-helium line spectrum. II. O. W. RICHARDSON and K. DAS (Proc. Roy. Soc., 1929, A, 125, 309—330; cf. this vol., 375).—The bands recently discovered by Sandeman (Proc. Roy. Soc. Edin., 1929, 49, 245) make it necessary to reconsider the structure of the band system formerly called $3^3S \rightarrow 2^3S$. Evidence is adduced in support of the view that the upper electronic level is a 2 state and the symbol $2^3S'$ is provisionally assigned to it. A detailed description is given of this system and also of the system $3^3S' \rightarrow 2^3S$ (R strong, P weak). The following values are calculated: for $2^3S'$: $\nu_e = 17733$, $\omega_0 = 2130$, $x\omega_0 = 67$, $B_0 = 26.54$ wave numbers, $r_0 = 1.119 \times 10^{-8}$ cm., D (heat of dissociation) = 1.42_5 volts; for $3^3S'$: $\nu_e = 8810$, $\omega_0 = 2184$ (?), $x\omega_0 = 43$ (?), $B_0 = 28.52$ wave numbers, $r_0 = 1.114 \times 10^{-8}$ cm., $D = 2.20_5$ volts. Two new progressions ending on 2^3S are also described. An investigation of vibrational and rotational structures of the initial levels of the bands indicates that these probably constitute the $n' = 5$ and $n' = 6$ progressions of $2^3S' \rightarrow 2^3S$. A new band in the yellow, of which the final state appears to be the vibrational state $n'' = 1$ of 2^3S , is described.

L. L. BIRCUMSHAW.

New regularities in the band spectrum of helium. III. G. H. DIEKE, S. IMANISHI, and T.

TAKAMINE (Z. Physik, 1929, 57, 305—325; cf. A., 1928, 677, 1295; this vol., 732).—Bands which correspond with the combinations of $4s$, $5s$, $6s$, $4d$, $5d$, and $6d$ terms with a new end term are investigated. The end term $2s'$ is expressed as $2\pi^3\Sigma$ and is analogous to the B -state of the hydrogen molecule. A number of bands have the $2p$ -state as end term.

A. J. MEE.

Probability of the forbidden s,d switch in the alkali metals. V. PROKORIEV (Z. Physik, 1929, 57, 387—393).—By investigating the anomalous dispersion of the forbidden lines, $1s-3d$, of the alkali metals the probability of switch was found. It is approximately equal for all the alkali metals and is of the order 10^{-5} to 10^{-6} . For caesium, the probability for the $1s-4d$ lines is approximately equal to that for the $1s-3d$ lines. The $1s-3d$ doublet of caesium was investigated and the intensity ratio of its components found to be 1.4 within an accuracy of 10%.

A. J. MEE.

Spectrum of beryllium. W. H. SANDERS and V. M. ALBERS (Physical Rev., 1928, [ii], 31, 151).—No lines of wave-length greater than 5271 Å. have been photographed with the vacuum spark, but some appear between 5000 and 8500 Å. when an air spark is used as a source. The band spectrum of the oxide is strong when the arc in air is used as source and weaker with the spark in air.

L. S. THEOBALD.

Spectra of boron. W. D. LANSING and W. F. TYLER (Trans. Illinois Acad. Sci., 1928, 21, 210—211).—The preparation of the material for a study of the spectral regions 2050—5200 and 4500—6880 Å. is described.

CHEMICAL ABSTRACTS.

Pressure shift in the spectrum of ionised nitrogen. W. E. PRETTY (Proc. Physical Soc., 1929, 41, 442—455).—The shifting of certain lines in the spectrum $N II$ caused by a change in the pressure of gas in the discharge tube is investigated. More than 80 lines in the region λ 6800—1850 were found to shift, and the amount in most cases was measured. The shift is in the direction of increasing wave-length in all cases. The shifts are considered in relation to the terms giving rise to the lines concerned and three new singlet terms identified. It is concluded that the phenomenon is in the main a Stark effect.

C. J. SMITHELLS.

Cathode phenomena in Geissler discharges through oxygen and nitrogen. (Miss) N. M. CARMICHAEL (Phil. Mag., 1929, [vii], 8, 362—368).—A search was made in the Geissler discharges through

oxygen and nitrogen for a primary dark space, the absence of which, in these gases, was not explained by a recent theory (cf. A., 1928, 677). The results were negative. A new dark space was discovered in the discharge through oxygen between the negative glow and the cathode dark space, and was investigated by the method of exploring electrodes; it appears to be a positive ion sheath between these two regions of the discharge. N. M. BLIGH.

Spectrum of the negative glow in oxygen. K. G. EMELEUS and (MRS.) F. M. EMELEUS (Phil. Mag., 1928, [vii], 8, 383—392; cf. Seeliger and Lindow, A., 1925, ii, 739).—A detailed investigation of the negative glow in oxygen was made, using a discharge tube with electrodes of degassed nickel. In addition to the visible and ultra-violet negative bands of oxygen, the ozone bands, and the nickel lines, there were present lines of O I, O II, and O III; O IV lines were not detected. The spectroscopic data and discharge conditions are correlated; the ionisation is treated with the help of the Langmuir analysis. Three groups of electrons are present and the number in each group able to effect ionisation at dissociation voltages is calculated irrespective of probability considerations. N. M. BLIGH.

Higher spark spectra of neon and argon in the extreme ultra-violet. J. C. BOYCE and K. T. COMPTON (Proc. Nat. Acad. Sci., 1929, 15, 656—658; cf. A., 1928, 338, 565, 1067).—By using an electrodeless ring discharge, the lines due to Ne III, Ne IV, A III, and A IV were investigated and their measurements and classification are tabulated. The lowest ionisation limit of Ne III was 63.2 volts and of A III 40.7 volts. N. M. BLIGH.

Afterglow of lamps containing neon, argon, and a mixture of neon with a little argon. M. J. DRUYVESTEYN (Z. Physik, 1929, 57, 292—304).—The afterglow of lamps filled with neon, argon, and neon with 0.5—3% of argon was investigated by visual and photographic methods. By comparing the spectrum of the afterglow with that of the principal discharge it is possible to find out whether the principal discharge is an excitation or a recombination glow. In pure neon the glow contains the lines due to atoms and positive ions. The strongest lines were the red arc lines, 1s—2p. The argon spectrum is similar. With 0.5—3% of argon, the neon lines were confined to the discharge glow, whilst the argon lines appeared only in the aurora. The following statements appear to be justified. In the first place, the glow in argon is chiefly an excitation glow. Secondly, the argon glow in the neon+argon tube is chiefly a recombination glow. Thirdly, the afterglow is a recombination glow for both the argon and neon+argon tubes. The use of the afterglow affords a simple means of separating lines due to atoms and positive ions. A. J. MEE.

Influence of foreign gases on the intensities of the magnesium resonance lines 4571 and 2852. J. G. FRAYNE (Physical Rev., 1929, [ii], 34, 590—596).—The 4571 line, which is weak in the arc, was obtained fairly prominently when magnesium vapour at 500° was excited in an evacuated tube by an

electrodeless short-wave discharge. The inert gases enhanced the line, the intensity relative to the triplet 3838 increasing up to about 20 mm. in argon and 10 mm. in neon and helium. At these pressures argon increased the line 100, neon 70, and helium 40 times; nitrogen and carbon monoxide increased it up to about 2 mm.; hydrogen caused a slight increase at about 2 mm. Intensity-pressure curves are given and analysed mathematically. Collisions of excited metastable atoms with the walls are shown to be of the second kind, and the enhancing action of the inert gases is shown to be one of reducing diffusion to the walls. All gases reduced the line 2852 in intensity, and also all singlets terminating on the 3^1P level. Increasing pressure of hydrogen reduced the line intensity faster than that of the singlets. Dissociation of the hydrogen molecule by magnesium atoms in the 3^1P state reduced radiation from that state. N. M. BLIGH.

New terms in the spectra of Al I, Ga I, and In I. W. D. LANSING (Physical Rev., 1929, [ii], 34, 597—598).—The spectra were investigated, using a tungsten vacuum furnace. Lines arising from the term sp^2-D were discovered in Al I. No emission lines of gallium were observed. A $2P-4P$ combination was found in In I from previous data. N. M. BLIGH.

Vacuum spark spectrum of aluminium. R. F. PATON and G. M. RASSWEILER (Physical Rev., 1928, [ii], 31, 151).—Forty lines between 2200 and 5000 Å. have been obtained with high vacua. L. S. THEOBALD.

Spectrum of phosphorus in the extreme ultra-violet. P. QUENEY (J. Phys. Radium, 1929, [vi], 10, 299—302).—The spectrum of phosphorus was investigated by the electrodeless discharge for the range 1200—2700 Å. Complete wave-lengths and intensities are tabulated. In addition to known lines about 250 new lines were found. N. M. BLIGH.

Band systems of titanium oxide. F. LOWATER (Proc. Physical Soc., 1929, 41, 557—568).—The bands of TiO have been extended towards the infra-red some 800 Å. further than the range previously known. Bands in the orange, red, and infra-red regions have been analysed into two systems, distinct from the blue-green system. One of these is due to the transition $^1\Pi \rightarrow ^1\Sigma$, the other to $^3\Sigma \rightarrow ^3\Pi$, the latter having the same final energy level as the blue-green system $^3\Pi \rightarrow ^3\Pi$. C. J. SMITHELLS.

Spectrum of gallium II and the $(4s4p^2)$ configuration in gallium I and indium I. R. A. SAWYER and R. J. LANG (Physical Rev., 1929, [ii], 34, 712—719; cf. Lang, A., 1928, 99; Rao, A., 1927, 390).—The spectrum of gallium excited in a hollow cathode discharge in helium was photographed in the region λ 10000—200, and about 90 lines excited were classified in singlet and triplet series of Ga II. Absolute term values are calculated and the lowest term is $(4s^2)^1S=165458$ corresponding with an ionisation potential for Ga II of 20.43 volts. Classified lines and term values are tabulated. The lines arising from combinations of $(4p^2)^4P$ and $(4p^2)^2S$ with $(4s4p)^2P$ of Ga I were identified and term values are given. For the indium spectrum in helium $(4p^2)^4P$

of In I was located, and its term values and combinations with $(4s4p)^2P$ are given. N. M. BLIGH.

Spark spectra of germanium. R. J. LANG (Physical Rev., 1929, [ii], 34, 697—711; cf. A., 1928, 99; Rao and Narayan, *ibid.*, 929).—The first three spark spectra of germanium were extended by the discovery of new terms and combinations: Ge II $4p^2\ ^2S$ and $p^3\ ^2P$. Ge III $4s^4\ S_0$, $5s^4\ S_0$, $4p^1P_1$, $5s^1P_1$, $4d^1D_2$, $4f^1F_3$, $4p^1D_2$, $4d^1P_1$, $4f^1D_2$, $4d^1D_2$, and possibly $5g^3G^1G$. Ge IV $d^{10}p^2P$, $d^{10}5g^2G$, d^8s^2D . A full classification of the lines of Ge II, Ge III, and Ge IV is given. N. M. BLIGH.

Absorption of light by bromine and iodine. P. BOVIS (J. Phys. Radium, 1929, [vi], 10, 267—272).—Films of solid iodine, liquid bromine, and solutions of bromine in organic solvents, a few microns thick, were prepared between quartz plates, and absorption spectra down to wave-length 0.290 μ obtained. All the spectra are characterised by two bands, the larger of which is in the region of shorter wave-length. This also applies to solutions, and the previous distinction between brown and violet solutions of iodine and bromine is attributed to the attenuation of the band in the visible region. The spectral absorption of chlorine, bromine, and iodine in the gaseous state shows a shift in the position of the two bands towards longer wave-length with increasing at. wt. The same bands exist in the liquid state, the weaker one occupying exactly the same position as in the vapour, but the bands partly overlap. As the physical state becomes denser the ultra-violet band extends until it becomes continuous with the violet band.

C. J. SMITHELLS.

Series in the arc spectrum of bromine. T. L. DE BRUIN and C. C. KIESS (Science, 1929, 69, 360—361).—The arc spectrum of bromine has been photographed beyond 9300 Å. in the infra-red, and with the help of Turner's data (A., 1926, 550) the structure of the arc spectrum of Br I has been worked out. Certain of the terms form a Rydberg series and give a calculated ionisation potential of 12.2 volts for the neutral bromine atom.

L. S. THEOBALD.

Resonance radiation of silver vapour. W. KAPUŚCINSKI (Bull. Acad. Polonaise, 1929, A, 284—286).—To examine the resonance radiation of silver vapour a silver wire was heated to 900° in a quartz vessel and the vapour illuminated by the light from a condensed spark passed between silver electrodes. The spectrum of the resultant fluorescence was photographed (exposure 10 hrs.). The two resonance lines (3280.66 and 3382.86 Å.) appeared much stronger in the fluorescence than in the control spectrum. The resonance radiation first became perceptible at 780° (pressure of silver vapour 10^{-3} mm.), and increased steadily in intensity to 900°. These results are further confirmed by the absence of fluorescence if the source of light is a condensed spark between copper electrodes. C. A. SILBERRAD.

Band spectrum of lanthanum monoxide. W. JEVONS (Proc. Physical Soc., 1929, 41, 520—545).—The spectrum has been observed from λ 8700 to 2850 Å., and the band-heads, mostly not hitherto recorded, are arranged into several systems. The analysis

differs in some respects from that of Mecke. A note on the general theory of electronic band spectra of diatomic molecules is given. C. J. SMITHELLS.

Hyperfine structure in spectral lines, especially those of singly-ionised praseodymium. R. C. GIBBS, H. E. WHITE, and J. E. RUEDY (Proc. Nat. Acad. Sci., 1929, 15, 642—646; cf. King, Astrophys. J., 1928, 68, 194).—The spectrum of Pr II was investigated with high dispersion over the region 3900—5000 Å., and the component separations of 33 lines exhibiting complex structure were measured. All of the completely resolved fine structures consisted of six components. This is shown to be in agreement with quantum theoretical requirements. Nine or ten weaker components are predicted. N. M. BLIGH.

Band spectra of the oxides of praseodymium, neodymium, and samarium. G. PICCARDI (Nature, 1929, 124, 618).—The oxides have been volatilised and their emission spectra between 8000 and 2400 Å. have been photographed. The most intense bands are: praseodymium 6475, 6282, 6022, 5765, 5692, 5597, 5352 Å.; neodymium 6580 Å.; samarium 6506 Å.

A. A. ELDRIDGE.

Zeeman effect for the arc spectrum of gold. A. S. M. SYMONS and J. DALEY (Proc. Physical Soc., 1929, 41, 431—441).—The Zeeman effect for about 50 gold lines has been observed, using a field strength of about 23,000 gauss. McLennan and McLay's assignment of terms to the Au I spectrum is verified to some extent, but modifications are suggested. Suggestions are made as to the identity of a few terms not previously identified. C. J. SMITHELLS.

Variations in the spectrum of the light emitted by quartz mercury lamps. T. TAKAHASHI and L. H. CLARK (J. Sci. Instr., 1929, 6, 273—277).—Variations in the intensity of the light emitted by quartz mercury lamps have been studied photometrically and shown usually to lead to the reversal of the intensities at the extreme ends of the spectra. They are due to irregularities in the curvature and thickness of the quartz envelope and may be eliminated by the insertion of a plane quartz (or pyrex) window in the side of the burner. J. GRANT.

Spectrum of the mercury arc in atmospheres of foreign gases. B. VENKATESACHAR and L. SIBAIYA (Indian J. Physics, 1929, 4, 179—193).—The behaviour of the mercury arc spectrum in the presence of carbon dioxide and of hydrogen has been observed. W. E. DOWNEY.

Fluorescent and phosphorescent excitation of mercury vapour by the resonance frequency and by lower frequencies. (LORD) RAYLEIGH (Proc. Roy. Soc., 1929, A, 125, 1—23).—Experiments are described in which the green band fluorescence is excited in dense mercury vapour by radiation of wave-length 3450 Å., and the spectrum of the fluorescence, consisting of the structureless bands 3300 and 4850 Å., has been photographed with excitation beginning at 3360 Å. and upwards. The fluorescence in the neighbourhood of the resonance line has been observed only with less dense vapour. When excitation extends over the resonance line the fluorescence shows a discontinuity of intensity, and is sharply

divided into "core effect," excited by a range of 0.1 Å. at the resonance line and attributed to line absorption, and "wing effect," excited by the region beyond the atomic line and attributed to band absorption. These effects are examined in a moving stream of vapour (Phillips' effect), the velocity of the stream being under control. Square silica tubes are used. The visual and ultra-violet effects can be separated in space, since the visual core and wing effects begin to pass along the vapour stream at lower velocities than the corresponding ultra-violet effects. With increased velocity of the stream the ultra-violet fluorescence eventually shows persistence also. Starting at atmospheric temperature in a vacuum, it is shown that by raising the temperature a continuous transition can be traced between Wood's "resonance radiation" and the phenomenon of the persistent ultra-violet core effect. L. L. BIRCUMSHAW.

Theory of intermittent action and series spectra. K. C. KAR (Z. Physik, 1929, 57, 416—428).—Mathematical. The Bohr principle of switches from one level to another is considered from the point of view of intermittent action, the theory of which has previously been put forward by the author. A. J. MEE.

Secondary diffraction maxima of spectral lines. A. G. SHENSTONE (Physical Rev., 1929, [ii], 34, 726—729).—The secondary diffraction maxima around a spectral line can be easily photographed under suitable conditions. The relative intensities usually show divergence from Rayleigh's theory, indicating peculiar forms of aberration due to modern spectrographic lenses. The practical difficulties introduced by the peculiar intensities are discussed. N. M. BLIGH.

Anomalous Zeeman effect, Stern and Gerlach's experiment, and the magneton. J. KUNZ (Prob. mod. Physik; Debye-Sommerfeld Festschr., 1928, 25—29; Chem. Zentr., 1929, i, 2619).—A discussion. A. A. ELDRIDGE.

Coarse structure of band spectra. A. KRATZER (Prob. mod. Physik, Debye-Sommerfeld Festschr., 1928, 149—156; Chem. Zentr., 1929, i, 2618).—The formula for the energy of a diatomic molecule is derived from wave-mechanics, and the general disposition of the band edges and the magnitude of the rotation terms are discussed. A. A. ELDRIDGE.

Effect of collisions on the structure of Fraunhofer lines. A. UNSOLD (Prob. mod. Physik; Debye-Sommerfeld Festschr., 1928, 95—104; Chem. Zentr., 1929, i, 2619).—The fact that the light intensity in the centre of a Fraunhofer line is not zero indicates that the theory takes no account of the effect of collisions. A. A. ELDRIDGE.

Emission lines accompanying absorption lines in the spectra of stars. W. H. MCCREA (Z. Physik, 1929, 57, 367—379).—The effect of repeated scattering of light in stellar atmospheres discussed by Franck is further investigated. The cases quoted by Franck of emission lines accompanying the absorption lines are easily explained by gas motion. A. J. MEE.

Absorption lines of the infra-red solar spectrum. C. G. ABBOT and H. B. FREEMAN (Smith-

sonian Miscell. Coll., 1929, 82, 1—17).—Langley's original bolographic investigations were extended with apparatus of higher resolving power, employing three glass prisms. The infra-red solar energy spectrum was recorded on moving photographic plates, three curves being impressed on a single plate. Greatly increased detail was obtained; the identification of the lines by comparator is described; intensities were assigned and wave-lengths determined. Full results for more than 1200 lines are tabulated. N. M. BLIGH.

Satellites of the X-ray lines $L\alpha$, $L\beta_1$, and $L\beta_2$. F. K. RICHTMYER and R. D. RICHTMYER (Physical Rev., 1929, [ii], 34, 574—581).—The X-ray satellites, faint lines which do not fit the energy level diagram, were investigated for the elements rubidium to tin, and were found to be of somewhat complex structure, with a continuous spectrum extending beyond them towards shorter wave-lengths. Tables are given of wave-lengths, values of ν/R , and of $\Delta\nu/R$, where $\Delta\nu$ is the difference in frequency between satellite and parent line, for five to seven satellites of $L\alpha$, four of $L\beta_1$, and five of $L\beta_2$. The empirical relation previously reported (cf. A. 1928, 939) was found to hold. N. M. BLIGH.

Scattering power of X-rays and the electron distribution of the H-ion. J. M. BLIJVOET and W. A. FREDERIKSE (Rec. trav. chim., 1929, 48, 1041—1046).—A quantitative investigation of the diffraction intensities of lithium hydride shows that the observed decline in the scattering power with increasing diffraction angle is in good agreement with that calculated from the atomic model of quantum mechanics. F. G. TRYHORN.

Ratio of intensities of modified to unmodified radiation in scattering of X-rays. E. ALBRECHT (Z. Physik, 1929, 57, 326—340).—The occurrence of the Compton effect is demonstrated by the scattering of hard X-rays from the lighter elements. The method used was that of absorption analysis. Monochromatic rays were used of wave-length 0.210 Å., from the spectrum of a Coolidge tube arranged with a filter. The observations were made with lithium, carbon, silica, aluminium, sulphur, and copper as scattering bodies. With increasing angle of scattering and decreasing atomic number the ratio of modified to unmodified radiation became greater. Lithium shows modified radiation only. The ratio $s_1/(s_1+s_2)$, where s_1 and s_2 represent the intensities of unmodified and modified radiation, respectively, is shown to be proportional to $e^{-c/N}$, where N is the atomic number of the element. The results are compared with those of other workers using softer rays. A. J. MEE.

Critical determination of the K -, L_1 -, and M_1 -levels for the lighter elements. B. C. MUKHERJEE and B. B. RAY (Z. Physik, 1929, 57, 345—353).—It is shown that the true K -absorption limit is calculable from accurate measurement of characteristic X-radiation and optical lines. The values of the L_1 and M_1 levels were also derived by the use of the Sommerfeld regular doublet interval. The curves of $\sqrt{\nu}/R$ against the atomic number were constructed and the discontinuities discussed. The values for the critical potentials of the lighter elements obtained by the

electron collision method are compared with those here derived.

A. J. MEE.

Diffraction of cathode rays. III. G. P. THOMSON (Proc. Roy. Soc., 1929, A, 125, 352—370; cf. A., 1928, 3, 938).—The metal films used in previous work on this subject were prepared from beaten foil thinned in a suitable reagent and were never free from holes. By a method involving cathode sputtering on to a base of cellulose acetate, perfectly continuous films of the order of 10^{-6} cm. thick have now been obtained, and cathode-ray diffraction patterns are described and discussed for films of gold, silver, lead, iron, and nickel. An unexpected structure is found for nickel (hexagonal closest packing), but the results for the other metals are in close agreement with those determined by X-ray analysis, with the exception of certain lead and iron films which probably contained compounds. The lowest voltages at which rings could be obtained have been determined for a number of films. A curve giving the variation of wave scattering with angle for the individual atoms is deduced by photometric measurements of the diffraction rings in gold. The curve falls much more steeply than the corresponding F curve for X-rays, indicating that the mean position of the scattering material is further from the centre of the atom. The fact that the present method gives a smooth curve is strong evidence that the crystals are distributed at random in the film.

L. L. BIRCUMSHAW.

Calculation of matrices for the hydrogen atom. W. GORDON (Ann. Physik, 1929, [v], 2, 1031—1056).—Mathematical.

R. A. MORTON.

Revision of the value of e/m derived from measurements of the Zeeman effect. H. D. BABCOCK (Astrophys. J., 1929, 69, 43—48).—Revision of the former value (*ibid.*, 1923, 58, 149) by elimination of uncertain lines, by the use of more recent analyses of the spectra of chromium and titanium and of the latest value for the velocity of light, gives, as the weighted mean of 48 determinations, $e/m = (1.7606 \pm 0.0012) \times 10^7$ e.m.u./g.

L. S. THEOBALD.

Masses of proton and electron. R. FURTH (Naturwiss., 1929, 17, 728—729; cf. this vol., 1123).—Preliminary. Following Eddington (this vol., 231) in certain respects, it is shown that it is possible to deduce, not only the charge, but also the mass of a proton or an electron from the fundamental magnitudes of the theory of relativity and the quantum theory.

R. A. MORTON.

Statistical interpretation of Maxwell's equations. M. S. VALLARTA (J. Math. Phys. Mass. Inst. Tech., 1929, 8, 155—161).—Mathematical.

Active nitrogen. P. K. KICHLU and S. BASU (Indian J. Physics, 1929, 4, 161—174).—Experimental evidence is adduced to support the views of Birge (Nature, 1924, 94, 642) with slight modification.

W. E. DOWNEY.

Detection of dissociation of halogen molecules effected directly by irradiation. H. SENFTLEBEN and E. GERMER (Ann. Physik, 1929, [v], 2, 847—864).—A method is described for detecting the dissociation of halogen molecules by the direct action of light.

The effective wave-lengths extend almost as far as the optically determined convergence frequencies, radiations on the short-wave side of 4722 and 5086 Å. being effective for chlorine and bromine, respectively. the convergences being at 4785 and 5107 Å. In the case of iodine, the convergence occurs at 4995 Å., whilst dissociation occurs directly for rays 4600—5000 Å. and is absent for the region 5000—5300 Å.

R. A. MORTON.

Chemical combination as an electrostatic phenomenon. XI—XIII. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 450—453, 478—482, 490—492; cf. this vol., 1129).—XI. The molecular configurations of ammonia, ammonium compounds, and some simple carbon compounds are discussed.

XII. The electrostatic forces within and between molecules of the general type XY_n are considered from the aspect of crystal lattice formation, and it is concluded that where n is greater than two, lattice formation is possible only if the Y ion is small relative to the central ion, and not easily polarised.

XIII. The forces causing deformation of the ions in crystal lattices are considered.

S. I. LEVY.

Structure of trebly-ionised chlorine. S. C. DEB (Nature, 1929, 124, 513).—Certain lines of trebly-ionised chlorine, due to the transition $M_2(N_1-N_2)$, have been found, and the chief lines of the group have been located by using Bowen's results (A., 1928, 210).

A. A. ELDRIDGE.

Equilibrium in a polyatomic gas according to the new statistics. H. LUDLOFF (Z. Physik, 1929, 57, 227—241).—Mathematical. Dissociation equilibria in molecules containing 3 or 4 equal atoms are discussed in a manner analogous with Gibson and Heitler's treatment of simple cases (A., 1928, 941). It is shown that the numerical value of the equilibrium constant depends on whether the molecule in question exists in enantiomorphic forms or not (cf. Hund, A., 1927, 809).

J. W. SMITH.

Geometrical treatment of Dirac's theory of the electron. V. FOCK (Z. Physik, 1929, 57, 261—277).—Mathematical.

J. W. SMITH.

Energy functions of the H_2 molecules. O. W. RICHARDSON and P. M. DAVIDSON (Proc. Roy. Soc., 1929, A, 125, 23—50).—The results given by the vibrational (cf. Kemble, A., 1926, 224) and rotational (cf. Birge, *ibid.*, 12) determinations of the terms in the expansion of the force function near the equilibrium position are in fair agreement, but the former method permits of far greater accuracy than the latter. The total energy of the H_2 molecules is calculated, and proof is obtained that the molecule in which the electron has total quantum number n breaks up into an unexcited atom and an atom in which the electron is excited to quantum number n . The estimated values of the dissociation energies of all the known electronic levels of the H_2 molecule are tabulated, together with several other constants of the levels. A formula is derived for the mean kinetic energy of a system of particles in motion under their mutual forces, some being held fixed and the others remaining in their neighbourhood, and this is applied to the case of two nuclei.

L. L. BIRCUMSHAW.

Thomson's experiment. S. C. KAR (Naturwiss., 1929, 17, 727).—Thomson's work (A., 1928, 938) with reference to the de Broglie theory of electron waves is discussed. Thomson's observations are consistent with light waves, although the deflection by means of magnetic and electric fields remains a difficulty.

R. A. MORTON.

Interaction of radiation and the electron. R. D. KLEEMAN (Science, 1929, 69, 380—381).—It has been shown thermodynamically that the electron may possess internal apart from kinetic energy, and that it can radiate in two entirely different ways: (i) on undergoing acceleration and (ii) on emitting a part of its internal energy as radiation, which is not necessarily connected with its motion. Further, the surrounding radiation gradually slows down its motion, which is attended by an increase in internal energy, and the force acting on it when placed in an electric field depends on its internal energy. The difficulties of the Bohr atom, and its antagonism to the Lewis-Langmuir atom, disappear in the light of the above.

L. S. THEOBALD.

Possible relation between Planck's constant h and the radiation pressure of circularly polarised rays. S. POKROVSKY (Z. Physik, 1929, 57, 278—282).—Mathematical.

J. W. SMITH.

Method for determining the temperature of glowing filaments. K. SCHESINGER (Ann. Physik, 1929, [v], 2, 933—975).—A method is described whereby the temperature of a glowing filament can be determined from the temperature variations in its characteristic vibrations when it is used as a stretched string.

R. A. MORTON.

Absorption law for the penetrating height-radiation. H. KULENKAMPF (Physikal. Z., 1929, 30, 561—567).—The decrease in intensity of ultra- γ -radiation effected in its passage through matter is influenced by the long-wave radiation which results from scattering. A method of calculation analogous to that used in the theory of radioactive disintegration is suggested as giving a good approximate description of the phenomena. The decrease in intensity of a primary monochromatic radiation is shown to depart considerably from the exponential law. The admixture of radiation of longer wave-length must also affect the other properties of the radiation.

R. A. MORTON.

Method for determining whether or not an electron has a magnetic moment comparable with that of a hydrogen atom. V. M. ALBERS and T. E. PHIPPS (Physical Rev., 1928, [ii], 31, 149).—A modification of the method suggested by Brillouin is proposed.

L. S. THEOBALD.

Dielectric cohesion of rare gases. M. CURIE and A. LEPAPE (J. Phys. Radium, 1929, [vi], 10, 294—298).—See this vol., 121.

Dependence of δ -radiation on outgassing of platinum foil. S. MATTHES (Ann. Physik, 1929, [v], 2, 631—645).—The initial intensity of δ -emission depends on the purity of the surface. Repeated heating to redness effects an increase in emission, but further heating to higher temperatures causes the emission to fall below the initial value. The changes

can be reproduced by recharging the surface with air or hydrogen.

R. A. MORTON.

Wave-mechanical character of the β -ray change. J. KUDAR (Z. Physik, 1929, 57, 257—260).—Mathematical.

J. W. SMITH.

Radioactivity. A. F. KOVARIK and L. W. MCKEEHAN (Bull. Nat. Res. Council, 1929, No. 51, 203 pp.).—A second revised printing of the Report of the Committee on X-rays and radioactivity first issued in 1925.

Search for element 87 by analysis of positive rays. K. T. BAINBRIDGE (Physical Rev., 1929, [ii], 34, 752—762).—Previous searches are surveyed critically. Predictions of spectral values, and estimates for the sensitivity of detection and identification by at. wt. determinations, radioactive means, physiological effects, X-ray and optical spectrum analysis are given. An intense homogeneous source of positive ions, by means of a tungsten filament heated at 1200—1300° Abs., was incorporated into a mass spectrograph, and positive ions of mass number 223 or 224 were looked for in the product obtained after attempting the chemical separation of caesium and eka-caesium from pollucite and lepidolite ores. Eka-caesium was not present to an extent greater than 3.5×10^{-7} and 7.3×10^{-6} in the caesium separated from the two ores, respectively. Measurements of the vapour pressures of the alkali metals by Langmuir and Kingdon (A., 1925, ii, 254) and by Killian (A., 1926, 653) by measurements of the positive ion current thermally produced from tungsten filaments in the vapour of these elements are shown to be highly accurate, and the method is applicable to the separation of isotopes and determinations of isotope intensity ratios.

N. M. BLIGH.

Cathode drop in an electric arc. S. S. MACKEOWN (Physical Rev., 1929, [ii], 34, 611—614).—According to Langmuir's theory developed by Compton (cf. A., 1927, 926) the electrons emanating from the cathode in the mercury arc are due primarily to the high electric field and not to thermal emission. Values for the electric field at the cathode surface are determined for varying percentages of current carried by positive ions. Assuming that the total cathode drop occurs in a distance less than one mean free path from the cathode, the theory is shown to be consistent with available data.

N. M. BLIGH.

Recombination of ions and of ions and electrons in gases. L. C. MARSHALL (Physical Rev., 1929, [ii], 34, 618—634).—By means of a new direct method, using constant radiation from a Coolidge tube as the ionising agent, together with a rotating commutator shutter, the X-ray exposure t' , the initial ion concentration n_0 , and the time of recombination t could be varied independently over a wide range. Results in air show that the coefficient of recombination α varies as a function of t' , t , and n_0 . The ions must therefore be non-uniformly distributed initially, and in pairs along the X-ray paths. As t' , t , and n_0 increase, α approaches a constant value between 0.8 and 0.9×10^{-6} . Diffusion probably plays an important part in the initial stages of the mechanism of recombination. In argon α is nearly constant, due to rapid

random distribution, at a value about half that for argon-oxygen mixtures. Values indicate that α is less for electrons and positive ions than for positive and negative ions, in agreement with the work of Kenty (cf. A., 1928, 1300). N. M. BLIGH.

Factors affecting the nature of ions in air. H. A. ERIKSON (Physical Rev., 1929, [ii], 34, 635—643; cf. this vol., 483).—It was found that drying agents such as calcium chloride and phosphorus pentoxide were insufficient, and that cooling by liquid air is essential. In air thus dried the initial positive ion transforms into the final ion very slowly, if at all. The ionising process itself gives rise to impurities affecting the ions, confirming Tyndall and others (cf. this vol., 6). The effect of water is modified by the presence of the impurities due to ionisation.

N. M. BLIGH.

Relative probabilities of the ionisation of K and L electrons of equal ionisation energy. G. L. PEARSON (Proc. Nat. Acad. Sci., 1929, 15, 658—664).—The intensities of X-ray lines were measured, using an X-ray tube on the target of which was a compound of two elements such that the values of the excitation voltage for the K series of one and the L series of the other were as nearly alike as possible. Lead selenide was used. Data were obtained on ratios of the values, for various sub-series, of the product of two factors, the probability that a cathode ray will produce an ionisation of the appropriate type, and the probability that the subsequent reorganisation will result in radiation of some line of the sub-series. Between two sub-series such as L_{21} and L_{22} , differing only in the inner quantum number, this product was proportional to the latter. A difference in azimuthal quantum number only between the K and L_{21} was found to have no appreciable effect; a difference in radial quantum number between K and L_{11} had a great effect. N. M. BLIGH.

Occurrence of ions in the decomposition of ozone and the ionisation of the stratosphere. H. HELLMANN (Ann. Physik, 1929, [v], 2, 707—731).—No ionisation is observed in the thermal decomposition of ozone, although the apparatus used is capable of detecting one ion pair for every 5×10^{15} molecules decomposing. The electrical conductivity of the upper layers of the atmosphere is therefore unlikely to be related to the presence of ozone.

R. A. MORTON.

Ultra-short waves and radiation from free electrons. D. S. KOTHARI and D. V. GOGATI (Indian J. Physics, 1929, 4, 175—178).—Theoretical.

W. E. DOWNEY.

Longitudinal distribution of photo-electrons. A. CARRELLI (Atti R. Accad. Lincei, 1929, [vi], 9, 1102—1110).—See this vol., 1121.

Hydrogen and the photo-electric emission from potassium. N. CAMPBELL (Physikal. Z., 1929, 30, 537—538; cf. Fleischer, this vol., 736).—Experiments as yet incomplete are consistent with the view that sensitisation is closely connected with two different processes. One is a gross change in the surface structure manifested by a change in colour and possibly arising from volatilisation of potassium. The other is in all probability a change in the atomic

structure of the surface due to the formation (or possibly the removal) of monatomic gas layers.

R. A. MORTON.

Electron scattering in atomic and molecular hydrogen. G. P. HARNWELL (Physical Rev., 1929, [ii], 34, 661—672; cf. this vol., 619).—By using an apparatus similar to that of Dymond (this vol., 368), electron scattering was investigated in hydrogen admitted from a discharge tube, containing more than 60% of atomic hydrogen. The electron energy spectrum was analysed into component peaks interpreted as due to elastic, inelastic, and ionising collisions. One inelastic loss at about 8 volts and several at about 12.5 volts were found. From the areas under the peaks the number of electrons scattered through a given angle was calculated and, plotted against scattering angle, gave similar results for atomic and molecular hydrogen, the former case agreeing well with the theoretical predictions of quantum mechanics. N. M. BLIGH.

Absorption coefficient for slow electrons in alkali metal vapours. R. B. BRODE (Physical Rev., 1929, [ii], 34, 673—678).—With the apparatus and method previously used for gases (A., 1925, ii, 617) the absorption coefficient for electrons was measured in the vapours of sodium, potassium, rubidium, and caesium. The curves connecting absorption coefficient with electron velocity in each case increase monotonically from high to low velocity except in the regions of the critical potentials, where a sharp peak is superimposed on the monotonic rise, and in general resemble the curve deduced from wave mechanics for hydrogen. N. M. BLIGH.

Effective cross-section and molecular structure for the isosteric series: N_2 -(CH)₄ and O_2 —[(NH)₂]₂—(CH₂)₂. E. BRUCHE (Ann. Physik, 1929, [v], 2, 909—932).—The effective cross-section in cm²/cm³ for acetylene and ethylene has been determined for electron velocities from 0 to 7 volt¹. Acetylene shows a sharp maximum at 1.55—1.7 volt¹ and an ill-defined maximum near 2.5 volt¹. Ethylene exhibits a sharp maximum at 1.35 volt¹, a minimum about 2 volt¹, and a second broader maximum near 3 volt¹. The form of the effective cross-section curve depends on the electronic configuration in the isosteric series Ne, HF, H₂O, NH₃, CH₄, each of these molecules having a completed octet. The molecules N₂ and C₂H₂ are also isosteric, and the series O₂-(NH)₂ [hypothetical], C₂H₄ exhibits a similar relationship. Grimm's hydride displacement law is discussed in relation to the cross-section curves, and it is concluded that the results on the whole conform with expectations. The introduction of hydrogen (provided no dipole is formed) effects a simple magnification of the field, which is more pronounced when several hydrogen atoms occur, e.g., the field for acetylene is greater than for nitrogen, whilst the field for ethylene is much greater than for oxygen. R. A. MORTON.

Conductivity of ions in crossed electric and magnetic fields. L. PAGE (Physical Rev., 1929, [ii], 34, 763—771; cf. this vol., 619).—Theoretical. Collisions of ions with one another are shown to be without effect, the transverse current at right angles to the fields being the same as in absence of collisions.

Collisions of free ions with neutral particles are investigated where the velocity of progression u is small compared with the speed v of thermal agitation. As the mean free path is increased the current parallel to the electric field increases to a maximum and then falls asymptotically to zero, the transverse current parallel to u rising from zero to a limiting value for infinite mean free path. Calculations of the Hall coefficient on the present theory, taking account of long free paths, show that the coefficient increases with increasing magnetic field. N. M. BLIGH.

Charges of mercury atoms in the canal-ray stream. W. JACOBI (Physikal. Z., 1929, 30, 568—575).—The stages of ionisation of the mercury atom have been studied by the simultaneous application of electric and magnetic fields to a mercury positive-ray stream (parabola method). In a hydrogen discharge containing a small quantity of mercury vapour, in addition to the hydrogen and Hg^+ parabolas it is possible to record parabolas b , c , and d (a being the Hg^+ parabola). The ratios $(e/m)_b$, $(e/m)_c$, $(e/m)_d$ are, respectively, equal to 7.9, 12, and 18.1 times $(e/m)_a$. These results are either due to the occurrence of multiply charged mercury atoms, Hg^{8+} , Hg^{12+} , and Hg^{18+} or to particles of smaller mass. Evidence is adduced which supports the hypothesis of multiple ionisation by definite stages rather than electron by electron. The results agree well with Stoner's scheme of electron distribution. R. A. MORTON.

Influence of surface layers on the electron emission from glowing metals. C. ZWIKKER (Physikal. Z., 1929, 30, 578—580).—In Richardson's formula for the saturation current i in the emission of electrons from hot wires, $i = AT^2 e^{-b/T}$, and the constants A and b depend on the surface condition of the metal. The relation between A and b for zirconium and hafnium wires covered superficially with various oxide layers follows the equation $b = c \log A + d$, c and d being constants. The change in A and b is probably due to gradual outgassing as the heating proceeds and adsorbed oxygen or nitrogen is set free. The line obtained by plotting $\log A$ against b for tungsten and platinum shows the same inclination as for zirconium and hafnium. This result is shown to follow from theoretical considerations.

R. A. MORTON.

Direct measurement of intensity distribution in molecular beams. J. B. TAYLOR (Z. Physik, 1929, 57, 242—248).—When an alkali-metal atom strikes a glowing tungsten wire, it parts with an electron and is re-emitted as a positive ion. By measuring the number of positive ions emitted from such a wire in various positions in the path of a molecular beam the number of alkali-metal atoms striking the wire per second can be determined, and hence the energy distribution in different parts of the beam deduced, with an accuracy of 1 in 10^3 .

J. W. SMITH.

Electron emission and diffraction by a copper crystal. H. E. FARNSWORTH (Physical Rev., 1929, [ii], 34, 679—696; cf. A., 1928, 453).—A narrow beam of variable-speed electrons was incident normally on the face of a copper crystal, and measurements were made of the total secondary electron current under the

same conditions as the angular distribution of scattered electrons for bombarding potentials from 0 to 250 volts. The total secondary electron curve shows maxima at 3 and 10.5 volts and changes of slope at higher voltages. These correspond with intense electron beams issuing from the crystal, and to other beams normal to the crystal contributing to the total secondary current. The two types of diffraction beams found are discussed, and their respective refractive indices considered (cf. Davisson and Germer, A., 1928, 1173). The diffraction beams are composed entirely of full-speed electrons. Evidence of a selective angular distribution of emitted electrons, differing from that of the scattered electrons, was obtained. N. M. BLIGH.

Total radiation from nickel and cobalt. C. L. UTTERBACK (Physical Rev., 1929, [ii], 34, 785—790).—Using a platinum-tellurium thermocouple and a high-sensitivity galvanometer at constant deflexion, measurements were made of the total radiation from nickel and cobalt for the range 630 — 1600° and 672 — 1590° Abs., respectively, measured by means of an optical pyrometer calibrated at the gold and palladium points, and by a platinum-platinum-rhodium thermocouple. The value of n in the formula $E = cT^n$ is evaluated, and a logarithmic graph of energy against temperature is given. N. M. BLIGH.

Photo-ionisation of some alkali vapours. F. L. MOHLER and C. BOECKNER (Bur. Stand. J. Res., 1929, 3, 303—314).—Relative measurements of photo-sensitivity as a function of wave-length have been made by the space-charge method, and absolute values at favourable wave-lengths measured by a direct method. The shape of the sensitivity curve for caesium is similar to published results and is independent of pressure. The atomic absorption coefficient k is 2.3×10^{-19} at the principal series limit. The curve for rubidium is similar and the value of k at the limit is 1.1×10^{-19} . For potassium the sensitivity is low at the limit 2856 \AA . and rises rapidly from 2600 to 2200 \AA .

C. J. SMITHELLS.

Dissociation of nitrogen by electron impact. L. A. TURNER and E. W. SAMSON (Physical Rev., 1929, [ii], 34, 743—746; cf. Herzberg, A., 1928, 931).—Using Kondratjev's method (A., 1926, 989), the $2p^2 3s^4 P - 2p^2 3p^4 P^0$ N I lines near 8200 \AA . were produced by bombarding N_2 molecules with electrons having energies of 23 ± 1 volts or more. Variations of currents and pressures indicated that the rate of production of excited atoms depends on a single impact and not on successive double impacts. The possible emission of the lines following the recombination with electrons of N^+ ions, shown by positive-ray experiments to be produced at this voltage, is discussed (cf. Kenty and Turner, this vol., 114). N. M. BLIGH.

Excitation potential of the negative bands of nitrogen. L. A. TURNER and E. W. SAMSON (Physical Rev., 1929, [ii], 34, 747—751).—The energy of the $0 \rightarrow 1$ negative band of nitrogen at 4278.1 \AA . was found to be 19.0 volts, by comparison with the energy of excitation of neon lines. This gives 15.8 volts for the ionising potential of nitrogen and 8.4 volts for the heat of dissociation (cf. Birge, this vol., 7). Peculiar effects in the excitation of the $2s - 2p$ lines of neon are discussed. N. M. BLIGH.

Dependence of the photo-electric conductivity of red mercuric iodide on the temperature. L. PIATTI (Nuovo Cim., 1929, 6, 14—35; Chem. Zentr., 1929, i, 2513).—The change of photo-electric conductivity previously observed when a vessel of water is interposed between the source of light and the mercuric iodide cell is attributed to infra-red rays. The method is applicable to the determination of the temperature of transition into the yellow variety.

A. A. ELDRIDGE.

Ionisation potentials and conductivities of metals. B. B. RAY and D. P. R. CHAUDHURI (Nature, 1929, 124, 512—513).—For metals possessing the same crystal structure, the product of the electrical conductivity with the ionisation potential varies inversely as the atomic number. Magnesium, calcium, strontium, rhodium, and bismuth exhibit discrepancies.

A. A. ELDRIDGE.

Absorption of ultra-violet light by organic substances. X. L. KWIECINSKI and L. MARCHLEWSKI (Bull. Soc. chim., 1929, [iv], 45, 591—611; cf. this vol., 9).—Paraldehyde, metaldehyde, and aldehyde-ammonia show no selective absorption. Acetaldehyde and propaldehyde are characterised by absorption bands with maxima at 2780 and 2800 Å., respectively, and minima at 2260 and 2340 Å. Methylglyoxal shows considerable absorption in the ultra-violet with a maximum at 2640 and a minimum at 2260 Å.

O. J. WALKER.

Absorption of ultra-violet light by benzene. L. KWIECINSKI and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1929, A, 255—263).—A re-investigation of the absorption spectrum of carefully purified benzene is described; the six bands had maxima at 2684, 2608, 2546, 2490, 2433, and 2390 Å. The absorption spectrum of benzene in various concentrations of alcohol has also been measured.

A. I. VOGEL.

Structure of absorption-resonators of organic chromophors. I. Structure of absorption-resonators of halochromic complexes of quinones and quinhydrones. D. RĂDULESCU and F. BĂRBULESCU. II. Polarity of substituents as determining factor in displacement of bands. D. RĂDULESCU and A. GEORGESCU. III. Phenomena of halochromism in sulphonation. D. RĂDULESCU (Z. physikal. Chem., 1929, B, 5, 177—198, 301—303).—I. Absorption curves of naphthacene and its derivatives have been compared. Where the distribution of electrons characteristic of the unsubstituted hydrocarbon is retained (as in a halochromic complex compound of naphthacenediquinone) the compound gives a spectrum very similar to that of the hydrocarbon, except for a displacement, the magnitude and direction of which depend on the polarity and strength of the substituent. Where the electronic skeleton is different (as in ketonic quinones and diquinones) the characteristic absorption spectrum of the hydrocarbon is not obtained. These observations are at variance with Pfeiffer's theory of local "absorption centres," but support the conception in which the resonator responsible for the characteristic selective absorption is assumed to be a complicated structure of linked valency electrons. Quinhydrones are complex compounds possessing the same absorption resonators

as the rest of the halochromic compounds of the corresponding quinones.

II. Alteration of the polarity of a substituent of a chromophor group displaces the characteristic absorption spectrum of the group and is unaccompanied by any appreciable distortion. By choosing a suitable chromophore group and graduating the polarity by the substitution of Cl, Me, OMe, etc. in the nucleus, it is found that the essential structure of the chromophore group remains unchanged. Increased negative polarity displaces the entire spectrum towards the red, sometimes by as much as 1000 Å. Conversely, the degree of displacement of a given spectrum affords a measure of the polarity of the substituent.

III. Preliminary. The transient colouring often observed during the sulphonation of hydrocarbons is due to the production of a complex compound. Spectroscopic observations show that the effect is quite general, but is especially marked with coloured hydrocarbons such as naphthacene and pyrene. Measurements of the absorption bands of naphthacene and its intermediate product show that the latter has the characteristic spectrum of the hydrocarbon displaced toward the red. It therefore possesses the same resonator system. It is possible to recover the unchanged hydrocarbon quantitatively from the sulphuric acid.

F. L. USHER.

Quantitative spectrographic studies in the ultra-violet. I. Hormones. W. GRAUBNER (Z. ges. exp. Med., 1928, 63, 527—551; Chem. Zentr., 1929, i, 2068).—Adrenaline, thyroxine, and the pituitary hormone give a specific band at 2800, 3250, and 2650—2670 Å., respectively. Thyroid extracts do not exhibit the thyroxine spectrum. Insulin preparations give a band at 2450—2850 Å., with a centre at 2750 Å. Ergotamine and ephedrine give absorption bands with heads at 3170 and 2570 Å., respectively. Combination of two hormones caused a shift of the absorption towards the red and disappearance of the characteristic bands.

A. A. ELDRIDGE.

Absorption of ultra-violet light by some hormones and allied substances. L. MARCHLEWSKI and B. SKARŻYŃSKI (Bull. Acad. Polonaise, 1929, A, 241—254).—Measurements of the absorption spectra of the following substances are described: *dl*-ephedrine hydrochloride in water (three bands with maxima at 2638, 2564, and 2508 Å.); *l*- and *ψ*-ephedrine hydrochloride in water (similar to the *dl*-compound); adrenaline hydrogen tartrate in water (one band, maximum at 2800 Å.); thyroxine in 0.01*N*-sodium hydroxide (broad band with maximum at 3110 Å.; cf. tyrosine, band with maximum at 2750 Å.); α -hydroxytyrosine in 0.1*N*-hydrochloric acid (one band, maximum at 2808 Å.).

A. I. VOGEL.

Ultra-violet absorption of the carbonyl group. K. L. WOLF and W. HEROLD (Z. physikal. Chem., 1929, B, 5, 124—130).—The substances containing the carbonyl group the data for which were collected comprised acids, aldehydes, and ketones of the aliphatic, heterocyclic, and homocyclic series. The log k_{\max} values for the first ultra-violet absorption bands of these substances in various alcoholic solutions are discussed, and for the ketones a new series of values is

put forward. Experiments with propaldehyde are quoted which show that the aldehyde bands are normal. Any reaction between aldehyde and alcohol to form an acid can be followed optically. The formation of aldehyde hydrates and acetals can be followed by investigating the ultra-violet absorption.

A. J. MEE.

Absorption spectrum of carbon disulphide in the near ultra-violet. E. D. WILSON (Astrophys. J., 1929, 69, 34—42).—The absorption spectrum of carbon disulphide vapour has been photographed under varied conditions favourable to the complete development of the band system between 2900 and 3800 Å. The wave-lengths of about 650 lines have been measured and their intensities have been compared photometrically. Certain regularities in the band system are indicated and some of the lines have been grouped into series.

L. S. THEOBALD.

Ultra-violet spectral absorption of lignin derivatives. E. HAGGLUND, F. W. KLINGSTEDT, and (in part) O. LUND (Svensk Kem. Tidskr., 1929, 44, 185—190).—By the action of alcohols and anhydrous hydrogen chloride on lignin from pine, birch, and beech woods various alkyl-lignins have been prepared (cf. Holmberg, B., 1926, 267) and their ultra-violet absorption spectra in alcoholic solution investigated. The absorption curves are all of the same type, consisting of a broad, continuous band, with minimum in each case about $\lambda=2590$ Å., and a second band, not completely traced ($\lambda=\text{about } 2330$ Å.), superimposed on a strong, continuous absorption. Comparison of these results with those of Herzog and Hillmer (this vol., 915) for coniferyl alcohol would seem to exclude a purely aliphatic character for the lignin unit which, the authors conclude, must contain at least one aromatic ring. The difference in the two sets of type-similar absorption curves depends on differences in the side chains attached to the ring system. The ultra-violet absorption spectrum of ligninsulphonic acid (from pine), which approximates in type to that of the isoamyl-lignins from birch and beech, shows that it contains the same unsaturated groups responsible for the selective absorption of the latter.

J. W. BAKER.

CH-band at 3143 Å. and a new NH-band at 2530 Å. T. HORI (Nature, 1929, 124, 480).—The CH-band at 3143 Å. appears to belong to a $^2\Sigma \rightarrow ^2\Pi$ system; it has a common final level $^2\Pi$ with the bands at 3900 and 4300 Å. The nuclear distance in the $^2\Sigma$ state is $r_0'=1.12 \times 10^{-8}$ cm. A new simple NH-band at 2530 Å. of comparatively small intensity has been observed; the corresponding transition is of $^1\Sigma \rightarrow ^1\Pi$ type. The nuclear separations of the molecule in the initial and final states are $r_0'=1.03 \times 10^{-8}$ cm. and $r_0''=1.06 \times 10^{-8}$ cm., respectively.

A. A. ELDRIDGE.

Ultra-violet dispersion frequencies, measurable in air, of the alkali halides. R. HILSON and R. W. POHL (Z. Physik, 1929, 57, 145—153).—A method for distilling substances on to surfaces as thin films is described. Curves are given for absorption in the region 180—250 mμ for alkali bromides and iodides and for reflexion from potassium iodide. If absorption is due to the removal of an electron from

the halogen anion and its return to the alkali cation, the lowest energy level should equal $Q+E-J$ (Q is the "Coulomb grating energy," E the halogen electron affinity, and J the ionisation potential of the alkali metal). This relation leads to frequencies near those observed. A trace of iodide in the chloride crystal causes selective absorption at frequencies given by the above relation, except that Q is the chloride grating energy, whilst E and J refer to the iodide.

A. B. D. CASSIE.

Influence of X-rays on the absorption spectra of alkali halide phosphors. (FRL.) A. ARSENJEWA (Z. Physik, 1929, 57, 163—172).—The intensities of the sharply-defined absorption bands of alkali halide phosphors containing lead as exciting ion are found to be diminished by exposure to X-rays, whereas in the case of phosphors containing thallium the intensities are increased. With potassium chloride phosphor containing lead, the maximum of the extreme short-wave excitation band is shifted slightly towards the short-wave side. Evidence has also been obtained of a doubling of the absorption bands in this case. In all cases irradiation by X-rays also develops a continuous absorption underlying the normal absorption bands, this continuum increasing in intensity towards the short-wave side. This abnormal absorption is not permanent, but disappears, recovery being slowest in the case of sodium chloride phosphors. The conclusion is also reached that all the above-described effects of X-rays on the absorption spectra of phosphors are independent of whether the phosphors contain "foreign colouring of the first kind" or whether this foreign colouring is removed before the investigation.

J. W. SMITH.

Cathodic luminescence spectra of rare earths extracted from samarskite, ishihawaite, and monazite of Ishikawa, Iwaki Province. Y. UZUMASA (Japanese J. Chem., 1929, 4, 7—9).

C. W. GIBBY.

Excitation of fluorescence in benzene at -183° by monochromatic light. J. STARKIEWICZ (Bull. Acad. Polonaise, 1929, A, 287—294; cf. Pringsheim and Reimann, A., 1925, ii, 181; Pringsheim, A., 1927, 186).—The fluorescence spectra excited in benzene at -183° by the almost monochromatic radiation from electrodes of zinc ($\lambda=2502$ and 2558 Å.) and of cadmium ($\lambda=2265$ and 2313 Å.) are in all respects similar to each other and to that obtained in similar circumstances by Reimann with a mercury lamp. It is therefore concluded that this independence of fluorescence on wave-length cannot be due, as in the case of the vapour, to collisions, but, as supposed by Pringsheim, to some intramolecular mechanism.

C. A. SILBERAD.

Thermoluminescence excited by X-rays. Further experiments on synthetically-prepared materials. F. G. WICK and (Miss) M. K. SLATTERY (Physical Rev., 1928, [ii], 31, 306).—Exposure of the sulphates of cadmium, calcium, sodium, and zinc containing a small amount of manganese to X-rays produces two types of thermoluminescence, one which appears quickly and is of short duration, and the other which appears more slowly and lasts longer. Both types are preserved at the temperature of liquid

air, but are destroyed by exposure to ultra-violet light of a definite frequency. L. S. THEOBALD.

Oxidation of carbon monoxide. M. PRETTE and P. LAFFITTE (Compt. rend., 1929, 189, 177—179).—An apparatus for studying quantitatively and continuously the phenomena which occur during the period of violet-red luminosity below the ignition temperature of mixtures of dry air and carbon monoxide (20—43.5%) has been devised. The luminosity corresponds with slow oxidation of the monoxide (this vol., 771), and the fact that it disappears before oxidation is complete is shown by the ignition of the remaining mixture when the pressure is reduced to 8 mm. of mercury. On the other hand, after an interval of 10 min., reduction of pressure will not effect combustion and the luminosity reappears at a temperature within 10—20° of the ignition point.

J. GRANT.

Phosphorescent flame of arsenic. H. J. EMELÉUS (J.C.S., 1929, 1846—1848; cf. A., 1927, 497).—The spectrum of the glow produced by heating arsenic in a current of air at temperatures between 250° and 360° consists of a continuous band between 4300 and 4900 Å., similar to that of the ordinary flame. The glow is inhibited by the vapours of benzene, ethyl alcohol, hexane, acetone, chloroform, amyl acetate, methyl alcohol, and chlorobenzene, but reappears on removal of the organic vapour or on raising the temperature by 12—30°.

C. W. GIBBY.

Light emission from phosphorescent flames of ether, acetaldehyde, propaldehyde, and hexane. H. J. EMELÉUS (J.C.S., 1929, 1733—1739; cf. A., 1927, 7).—The spectra of phosphorescent flames of acetaldehyde, propaldehyde, and hexane all give the same series of bands degraded towards the red between 5000 and 3360 Å. In each case the combustion of the substance was incomplete. Acetaldehyde was found in the products of combustion of ether, but not of propaldehyde or hexane.

C. W. GIBBY.

Infra-red absorption spectrum of hydrogen sulphide. A. H. ROLLEFSON (Physical Rev., 1929, [ii], 34, 604—610).—Using a prism-grating spectrometer a narrow intense absorption band was observed at 4.2 μ . but could not be resolved. The 5.6 μ band observed by Coblentz was not found and was probably due to an impurity. Thirty-four lines of the band in the region of 8.0 μ were observed and tabulated.

N. M. BLIGH.

Infra-red absorption spectra of organic nitrates. E. K. PLYLER and P. J. STEELE (Physical Rev., 1929, [ii], 34, 599—603).—Methyl, ethyl, propyl, and butyl nitrates were studied in the region 1.0—7.5 μ . Two absorption bands at 1.4 and 2.96 μ are attributed either to an O-H linking or to water. All other bands are attributed to the carbon-hydrogen linking, and as an additional CH₂ group is introduced the intensity of all bands decreases and a shift of from 0.01 to 0.06 μ to longer wave-length occurs. No characteristic absorption spectra of the NO₂ group were found. An intense absorption band was observed at 6.7 μ .

N. M. BLIGH.

Near infra-red absorption spectra of some halogen derivatives of ethane. B. J. SPENCE and

M. A. EASLEY (Physical Rev., 1929, [ii], 34, 730—742; cf. A., 1928, 1170).—Infra-red absorption spectra (0.8—3 μ) of 14 halogen derivatives of ethane were studied. A large number of new absorption bands were discovered, and full data are tabulated. Bands were not observed for compounds containing no hydrogen. The other spectra showed a close similarity, particularly when the halogens were interchanged.

N. M. BLIGH.

Intensity measurements in the Raman effect and the distribution law of Maxwell and Boltzmann. L. S. ORNSTEIN and J. REKVELD (Physical Rev., 1929, [ii], 34, 720—725).—By considerations similar to Einstein's treatment of Planck's law a relation is deduced for the ratio of intensities between Stokes and anti-Stokes lines in the Raman effect, and is shown to give good agreement with experimental results on carbon tetrachloride. A precision measurement of the constant h/k can be developed.

N. M. BLIGH.

Vibrational selection principles in the Raman effect. J. H. VAN VLECK (Proc. Nat. Acad. Sci., 1929, 15, 754—764; cf. Manneback, this vol., 866).—Theoretical. A proof is given of the proposition of the usual absence of all displacements in the vibrational quantum number except the fundamental.

A. J. MET.

Raman spectra of polyatomic gases. R. G. DICKINSON, R. T. DILLON, and F. RASSETTI (Physical Rev., 1929, [ii], 34, 582—589; cf. Rasetti, this vol., 241, 627, 975; Wood, *ibid.*, 627).—Raman spectra of gaseous carbon dioxide, nitrous oxide, ammonia, methane, and ethylene were photographed using the mercury line λ 2536 Å. for excitation. Vibrational transitions were observed for each gas, and rotational transitions for ammonia and methane. Values are listed for the frequency shifts due to vibrational transitions. Raman spectra for liquid ammonia were photographed, and gave the frequency shifts 3298.4 and 3214.5. For gaseous ammonia, pure rotational transitions gave the value $I_0 = 2.79 \times 10^{-40}$, and for methane the positive and negative branches of the 3022.1 band gave the value $I_0 = 5.17 \times 10^{-40}$ for the moment of inertia. The relations between these data and infra-red absorption data are discussed.

N. M. BLIGH.

Raman effect in liquids. A. S. GANESAN and S. VENKATESWARAN (Indian J. Physics, 1929, 4, 195—280).—Results for a number of representative compounds are given. The shifts below are given in wave numbers per cm. All the paraffins show a prominent band corresponding with shifts of 2850—2960, and resolved into five components; the relation of the constant of spacing, about 27, to the rotational frequency of the molecule is discussed. Carbon disulphide shows no correspondence between molecular frequencies from Raman and infra-red absorption measurements. Chloroform and bromoform illustrate the influence, among the halogen derivatives of methane, of the mass of the substituents on the positions of the Raman lines. For the alcohols, the structure of the band shifted about 2960, its development up the series, and the influence of isomerides are discussed. The fatty acids show a

general continuous spectrum, and glycerol a prominent one, the origin of which is discussed. A strong line is characteristic of the carbonyl groups and of the nitro-compounds, shifted by 1700 and 1347, respectively. Characteristic differences for aliphatic and aromatic compounds between 3 and 10 μ are pointed out. The Raman spectra of the xylenes illustrate the influence of substitution. The cases of ethyl ether and anisole are considered. *cyclo*Hexane illustrates the lines of open-chain and cyclic compounds; the aliphatic 2853—2935 band and the 800 band are very prominent. Pyridine and benzene lines are compared; in the former the additional line 1027 is the most prominent; corresponding lines in the two liquids are polarised to nearly the same extent, indicating molecular structural similarity. Quinoline gives a prominent fluorescence spectrum, the Raman spectrum being similar to that of naphthalene with 1370 most prominent in each. Sulphuric acid gives a continuous spectrum in addition to the lines; hydrochloric acid shows only water bands sharpening with the concentration; nitric acid shows a number of prominent lines in addition to the water band, which is resolved into three sharp components as in ice. Potassium and sodium carbonate solutions give a prominent line at 1064, identified with the inactive frequency of the CO_3 ion. The 3 μ band of water consists of a prominent component 2.9 and also 2.77 and 3.13 μ ; the structure of the band in ice, in hydrated crystals, and in electrolytes, and the effect of temperature on the band, are discussed. The non-correspondence of molecular frequencies from Raman lines and direct infra-red measurements is discussed and explained on the wave-mechanical treatment of dispersion. Raman lines for aliphatic compounds are generally more polarised than for aromatic, indicating a close analogy to the classical scattering. Full tabulations of Raman lines are given.

N. M. BUGH.

Raman spectra from acetone. R. T. DILLON and R. G. DICKINSON (Proc. Nat. Acad. Sci., 1929, 15, 699—702).—The measurements of Williams and Hollaender (this vol., 866) on the Raman spectra from acetone do not agree with this redetermination. Seven mercury lines are concerned in the production of Raman lines. A table showing the frequency differences of the modified lines is given. A. J. MEE.

Raman spectra of some organic and inorganic compounds. A. PETRIKALN and J. HOCHBERG (Z. physikal. Chem., 1929, B, 4, 299—311; cf. this vol., 741, 865).—Measurements of the Raman spectra of 15 further organic compounds confirm the usefulness of these spectra in elucidating the nature of the interatomic linkings in organic molecules. The results are summarised along with those given in previous papers. The Raman spectrum of stannic chloride consists of two narrow doublets and is quite different from that of carbon tetrachloride. The cyanide radical in a concentrated solution of potassium cyanide gives a single line of wave-length 4.80 μ as compared with 4.41—4.48 μ obtained with organic compounds containing the $\cdot\text{CN}$ group. The oscillator in this case is the free cyanide ion.

O. J. WALKER.

Relation between Raman lines and infra-red bands. C. P. SNOW (Phil. Mag., 1929, [vii], 8,

369—379).—The Langer-Dieke account (cf. this vol., 379, 490) of the relation between Raman lines and infra-red bands is discussed. For oxygen, nitrogen, and carbon monoxide a similar scheme to that of Dieke for hydrogen chloride must be used, and for the three gases the position of the central Raman line should not coincide with the electronic vibration frequency. There is experimental evidence of vibration-rotation bands of oxygen and nitrogen. Evidence in favour of absorption by oxygen was obtained with an infra-red vacuum spectrometer; the intensity of absorption for a metre path of oxygen has 5% as its upper limit. The Raman effect for carbon dioxide is in agreement with the Langer-Dieke account, and some suggestions are advanced on the transitions to be expected; the effect for hydrogen gives results not yet explained by the theory. N. M. BUGH.

Raman spectra of calcite, aragonite, and aqueous solution of potassium carbonate. M. KIMURA and Y. UCHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 199—204).—Raman lines of calcite are given for light incident (i) perpendicular and (ii) parallel to the optic axis. The inactive frequency $\lambda=9\mu$ always appeared strongly. The frequency $\lambda=11.4\mu$ appeared strong in i, weak in ii. The external frequency $\lambda=36\mu$ always appeared almost as strong as $\lambda=9\mu$. Aragonite was illuminated along and perpendicular to the acute bisectrix of the axes, but no peculiarities were noted. The intensity of the inactive frequency and of the external frequency ($\lambda=36\mu$) suggests that the oxygen atoms determine the field in which the calcium ion moves.

A. B. D. CASSIE.

Raman spectrum of gypsum. R. G. DICKINSON and R. T. DILLON (Proc. Nat. Acad. Sci., 1929, 15, 695—699).—The change of frequency on scattering at gypsum was determined and compared with that for a solution of ammonium sulphate. There are eight different frequency shifts for gypsum. The two largest are probably due to water of crystallisation, whilst the smaller ones are due to the sulphate ion. The multiplicity of lines found from gypsum may be explained on Brester's theory of the multiplication of characteristic frequencies due to removal of symmetry.

A. J. MEE.

Raman spectra of crystals. K. S. KRISHNAN (Indian J. Physics, 1929, 4, 131—140).—The Raman spectra of quartz, calcite, topaz, and selenite have been observed. Selenite shows lines corresponding with ice and two lines of somewhat longer wave-length than the prominent line shown by solutions of sulphates in water.

W. E. DOWNEY.

Raman effect in crystals. C. SCHAEFER, F. MATOSI, and H. ADERHOLD (Physikal. Z., 1929, 30, 581—585).—The following wave-lengths correspond with Raman lines observed with crystals: calcite 62.1, 35.4, 13.95 (weak), 9.18, 6.9 μ (weak); sodium nitrate 105 (weak), 53.65, 13.7 (weak), 9.3, 7.17 μ ; gypsum 24.5 (weak), 9.9, 8.85 μ (weak). Nitric acid solution gave 7.8, 9.53, 13.9, and 14.3, the alleged 12 μ line being absent. Dilute sulphuric acid (1 : 4) gives 9.4 (weak) and 10.02 μ . Carbon disulphide: 11.8 and 12.45 (weak), 15.15 μ . Infra-red investigations on calcite indicate two series of vibrations, "outer"

and "inner." For the former poor agreement with Raman lines is obtained, whilst for the latter the $9.1\ \mu$ line is optically inactive and a line at $11.38\ \mu$ is missing from the Raman spectrum. The $9.1\ \mu$ vibration is the least and the $11.38\ \mu$ vibration the most symmetrical. The Raman lines for the CO_2 and NO_2 groups exhibit a fairly close analogy. Infra-red data on gypsum indicate bands at 8.74 and $14.84\ \mu$. Raman lines at 2.84 and $2.95\ \mu$ observed with gypsum arise from the water of crystallisation. The relationship between the infra-red bands for carbon disulphide and the Raman lines remains obscure.

R. A. MORTON.

Raman effect from powdered crystals. A. C. MENZIES (*Nature*, 1929, 124, 511—512).—Raman lines were obtained by reflexion from powdered potassium nitrate.

A. A. ELDRIDGE.

Primary photo-electric current in antimony glance. K. H. VOIGT (*Z. Physik*, 1929, 57, 154—162).—The photo-electric primary current with antimony sulphide has been investigated with respect to its change with time, with the intensity of the light, and with the accelerating voltage applied. The decrease in the primary current after shutting off the light is in agreement with the views of Gudden and Pohl (cf. A., 1921, ii, 145; 1923, ii, 718; 1925, ii, 343).

J. W. SMITH.

Photo-electric behaviour of salts. J. WERNER (*Z. Physik*, 1929, 57, 192—226).—It has been shown that cadmium iodide, lead chloride, and potassium nitrate are all photo-sensitive, and that the photo-electric effects to be observed are due to the salts themselves and not to photochemical decomposition products. Using an accelerating potential of 40 volts, the photo-electric current decreases rapidly with time, but finally reaches a constant value. This is analogous to the behaviour of metals, and is due to the lowering of the concentration of free electrons in the surface, the latter being determined by the ratio of the velocity of the liberation of electrons to the velocity of their emission. On screening off the light or on application of a retarding potential a recovery is observed. The recovery process differs in the two cases. Recovery in the light under the influence of a retarding field is brought about by the decrease in the surface concentration of free electrons being neutralised by the further liberation of electrons; this can also be partly effected by lowering the accelerating potential. Recovery in the dark is brought about by the return of previously emitted electrons to the surface.

As in the case of metals, outgassing at first increases the photo-electric sensitivity of cadmium iodide, but a maximum is soon reached, after which a decrease is observed. Very complete outgassing stops the effect completely. Water vapour seems to exert a specific influence in this respect, since, after a preparation has been rendered completely insensitive by thorough outgassing, the admission of dry gas causes no change, whereas when a little moisture is introduced recovery is rapid.

J. W. SMITH.

Dielectric constants of argon and neon. A. B. BRYAN (*Physical Rev.*, 1929, [ii], 34, 615—617; cf. A., 1928, 1076).—Using the heterodyne beat method, the values found relative to 1.000589 for air were 1.000574

and 1.000148 for argon and neon, respectively, at N.T.P. (cf. Braunmühl's value for argon 1.000571; A., 1927, 294).

N. M. BLYTH.

Dipole moment of hydrocyanic acid and of some nitriles. O. WERNER (*Z. physikal. Chem.*, 1929, B, 4, 371—392).—The dipole moments of hydrocyanic acid, aceto-, propio-, butyro-, and benzo-nitrile have been determined by measuring the dielectric constants of dilute solutions of these substances in benzene. An improved resonance method is described which makes use of a piezoelectric quartz crystal for maintaining a constant frequency. The dipole moments of the nitriles in the aliphatic series increase with the length of the carbon chain. The dipole in these substances extends more over the whole molecule, whereas in the alcohols and amines the dipole is localised at the strongly deformed OH and NH_2 groups, respectively. It is calculated that the dipole moment would reach a limiting value in the nitrile series at the member $\text{C}_6\text{H}_{13}\cdot\text{CN}$. Hydrocyanic acid in its dielectric properties fits in regularly as the first member of the series and therefore has the nitrile structure. The dielectric constant and density of solid hydrogen cyanide have been redetermined ($\epsilon^{40} = 3.4 \pm 0.2$, $d^{40} = 0.925 \pm 0.005$).

O. J. WALKER.

Range of validity of the method of dilute solutions for the determination of dipole moments. O. WERNER (*Z. physikal. Chem.*, 1929, B, 4, 312—320).—The importance of the three terms which go to make up the total polarisation of a molecule, as determined by the method of dilute solutions, is discussed. The polarisation due to the deformation of the atoms cannot be determined with certainty and, in the case of heteropolar substances with large molecular volume, can no longer be considered as a small correction factor to be added to the orientation polarisation of the whole molecule. Measurements of the dielectric constants of solutions of tetraisoamylammonium picrate in benzene show that that substance is dissociated even in this solvent. The dilute solution method is therefore not applicable in such a case for determining dipole moment.

O. J. WALKER.

Temperature variation of the dipole moment. O. WERNER (*Z. physikal. Chem.*, 1929, B, 4, 393—400).—The distinction between rigid and non-rigid (flexible) dipoles is discussed (cf. Hojendahl, "Studies of Dipole Moment," 1928), and it is suggested that the two types of dipole may be distinguished by studying the temperature dependence of the dipole moment. A variation of the moment with the temperature would indicate the presence of an equilibrium, i.e., of a flexible dipole. This is illustrated by measurements of the dipole moment of benzonitrile (rigid dipole) and of quinol diethyl ether (flexible dipole) in dilute benzene solution at 20° , 40° , and 60° . The moment of benzonitrile is constant at the three temperatures, whereas that of the quinol ether increases by 16% from 20° to 60° . The application of the above view to the elucidation of the structure of pentaerythritol is indicated.

O. J. WALKER.

Electric moments of aromatic *p*-diamines. A. WEISSBERGER and R. SANGEWALD (*Z. physikal. Chem.*, 1929, B, 5, 237—240; cf. Williams, A.,

1928, 1180).—The dipole moments of tetramethyl-*p*-phenylenediamine and tetramethylbenzidine have been determined in *N*-benzene solution and found to be 1.23×10^{-18} and 1.25×10^{-18} e.s.u., respectively. These values support the general observation that corresponding disubstitution products of these types have similar dipole moments. The results further indicate that the figure given by Williams for the dipole moment of *p*-phenylenediamine is too low, and cannot therefore be used in favour of a "folded" formula for benzidine.

F. L. USHER.

Influence of solvents and other factors on the rotation and rotation-dispersion of optically active compounds. XXVII. Derivatives of lactic acid. T. S. PATTERSON and A. LAWSON (J.C.S., 1929, 2042—2051).—The rotations of a number of esters of lactic acid have been determined in light of six different wave-lengths at temperatures from 0° to 140°. The results show that the lactic acid formerly described as *d*-lactic acid should be called *l*-lactic acid. The general behaviour of the lactates seems to be similar to that of the tartrates.

C. W. HART-JONES.

Influence of position isomerism on specific properties. N. SCHOORL (Rec. trav. chim., 1929, 48, 935—937).—The molecular refractions (Gladstone-Dale; Lorentz-Lorenz), molecular coefficients of refraction (Eisenlohr, A., 1920, ii, 717), and parachors of *o*-, *m*. p. 29.3°, d_4^{20} 1.0465, n_D^{20} 1.5453, *m*-, *m*. p. 8°, d_4^{20} 1.0336, n_D^{20} 1.5398, and *p*-cresols, *m*. p. 33.6°, d_4^{20} 1.0341, n_D^{20} 1.5395, are calculated. The values for the *m*- and *p*-derivatives are in closer agreement in all cases, and the largest difference for the *o*-compound is for the parachor ($o < p < m$).

H. BURTON.

Valency. XIII. Molecular structure of the quadrivalent derivatives of tellurium. T. M. LOWRY and F. L. GILBERT (J.C.S., 1929, 2076—2091).—The properties of the quadrivalent derivatives of tellurium are discussed in the light of the structure recently assigned to the β -compounds by Drew (this vol., 546). Drew's conclusion that the conversion of the α - into the β -dihalides involves the wandering of a methyl group from one tellurium atom to another is verified, but the contrast between these salts is not sufficient to class the β -salts as necessarily complex and the α -salts as always monomeric. There is strong *a priori* evidence for the view that the solid phase of the α -compounds may have a similar structure to that assigned by Drew to the β -compounds. According to this view, the solid may be a complex salt $[\text{TeMe}_3]^+[\text{TeMeI}_4]^-$ or an aggregate of the two components TeMe_3I , TeMeI_3 . In the case of the complex salt all the atoms are covalently linked to tellurium and may be expected to contribute to the colour of the ion, but in the case of the double salt, one of the iodine atoms should be colourless as in TeMeI_3 . The existence of a labile red and a stable purple solid form of the bromotri-iodide (Drew) $\text{TeMe}_3\text{Br}, \text{TeMeI}_3$ or $[\text{TeMe}_3]^+[\text{TeMeBrI}_3]^-$ could be explained by formulating the red crystals as the double salt and the purple crystals as the complex salt. The existence of an orange high-temperature and a purple low-temperature form of *cyclotelluripentane* di-iodide (Morgan and Burgess, A., 1928, 435) is

similarly explained. The absorption spectra of many of the β -salts have been examined, and the molecular extinction coefficients determined from 2000 to 5000 Å. The conductivities of the β -methyl and -ethyl bases have been determined in aqueous solution, and those of various salts in the fused state and in non-aqueous solvents. The solubilities of α -dimethyltelluronium di-iodide in various organic solvents at 25° are given. The parachor of diphenyl telluride gives a value of 77.4 units per atom of tellurium. The values determined from the α - and β -dihalides of the methyl and ethyl series are considerably less.

C. W. HART-JONES.

Theory of the valency octet in the "torular" atom model. I—VII. D. RĂDULESCU (Bul. Soc. Stiinte Cluj, 1928, 4, 263—279, 280—291, 292—305, 306—311, 312—322, 323—325, 326—332; Chem. Zentr., 1929, i, 1783—1784).—Theoretical.

A. A. ELDRIDGE.

Para- and ortho-hydrogen. K. F. BONHOEFFER and P. HARTECK (Z. physikal. Chem., 1929, B, 5, 292).—An explanatory note regarding a passage in an earlier paper (cf. this vol., 982).

F. L. USHER.

Homogeneity of water. K. F. BONHOEFFER and P. HARTECK (Z. physikal. Chem., 1929, B, 5, 293—296).—From consideration of the various terms in Nernst's expression for vapour pressure it is shown that the ortho and para modifications of a liquid should have different vapour pressures; hence fractional distillation, sublimation, or condensation should lead to a change in the proportion of the constituents and to the possibility of detecting a difference in their vapour pressures. Theoretical considerations, supported by some preliminary fractionation experiments with water, made it evident that fractions with different vapour pressures could not be expected with the usual experimental arrangement owing to the high velocity with which equilibrium between the ortho and para components is established. Single fractionations were therefore carried out with conductivity water at a low temperature as rapidly as possible and the vapour pressures of the distillate and residue measured quickly and accurately. Even under these conditions no difference could be detected. The negative result is attributed entirely to the high velocity of transformation of one modification into the other.

F. L. USHER.

General principles of oxidation-reduction reactions and of chemical combinations. II, III. B. JIRGENSONS (Z. Elektrochem., 1929, 35, 473—477, 477—483; cf. this vol., 896).—A discussion of the application of the electronic theory of valency to inorganic oxidation-reduction reactions and to the structure of various organic compounds.

H. T. S. BRITTON.

Numerical approximations neglected in both chemistry and physics. R. PANEBIANCO (Schola et Vita, 1929, 4, 163—172).—The errors introduced into chemical and physical data by the neglect or the incorrect application of the theory of approximations are pointed out and discussed with illustrative examples.

L. S. THEOBALD.

Determination of the configuration of stereoisomeric ethylene derivatives. K. VON AUWERS

and L. HARRIS (Z. physikal. Chem., 1929, 143, 1—20).—The relationships between the b. p., densities, refractive indices, and specific elevations of the esters of stereoisomeric substituted acrylic acids correspond in general with those between *o*- and *p*-benzene derivatives of analogous structure, in accordance with Langseth's assumption. It is therefore legitimate in these cases to reach conclusions regarding configuration. Numerous exceptions, however, exist; the rule is not valid for the comparison of the esters of maleic and fumaric acids with those of *o*- and terephthalic acids, neither can the configuration of the oximes be deduced by comparison of the physical constants with those of phenols. H. F. GILLBE.

Molecular structure of triatomic gases. P. N. GHOSH and P. C. MAHANTI (Physikal. Z., 1929, 30, 531—537).—Triatomic molecules may possess a symmetrical linear structure, an unsymmetrical linear form, or a structure of the form of an isosceles triangle. From data on the dielectric constant and the refractivity of carbon dioxide $(\epsilon-1) \times 10^{-7}$ is equal to $(n_{\infty}^2-1) \times 10^{-7}$, indicating a symmetrical linear structure. The analysis of infra-red spectra and the Raman effect supports this conclusion. For sulphur dioxide $\epsilon > n_{\infty}^2$, indicating an unsymmetrical structure. The dipole moment is large, so that the triangular model is more probable than the unsymmetrical linear form, a conclusion supported by the infra-red data. For carbon disulphide $\epsilon = n_{\infty}^2$, indicating that the linear structure shown by carbon dioxide is reproduced in conformity with the spectroscopic data. For nitrogen peroxide $\epsilon > n_{\infty}^2$ and the unsymmetrical molecule is more likely to exhibit the triangular than the linear form. R. A. MORTON.

Molecular energy and structure. G. BECK (Z. anorg. Chem., 1929, 182, 332—342).—Various regularities in the properties of molecules are derived on the assumption that the electrons in a molecule in the solid state comport themselves as a quasi-ideal gas. H. F. GILLBE.

Properties of salt-like compounds and atomic structure. A. HANTZSCH and H. CARLSOHN (Z. Krist., 1929, 69, 556; Chem. Zentr., 1929, i, 1889).—Polemical (cf. Fajans, A., 1928, 1170).

A. A. ELDRIDGE.

[Properties of salt-like compounds and atomic structure.] K. FAJANS (Z. Krist., 1929, 69, 557; Chem. Zentr., 1929, i, 1889—1890).—A reply to Hantzsch and Carlsohn (preceding abstract).

A. A. ELDRIDGE.

Shell charge and proton migration. E. WIERBERG (Z. physikal. Chem., 1929, 143, 97—118).—Theoretical. It is assumed that when a proton is detached from one central atom to combine with another it moves from the atom with the greater effective repelling force, as measured by the charge contributed by the outer electron shell. General definitions of acidity and basicity are given, and the acidic or basic properties of various atomic groupings are discussed and explained on the assumption of proton migration in the direction indicated by this rule. Different stabilities are predicted for ammonium and oxonium compounds, and the hydrolysis of certain

sodium compounds, e.g., sodamide and sodium methide, is explained. F. L. USHER.

Evaluation and interpretation of parachors. S. A. MUMFORD and J. W. C. PHILLIPS (J.C.S., 1929, 2112—2133).—The mean CH_2 parachor increment adopted by Sugden (cf. A., 1924, ii, 662) is too small. New values calculated for the various atomic and structural constants have been obtained by the aid of a corrected increment, and lead to an improvement in the agreement between observed and calculated values, especially in the case of compounds of high mol. wt. They also afford a rational interpretation of parachor variations on the basis of intramolecular strain. The interatomic stresses in substituted ring systems, in branched-chain derivatives, and in compounds containing accumulated negative groups are considered. The departure of the parachor from additivity in such compounds is accounted for by the introduction of strain constants, the value of which is shown to give a measure of the alteration in the effective size of the central atom of the group. The parachors of hydroxy-compounds and amines are brought into line with those of non-associated compounds by assuming the effective volume of the hydrogen atom to decrease with increasing electron affinity of the atom to which it is attached. By assigning a higher value to halogen ions than to bound halogen atoms, the apparent parachor anomaly of fused salts (Sugden and Wilkins, this vol., 983) is overcome. A method for estimating such ionic parachors is indicated. The conclusions of Sugden and co-workers with respect to different types of interatomic linkings are not invalidated.

C. W. HART-JONES.

Determination of molecular forces from the viscosity of a gas. H. R. HASSÉ and W. R. COOK (Proc. Roy. Soc., 1929, A, 125, 196—221; cf. A., 1927, 616).—The law of variation of viscosity of a gas with temperature has been determined on the basis of Lennard-Jones' molecular model (A., 1925, ii, 91), and an equation is derived for the special case where the mutual actions of the molecules are represented by repulsive and attractive forces of the types λr^{-9} and μr^{-5} , respectively. The calculated values for argon, hydrogen, nitrogen, carbon dioxide, air, and mercury vapour are in fair agreement with experiment over a limited range of temperature, but no agreement is found in the cases of helium and neon. The values of the force constants λ and μ are calculated and compared with those deduced from the equation of state, using the same molecular model; excellent agreement is obtained in the values of λ , but those of μ show a divergence. It is possible that the value of the index m is incorrect. L. L. BIRCHMISHAW.

Dimensions of diatomic molecules. J. K. SYRGIN (Z. physikal. Chem., 1929, B, 5, 156—159).—Mathematical. Diatomic homopolar molecules are assumed to be rigid quadrupoles. Their moments can be calculated from the critical constants. From the size of the moment, the dimensions of the quadrupole can be obtained. Results are given for a number of diatomic gases, which are in good agreement with the nuclear distances obtained by a study of spectra. A. J. MEE.

X-Ray diffraction by amorphous solids. P. KRISHNAMURTI (Indian J. Physics, 1929, 4, 99—108).—The changes in the X-ray diffraction maxima of ordinary rosin, shellac, and a synthetic resin of composition $(C_7H_8)_n$ have been observed over the temperature range 28—120°. For shellac and the synthetic resin the contraction of the halo is greatest between 28° and 45°, whilst for rosin the maximum changes take place at about 65°.

W. E. DOWNEY.

Ionisation spectrometer for long-wave X-rays. H. KULENKANPFF and B. WOERNLE (Physikal. Z., 1929, 30, 551—554).—A preliminary account of a new instrument.

R. A. MORTON.

Effect of X-rays on certain optical properties of liquids and glass. F. ALLISON (Physical Rev., 1928, [ii], 31, 306).—In sucrose and tartaric acid solutions, X-rays increase the induced right-handed rotation approximately in proportion to the concentration. X-Rays induce in glass in a magnetic field a small rotation opposite to the Faraday rotation.

L. S. THEOBALD.

Influence of crystal habit on the Debye-Scherrer diagram. J. BOHM and F. GANTER (Z. Krist., 1928, 69, 17—25; Chem. Zentr., 1929, i, 2013).

Isomorphism and homology. P. C. RAY (Nature, 1929, 124, 480—481).—Ammonium and potassium beryllium fluorides are complex salts having the bivalent anion BeF_4 , although partly further dissociated. Double salts, $X_2BeF_4 \cdot YSO_4 \cdot 6H_2O$ ($X=K$ or NH_4 , $Y=Ni$, Co , or Zn ; $X=K$, $Y=Co$; $X=NH_4$, $Y=Fe$, Mn , Mg , or Cd), have been prepared. These salts are isomorphous with the double sulphates and fluoberyllates.

A. A. ELDRIDGE.

Favourable direction of growth of some metal crystals. S. TSUBOI (Mem. Coll. Sci. Kyoto, 1929, A, 12, 223—226).—The directions of growth of crystals of aluminium, lead, zinc, cadmium, and bismuth have been investigated, when crystallisation was made to take place in one direction by drawing up a wire from the molten metal. Aluminium and lead generally grew in a direction parallel to the (100) axis of their face-centred cubic crystals, and the other three metals nearly perpendicular to the principal axis of their hexagonal crystals. The most favourable direction is closely connected with the form of the crystal lattice.

C. W. GIBBY.

Examination of ice crystals by X-rays. U. YOSHIDA and S. TSUBOI (Mem. Coll. Sci. Kyoto, 1929, A, 12, 203—207).—Ice formed on the surface of still water, in ice columns in the ground, and in icicles has been examined by means of X-rays. The direction of growth is in each case parallel to the basal plane of the hexagonal ice crystal. No such regularity is found in ice produced by sudden cooling.

C. W. GIBBY.

Method of producing long single crystals of metal. Factors influencing crystal orientation and perfection. A. GOETZ and M. F. HASLER (Proc. Nat. Acad. Sci., 1929, 15, 646—656).—General methods of producing large crystals are discussed. A two-stage method is described for the production of

crystals of any desired length with a constancy of diameter to less than 2%; the progressive crystallisation of molten metal (bismuth) in a glass or quartz tube is followed by the remelting of the metal in the tube and starting a new crystallisation by drawing out the tube and metal together by means of a mechanical device effecting and controlling the speed of introduction of the tube into a furnace and its withdrawal. The zone of crystallisation is located and the effects of a strong magnetic field and the temperature gradient on the orientation were studied. Variation of gradient and of strain applied to the crystal influenced the orientation. N. M. BLIGH.

Theory of recrystallisation of pure metals. U. DEHLINGER (Ann. Physik, 1929, [v], 2, 749—793).—The recrystallisation temperature is found on the basis of experiment to be best defined as that temperature at which the velocity of recrystallisation undergoes a sudden change. Recrystallisation involves at least two successive processes. One is a loosening of inner forces (Verhakungen) which is not detectable by X-ray analysis, but nevertheless fixes the recrystallisation temperature and the time factors. The other is the recovery or grain-formation as a result of inner elastic forces persisting in the deformed state. An extended theoretical discussion is given.

R. A. MORTON.

Morphological and structural relationships of meteoric iron in relation to its evolution. J. LEONHARDT (Neues Jahrb. Min., 1928, 58, A, 153—212; Chem. Zentr., 1929, i, 1915—1916).—An X-ray, microscopical, and goniometric study shows that the structure of meteoric iron is affected by secondary processes of growth and metamorphosis.

A. A. ELDRIDGE.

X-Ray study of iron-nitrogen compounds. A. OSAWA and S. IWAIZUMI (Z. Krist., 1928, 69, 26—34; Chem. Zentr., 1929, i, 2012).—In the nitride Fe_4N , cubic, a 3.86 Å., d_{calc} 6.57, the iron atoms form a face-centred lattice with one nitrogen atom in the unit cell. In the nitride Fe_2N , hexagonal, a 2.743 Å., $c:a$ — 1.59, 5.02, the iron atoms form a close-packed hexagonal lattice with one nitrogen atom in the unit cell.

A. A. ELDRIDGE.

Structural investigation of Heusler's alloy. S. VALENTINER and G. BECKER (Z. Physik, 1929, 57, 283—291).—X-Ray spectrograms of alloys of the composition $Al(Cu,Mn)_3$ were obtained, and combined with metallographic observations, including the change of length on tempering, lead to the result that the magnetic properties of Heusler's alloy cannot be attributed to any particular lattice arrangement.

A. J. MEE.

Internal strain of uniformly distorted aluminium crystals. K. YAMAGUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 151—169; cf. this vol., 248).—X-Ray analysis shows that the internal strain within a uniformly distorted aluminium crystal is chiefly due to the elastic curvature of the crystal which is necessarily produced by slipping of a limited area on the slip plane, so long as the strain due to slip does not exceed about 0.2 or 0.3. The amount of rotation of the slip plane (cf. Taylor, A., 1928, 695) increases gradually and almost linearly

with increasing amount of shear. Specimens with higher resistance to slipping are also the most strained internally for the same amount of shear, thus showing the close relationship of the internal strain and the work-hardening of the metal. J. W. SMITH.

Crystal structure of the chlorides of certain bivalent elements. L. PAULING (Proc. Nat. Acad. Sci., 1929, 15, 709—712).—Results given by Bruni and Ferrari (A., 1926, 995) were used to deduce the atomic arrangement of the bivalent chlorides of cadmium, magnesium, nickel, and cobalt. It has also been shown that other representatives of the same class are manganese, zinc, ruthenium, rhodium, palladium, iridium, and platinum chlorides. The structure found is one closely resembling the cadmium iodide structure. Each cation is surrounded by six chloride ions approximately at the corners of a regular octahedron, six edges of which are shared with other octahedra so as to form a layer. It seems probable that the cadmium chloride structure is the stable one for substances of the type MX_2 where the cation M has a co-ordination number 6 and the anion has a small polarisability. A. J. MEE.

Crystal structure of strontium. F. SIMON and E. VOHSEN (Proc. Nat. Acad. Sci., 1929, 15, 695; cf. A., 1928, 694).—The higher value found by King (this vol., 749) than by the authors (*loc. cit.*) for the unit cube edge of strontium is due to the fact that King worked at the ordinary temperature, whereas the authors used liquid air temperatures. When this is corrected for, the values obtained by both sets of observers agree to within the experimental error, and also agree with those obtained by Ebert (this vol., 631). A. J. MEE.

Crystal structure of some binary compounds of the platinum metals. II. L. THOMASSEN (Z. physikal. Chem., 1929, B, 4, 277—287; cf. this vol., 630).—Four further compounds have been investigated. The following have the pyrites structure: palladium diarsenide, PdAs_2 (a 5.970 ± 0.004 Å.), platinum diphosphide, PtP_2 (a 5.683 ± 0.004 Å.), rhodium disulphide, RhS_2 (a 5.574 ± 0.005 Å.). Platinum monoantimonide, PtSb (a 4.130 ± 0.004 , c 5.472 ± 0.005 Å.), has a nickel arsenide structure. None of these substances is ferromagnetic. A new determination of the structure of platinum diarsenide, PtAs_2 , gave a value of $a = 5.957 \pm 0.003$ Å. O. J. WALKER.

X-Ray investigations of manganese nitrides. G. HAGG (Z. physikal. Chem., 1929, B, 4, 346—370).—X-Ray investigations of the system manganese-nitrogen show the existence of four nitride phases. The manganese nitrides were prepared by heating powdered manganese in presence of gaseous ammonia. The phase with the lowest nitrogen content is homogeneous at about 2% N and can exist only above 500° . The manganese atoms are arranged in a face-centred tetragonal lattice (for 2.2% N $a = 3.765$, $c = 3.684$ Å.), but there is no indication of a regular arrangement of the nitrogen atoms. The next higher nitride phase is homogeneous between 6.0 and 6.5% N at 400° and below. The manganese atoms have a face-centred cubic lattice (a 3.855 — 3.860 Å. at 400°). In the third phase the manganese atoms are arranged in a

hexagonal lattice with most dense spherical packing, the nitrogen atoms being distributed at random in the spaces between them. At 400° the lattice dimensions increase from a 2.773 , c 4.520 Å. for 9.2% N to a 2.828 , c 4.528 Å. for 11.9% N. The fourth phase has a face-centred tetragonal arrangement of the manganese atoms, the dimensions increasing from a 4.194 , c 4.031 Å. for 13.5% N to a 4.207 , c 4.129 Å. for 14% N. The cubic and hexagonal phases are analogous to two phases in the system iron-nitrogen. The manganese nitrides can exist in a stream of ammonia at atmospheric pressure even when their nitrogen fugacity is greater than 1 atm.

O. J. WALKER.

Polymorphism of sodium sulphate. I. Thermal analysis. F. C. KRACEK (J. Physical Chem., 1929, 33, 1281—1303).—Heating and cooling curves for sodium sulphate over the range 190 — 280° indicate that five distinct modifications of this substance exist, but owing to hysteresis in the inversions the equilibrium temperatures cannot be definitely fixed. Approximate values are quoted, however, and the five phases are identified with those of previous workers. L. S. THEOBALD.

Polymorphism of sodium sulphate. II. Densities of anhydrous sodium sulphate at 25° . F. C. KRACEK and R. E. GIBSON (J. Physical Chem., 1929, 33, 1304—1308; cf. preceding abstract).—Density determinations at $25^\circ \pm 0.01$ show that sodium sulphate can exist in at least two modifications at the ordinary temperature and pressure. These forms are thenardite or $\text{Na}_2\text{SO}_4\text{-V}$, d 2.664 ± 0.001 , and $\text{Na}_2\text{SO}_4\text{-III}$, d 2.697 ± 0.001 , which is the modification finally left when thenardite is heated above 200° and then cooled. Persistent inclusions of air or liquid in the crystals of sodium sulphate limit the accuracy of d . L. S. THEOBALD.

Structural relations of alkali sulphates. B. GOSSNER and F. MUSSGUNG (Z. Krist., 1929, 69, 446—454; Chem. Zentr., 1929, i, 1891).—The lattice constants of sodium sulphate are: a 9.79 , b 5.89 , c 12.31 Å., the corresponding axial ratio being $a:b:c = 1.662:1:2.090$. The unit cell contains 8 mols., $d_{\text{calc.}}$ 2.673 , space-group V_2^4 . Results for the molecules LiKSO_4 , $\text{NaK}_3(\text{SO}_4)_2$, K_2SO_4 , and Na_2SO_4 are compared. A. A. ELDRIDGE.

Lattice constants of copper sulphate. B. GOSSNER and K. BRUCKL (Z. Krist., 1929, 69, 422—426; Chem. Zentr., 1929, i, 1891—1892).—The lattice constants are: a 6.07 , b 10.78 , c 5.89 Å., with 2 mols. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the unit cell, the corresponding axial ratio being $a:b:c = 0.563:1:0.546$ (goniometric, $a:b:c = 0.5721:1:0.5554$).

A. A. ELDRIDGE.

Crystal structure of anhydrous alums $\text{R}'\text{R}''(\text{SO}_4)_2$. L. VEGARD and A. MAURSTAD (Z. Krist., 1929, 69, 519—532; Chem. Zentr., 1929, i, 1892).—The following constants (Å.) for the hexagonal unit cells were obtained: $\text{KAl}(\text{SO}_4)_2$, a 4.706 , c 7.960 ; $\text{NH}_4\text{Al}(\text{SO}_4)_2$, a 4.724 , c 8.225 ; $\text{NH}_4\text{Fe}(\text{SO}_4)_2$, a 4.825 , c 8.310 ; $\text{KCr}(\text{SO}_4)_2$, a 4.737 , c 8.030 . The unit cell contains 1 mol.; space-group D_3^2 .

A. A. ELDRIDGE.

Lattice constants and the space-groups of barium and strontium carbonates. T. A. WILSON (Physical Rev., 1928, [ii], 31, 305).—The fundamental lattice for both carbonates is the simple orthorhombic Γ_0 , and the unit cell contains 4 mols. That of barium carbonate has a_0 5.252 ± 0.001 , b_0 8.828 ± 0.002 , c_0 6.544 ± 0.001 Å., 4.291 ± 0.004 ; the corresponding values for strontium carbonate are 5.118 ± 0.003 , 8.404 ± 0.005 , 6.082 ± 0.004 Å., 3.722 ± 0.006 . The space-group of barium carbonate is $2D_1-16$ ($X-a$), and that of strontium carbonate probably the same. L. S. THEOBALD.

Cobaltamine chloratosulphates and perchloratosulphates, and a comparison of the lattice constants of cobaltates and chromiates. O. HASSEL and H. KRINGSTAD [with I. OFTEDAL] (Z. anorg. Chem., 1929, 182, 281–288).—Hexamminocobaltic chloratosulphate, prepared from the corresponding chloride by liberation of the base with moist silver oxide and neutralisation with a mixture of sulphuric acid and chloric acid, is sparingly soluble in water and forms yellow octahedra. Pentammineaquo- and hexammino-cobaltic perchloratosulphates have been prepared in a similar manner. The lattice constants in Å. of these three complexes, all of which crystallise in the cubic system, are 10.80 ± 0.01 , 10.89 ± 0.01 , and 10.95 ± 0.01 , respectively. Tetramminediaquocobaltic perchloratosulphate, obtained from the chloride, forms reddish-violet, hexagonal prisms, and the trihydrate of triaminotriaquocobaltic perchloratosulphate, prepared from triaminotritritocobaltic chloride by direct treatment in acetic acid solution with a mixture of sulphuric and perchloric acids, forms deep reddish-violet prisms; although both substances crystallise in the hexagonal system, the elementary cell containing 4 mols., the X-ray diagrams differ considerably. Other lattice constants which have been measured are: pentammineaquo-cobaltic chloratosulphate, 10.73 ± 0.01 ; hexamminochromic perchlorate, 11.545 ± 0.005 ; pentammineaquo-chromic perchlorate, 11.47 ± 0.00 ; pentammineaquo-chromic bromatosulphate, 10.535 ± 0.005 Å. The approximately constant difference between the lattice constants of the hexammino- and pentammineaquo-compounds indicates a constant change of volume by substitution of ammonia by water, whereas by the substitution of cobalt by chromium more complex relationships exist. The larger lattice dimensions of the chromium compounds are to be expected in view of the greater nuclear charge.

H. F. GILLBE.

Fine structure of the chemical elements. J. BECKENKAMP (Zentr. Min. Geol., 1929, A, 65–79; Chem. Zentr., 1929, i, 1890).

Crystal structure. II. A. NOLD (Z. Krist., 1929, 69, 427–445; Chem. Zentr., 1929, i, 1890).

Lattice constant of barium telluride. V. M. GOLDSCHMIDT [with E. BROCH and I. OFTEDAL] (Z. Krist., 1929, 69, 411–414; Chem. Zentr., 1929, i, 1891).—New values (± 0.002 Å.) are 6.986 and 6.984 Å., in accord with the earlier value 6.986 .

A. A. ELDRIDGE.

Change [of crystal structure] of rubidium halides by pressure. L. PAULING (Z. Krist., 1928,

69, 35–40; Chem. Zentr., 1929, i, 2011).—The caesium chloride structure for the high-pressure modifications of rubidium halides is supported.

A. A. ELDRIDGE.

Translation lattice of methylcellulose. X-Ray investigations on cellulose derivatives. II. C. TROGUS and K. HESS (Z. physikal. Chem., 1929, B, 4, 321–345; cf. A., 1928, 1225).—Two forms of trimethylcellulose, one preserving the natural fibre structure of ramie and the other corresponding with the mercerised fibre, have been studied. The diagrams for both agree with a 21.3, b 25.6, c 11.3 Å. The digonal helical axis is lacking in both. Within the limitations of technique the diagram to be expected from the net plane distances is reproduced experimentally. Reference is made to the uncertainty of conclusions connecting intensity measurements and constitutional problems regarding cellulose and also of the calculation of micellar magnitudes from the breadth of interference fringes. The interpretation of the digonal helical axis in the fibre diagrams of cellulose and cellulose hydrate in the sense of principal valency chains is scarcely to be reconciled with the methylcellulose diagram without recourse to special hypotheses. R. A. MORTON.

Reversible and irreversible lattice changes of cellulose triacetate. X-Ray investigations of cellulose derivatives. III. K. HESS and C. TROGUS (Z. physikal. Chem., 1929, B, 5, 161–176; cf. preceding abstract).—When fibrous cellulose triacetate is allowed to swell in cyclohexanone, methyl alcohol, benzene, pyridine, or a chloroform-methyl alcohol mixture, an expansion of the lattice at right angles to the fibre is observed, and the original dimensions are regained when the solvent is removed by drying or displacement. If, however, the material is completely dispersed in chloroform the lattice is destroyed, and on reprecipitation with methyl alcohol a different lattice is formed. The change in the lattice structure corresponds with a marked difference in external properties, the reprecipitated material consisting of doubly refracting crystalline needles, possessing when swollen a lower elastic limit, and incapable of forming a film on drying. The lattice of this second form remains unchanged when the substance is moistened with organic liquids. The nature of the process of dissolution is discussed in the light of the observations. F. L. USHER.

Silk fibroin. II. O. KRATKY (Z. physikal. Chem., 1929, B, 5, 297–300; cf. Brill, A., 1924, i, 102).—A preliminary account of the application of improved experimental methods (cf. Weissenberg, this vol., 493) to the X-ray examination of silk fibroin. F. L. USHER.

Crystal structure of tartaric acid, isohydrobenzoin, and rubidium tartrate. A. REIS and W. SCHNEIDER (Z. Krist., 1928, 69, 62–76; Chem. Zentr., 1929, i, 2524).—Tartaric acid and isohydrobenzoin crystallise in space-group C_2^2 , with 2 mols. in the unit cell. The following values, respectively, are recorded: $T_{(100)}$ 7.68, 12.40; $T_{(010)}$ 6.03, 7.92; $T_{(001)}$ 6.18, 5.81 Å.; β $100^\circ 17'$, $92^\circ 53'$. Rubidium tartrate, $Rb_2C_4H_4O_6$, crystallises in space-group D_2^4 (D_2^3) with

6 mols. in the unit orthohexagonal cell; $T_{(010)}$ 7.17, $T_{(001)}$ 13.19 Å. A. A. ELDRIDGE.

Crystal structure of anhydrous mesotartaric acid and tartrates. W. SCHNEIDER (Z. Krist., 1929, 69, 49—61; Chem. Zentr., 1929, i, 2523—2524).—The smallest (triclinic) translation cell has $T_{(100)}$ 9.24, $T_{(010)}$ 6.33, $T_{(001)}$ 5.45 Å.; α 70.5°, β 78.0°, γ 79.5°, and contains 2 mols. of $C_4H_4O_6$. The thallium salt contains 4 mols. of $Tl_2C_4H_4O_6$; $T_{(100)}$ 13.66, $T_{(001)}$ 7.63 Å.; β 86° 37'. Potassium mesotartarate dihydrate has $a:b:c=1.019:1:1.600$; α 95° 44', β 102° 52', γ 61° 46'; the unit cell contains 2 mols. of $K_2C_4H_4O_6 \cdot 2H_2O$; $T_{(100)}$ 7.02, $T_{(001)}$ 11.02 Å.

A. A. ELDRIDGE.

X-Ray studies on pentaerythritol. H. MARK and G. VON SUSICH (Z. Krist., 1928, 69, 105—117; Chem. Zentr., 1929, i, 2520—2521).—The following values were obtained: a 6.09, c 8.79 Å.; 2 mols. $C_5H_{12}O_4$ in the unit cell; space-group C_2^1 or S_6^1 .

A. A. ELDRIDGE.

Crystal structure of pentaerythritol, pentaerythrityl tetra-acetate, and dibenzylidenepentaerythritol. F. A. VAN MELLE and H. B. J. SHURINK (Z. Krist., 1928, 69, 1—16; Chem. Zentr., 1929, i, 2521).—Studies on the crystal structure of compounds CX_4 are discussed. Pentaerythrityl tetraacetate has space-group C_{4h} . Dibenzylidenepentaerythritol has $c:a=6.09$; J_{0001} 36.7 Å.; the unit cell contains 3 mols.

A. A. ELDRIDGE.

Crystalline form of thiophen and its solid solutions with benzene. G. BRUNI and G. NATTA (Rec. trav. chim., 1929, 48, 860—863).—The axial ratios $a:b:c=0.771:1:0.704$ have been found for benzene crystals at about -170° in an X-ray examination using a calcium anticathode. These results confirm those of Cox (A., 1928, 1081). Thiophen crystallises with a tetragonal cell with an axial ratio $c/a=1.32$, containing 4 mols. At about -170° the dimensions of the cell are a 7.22, c 9.53 Å.; $v=497.10 \times 10^{-24}$ cm³, d_{calc} 1.123. Benzene and thiophen are not isomorphous, but exhibit isodimorphism by reason of their similar crystalline form and dimensions. Solid solution crystals separating from mixtures containing 75—50% of thiophen give photograms identical with those of thiophen, the contractions in the lattice dimensions varying from 0.01 to 0.03 Å.

F. G. TRYHORN.

Crystal structure of tysonite and some artificial lanthanide fluorides. I. OFTEDAL (Z. physikal. Chem., 1929, B, 5, 272—291).—Powder diagrams of tysonite ($[Ce, La]F_3$), and of specimens of lanthanum, cerium, praseodymium, neodymium, and samarium fluorides prepared in the laboratory have been made. A common structure is proposed for all the substances named: a hexagonal elementary cell with c -axis of the order 7 Å. and axial ratio 1.77, containing two metal ions. From the Laue diagram of tysonite it is inferred that the above is a pseudo-cell, the smallest cell compatible with the diagram being three times as large, and containing 6 mols. of RF_3 . The axial ratio is about 1.023 for all the substances.

F. L. USHER.

Technique for X-ray examination of crystal structures with many parameters. W. L. BRAGG

and J. WEST (Z. Krist., 1928, 69, 118—148; Chem. Zentr., 1929, i, 2012).

Structure of diopside, $CaMg(SiO_3)_2$. B. WARREN and W. L. BRAGG (Z. Krist., 1928, 69, 168—193; Chem. Zentr., 1929, i, 2013).

Fine structure of brookite. J. H. STURDIVANT and L. PAULING (Z. Krist., 1929, 69, 557—559; Chem. Zentr., 1929, i, 1892).—Schroder's results (*ibid.*, 1928, 67, 485) are based on an error.

A. A. ELDRIDGE.

Crystal structure of the A -modification of sesquioxides of the rare-earth metals. L. PAULING (Z. Krist., 1929, 69, 415—421; Chem. Zentr., 1929, i, 1891).—Contrary to Zachariasen's view, a structure having symmetry D_{3d}^5 is proposed.

A. A. ELDRIDGE.

Comparative X-ray examination of magnesium silicates. B. GOSSNER and F. MUSSGÜNG (Neues Jahrb. Min., 1928, 58, 213—252; Chem. Zentr., 1929, i, 1892).—Prismatin (SiO_2 33.20, Al_2O_3 42.36, Fe_2O_3 0.30, FeO 5.81, MgO 11.76, Na_2O 5.07, K_2O 0.83, H_2O 1.62%, d 3.280) forms a rectangular parallelepiped, a 13.86, b 16.02, c 6.78 Å. (calc. $a:b:c=0.865:1:0.423$), and is considered to be $3Al_2O_3 \cdot 4MgSiO_3$ with 4 mols. in the unit cell. Kornerupin has c 6.8 Å. Sapphirin has $a:b:c=0.667:1:0.691$, $\beta=105^\circ 29'$ (approx.), with 8 mols. of $2Al_2O_3 \cdot Mg_2SiO_4$ (partial replacement of $SiMg$ by Al_2) in the unit cell. Actinolite has $a:b:c=0.536:1:0.290$, $\beta=105^\circ 36'$. Glaucophane, with 4 mols of $NaAlSi_2O_6 \cdot 2MgSiO_3$ in the unit cell, has $a:b:c=0.543:1:0.300$, $\beta=104^\circ 10'$.

A. A. ELDRIDGE.

Aenigmatite and its position in the silicate system. B. GOSSNER and F. MUSSGÜNG (Zentr. Min. Geol., 1929, A, 5—11; Chem. Zentr., 1929, i, 1914).—The unit cell has a 18.3, b 18.3, c 10.6 Å., α 96.5°, β 96.5°, γ 113.5°.

A. A. ELDRIDGE.

Thortveitite. B. GOSSNER and F. MUSSGÜNG (Zentr. Min. Geol., 1929, 1—5; Chem. Zentr., 1929, i, 1915).—Thortveitite, monoclinic, $2SiO_2 \cdot Se_2O_3$, has a 6.56, b 8.58, c 4.74 Å., β 103° 8', whence $a:b:c=0.767:1:0.552$. The unit cell contains 2 mols.; space-group C_{2h}^2 .

A. A. ELDRIDGE.

Magnetic birefringence in solutions and its relation to crystal structure and properties. M. RAMANADHAM (Indian J. Physics, 1929, 4, 109—130).—Benzene, naphthalene, phenanthrene, azobenzene, and anthracene show positive magnetic double refraction in ascending order of magnitude. Nitro-aromatic compounds, maleic acid, nitrates, and nitrites also give the effect. The known magnetic and optical properties of these various crystalline compounds have been related to the magnetic birefringence exhibited by them, on the assumption that the molecules inside the crystal are all parallel.

W. E. DOWNEY.

Anomalous diamagnetism of graphite. S. PARAMASIVAN (Indian J. Physics, 1929, 4, 141—146).—Seven varieties of amorphous carbon have been found to show specific diamagnetic susceptibility between 0.36×10^{-6} and 0.53×10^{-6} . Graphite gives values 3.5×10^{-6} to 4.2×10^{-6} , diamond 0.47×10^{-6} , and graphitic anthracite 0.97×10^{-6} . W. E. DOWNEY.

Structure of the atomic magnet in ferromagnetic materials. R. FORRER (*J. Phys. Radium*, 1929, [vi], 10, 247—262).—A fine metal wire is annealed, stretched to the breaking point, wound on a mandrel six times the wire diameter to give it a slight permanent curvature, and straightened by inserting it into a capillary tube. Such a wire gives a very simple magnetisation curve in which the reversible and irreversible components are almost completely separated. It is concluded from comparisons with models that in nickel there are two magnetic moments at right angles to each other. This doublet may be oriented without respect to the crystallographic axes and is influenced by a magnetic field. In ferromagnetic materials the hysteresis cycle results from a rotation and inversion of the magnetic multiplet. The multiplet is deformable, and may close up under the action of an intense field, resulting in saturation. Similar considerations lead to the assumption of a tri-rectangular triplet in electrolytic iron.

C. J. SMITHELLS.

Degeneration of paramagnetism at high temperatures. A. SCHIDLÖF (*Helv. phys. Acta*, 1928, 1, 578—600; *Chem. Zentr.*, 1929, i, 2392).

Degeneration of electron rotation and magnetism at low temperatures. A. SCHIDLÖF (*Helv. phys. Acta*, 1928, 1, 601—612; *Chem. Zentr.*, 1929, i, 2392).

Fused paramagnetic salts. L. A. WELO (*Nature*, 1929, 124, 575—576).—Values of c and 0 for solid and fused hydrated salts are tabulated, and curves are given. Coalescence of the salts may be mistaken for fusion.

A. A. ELDRIDGE.

Magnetic quadrupole moment of the iron atom. N. S. AKULOV (*Z. Physik*, 1929, 57, 249—256; cf. this vol., 248, 752).—Mathematical. Expressions are derived for the dipole energy density of a body-centred lattice and also for its quadrupole energy density. These are applied to the case of the iron atom. The quadrupole moment of the iron atom is calculated by two entirely independent methods, the results being in satisfactory agreement (4.50×10^{-29} and 4.54×10^{-29}).

J. W. SMITH.

Hall effect, electrical conductivity, and thermo-electric power of the copper-tin series of alloys. E. STEPHENS (*Phil. Mag.*, 1929, [viii], 8, 273—289; cf. this vol., 384).—The resistance of the alloys was determined, with annealing, until a constant value was obtained. The temperature coefficient of resistance, thermo-electric power, and Hall effect were then determined for the alloys in this final state. Singular points corresponding with both Cu_3Sn and Cu_2Sn were obtained in each of the curves relating these constants and the concentration of one metal in the alloy. The Hall effect, although negative for copper and tin, is positive for Cu_3Sn and Cu_2Sn and for alloys of composition ranging between 74% Cu, 26% Sn, and 4% Cu, 96% Sn. Cu_3Sn has the maximum positive Hall coefficient 0.000935, or approximately one half that of Cu_3Sb . The effect of annealing on the resistivity of the alloys depends on their composition.

N. M. Blich.

Barkhausen effect in iron, nickel, and permalloy. I. Measurement of discontinuous

change in magnetisation. R. M. BOZORTH (*Physical Rev.*, 1929, [ii], 34, 772—784).—The magnetic material was placed in a slowly and uniformly changing magnetic field, and the discontinuities in the magnetisation, characteristic of the Barkhausen effect, were followed through the *E.M.F.* created in a surrounding coil of wire. It was found that the changes in magnetisation taking place suddenly in large groups of atoms account quantitatively for the whole change in magnetisation which corresponds with the steeper part of the hysteresis loop. The magnetic moments of only a very small number of atoms are reversed in groups smaller than 10^{10} atoms, or a volume of 10^{-13} c.c. The maximum size of the discontinuities for each material was found to be about the same, corresponding with the complete reversals of the elementary magnets in a volume of about 10^{-6} c.c. Previous discordant results are attributed to different decay rates of eddy currents.

N. M. Blich.

Theory of magneto-optical phenomena in crystals. J. BECQUEREL (*J. Phys. Radium*, 1929, [vi], 10, 313—320, and *Z. Physik*, 1929, 58, 205—216).—See this vol., 1134.

Paramagnetic properties of rare earths. B. CABRERA and A. DUPÉRIER (*Anal. Fis. Quím.*, 1929, 27, 671—682).—See this vol., 982.

Magnetic susceptibility of nitric oxide at 296° and 216° Abs. F. BITTER (*Proc. Nat. Acad. Sci.*, 1929, 15, 638—642).—By an improved form of the method of hanging a test body surrounded by the gas to be measured in an inhomogeneous magnetic field, results were obtained in good agreement with the theoretical calculations of Van Vleck (cf. A., 1928, 572).

N. M. Blich.

Problem of magnetism. W. GERLACH (*J. Phys. Radium*, 1929, [vi], 10, 273—282).—Methods for the direct measurement of the moment of a free atom from photomicrographs of atomic rays under the influence of a magnetic field are described. Simple patterns are obtained for atoms having a magnetic moment of one Bohr magneton; more complicated patterns indicate the existence of atoms with more than one magneton. The orientation of the atoms appears to correspond with a maximum moment; birefringence expected for paramagnetic gases is not observed. Another method of atomic moment determination is that of Weiss from susceptibility measurements and the Curie constant. From calculations on the paramagnetic saturation of gadolinium sulphate it is shown that the moments of the gadolinium ion calculated with Langevin's theory by the method of atomic rays, and indirectly with the laws of space quantisation, respectively, are in the same numerical relation as the Weiss and Bohr magneton. Becquerel's magneto-optical measurements on paramagnetic saturation are a proof of space quantisation. Direct measurements of the susceptibility of potassium vapour were attempted, and the calculated Curie constant is in good agreement with that calculated from the Bohr magneton. It is concluded that the susceptibility of diamagnetic gases is independent of the temperature and pressure. Ferromagnetism and its relation to dia- and para-magnetism is briefly discussed.

N. M. Blich.

Superstructure and magnetic susceptibility in the system copper-gold. H. J. SEEMANN and E. VOGT (Ann. Physik, 1929, [v], 2, 976—990).—The variation of diamagnetic susceptibility with concentration has been measured for the gold-copper mixed crystal series. Alloys of the composition Cu_3Au and CuAu in certain circumstances exhibit super-imposed structure lines consistent with a regular arrangement of the constituent atoms; e.g., the corners of the elementary cube may be occupied by gold atoms and the face-centres by copper atoms. The relation between susceptibility and the appearance of super-structure has been determined for alloys of the composition Cu_3Au and CuAu , and it is found that for the former an increase and for the latter a decrease in diamagnetic susceptibility accompanies the production of regular atomic distribution in the lattice. Control experiments on alloys differing in composition from the whole-number ratios indicated no difference in susceptibility for quenched and slowly-cooled specimens. No explanation is available for the difference in sign of the effect with Cu_3Au and CuAu . R. A. MORTON.

Magnetic susceptibility of caesium in the solid and liquid state. C. T. LANE (Phil. Mag., 1929, [vii], 8, 354—362; cf. Crow, A., 1926, 14; Sucksmith, A., 1926, 782; McLennan, A., 1927, 1017).—Determinations were made with highly purified caesium, using the Gouy method for the liquid and a modified form of this method for the solid metal. Caesium was found to be paramagnetic; the values for the specific susceptibility were $+0.22 \times 10^{-6}$ and $+0.20 \times 10^{-6}$ in the solid and liquid state, respectively, in good agreement with the value for the solid state calculated on Pauli's theory. N. M. BLIGH.

Electrical conductivities of liquid alkali-metal amalgams. D. BOOHARIWALLA, G. R. PARANJPE, and M. PRASAD (Indian J. Physics, 1929, 4, 147—160).—The liquid sodium, potassium, and lithium amalgams show break points in the conductivity-concentration curves as pointed out by Hine (cf. A., 1917, ii, 287). The conduction has been shown to be metallic and not electrolytic. W. E. DOWNEY.

Specific resistance and purity of sodium electrolysed through soda-glass. J. R. NIELSEN (Physical Rev., 1928, [ii], 31, 304).—The specific resistance for solid sodium, containing 0.08% K as the only detectable impurity, between 30° and 90° is $4661 \times 10^{-9} \times (1 + 0.00484t)$ and for liquid sodium below 160° , $9828 \times 10^{-9} \times [1 + 0.00354(t - 100) + 0.00000039(t - 100)^2]$. L. S. THEOBALD.

Electrical conductivity of natural and artificial sodium chloride crystals. A. D. GOLDHAMMER (Z. Physik, 1929, 57, 173—185; cf. Salessky, this vol., 384).—Between 120° and 200° sodium chloride crystals obey Ohm's law up to 600 volts. The temporary production of polarisation and its magnitude are determined by the temperature and potential applied. Quantitative conductivity measurements show that crystals should be divided into two groups: (a) natural crystals and old synthetic crystals, and (b) synthetic crystals, with or without the addition of foreign ions. The con-

ductivity of the crystals is shown to be strongly dependent on the presence of small quantities of foreign ions introduced into the crystal lattice during preparation of the crystal. J. W. SMITH.

Mechanism of metallic conduction. H. M. BARLOW (Phil. Mag., 1929, [vii], 8, 289—304).—The electron fluid theory of conduction recently proposed (cf. this vol., 496) is developed. It is shown that the application of an *E.M.F.* to a metal bar involves a distortion of the electron orbits; the larger is the number of valency electrons the greater is the work necessary for distortion and the higher is the resistance of the conductor. The new theory is developed mathematically with regard to the ordinary phenomena of conduction and their relation to thermal conductivity. N. M. BLIGH.

Internal specific heat. I. W. JAZYNA (JACYNO) (Z. Physik, 1929, 57, 341—344).—Theoretical. Using the assumption of uniform energy distribution, the "heat-mol. wt." and the "internal absolute" specific heat of gases are calculated. Results are given for sixteen common gases. A. J. MEE.

Recrystallisation of substances of low m. p. and of ice. G. TAMMANN and K. L. DREYER (Z. anorg. Chem., 1929, 182, 289—313).—The recrystallisation at constant temperature of transparent substances such as camphor, pinene hydrochloride, and ice has been studied by direct visual observation. The nature of the displacement experienced by the particles is determined by the orientation of adjacent crystals, but the velocity of this displacement is governed by the concentration of minute films of impurities which separate on the surface of the particles; such films have been isolated as honey-combed structures after removal of the crystal. This view is supported by the observation that decrease of the amount of impurities present results in an increase of the recrystallisation velocity, and that mechanical working causes the recrystallisation velocity to diminish on account of the more rapid separation of the impurities. H. F. GILLBE.

Alternation in the heats of crystallisation of the normal monobasic fatty acids. IV. W. E. GARNER and (Miss) A. M. KING (J.C.S., 1929, 1849—1861; cf. A., 1924, ii, 239; 1926, 1087).—The following values have been obtained for the heats of crystallisation of these acids: margaric, 12.22; tricosoic, 17.60; pentacosic, 20.00; behenic, 18.75; lignoceric, 21.10; cerotic, 52.25 kg.-cal./mol. Q and Q/T when plotted against the number of carbon atoms give linear relationships for both the odd and even acids. The equation for the setting points of the odd acids is $T_s = (0.9651n - 4.49)/(0.002505n - 0.0071)$ and gives a convergence temperature of 112.2° . Cerotic acid is an exception, but X-ray analysis shows it to be a mixture of at least two acids. Detailed study of the transition of the α and β forms of the odd acids has been made, and the heats of transition $\alpha \rightarrow \beta$ have been found to be constant for margaric, tricosoic, and pentacosic acids at an average value of 1.55 kg.-cal./mol. There is a discontinuity in the curve of these heats plotted against number of carbon atoms per molecule between C_{11} and C_{13} . For acids

above C_{11} the β — change does not easily take place.

C. W. HART-JONES.

M. p. of chromium. C. J. SMITHELLS and S. V. WILLIAMS (*Nature*, 1929, **124**, 617—618).—Preliminary determinations give 1920° , or a rather higher temperature, as the m. p. of chromium.

A. A. ELDRIDGE.

Intensively dried liquids. J. W. SMITH (*Phil. Mag.*, 1929, [vii], **8**, 380—383).—Experimental data on intensively dried liquids are reviewed. The work of Smits (A., 1928, 1189) and Lenher (this vol., 872) indicates that Baker's results for such liquids are not conclusive evidence of inner complexity of the liquid system, and that the abnormal effects may be due to a slowness in attaining an equilibrium state. The rate of distillation of super-dried nitrogen tetroxide gradually rose when determined after long undisturbed periods.

N. M. BLIGH.

Vapour pressures of lead iodide, cuprous iodide, cuprous bromide, silver iodide, and silver bromide by a modified transference method. K. JELLINEK and A. RUDAT (*Z. physikal. Chem.*, 1929, **143**, 55—61).—The following latent heats of evaporation, in kg.-cal./mol., have been calculated from vapour-pressure measurements at 900 — 1200° : lead iodide, 27.70; cuprous iodide, 18.30; cuprous bromide, 18.10; silver iodide, 38.60, and silver bromide, 40.80. The vapour density of cuprous iodide at 900 — 1100° corresponds with the formula CuI , whereas the bromide possesses the double formula.

H. F. GILLBE.

Vapour pressure of thallium and lead halides. F. VOLMER (*Physikal. Z.*, 1929, **30**, 590—596).—The vapour pressures of thallium chloride, bromide, and iodide, lead chloride, and bromide at various temperatures have been measured in nitrogen by the streaming method. Lead iodide tends to decompose in nitrogen. The vapour pressures of silver halides are too small to be measurable by this method up to 750° , above which temperature decomposition occurs.

R. A. MORTON.

Vapour pressure of titanium tetrachloride. K. ARII (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1929, **8**, 714—718).—The vapour pressure of titanium tetrachloride between 20° and 135° can be represented by $\log p_{(\text{mm.})} = 7.64433 - 1974.6/T$. The molecular latent heat of vaporisation is calculated to be 8960 g.-cal. at 25° and 8620 g.-cal. at the b. p.

C. W. GIBBY.

Vapour pressure of thionyl chloride. K. ARII (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1929, **8**, 719—722).—The vapour pressure of thionyl chloride between 20° and 75° may be expressed by $\log p_{(\text{mm.})} = 7.60844 - 1648.21/T$. The b. p. was found from the p - T curve to be $75.7^\circ/760$ mm., and the molecular latent heat of vaporisation was calculated to be 7553 g.-cal. at 25° and 7482 g.-cal. at the b. p.

C. W. GIBBY.

Constants of chlorine fluoride. O. RUFF and F. LAASS (*Z. anorg. Chem.*, 1929, **183**, 214—222).—The chlorine fluoride, prepared by a method previously described (this vol., 40) and purified by redistilling five times, had m. p. $-154^\circ \pm 0.5^\circ$. Vapour pressures between -150° and -105° have been determined

and the results are represented by the equation $\log p = 15.738 - 3109/T + 1.538 \times 10^5/T^2$. This gives -100.8° as the b. p., approximately -14° as the critical temperature, and -2.27 kg.-cal./g.-mol. as heat of vaporisation. The heat of formation of hydrogen fluoride has been found to be 62.3 kg.-cal. (cf. Wartenberg and Fitzner, A., 1926, 476) and the heat of reaction between chlorine fluoride and hydrogen 58.6 kg.-cal. From these values and the heat of formation of hydrogen chloride, 22.0 kg.-cal., the calculated heat of formation of chlorine fluoride is 25.7 kg.-cal.

M. S. BURR.

General method of measuring the partial pressure of mercury [over any amalgam] at the ordinary temperature. L. L. HIRST and A. R. OLSON (*J. Amer. Chem. Soc.*, 1929, **51**, 2398—2403).—The vapour pressure is calculated from the pressure change which is produced in a mixture of ethylene, hydrogen, and mercury vapour by mercury resonance radiation at 2536 Å. which has traversed a layer of the mercury vapour. The activities at 26° of some thallium amalgams, calculated from the results, substantially agreed with those found by Richards and Daniels (A., 1920, ii, 34). The broadening of the absorption line of mercury for its own resonance light by hydrogen was investigated and the change in the atomic absorption coefficient of mercury in presence of hydrogen was determined.

S. K. TWEEDY.

Vapour tensions and vapour densities of ethylene and nitrous oxide. G. T. BRITTON (*Trans. Faraday Soc.*, 1929, **25**, 520—525).—A method for the measurement of vapour tension and vapour density simultaneously is described. The measurement of the latter is carried out by determining the buoyancy correction to be applied when an aluminium weight of known volume is weighed in the vapour, using a McBain and Bakr sorption balance. The pressure-temperature equation of Batschinski fits the data well in the form $t + c - K \times p^{1/4}$.

F. J. WILKINS.

Limiting values for the expansion and pressure coefficients of helium, hydrogen, and nitrogen. W. HEUSE and J. OTTO (*Ann. Physik*, 1929, [v], **2**, 1012—1030).—By means of a new method it is found that the isotherms of helium, hydrogen, neon, argon, nitrogen, and oxygen in the region 0.4—1 mm. of mercury follow a linear course, the inclinations being consistent with data obtained at higher pressures. From the expansion and pressure coefficients of helium, hydrogen, and nitrogen measured at different pressures the limiting value at $p=0$ is calculated. Thermodynamic relations applied to the isotherm inclinations at 0° and 100° for higher pressures lead to the values $\gamma = 0.0036609$ and $T_0 = 273.16$. The method of linear extrapolation to $p=0$ gives $\gamma = 0.0036610$. Taking earlier data into account, the values $\gamma = 0.0036608$ and $T_0 = 273.16$ are obtained as means.

R. A. MORTON.

Generalisation of the virial of Clausius. S. RAY (*Bull. Acad. Polonaise*, 1929, **A**, 233—239).—Mathematical. The virial of Clausius is applied to the case of a volume of gas enclosed within impervious walls disposed symmetrically with respect to the co-ordinate axes.

A. I. VOGEL.

Entropy of hydrogen. W. H. RODEBUSH (Proc. Nat. Acad. Sci., 1929, 15, 678—680; cf. Fowler, A., 1928, 469; Giauque and Johnston, this vol., 138).—If an equilibrium condition is assured between the two kinds of molecules of hydrogen (cf. Bonhoeffer, this vol., 479; Eucken, *ibid.*, 497) by making specific heat measurements on hydrogen which has been kept at a low temperature for a long time, the discrepancy can probably be removed between the entropy values as obtained from thermal data and indirectly from the equilibrium between hydrogen, oxygen, and water. A corrected value can be obtained theoretically when account is taken of rotational energy. N. M. BLIGH.

Isotherms of hydrogen, carbon monoxide, and their mixtures. G. A. SCOTT (Proc. Roy. Soc., 1929, A, 125, 330—344).—The isotherms of hydrogen, carbon monoxide, and mixtures of the two in the molecular proportions 2 : 1, 1 : 1, and 1 : 2 have been determined at 25° over a pressure range up to 170 atm. The method employed consists in filling a vessel of known constant volume at a known constant temperature with the gas or mixture under investigation up to a given measured pressure, and on releasing the gas, determining its volume at atmospheric pressure. Full details are given of the apparatus, comprising a high-pressure vessel, its filling system, a glass measuring system, an accurate pressure balance, and a water-bath. The isotherms are expressed by equations of the form $pv_A = a + bp + cp^2$, and the values of a , b , and c for hydrogen are calculated to be 1.09090 , 0.6511×10^{-3} , and 0.033×10^{-6} , respectively; for carbon monoxide, 1.09196 , -0.4393×10^{-3} , and 3.55×10^{-6} ; for the 2:1 mixture, 1.09109 , 0.4626×10^{-3} , and 0.947×10^{-6} ; for the 1:1 mixture, 1.09122 , 0.3281×10^{-3} , and 1.28×10^{-6} , and for the 1:2 mixture, 1.09142 , 0.1514×10^{-3} , and 1.88×10^{-6} . The mixtures show deviations both from the law of additive volumes and from that of additive pressures, and behave in general very similarly to the hydrogen-nitrogen mixtures studied by Verschoyle (A., 1926, 894). The constant b_{12} for the force acting between a molecule of hydrogen and a molecule of carbon monoxide at 25° has been calculated from the isotherms (cf. Lennard-Jones and Cook, A., 1927, 727), and is found to be 0.50, 0.51, and 0.62×10^{-3} for the three mixtures containing 66.3, 51.7, and 33.1% of hydrogen, respectively. L. L. BIRCUMSHAW.

Compressibilities and thermal pressure coefficients of certain liquids. J. H. HILDEBRAND (Physical Rev., 1929, [ii], 34, 649—651).—A small error is corrected in the values recently obtained by Westwater and others (cf. A., 1928, 228) for the compressibilities of a number of organic liquids, and the corrected values are found to be in good agreement with those found by Freyer and others (cf. this vol., 637). Values are given for a constant from which the coefficients of thermal pressure or of compressibility at various temperatures can be calculated by the aid of existing data for the densities and coefficients of expansion, and their values and those of the constant are listed for the eight organic liquids.

N. M. BLIGH.

Compressibility of crystals. R. F. MEHL and R. H. CANFIELD (Nature, 1929, 124, 478—479).—

Rashevsky's views (this vol., 499) are criticised, the genuineness of the compressibility coefficient being regarded as established by consideration of (a) internal evidence from the inter-relationships of the generally accepted compressibility coefficients among themselves and with other physical properties, and (b) the possible volume of internal voids.

A. A. ELDRIDGE.

Viscosity, heat conductivity, and diffusion in gas mixtures. II. Viscosity of hydrogen-nitrogen and hydrogen-carbon monoxide mixtures. M. TRAUTZ and P. B. BAUMANN. III. Viscosity of hydrogen-ethylene mixtures. M. TRAUTZ and F. W. STAUF. IV. Viscosity of binary and ternary rare-gas mixtures. M. TRAUTZ and K. F. KIPPAN (Ann. Physik, 1929, [v], 2, 733—736, 737—742, 743—748; cf. A., 1926, 118, 671; 1927, 194).—II. Measurements have been made of the viscosities of air, hydrogen, and nitrogen at a series of temperatures between -78° and 250°. The Sutherland formula applies when the constant is 101.1 for carbon monoxide and 102.7 for nitrogen. The viscosity isotherms for the systems hydrogen-carbon monoxide and hydrogen-nitrogen have been determined. Maxima can appear only at very low temperatures, e.g., -100° to -150°; at -78° the isotherms on the non-hydrogen side are nearly horizontal.

III. The viscosities of hydrogen and of ethylene have been determined and the results agree well with the Sutherland formula (when the constants are 82.8 and 238.9, respectively) for the range -40° to 250°, the agreement being less satisfactory from -40° to -78°. The isotherms in the viscosity/molar fraction curves exhibit a marked maximum which becomes flatter with rise of temperature. The position of the maximum is shifted in the direction of lower hydrogen content as the temperature rises.

IV. The viscosities at various temperatures have been measured for the binary systems hydrogen-helium, helium-neon, helium-argon, neon-argon, and the ternary system helium-neon-argon. The results conform very closely to theoretical requirements and it is shown to be possible to analyse mixtures of inert gases by measurement of viscosities and densities.

R. A. MORTON.

Mixtures of alcohol and ethyl ether. DESMAROUX (Mem. Poudres, 1928, 23, 198—229).—The densities of mixtures of ethyl alcohol and ether at 0° have been determined; there is always a contraction on mixing, which passes through a maximum at an equimolecular mixture. Mixtures of alcohol with a light essential oil showed a dilatation reaching a maximum at 40 mol.-% of oil. Only small variations in molecular volume were found in mixtures of ether with the essential oil. The partial vapour pressures of alcohol and ether over mixtures have been determined at 0°; they show positive deviations from Raoult's law. Similar measurements have been made with alcohol-oil and ether-oil mixtures. The heats of admixture of alcohol and ether at 0° are negative, showing a maximum cooling at about 66 mol.-% of ether. Mixtures of the oil with alcohol and with ether behave similarly. The electrical conductivity of mixtures of alcohol with the essential

oil diminishes linearly as the oil content rises. In mixtures of alcohol and ether it diminishes as ether is added, at first slowly and then more rapidly. The f.-p. curve for mixtures of alcohol and ether shows three maxima, corresponding with compounds of 1 mol. of alcohol with 1, 3, and 5 mols. of ether.

C. W. GIBBY.

Viscosity isotherms of binary mixtures. I. Benzene-sulphur monochloride. II. Nitrobenzene-sulphur monochloride. F. DE CARLI (*Gazzetta*, 1929, 59, 495—501, 502—506).—I. The system benzene-sulphur monochloride has a eutectic point at -92° corresponding with about 4% of benzene. The viscosity isotherms at 15.5° and 20° are continuous and show neither maximum nor minimum. With increasing percentage of benzene the fall in viscosity at 20° is considerably more rapid than at 15.5° . It is inferred from Batschinski's rule that sulphur monochloride is associated, but that dissociation is promoted by the presence of benzene.

II. Evidence of an unstable compound, $\text{PhNO}_2 \cdot \text{S}_2\text{Cl}_2$, m. p. -18° , is obtained from the thermal diagram for the system nitrobenzene-sulphur monochloride. The density in this system varies linearly with the composition at 20° . The viscosity isotherm at 20° is partly linear, but between 50 and 80% of nitrobenzene the viscosity is lower than that calculated from the mixture law; the divergence is less than in the 3° isotherm, in which the observed viscosity is lower throughout than the calculated.

F. G. TRYHORN.

Partial pressures of binary solutions. R. W. DORNT (*J. Physical Chem.*, 1929, 33, 1309—1331).—Measurements of the partial pressures have been made for mixtures of ethyl alcohol and water at 25° , and for mixtures of benzene and carbon disulphide at 20° , 25° , and 30° , by the use of an interferometer. Bancroft's equation (this vol., 255, 638) holds over a wide range of concentration, especially in the second system, and it can be successfully applied to the data of Campbell (*Trans. Faraday Soc.*, 1910, 10, 197) and others on various binary systems containing one volatile component. Data for the system ethyl alcohol-water obtained by a distillation method and by the interferometer method are compared and the latter is shown to be untrustworthy unless an empirical calibration is used.

L. S. THEOBALD.

Reactivity of atoms and groups in organic compounds. IX. Vapour pressures, densities, and refractive indices of binary mixtures. S. W. PRENTISS (*J. Amer. Chem. Soc.*, 1929, 51, 2825—2832).—An apparatus for the measurement of vapour pressures by a static method is described. Determinations of the vapour pressures at 20° of binary mixtures of nitrobenzene, acetone, *n*-butyl alcohol, and benzene with pyridine or ethyl iodide, the densities at 25° of similar mixtures of nitrobenzene, acetone, *tert*-butyl alcohol, and benzene with pyridine or ethyl iodide, and refractive indices at 25° of benzene and nitrobenzene with pyridine or ethyl iodide show that the deviations from the ideal solution laws bear no relation to the "adjuvance" of the solvent (Norris and Prentiss, this vol., 47).

H. BURTON.

Physico-chemical measurements of azeotropic mixtures. W. HERZ and (MISS) M. LEVI (*Z. anorg. Chem.*, 1929, 183, 340—346).—Some of the physico-chemical properties of azeotropic mixtures of the following pairs of liquids have been determined at 20° , 30° , 40° , and 50° , and compared with the values calculated from the mixture rule: methyl alcohol-ethyl acetate, methyl alcohol-ethylene chloride, and ethyl alcohol-ethylene chloride. The b. p. of these mixtures all lie below the b. p. of their components. The density, viscosity, surface tension, and possibly also the heat of vaporisation are lower for the azeotropic mixture than is calculated by the mixture rule, whilst the specific heat is higher.

M. S. BURR.

Glass. IV. Viscosity data for liquid dextrose and dextrose-glycerol solutions. G. S. PARKS and W. A. GILKEY (*J. Physical Chem.*, 1929, 33, 1428—1437; cf. this vol., 980).—The viscosities of undercooled liquid dextrose have been measured by methods of shear at temperatures between 28° and 110° . Five different samples gave slightly different viscosity-temperature curves between 28° and 60° , probably owing to varying proportions of α - and β -glucose in the samples and to variable but small amounts of water. The "hardening point" has been arbitrarily defined as the temperature at which $\eta = 10^{13}$ poises; this occurs at 25° with dextrose. The system dextrose-glycerol gives fairly stable organic glasses when correctly cooled, and the viscosities and hardening points for glasses of various compositions in this system have also been determined.

L. S. THEOBALD.

Critical state. IV. Solutions in ethyl ether. E. SCHROER (*Z. physikal. Chem.*, 1929, 142, 365—390; cf. this vol., 498).—The limiting curves in the temperature-density and temperature-pressure diagrams have been determined for solutions of triphenylmethane, phenanthrene, benzil, and of resorcinol in ethyl ether. The temperature-density curves are made up of two parts corresponding with two distinct systems, viz., a small amount of dissolved substance in a large amount of solvent phase, and a large amount of dissolved substance in a small amount of solvent. In the temperature-pressure diagrams the pressure increases linearly with the temperature up to the critical point, after which the curve begins to bend towards the temperature axis. The elevations of the critical temperature and of the critical pressure are directly proportional to the number of dissolved molecules up to fairly high concentrations. The critical opalescence is much more intense with the solutions than with pure ether. In certain cases the phenomenon of retrograde condensation was observed isothermally and quantitatively. Isothermals of some of the solutions have been determined and are found to be displaced in the direction of the liquid state compared with the isothermals of pure ether. This displacement is strongest in the region of high compressibility of pure ether. The isometric lines of solutions are linear, i.e., $(\partial p / \partial t)_v$ is constant above the critical temperature.

O. J. WALKER.

Demixing curves with more than one inflexion. P. A. MEERBURG (*Rec. trav. chim.*, 1929, 48, 935—

959).—A second maximum in the miscibility curve of castor oil and 89.9 vol.-% of ethyl alcohol occurs on the addition of small amounts of sesame oil. The critical solution temperature in the castor oil-alcohol curve occurs at 27.4° with a mixture containing 62.5% of castor oil. This critical solution temperature increases to about 40° at practically constant percentage of castor oil on the addition of sesame oil. The new critical solution temperature occurs in mixtures containing 10–15% of castor oil and increases from 19° to 55° as the percentage of sesame oil rises from 2.94 to 10.52%.

F. G. TRYHORN.

Determination of temperature of completion of solidification of mixed crystal series by heating curves. R. RUER and K. KREMERS (Z. anorg. Chem., 1929, 183, 223–224).—For determining the completion of solidification of mixed crystals the breaks in the heating curve are more sharply defined than those of the cooling curve. It is therefore more satisfactory to employ the heating curve, especially in metallic systems which have high heat conductivity and fusion velocity. A correction of +3° should be applied to the temperature at which fusion begins.

M. S. BURR.

Transition of austenite into martensite in hardened steel. E. SCHIEL (Z. anorg. Chem., 1929, 183, 98–120).—Dilatometric measurements have been made with hardened steel with the view of determining the conditions governing the transition of austenite into martensite during cooling. Since the transition velocity is very great over the whole temperature range of +300° to –200° the main factor cannot be diffusion. The measurements show that the transition is caused by internal mechanical stresses, since diminution of these forces, e.g., by keeping the steel at the ordinary temperature for several days, retards the formation of austenite. When viewed under the microscope the transition process resembles the formation of twin crystals under the influence of mechanical forces. H. F. GILLBE.

Absorption velocity of gases by liquids. II. Absorption of carbon dioxide by sodium hydroxide solution. S. HATTA (J. Soc. Chem. Ind. Japan, 1929, 32, 809–814; cf. this vol., 150).—With the apparatus used previously, the author has studied the velocity with which carbon dioxide mixed with air is absorbed by sodium hydroxide solution (N, 2.14N, 3.16N, and 4.15N) at 20° and 30° and sometimes under 1.53 atm. pressure. Under the same conditions, the rate of absorption is always less than that obtained with potassium hydroxide. The curves representing the relation between the absorption velocity and the concentration of the free alkali are quite different in the two cases. For sodium hydroxide the velocity decreases continuously as the free alkali decreases, but discontinuities are observed with potassium hydroxide. This is attributed to differences in the chemical reaction between carbon dioxide and the two alkalis. Although the method used is not very accurate, it would seem that the reaction velocity is proportional to p^n , where p is the pressure of the carbon dioxide and $n < 1$.

K. KASHIMA.

Solubility of iodine in gaseous carbon dioxide. H. BRAUNE and F. STRASSMANN (Z. physikal. Chem., 1929, 143, 225–243).—The vapour pressure of iodine, and the increased saturation concentration of iodine in the gas phase in presence of carbon dioxide at 1–50 atm. pressure, have been determined over the temperature interval 32.6–98.5°. The molecular attraction coefficient for iodine and carbon dioxide varies inversely as the temperature and decreases rapidly at high carbon dioxide concentrations; the heat change for the dissolution of iodine in carbon dioxide at M -concentration is about 1000 g.-cal./mol. The experimental results are correlated with those of Quinn (A., 1928, 470).

H. F. GILLBE.

Solubility of sodium salicylate in alcohol. W. SCHNELLBACH (Amer. J. Pharm., 1929, 101, 586–587).—One g. of sodium salicylate dissolves in 7.52 g. of U.S.P. alcohol (d_4^{25} 0.8083) at 25°.

E. H. SHARPLES.

Calcium oxalate and its solubility in the presence of inorganic salts with special reference to the occurrence of oxaluria. (MLLE.) G. HAMMARSTEN (Compt. rend. Lab. Carlsberg, 1929, 17, No. 11, 1–85).—Neutral calcium oxalate forms three hydrates. The dihydrate and trihydrate are readily converted into the monohydrate, which is the stable form above 0°. The rate of conversion varies largely with the temperature, and, in the case of the trihydrate, is accelerated by oxalate ions. The solubility of calcium oxalate in water and in solutions of sodium, potassium, lithium, rubidium, and ammonium chloride, and of sodium and potassium sulphate at 37° has been determined. The results are not in good agreement with the Debye-Huckel theory. The solubilities have also been measured in solutions of primary and secondary sodium phosphates, in mixtures of the latter with sodium chloride, in magnesium chloride, and in mixed magnesium chloride-sodium chloride solutions.

C. W. GIBBY.

Solubility relationships and solvation in non-aqueous salt solutions. P. P. KOSAKIEWITZ (Z. physikal. Chem., 1929, 143, 216–224).—The alkali metal halides diminish the solubility of carbon dioxide in methyl, ethyl, and *n*-butyl alcohols and in acetone, the magnitude of the effect diminishing in the order: lithium, sodium, and iodine, bromine, chlorine for ethyl alcohol, and lithium, sodium, and iodine, chlorine, bromine for methyl alcohol. In concentrated solution the salt molecules combine with 3–5 mols. of solvent, and in very dilute solution with 7–10 mols.

H. F. GILLBE.

Solubility of sodium and calcium in their chlorides and in chloride mixtures. R. LORENZ and R. WINZER (Z. anorg. Chem., 1929, 183, 121–126).—The solubility of sodium in sodium chloride is 4.2% at 800° and 15–20% at 850°, whilst at higher temperatures the metal phase disappears. The total solubility of sodium and calcium at constant temperature in a fused mixture of sodium and calcium chlorides increases in an approximately linear manner with the calcium chloride concentration, and increases rapidly with rise of temperature. H. F. GILLBE.

Wo. Ostwald's "solid-phase rule" and the solubility of casein in sodium hydroxide. S. P. L. SØRENSEN and J. SLÁDEK (*Kolloid-Z.*, 1929, 49, 16—35).—The authors' physico-chemical interpretation of the abnormal solubility relations of globulin and other proteins is compared with Wo. Ostwald's colloid-chemical explanation. Measurements of the solubility of casein in dilute solutions of sodium hydroxide show that with constant amounts of sodium chloride and hydroxide and increasing amounts of casein, the quantity of casein which dissolves increases so long as the proportion of casein to sodium hydroxide does not become very great; at the same time, the p_H of the solution falls. On the other hand, the percentage of casein which is dissolved by a constant amount of sodium hydroxide diminishes as the total quantity of casein increases. With a constant quantity of sodium chloride and of casein, the amount of casein which passes into solution is increased by using larger quantities of sodium hydroxide and the p_H of the solution increases. The distribution of the sodium hydroxide between the solution and the solid phase is such that the excess of sodium hydroxide in the solution (C_{NaOH}) increases with the amount of sodium hydroxide used more rapidly than the amount of dissolved casein (C_N), so that the relation falls with increasing p_H . Increase in the concentration of sodium chloride has the effect of raising the solubility of casein in dilute solutions of sodium hydroxide, and of decreasing the solubility in dilute hydrochloric acid. It seems that addition of increasing amounts of sodium chloride displaces the isoelectric reaction of casein in the acid direction. The increase in solubility brought about by sodium chloride in alkaline solutions becomes more pronounced until a concentration $2N$ is reached, and at higher concentrations the solubility falls again, probably as the result of the formation of compounds between casein and sodium chloride or its ions. E. S. HEDGES.

Solubility of oxygen in solid iron. W. KRINGS and J. KEMPKENS (*Z. anorg. Chem.*, 1929, 183, 225—250).—The solubility of oxygen in solid iron has been determined by a kinetic method. Mixtures of hydrogen and water vapour of definite composition were passed over iron or iron oxide at 715° until no further change in weight of the solid took place. The pressure of oxygen in the gaseous phase was determined from the amount of water vapour by the equilibrium relation $2H_2O \rightleftharpoons 2H_2 + O_2$ and the value plotted against percentage of oxygen in the solid. Starting with iron, for example, the percentage of oxygen present in the iron increases as the pressure of oxygen increases until a certain maximum limiting pressure is reached. This represents the pressure at which the iron is saturated with oxygen, and formation of ferrous oxide begins. The solubility is thus found to be $0.11 \pm 0.015\%$, which is greater than the values for technical iron based on metallographic observations or on the relation between oxygen content and physical properties. On the other hand, it is below that found by other investigators by a static method. It is claimed that the kinetic method possesses considerable advantages over

the static. The suitability of a number of different materials for combustion boats has been tested.

M. S. BURR.

Distribution equilibrium of silver between lead and aluminium. Test of the distribution law for condensed systems. R. LORENZ and F. ERBE (*Z. anorg. Chem.*, 1929, 183, 311—339).—The system aluminium-silver-lead has been investigated at 750° and 1000° over a large concentration interval. Lead and aluminium are practically immiscible with one another and their great density difference facilitates the separation of the two phases. Silver is miscible with both, but does not appreciably influence their mutual solubility, except at very high concentrations. The results are tabulated and ternary diagrams showing weight percentages and atomic percentages at 1000° are given. At both temperatures the distribution ratio, silver in aluminium to silver in lead, remains approximately constant at low concentrations, i.e., is in agreement with the ideal distribution law. It then slowly increases to a maximum, after which it falls rapidly. Values for 1000° are, throughout, smaller than for 750° . The results are discussed from the point of view of van Laar's distribution law. For lack of exact values for van der Waals' constants of the distributing material, the results cannot be made to agree quantitatively with van Laar's law, but they agree a little better with the latter than with the ideal distribution law. Some experiments have also been carried out using tin instead of silver, and the results recorded, but as all three metals become completely miscible at moderately high concentrations of tin, the results are useless for the purposes of the investigation.

M. S. BURR.

Sorption of sulphur dioxide, carbon dioxide, and nitrous oxide by activated carbon. D. O. SHIELDS (*J. Physical Chem.*, 1929, 33, 1386—1397).—The adsorption of carbon dioxide, nitrous oxide, and sulphur dioxide by an activated gas-mask charcoal at $25^\circ \pm 0.03$ has been determined from 0 to 40 mm. pressure for the first two gases, and from 0 to 22 mm. for the last. In the case of carbon dioxide, adsorption is reversible, but with the other two gases, especially the last-named, hysteresis occurs. As is to be expected from their similar electronic configurations, carbon dioxide and nitrous oxide give isotherms which nearly coincide, whilst the curves obtained by plotting the volume of liquid adsorbed against the quotient p/P , where p is the equilibrium pressure observed during adsorption and P is the saturation pressure at 25° , coincide exactly for these two gases. The order of adsorption differs from that obtained with silica gel (Patrick and others, *A.*, 1925, ii, 508), being greatest with sulphur dioxide and least with carbon dioxide. The adsorption of nitrous oxide and carbon dioxide can be represented by Patrick's equation, $V = K(p/P)^{1/n}$. L. S. THEOBALD.

Adsorption of mercury vapour by activated charcoal. D. O. SHIELDS (*J. Physical Chem.*, 1929, 33, 1398—1402).—The adsorption of mercury vapour by activated charcoal at the ordinary temperature in a vacuum is of the order of 0.2 mg. per g. of charcoal. No definite indication of adsorption in the presence

of air was obtained. The results are of the same order of magnitude as those of Coolidge (A., 1927, 928), but differ from those of Zelinski and Rakuzin (A., 1926, 1090), whose method is shown to be untrustworthy.

L. S. THEOBALD.

Calorimetric determination of heats of adsorption. A. MAGNUS and H. GIEBENHAIN (Z. physikal. Chem., 1929, 143, 265—277).—An extremely sensitive calorimeter whereby heats of adsorption may be experimentally determined is described. The heats of adsorption Q of carbon dioxide on silica and on carbon remain approximately constant over the pressure range for which Henry's law is valid; at higher pressures Q undergoes a linear decrease with increase of pressure, the rate of decrease diminishing at the highest pressures studied. With rise of temperature Q decreases.

H. F. GILLBE.

Adsorption of phosphoric acid by stannic sulphide. R. CHANDELLE (Bull. Soc. chim. Belg., 1929, 38, 255—258).—There is a definite but small adsorption of phosphoric acid by stannic sulphide. If the phosphorus in a bronze is determined by removing the metal as sulphide and precipitating with magnesia mixture there is a loss of about 0.2% of the total phosphorus due to adsorption. The formation of basic compounds of tin should be avoided, since these increase the adsorption of phosphoric acid.

O. J. WALKER.

Probable role of ammoniacal complexes in the adsorption of copper and nickel salts by ferric hydroxide. (MLLE.) L. S. LEVY (Compt. rend., 1929, 189, 426—428).—Extension of earlier experiments (this vol., 1001) has shown that the influence of ammonia on the formation and stabilisation of complex salts depends on the concentration of the ammonia and that only the portion of the copper or nickel salt liberated by hydrolysis of the complex ion is capable of being adsorbed. An excess of ammonia has no influence except in so far as it alters the p_H value of the medium (cf. Geloso, A., 1927, 407).

J. GRANT.

Adsorption of aerosols by solids. A. ÅSTRÖM (Svensk Kem. Tidskr., 1929, 41, 190—203).—The preparation and properties of aerosols are discussed. The degree of adsorption is determined by counting the number of particles in unit volume of the aerosol, before and after passage of the filter, the ultra-microscope being employed; it is necessary to take the mean of a large number of observations in order to secure trustworthy results. An alternative method is to measure the Tyndall effect, using the apparatus of Tolman and Vliet (A., 1919, ii, 180), the intensity being proportional to the concentration of the disperse phase. Particles of size ranging from 50 to 100 μ are the most difficult to adsorb. Passage through cotton and woollen filters showed that the degree of adsorption increased with the thickness of material, but was not directly proportional to this; direct proportionality exists, however, between the rate of passage through the filter and the amount of unadsorbed solid. Adsorption is rendered more complete if the air charged with the aerosol is passed intermittently through the filter instead of in a steady

stream. The above experiments were made using aerosols formed by condensation of superheated vapours in a continuous current of air, as such are relatively homogeneous. Aerosols prepared by dispersion (e.g., by detonation) give untrustworthy results owing to the rapidity with which they aggregate.

H. F. HARWOOD.

Determination of maximum adsorption of activated charcoal. H. BURSTIN and J. WINKLER (Przemysl Chem., 1929, 13, 114—119).—For the system activated charcoal-benzene the maximum adsorption is $A_{\max} = kQ$, where Q is the heat of wetting; k was determined experimentally.

CHEMICAL ABSTRACTS.

Heterogeneous splitting reactions. H. DOHSE and W. KALBERER (Z. physikal. Chem., 1929, B, 5, 131—155).—The elimination of water from isopropyl alcohol at the surface of bauxite is investigated as an adsorption phenomenon, and the part reactions are discussed. The kinetics of the decomposition show that it may be regarded as a continuous reaction of a surface layer which becomes gradually diminished by the adsorption of reaction products. The heat of activation is 39,000 g.-cal. The inhibitive effect of water on the reaction is investigated. If water is removed the reaction is of zero order, and the heat of activation is then 26,000 g.-cal. The difference between these two quantities of heat corresponds with the heat of desorption of water. The adsorption isotherms of water, propylene, and isopropyl alcohol on the surface of bauxite were obtained at different temperatures in the neighbourhood of the reaction temperature. For small densities on the surface the unimolecular constant is independent of the quantity adsorbed, but it decreases rapidly with increasing densities.

A. J. MEE.

Regional absorption of dyes by growing crystals. A. G. MILLIGAN (J. Physical Chem., 1929, 33, 1363—1373).—Crystals of potassium alum separating from a saturated solution coloured by chlorazol-sky-blue FF show a modified habit and an intense blue coloration in the centre of each cubic face. This regional deposition of the dye favours the development in area of the absorbing face by retarding the deposition of salt upon it. Croceine-scarlet 3B has a similar effect, but the absorption in this case is weaker and the inhibition of growth is less marked. Regional absorption also occurs with methyl-violet, but other dyes are either salted out by the saturated solution of alum or are not absorbed (methylene-blue, acid-green G, etc.). Sodium chlorate and phloxine or croceine-scarlet 3B, and oxalic acid and rhodamine B also showed this phenomenon, and Rochelle salt and croceine-scarlet 3B, chlorazol-sky-blue FF, and acid-green G showed it to a marked degree, but little or no alteration of habit occurred in these last three cases. Rochelle salt and acid-green G gave the only instance of absorption of the dye simultaneously on two forms of the crystal. An hypothesis to account for regional absorption is tentatively advanced.

L. S. THEOBALD.

Adsorption phenomena in systems of several constituents. C. WAGNER (Z. physikal. Chem.,

1929, 145, 389—396).—From measurements of the surface tension of aqueous solutions of aniline-phenol mixtures the quantities of each of these substances adsorbed by powdered charcoal at an air-water interface have been determined. Below certain limiting concentrations at which blocking of the surface occurs, the presence of one constituent favours the adsorption of the other, showing that the mutual effect of the molecules is an important factor in the adsorption. The nature of this attractive force remains uncertain. In the case of aniline the ratio (amount of aniline adsorbed)/(concentration of aniline in solution) increases with increasing concentration of aniline. A qualitative explanation of these two results is given by taking into account the effect of the reciprocal action of phenol-phenol and aniline-phenol molecules in the adsorption layer on the work of adsorption of phenol. F. L. USHER.

Frenkel adsorption isotherm. F. J. WILKINS and A. F. H. WARD (*Nature*, 1929, 124, 482).—An algebraic error is corrected (cf. Frenkel, *Z. Physik*, 1924, 26, 133). A. A. ELDRIDGE.

Theory of liquid film formation. C. W. FOULK (*Ind. Eng. Chem.*, 1929, 21, 815—817).—It has been established that pure liquids do not foam; that some substance must be molecularly or colloiddally dispersed in a liquid to make it foam; that foams can be produced whether the added substance is positively or negatively adsorbed at the surface; and that certain substances have the property of destroying foam and preventing its formation. A study of the mechanical aspects of liquid film formation leads to the view that liquid films are always the result of the approach to each other on the liquid side of two already formed surfaces. Several examples are given and the view is supported by energy considerations. A new theory of film formation is developed which aims at explaining why in the case of solutions two surfaces when very close to each other resist a mechanical push to bring them together, whilst there is no such resistance in the case of the surfaces of a pure liquid. Starting from the fact that in solutions the solute is either more or less concentrated in the surface layer than in the interior of the liquid, it is maintained that such a system will resist a force tending to bring about an equality of concentration, that is, it will resist a tendency to mix the surface layer with the rest of the liquid. A resistance will therefore be set up when two such surfaces are brought together by some small mechanical force. The theory explains why the effect is the same whether the surface tension is raised or lowered by the dissolved matter. The view is expressed that film formation and film stability are separate questions which have often been confused in the literature.

E. S. HEDGES.

Growth of silver iodide films. U. R. EVANS and L. C. BANNISTER (*Proc. Roy. Soc.*, 1929, A, 125, 370—394).—A study has been made of the relation between the weight increment and the interference colour due to the iodide film which is formed on exposure of silver foil to solutions of iodine in chloroform. The experimental results do not support the assumption, made by previous investigators, that the

thickness of the film can be judged by dividing the thickness of the air film required to give the same colour by the refractive index of the film material; this method, in fact, gives values too low at great thicknesses and too high at small thicknesses. A new colour method is described which is more accurate for small specimens than direct weighing. A short pre-exposure to air at ordinary temperatures does not measurably affect the growth of iodide films, although exposure for 30 min. at 400° considerably retards film formation, and a preliminary heating in a vacuum, with hydrogen as the residual gas, accelerates it. Electrometric and nephelometric methods have been used to determine the film thickness, and are compared with the gravimetric procedure. The rate of growth of the film has been studied under different conditions of solvent, stirring rate, abrasive treatment, temperature, and concentration of solution. Other things being equal, violet solutions cause much quicker growth of films than brown solutions, and coarsely abraded surfaces are attacked more rapidly than finely abraded. The velocity of film growth is increased by stirring. The fact that the rate of thickening decreases with the thickness indicates that the process is essentially controlled by diffusion through the solid film. The concentration factor indicates that the molecular condition of the free iodine in the film is never less complex than I_2 , but the small temperature coefficient excludes the possibility of gaseous diffusion through large apertures. The effect of varying the solvent makes it highly improbable that the solution, including the solvent, enters the pores. The mechanism of film growth which best fits the experimental data is that the iodine passes through pores of a few molecular diameters in loose union with the silver iodide of the walls, a process intermediate in character between gaseous diffusion and diffusion in solid solution. This conception is supported by previous work on films other than iodides.

L. L. BIRCUMSHAW.

Velocity of crystallisation. I. E. N. GAPON (*Ukraine Chem. J.*, 1929, 4, 161—192).—The velocity of crystallisation of ammonium oxalate, sodium oxalate, potassium sulphate, potassium dichromate, sodium picrate, potassium alum, ammonium alum, and potassium nitrate was determined by two methods. The first consists in adding a known weight of a salt to 250 c.c. of a solution of the salt of known supersaturation, at either 0° or 25°, and stirring vigorously (1500—1800 r.p.m., at which velocity of stirring the velocity of crystallisation becomes independent of the intensity of stirring). A sample is withdrawn every $\frac{1}{2}$ min. The second ("compensation") method consists in determining the velocity of crystallisation of a solution of a degree of supersaturation and of three other solutions with supersaturation values $C_1/2$, $C_1/2^{1/2}$, and $C_1/2^{1/3}$ and in the presence of twice the number of crystallisation centres. From these experiments it appears that the two factors which determine crystallisation from a supersaturated solution are dehydration of the ions and adsorption, and also that for the majority of the salts the process of crystallisation consists of two stages, the initial and the normal. In the initial stage if the velocity is

determined by adsorption its order will be unity as, for instance, in the first $\frac{1}{4}$ — $1\frac{1}{4}$ min. of the crystallisation of a supersaturated solution of sodium oxalate, and most of the other salts. If, however, the velocity is determined by dehydration of the ions, then the order of the reaction will be equal to the number of ions dehydrated, *e.g.*, crystallisation of sodium picrate at 25°. In the normal stage the order is always bimolecular.

A. FREIMAN.

Trichloroacetic acid as a cryoscopic medium for organic compounds and binary salts. P. WALDEN (Rec. trav. chim., 1929, 48, 880—884).—The high cryoscopic constant (122) of trichloroacetic acid renders it a useful medium for mol. wt. determinations of organic compounds, especially for those in dilute solution. Typical organic compounds have normal mol. wt. in this medium. On the other hand, typical binary salts which in aqueous solution are classed uniformly as strong, may behave in trichloroacetic acid solution in different ways, ranging from double or triple association to complete dissociation. Both cation and anion have a marked influence on the mol. wt. Salts of a given cation, *e.g.*, NMe_4^+ , with a series of equivalent, strong anions, *e.g.*, Cl^- , Br^- , I^- , NO_3^- , may behave quite differently, exhibiting molecular states between association ($x=2$) and complete dissociation. Salts of a given anion, *e.g.*, I^- , Cl^- , or the picrate ion, change in molecular condition with change of cation. The degree of association of salts of alkylated ammonium bases varies with the size of the alkyl group and the degree of alkylation. In view of the low dielectric constant of trichloroacetic acid the high dissociation of many of these salts cannot be referred to high ionisation of the type $\text{MA}=\text{M}^++\text{A}'$, but must be attributed to acidolysis of the type $\text{M}^+\text{A}' + x\text{CCl}_3\cdot\text{CO}_2\text{H} = \text{M}^+\text{CO}_2\cdot\text{CCl}_3 + (x-1)\text{CCl}_3\cdot\text{CO}_2\text{H} \rightarrow \text{AH}$. It appears that through the action of the solvent even strong acids may be driven out of combination with strong bases, and ions such as SCN^- , NO_3^- , or $\text{C}_6\text{H}_5(\text{NO}_2)_3\cdot\text{O}^-$ may be converted into non-ionising compounds. The results indicate that as a result of mass action and catalytic effects a solvent may completely alter the accepted affinity relationships of acids and bases.

F. G. TRYHORN.

Apparent hydration of ions. III. Densities and viscosities of saturated solutions of ammonium chloride in hydrochloric acid. J. W. INGHAM (J.C.S., 1929, 2059—2067).—The solubility of ammonium chloride in aqueous solutions of hydrochloric acid of concentrations up to 13*N* and the densities and viscosities of the saturated solutions have been determined at 25°. The density is a linear function of the acid and salt concentrations, and the solution volume of the ammonium ion is calculated to be 19.64. The effect of the chloride ion on the viscosity is approximately equal and opposite to that of the ammonium ion, and both effects remain practically constant over a wide range of concentration, indicating that neither ion is hydrated. From the viscosity data the solution volume of the ammonium ion is calculated to be 14. It seems probable that the viscosity is determined principally by the number of particles present in the

solution and on their sizes compared with that of the water molecule, the predominating species.

R. CUTHILL.

Dependence of equivalent refraction of strong electrolytes in solution on concentration. XI. Addition to "refractometric experiments" of Fajans and co-workers. W. GEFFCKEN (Z. physikal. Chem., 1929, B, 5, 81—123).—The dependence of equivalent refraction on concentration in the range from 2*N* to practically saturated solutions at 25° was investigated for a number of strong electrolytes. The solutions examined were potassium fluoride, sodium, potassium, rubidium, caesium, and ammonium chlorides, sodium iodide, sodium and potassium nitrates, zinc sulphate, lithium, aluminium, and mercuric perchlorates. The expression for calculating the equivalent refraction of a dissolved substance can be written as $R = \text{const.} (\phi + \pi)$, where ϕ is a simple function of the density and concentration of the solution, and π is a function of the refractive index and concentration. It is possible to make use of this equation to obtain, graphically, the density of a solution from its concentration, and *vice versa*, with errors of 0.01% for the density, and 0.1% for the concentration. A useful control method for observations of density and refractive index is outlined. A new method for the preparation of pure sodium iodide by the electrolytic reduction of sodium iodate is given. There is a very approximate linear relationship between refraction and concentration. Deviations are shown by sodium iodide and potassium fluoride. There is some confirmation for the assumption that with increasing concentration of electrolyte there are formed combinations of oppositely charged ions which are directly in contact with each other without the intervention of water molecules, thus giving rise to an undissociated fraction. A rough evaluation of the undissociated part on the basis of variation of refraction with concentration leads to reasonable results. The extrapolated values of the equivalent refraction of electrolytes at infinite dilution are shown to be strictly additive.

A. J. MEE.

Size of gas bubbles in liquids. R. SCHNURMANN (Z. physikal. Chem., 1929, 143, 456—474; cf. this vol., 903).—The size of the bubbles formed by forcing air through filters of various types into different liquids has been found to be determined by the viscosity of the liquid. In ionised liquids a subsidiary factor is the charge on the bubble, but this is effective only when the viscosity of the electrolyte solution is of the same order as that of water. The bubble size is independent of the nature of the filter used. These facts explain the author's results on the determination of the pore diameter of porcelain filters by the bubble pressure method. A picture of the process of formation of visible bubbles is given.

F. L. USHER.

Velocity of elutriation and particle size. A. H. M. ANDREASEN and J. J. V. LUNDBERG (Kolloid-Z., 1929, 49, 48—51).—Experiments on the relation between elutriation velocity and particle size in the case of graded pulverised flint show that Stokes' law can be applied.

E. S. HEDGES.

Theory and methods of ultracentrifuging. O. LAMM (Z. physikal. Chem., 1929, **143**, 177—190).—The mathematical theory for the sedimentation and diffusion of a dissolved substance in a centrifugal field is developed. The optical refraction method of observing concentration changes has been applied to the experimental study of the ultracentrifuge, and experiments with solutions of starch and proteins demonstrate the usefulness of the method for the study of solutions containing two or more substances.

H. F. GILLBE.

Interference colours of finely disperse precipitates in transmitted light. G. P. VORONKOV and G. I. POKROVSKI (Kolloid-Z., 1929, **49**, 1—3).—When water vapour from the air condenses on a glass slide cooled to -15° or -20° , or when the vapour of benzoic acid condenses on a cool glass slide, the film produced exhibits interference colours when viewed by transmitted light. A theory is advanced in explanation.

E. S. HEDGES.

Nucleus formation in the condensation of vapours in non-ionised dust-free air. E. X. ANDERSON and J. A. FROENKE (Z. physikal. Chem., 1929, **142**, 321—350).—A critical summary of earlier work dealing with nucleus formation in the condensation of vapour is given. An improved form of cloud condensation apparatus for the measurement of the expansion necessary for the various stages of condensation of a vapour is described. A volume of air saturated with water vapour must expand to 1.2006 ± 0.0007 times its volume before condensation commences. The value of 1.252 found by Wilson is therefore too high.

O. J. WALKER.

[Stability of coarse particles in solutions. IV. Formation and removal of liquid sheaths in suspensions of *Bulus alba*. Reversible sol-gel transformation; thixotropism.] H. WERNER (Ber., 1929, **62**, [B], 2474).—The author's experiments (this vol., 878) are in harmony with the conceptions of Ostwald (this vol., 137).

H. WREN.

Theory of stability of disperse systems. II. Stability of hydrosols of Prussian-blue. E. N. GAPON (Ukraine Chem. J., 1929, **4**, 155—159; cf. A., 1928, 949).—The stability at the ordinary temperature of dispersed systems of Prussian-blue in water for varying proportions of potassium ferrocyanide and ferric chloride has been found to decrease with increasing concentration of ferric chloride.

A. FREIMAN.

Emulsions and the effect of hydrogen-ion concentration on their stability. J. C. KRANTZ, jun., and N. GORDON (Coll. Symp. Mon., 1928, **6**, 173—206).—The particle size and viscosity are affected by the p_H value for gum tragacanth emulsions, but not for gum arabic emulsions, except that for the latter the particle size increases at $p_H > 7$. Fischer's hydrate theory appears to be substantiated by emulsions prepared with gum tragacanth. The stability of various emulsions has been determined. The surface tension of water-in-oil emulsions is unaffected by changes in p_H of the internal phase; unstable emulsions have a lower viscosity than stable emulsions. Variations in particle size, up to 30μ , do not affect the stability. CHEMICAL ABSTRACTS.

Change of viscosity of sols and of precipitating concentrations of electrolytes with purity, and change of ratio of precipitating concentrations with temperature of coagulation. V. GORE and N. R. DHAR (J. Indian Chem. Soc., 1929, **6**, 641—652; cf. this vol., 506).—The viscosity of ferric, stannic, ceric, zirconium, and thorium hydroxide sols increases steadily with the elimination of impurities, supporting the view that the increase of viscosity is due to decrease of electric charge as a result of the removal of adsorbed electrolyte. By reversing the process and adding electrolytes to the pure, unstable, and highly viscous sols of ferric, stannic, and zirconium hydroxides, stability and electric charge increase, owing to adsorption of electrolyte, whilst viscosity diminishes. The coagulum from an impure stannic hydroxide sol is white, but from a highly purified and viscous sol it is almost transparent, indicating that increase in hydration has accompanied purification. The ratio of the precipitating concentrations of uni- and bi-valent ions decreases as the purity and viscosity of the sols increase. On raising the temperature the ratio of the precipitating concentrations of uni- and bi-valent ions with ferric, stannic, and ceric hydroxide sols becomes less, but the relative diminution in the ratio, as the temperature increases from 30° to 60° , is the same for any one sol no matter what its degree of purity may be. No definite relationship could be established between the viscosity and purity of the sols of arsenious and antimony sulphides, Prussian-blue, cupric and uranium ferrocyanides, mastic, and gamboge, since they are all progressively hydrolysed on dialysis.

M. S. BURR.

Relation of dielectric constant of emulsions to the concentration of the disperse phase and the degree of dispersion. A. PIEKARA (Kolloid-Z., 1929, **49**, 97—102).—See this vol., 27.

Role of dielectric constants, polarisation, and dipole moment in colloid systems. VI. Swelling of cellulose acetate in binary mixtures. II. I. SAKURADA (Kolloid-Z., 1929, **49**, 52—60).—Experiments have been made to determine the connexion between swelling and polarisation in binary mixtures consisting of benzene, carbon tetrachloride, or carbon disulphide as one component and one of the lower aliphatic alcohols as the other component. A binary system consisting of a dipole-free liquid and an aliphatic alcohol always gives a swelling maximum. Cellulose acetate swells more strongly in mixtures of alcohol with benzene than in those with carbon tetrachloride or carbon disulphide. Equimolecular concentrations of cellulose acetate swell to a practically equal extent in dilute solutions of alcohol in benzene, irrespective of the alcohol used, but at higher concentrations the swelling becomes less with increasing molecular complexity of the alcohol. Curves were constructed showing the deviations of the experimental values of total polarisation, dielectric constant, and swelling from the values calculated by means of the arithmetical mixture rule, and it is shown that all the curves take a similar course. E. S. HEDGES.

General solvation equation for colloid systems. Wo. OSTWALD (Kolloid-Z., 1929, **49**, 60—74).—

Measurements of the swelling of caoutchouc and gutta-percha in benzene, nitrocellulose in acetone, and isoelectric gelatin and hæmoglobin in water confirm Ostwald's equation $P = cRT/M + bc^n$, where P is the observed osmotic pressure, c is the weight in g. of substance swelling in 1 c.c. of liquid, and b and n are constants. The solvation constant n generally has a value of approximately 2, whilst b is a characteristic colloid-chemical constant for each material. The view is confirmed that not only gels, but also sols can swell and that the "osmotic" pressure of a sol in a cell of micellar thickness is composed of the ordinary van 't Hoff pressure plus solvation pressure.

E. S. HEDGES.

Effect of ultra-violet light on colloids. I. P. LAL and P. B. GANGULY (J. Indian Chem. Soc., 1929, 6, 547—556).—Since both negative and positive sols are coagulated by ultra-violet light the effect cannot be satisfactorily explained as the result of the generation of electrons by the radiation. A study of the p_H values of the clear filtrate from an ultra-filter, before and after coagulation, has shown that these change appreciably, increasing in some cases and decreasing in others. These variations in p_H value have been interpreted on the basis of known chemical and photochemical reactions, and the coagulation of colloids by the action of ultra-violet light is ascribed to the destruction of the stabilising agents in the chemical changes brought about by the light.

M. S. BURR.

Action of X-rays on colloidal solutions. S. S. BHATNAGAR, R. S. GUPTA, K. G. MATHUR, and K. N. MATHUR (Z. Physik, 1929, 56, 684—693).—The velocity of cataphoresis of sols exposed to X-rays and those not so exposed, together with the stability of the two sets after the addition of electrolytes, have been measured. The exposures varied for different sols between 2 and 3 hrs. The following colloids were used: gold, silver, copper, copper hydroxide (positive and negative), and ferric hydroxide. To investigate the stability of the sols after addition of 0.02N-potassium chloride solution, and find whether it varied on exposure to X-rays, the optical transmission of the sols was determined by means of a thermopile. Only in the case of silver and copper (both prepared by Bredig's method) did the colour of the sol change after exposure. There was no change in the coagulation value of the copper sol. Except in the case of partly dialysed sols (ferric and copper hydroxides) there was no marked change in the velocity of cataphoresis before and after exposure. These results are discussed.

A. J. MEE.

Preparation of jellies of some inorganic substances. S. PRAKASH and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 587—598; cf. A., 1926, 676; 1927, 934).—The conditions necessary for the formation of gels of the following inorganic substances are given, and their properties described: ferric borate, molybdate, and tungstate; thorium phosphate and molybdate; stannic arsenate, phosphate, tungstate, molybdate, and borate.

M. S. BURR.

Silicic acid gels. I. Time of setting of gels. M. PRASAD and R. R. HATTIANGADI (J. Indian Chem. Soc., 1929, 6, 653—663).—Silicic acid gels

have been prepared by the action of ammonium acetate solution, with or without acetic acid, on solutions of sodium silicate. The time of setting has been determined by measuring the variation with time of the light scattered by the gel. The intensity of scattered light is found to increase more and more slowly until it reaches an approximately constant value. The time required for this is the time of setting. When there is no added acetic acid the time of setting decreases as the concentration of ammonium acetate increases up to a certain limit. At higher concentrations no gels, but only flocculent precipitates, are obtained. The gels are alkaline to litmus and no minimum value of the setting time is observed. The gels obtained with ammonium acetate acidified with acetic acid are alkaline, neutral, or acid to litmus; this depends on the concentration of ammonium acetate and acetic acid used, i.e., on the hydrogen- and hydroxyl-ion concentration. All mixtures set in a minimum time when they are slightly alkaline or neutral to litmus and the value of this minimum time is smaller the greater is the silica content of the mixture. Highly alkaline and highly acidic mixtures take a long time to set. The gels differ in appearance according as they are prepared from high or low concentrations of acidified ammonium acetate, the former being more transparent, and hence probably forming smaller aggregates, than the latter.

M. S. BURR.

Diffusion in gels. V. MORAVEK (Kolloid-Z., 1929, 49, 39—46).—The diffusion of lead nitrate into dilute solutions of potassium dichromate contained in gels of gelatin, agar, and mixed gelatin-agar has been studied. The time course of the diffusion is in accordance with a parabolic equation, but certain irregularities were observed when the concentration of the diffusing lead nitrate was varied. In gelatin and in the mixed gels, the curve connecting rate of diffusion with concentration of the lead nitrate passes through two maxima. This behaviour is ascribed to the formation of compounds between gelatin and the potassium dichromate. The form of the curve also depends on the concentration of potassium dichromate in the gel. In agar gels the rate of diffusion is directly proportional to the concentration of lead nitrate in the superimposed solution and the rate was scarcely affected by increasing the concentration of agar. The formation of periodic structures in these experiments is related to a dynamic equilibrium between the gel and the aqueous phase.

E. S. HEDGES.

Behaviour of swollen gelatin in water vapour. E. H. BUCHNER (Rec. trav. chim., 1929, 48, 1047—1051).—Lloyd's observations (A., 1920, i, 452) on the behaviour of swollen gelatin (acid or alkali treatment) are confirmed. The loss of water from the swollen gelatin when kept in a saturated vapour (cf. *loc. cit.*) is due either to a change in the hydrogen-ion concentration of the gelatin or to surface forces.

H. BURTON.

Osmosis in ternary liquids through a membrane permeable to two of the three substances. F. A. H. SCHREINEMAKERS (Rec. trav. chim., 1929, 48, 926—930).—Theoretical. When demixing into

two or more liquid phases does not occur in an osmotic system of the type $L_0[M(WY)|L]$, osmotic equilibrium is possible only when L_0 and L have the same compositions. In the case of the systems $L_0(Y+W)|M(WY)|L(X+Y+W)$ and $L_0(W)|M(WY)|L(X+Y+W)$ osmosis will continue until the left-hand side has been completely absorbed by the right-hand side liquid.

F. G. TRYHORN.

Donnan membrane equilibrium. Change of protein solutions by heating, its effect on the membrane equilibrium, and its relation to the viscosity. K. SHIGI (Kyoto J. Med., 1928, 25, 706—710).—*N*-Hydrochloric acid or sodium hydroxide was added to egg-white and the mixture was heated at 490° for various periods. With acid, no change of membrane potential occurs under 60 min. After 80 min. the potential gradually falls and becomes zero after 150 min. With sodium hydroxide a change in viscosity is observed after 10 min.

CHEMICAL ABSTRACTS.

Use of flat membranes for dialysis and for the determination of the osmotic pressures of colloidal solutions. J. ZAKOWSKI (Chem. Fabr., 1929, 427—429).—It is practically impossible to prepare collodion membranes of the customary sack-like form which possess a uniform degree of porosity throughout. This condition is more easily attained if the membranes employed are flat, and types of apparatus are described in which membranes of this description are used.

H. F. HARWOOD.

Cataphoretic migration velocity of zeolite suspensions. A. VON BUZAGH (Kolloid-Z., 1929, 49, 35—39).—Measurements have been made of the cataphoretic migration velocity of electro-dialysed chabasite and electro-dialysed synthetic aluminium silicate particles in presence of various electrolytes. Small concentrations of alkali hydroxides raise the ζ -potential, but higher concentrations lower it. Hydroxides of calcium and barium lower the ζ -potential at all concentrations. The chlorides of uni- and bi-valent cations have a discharging effect in the following order: $\text{Na} < \text{K} < \text{Ca} < \text{Ba}$. Aluminium and thorium chlorides discharge the particles at low concentrations, at higher concentrations they reverse the charge, and at still higher concentrations a further discharging effect in the positive region is observed.

E. S. HEDGES.

Equilibrium constants of reactions involving hydroxyl. D. S. VILLARS (Proc. Nat. Acad. Sci., 1929, 15, 705—709).—Mathematical. The equilibrium constants are calculated from the heat of dissociation of the hydroxyl group. A. J. MEE.

Cryoscopic determination of molecular equilibria of resorcinol in aqueous solutions of potassium chloride and of sodium chloride. F. BOURION and C. TUTTLE (J. Chim. phys., 1929, 26, 291—311).—The view previously suggested (cf. this vol., 648, 759), that the higher cryoscopic constant obtained with solutions of resorcinol in aqueous alkali chloride solutions can be attributed to adsorption of water by the ions or molecules of the dissolved salt, is discussed and it is shown that there is a parallelism between the degree of hydration derived

from this assumption and that calculated by other methods.

O. J. WALKER.

Chemical-kinetic and cryoscopic determination of equilibria in *p*-toluidine solution. Aminolysis. H. GOLDSCHMIDT and E. OVERWIEN (Z. physikal. Chem., 1929, 143, 354—388; cf. A., 1907, ii, 244).—The behaviour of various inorganic and organic acids in the basic solvent *p*-toluidine has been studied. That the acids differ in strength just as in aqueous solution is shown by conductivity measurements and by the different velocities with which they catalyse the intramolecular reaction diazoaminotoluene \rightarrow aminoazotoluene. Although the reaction velocities and conductivities run parallel for a given series of catalysing acids, the velocity coefficients do not decrease as rapidly as the equivalent conductivities. Addition of bases decreases the reaction velocity and increases the conductivity to an extent depending on the amount of salt formation taking place between the acid and the added base. The aminolytic constant $[\text{salt}]/[\text{acid}][\text{base}]$ obtained by the cryoscopic method is smaller than when calculated from reaction velocity measurements, but the series order for the acids used is the same for both. The amount of salt formation depends on the strength of the added base and of the acid used.

F. L. USHER.

Equilibrium between amylene and trichloroacetic acid in non-aqueous solvents. L. M. ANDREASOV (Ukraine Chem. J., 1929, 4, 143—148).—The equilibrium has been examined at 25° and 50° in benzene and carbon tetrachloride. The data are inconsistent with the supposed formation of double molecules of the acid.

A. FREMAN.

Electrolytic dissociation constant of hydrogen peroxide. V. A. KARGIN (Z. anorg. Chem., 1929, 183, 77—80).—The difficulty of measuring the acid dissociation constant of hydrogen peroxide is discussed; by potentiometric titration with potassium hydroxide solution using the glass electrode the value $K = 1.55 \times 10^{-12}$ at 20° is obtained. H. F. GILLBE.

Electrical dissociation of dibasic acids. V. Dissociation constants of the three hydroxybenzoic acids. E. LARSSON [with N. HOLMBERG] (Z. anorg. Chem., 1929, 183, 30—36).—The acidic and phenolic ionisation constants of salicylic and *m*- and *p*-hydroxybenzoic acids and the ionisation constants of their ethyl esters have been determined potentiometrically; the second constants for the *o*-, *m*-, and *p*-acids are 4×10^{-14} , 1×10^{-10} , and 4×10^{-10} , respectively, and the constants for the esters are 3×10^{-11} , 8×10^{-10} , and 5×10^{-9} , respectively. By consideration of the influence of the ionised carboxyl group on the hydroxyl group the values 1.1, 3.4, and 2.8 are derived as the distances in Å. between the site of the electric charge and the hydroxyl hydrogen atom in the *o*-, *m*-, and *p*-hydroxybenzoate ions.

H. F. GILLBE.

Determination of the tertiary dissociation constant of phosphoric acid. I. N. KUGELMASS (Biochem. J., 1929, 23, 587—592).—Hydrolysis of the tertiary phosphates gives 1.02×10^{-12} at 20° and 1.48×10^{-12} at 38°.

S. S. ZILVA.

Dissociation of alkaloid salts (caffeine, colchicine). M. GOURSAT (J. Pharm. Chim., 1929, [viii], 10, 263—267).—Potentiometric measurements of the p_H of mixtures of equivalent quantities of a solution of caffeine (14.98 g./litre) and 0.1*N*-solutions of sulphuric, hydrochloric, tartaric, oxalic, and benzoic (0.01*N*) acids show that the salts are completely dissociated in solution, the p_H value being the same as that of the free acid. Similar results are obtained with colchicine (3.99 g./litre) and 0.01*N*-solutions of the same acids, and in agreement with this, both alkaloids are completely extracted with chloroform from their solutions in acids. J. W. BAKER.

Hydrolysis of aluminium salts of strong acids. V. ČUPR (Coll. Czech. Chem. Comm., 1929, 1, 467—476).—The hydrogen-ion concentrations of 0.5—0.01*M*-solutions of aluminium sulphate, chloride, bromide, chlorate, perchlorate, and nitrate at 20°, of the sulphate, chloride, and bromide at 25°, and of 0.2—0.01*M*-solutions of aluminium potassium, aluminium sodium, and aluminium ammonium sulphate at 20° have been measured with the quinhydrone and hydroquinhydrone electrode. In dilute solutions the ratio $[H]/[\text{concentration}]$ varies in approximately the same manner for the simple salts with the exception of the sulphate; differences appear in more concentrated solutions. A. I. VOGEL.

Germanium. V. Hydrolysis of sodium germanate and the dissociation constants of germanic acid. W. PUGH (J.C.S., 1929, 1994—2001; cf. this vol., 997).—The hydrolysis of sodium germanate at 20° has been determined over a concentration range of 0.001—0.100 g.-mol./litre, the hydrolysis constant at the highest dilutions having the value of about 0.054, which gives 1.9×10^{-13} for the second dissociation constant of the acid. Electrometric titration of sodium germanate with hydrochloric acid yields a titration curve of the form characteristic of dibasic acids and gives a value of 2.6×10^{-9} for the first dissociation constant of the acid. Roth and Schwartz' value (A., 1926, 350) therefore seems much too high. R. CUTHILL.

Electrolytic dissociation of some metal malonates. H. L. RILEY and (Miss) N. I. FISHER (J.C.S., 1929, 2006—2010).—If the degree of dissociation of an electrolyte is largely influenced by the readiness of the cation to accept electrons and of the anion to donate electrons, it would be expected that salts consisting of an anion which readily forms stable complex ions and a cation which departs considerably from the inert gas structure would not be very highly dissociated. In confirmation of this view it is found by conductivity measurements at 25° that the tendency to dissociation of magnesium, cadmium, zinc, and cupric malonates diminishes in this order. R. CUTHILL.

Physico-chemical studies of amino-acids. G. TAKAHASHI and T. YAGINUMA (Japan. J. Chem., 1929, 4, 15—31; cf. this vol., 141).—The b. p. of the *l*-ethyl ester of leucine at pressures between 4 and 480 mm., the solubility of *l*-leucine in water between -0.2° and 81°, and the densities of the solutions are recorded. The system *l*-leucine-HCl-H₂O has been investigated at 15° and 30°, establishing the exist-

ence of the compounds *l*-leucine hydrochloride hydrate, C₆H₁₃O₂N.HCl.H₂O, and β-*l*-leucine hydrochloride ethyl ester, C₆H₁₂O₂N.C₂H₅.HCl. The optical rotation and dispersion of mixtures of *l*-leucine, hydrochloric acid, and water have been determined. C. W. GIBBY.

Lowest temperatures at which oxides show reduction by hydrogen. J. L. ST. JOHN (J. Physical Chem., 1929, 33, 1438—1440).—Reduction by hydrogen becomes appreciable at 140° in the case of copper oxide, at 185° with lead monoxide, at 280° with cadmium oxide, at 310° with zinc oxide, and at 185° with arsenic trioxide. A connexion between the temperatures of initial reduction and the heats of formation of these oxides is suggested.

L. S. THEOBALD.

Hydrogen reduction equilibria of metal chlorides, bromides, and iodides at high temperatures, and the chemical constants of chlorine, bromine, and iodine. K. JELLINEK and A. RUDAT (Z. physikal. Chem., 1929, 143, 244—264).—The equilibria attained in the reduction of lead and manganous chlorides, and lead, silver, and cuprous bromides and iodides for temperatures at which the halides exert appreciable vapour pressures have been determined. Since the integration constants of the dissociation equilibria of the lead halides are considerably greater than the integration constants of the vapour-pressure equations of the corresponding condensed halogens, the conclusion is reached that the entropies of the crystalline halogens at 0° Abs. are appreciably greater than zero.

H. F. GILLBE.

Equilibrium CO₂ + C = 2CO. F. J. DENT and J. W. COBB (J.C.S., 1929, 1903—1912).—Investigation of the above equilibrium at 800°/1 atm., using various forms of carbon, has shown that the equilibrium composition depends on the character of the carbon and the pre-treatment which it has received. With graphite in presence of sodium carbonate as catalyst, the equilibrium mixture of gases contained 13.8% CO₂. Samples of coke impregnated with sodium carbonate and of coconut charcoal gave initially much smaller equilibrium concentrations of carbon dioxide, but repeated heating at 900° in a vacuum resulted in the concentration gradually rising to 13.8%, due apparently to progressive surface graphitisation, a change which was brought about with the coke more readily than with the charcoal. Sodium carbonate appears, below 1000°, to retard graphitisation. The reactivity of coke diminishes as reaction proceeds; the equilibrium composition of the gas phase before partial gasification is not the same as after, since the more active portions of the coke gasify first. R. CUTHILL.

Connexion between the different hydrates of a salt. W. BRÜLL (Z. anorg. Chem., 1929, 183, 347—352).—Theoretical. In the detection of the different hydrates of a salt by the dehydration method, it is necessary to carry out isothermal or isobaric dehydration at very varying temperatures and pressures, respectively, as, owing to the intersection of the T -log p curves, the region of stability of a given hydrate may not be realisable under the conditions of any single experiment.

M. S. BURR.

Equilibria between metals and salts in fluxes. XVIII. Equilibrium between calcium and sodium and their chlorides when lead and antimony are present in the metal phases. R. LORENZ and R. WINZER (Z. anorg. Chem., 1929, **183**, 127—139).—Addition of lead to the metal phase displaces the equilibrium $\text{Ca} + 2\text{NaCl} \rightleftharpoons \text{CaCl}_2 + 2\text{Na}$ to the right, but the effect does not conform to the law of mass action; the displacement increases until the ratio $\text{Pb}/(\text{Ca} + \text{Na})$ is about 8, after which further addition of lead produces no further change, and the mass action law is then applicable to the equilibrium. The influence of antimony resembles that of lead, but the magnitude of the maximum displacement is different. H. F. GILLBE.

Isotherms of the ternary system containing water, alkali sulphate, and a sulphate of the vitriol type. I. A. BENRATH (Z. anorg. Chem., 1929, **183**, 296—300; cf. this vol., 650).—The isotherms for the system $\text{MnSO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ at 50° have been determined, and also a certain amount of data at 11°, 25°, 30°, and 41° has been obtained. The results indicate the existence of the salt $\text{MnSO}_4 \cdot 3\text{Na}_2\text{SO}_4$, in addition to the compound $\text{MnSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ previously found (*loc. cit.*). M. S. BURR.

Uranyl formate. A. COLANI (Bull. Soc. chim., 1929, [iv], **45**, 624—626).—The system uranyl formate—formic acid—water has been studied at 25°. A solution of uranyl formate monohydrate slowly deposits the basic formate $\text{UO}_3 \cdot 2\text{H}_2\text{O} \cdot \text{UO}_2(\text{HCO}_2)_2 \cdot \text{H}_2\text{O}$, the solubility of which increases with the concentration of formic acid. The solubility of the monohydrate decreases with increase of acid concentration. O. J. WALKER.

Reciprocal salt pair $\text{MgSO}_4\text{--}2\text{NaNO}_3\text{--H}_2\text{O}$. II. W. SCHRODER (Caliche, 1929, **11**, 154—162).—See this vol., 267.

The general thermodynamical integrating factor of the entropy function. A. PRESS (Z. Physik, 1929, **56**, 131—146).

Methods of calorimetry and the question of allotropy in the case of heats of dissolution of potassium nitrate and chloride. W. A. ROTH and C. EYMANN (Z. physikal. Chem., 1929, **143**, 321—353; cf. A., 1928, 22).—A review of the literature relating to the heat of dissolution of potassium nitrate in water reveals large discrepancies in the absolute values assigned to it by different workers, in spite of the good agreement between the results obtained by individuals. Fresh experiments have been undertaken in order to ascertain how far these discrepancies are to be attributed to defects in the calorimetric methods used and to inhomogeneity of the material. A specimen heated for a long time at 160° and then chilled at -16° gave a value about 1% lower than the values obtained when the salt had been cooled slowly from above its transition temperature, corresponding with an admixture of 8.5% of the β -modification, which, however, could not be prepared pure by this treatment. On the other hand, the results are influenced to a far greater extent by the type of calorimeter employed. If the course of the thermal change is different in the calibration and

the actual measurement, the usual method gives uncertain results, particularly if vacuum vessels or metal vessels of small size are used. A metal calorimeter completely immersed in water is the most satisfactory. These restrictions do not apply to adiabatic methods, which are, however, more difficult in use. The most suitable method is an adiabatic compensation method, in which the thermal effect is exactly neutralised by heat generated electrically within the calorimeter, an additional advantage being that the determination is made at a definite temperature. This method was therefore used, in conjunction with an immersed metal calorimeter, as a control in the measurement of the heats of dissolution of potassium nitrate and chloride. The following values are given: $\text{KNO}_3 \cdot 350\text{H}_2\text{O}$, -8.418 kg.-cal. per mol./21.0°; $\text{KCl} \cdot 150\text{H}_2\text{O}$, -4.322 kg.-cal. per mol./21.0°; heat of neutralisation of 1 mol. of oxalic acid in $1170\text{H}_2\text{O}$, $+28.11$ kg.-cal./20.0°. It is considered that many of the accepted thermo-chemical constants for solids are inexact. F. L. USHER.

Determination of heats of dilution of hydrated salts (second method). J. PERREU (Compt. rend., 1929, **189**, 462—465; cf. this vol., 1014).—To determine the heats of dilution (L) and of addition (A) where these are very small the method adopted consisted in immersing a small bulb containing varying amounts of water (π) in varying amounts (P) of saturated solution of concentration p contained in a calorimeter, breaking the bulb, and measuring the heat evolved (q). This process is repeated until the total heat evolved is equal to that of dissolution in a large excess of water. The results are plotted on a $-q$ curve, and A is determined as $(100M/p)(dq/d\pi)$. The values of A thus determined are: $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ -0.875 ; $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ -0.45 ; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ -0.95 ; $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ -0.25 ; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ -0.10 . L for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ deduced in this way is -2.48 , agreeing well with -2.44 determined directly. C. A. SILBERRAD.

Adiabatic calorimetry. I. **Temperature changes of the order of 1°.** E. LANGE and E. O. ROUNSEFELL (Z. physikal. Chem., 1929, **142**, 351—364).—Improvements in calorimetric technique which have been evolved in the course of several years' work on heats of dilution and of dissolution (cf. Lange and others, 1925 onwards) are described. Amongst the points dealt with are the measurement of temperature changes of the order of 1° by means of mercury thermometers graduated to 0.01° and 0.001°, an electrical glass capillary heater for calibration purposes, and an electrically controlled speed regulator for maintaining constant speed of the stirring motor. The possibility and mode of prevention of errors due to heat exchange between the calorimeter contents and surroundings, and also of those due to evaporation and condensation effects, are discussed. O. J. WALKER.

Thermo-chemistry of hypochlorous acid and some of its salts in aqueous solution. B. NEUMANN and G. MÜLLER (Z. anorg. Chem., 1929, **182**, 235—254).—The heats of the reactions $\text{Cl}_2 + 2\text{MOH}_{\text{aq.}} = \text{MOCl}_{\text{aq.}} + \text{MCl}_{\text{aq.}}$ and $\text{HOCl}_{\text{aq.}} + \text{MOH}_{\text{aq.}} = \text{MOCl}_{\text{aq.}} + \text{H}_2\text{O}$ have been determined when M is

lithium, sodium, potassium, calcium, strontium, or barium. For the second reaction the mean value obtained is 8440 g.-cal./mol. and is lower than those given by Thomsen (9976 g.-cal.) and Berthelot (9600 g.-cal.). The heat of dilution of hypochlorous acid increases with the concentration of the acid, and the heat of dissolution of chlorine monoxide (1 mol.) in water (2072 mols.) is found to have a mean value of 8737 ± 7 g.-cal. The heats of formation of aqueous solutions of hypochlorous acid and the hypochlorites of the above bases from their respective elements have been evaluated from these and other data. The values of $[H, Cl, O, aq.]$ vary from 30,366 g.-cal. when calcium hydroxide is used to 30,550 g.-cal. with lithium hydroxide, the mean value from the six hydroxides being $30,439 (\pm 0.1\%)$ g.-cal. The values for the hypochlorites are sodium 82,803, potassium 85,748, lithium 92,190, calcium 180,642, strontium 181,446, and barium 179,420 g.-cal./g.-mol. Other data are also evaluated.

Concentrated solutions of hypochlorous acid containing 16–22% $HClO$ have been prepared by the addition of a slight excess of freshly-precipitated mercuric oxide to water saturated at 0° with chlorine and distillation at 18–20 mm. pressure. Addition of liquid chlorine monoxide to this product gave a chlorine-free solution containing 30% $HClO$.

L. S. THEOBALD.

Calorimetric researches. XVIII. The two hydrobenzoin. P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1929, 48, 1031–1034).—The heats of combustion at 15° of *d*- and *l*-hydrobenzoin are respectively Q_v 1719.3, Q_p 1720.8, Q_v 1719.0, Q_p 1721.1 g.-cal. For the racemic compound obtained by the reduction of benzoin with aluminium ethoxide in boiling decalin the values Q_v 1718.6, Q_p 1720.0 were found. The heat of racemisation according to these data is 1.0 g.-cal.

F. G. TRYBORN.

Transference of water and its dependence on concentration in the electrolysis of sodium chloride solutions. (Miss) M. TAYLOR and E. W. SAWYER (J.C.S., 1929, 2095–2106).—Transport experiments have been made at 25° with 0.5*N*-solutions of sodium chloride containing carbamide, this substance having been shown by control experiments not to migrate under the influence of the electric field. A transportation of water towards the cathode was detected, the amount transported per faraday being rather greater than in Washburn's experiments with *N*-solutions (A., 1915, ii, 311). R. CUTHILL.

Electrical conductivity of salts of alkaloids in pure and in mixed solvents. J. N. RAKSHIT (J. Indian Chem. Soc., 1929, 6, 607–612).—Molecular conductivities of the hydrochlorides of morphine, codeine, narcotine, and cotarnine, in mixtures of alcohol and water varying in composition from pure alcohol to pure water, have been determined at 35° and at different dilutions. Molecular conductivity in all cases decreases as the water in the solution is replaced by alcohol, whilst the dilution of the salt remains constant. The relative variations are not the same for all the salts.

M. S. BURR.

Conductivity measurements in very dilute alcoholic solutions. L. THOMAS and E. MARUM

(Z. physikal. Chem., 1929, 143, 191–215).—The conductivities of the sodium and piperidinium salts of trinitro-*m*-cresol and of hydrochloric and picric acids in dilute aqueous solution have been determined, the extrapolated values of λ_∞ for the sodium salts being 80.3, 127.5, and 81.3, and for the piperidinium salts 66.3, 113.5, and 67.3, respectively. The following values of λ_∞ in methyl and ethyl alcohol, respectively, have been extrapolated from conductivity measurements at dilutions up to 45,000 litres; sodium chloride 100.5, 43.0; sodium bromide 104.8, 44.9; sodium iodide, 110.3, 47.8; sodium picrate 94.7, 45.8; sodium trinitro-*m*-tolylloxide 92.7, 44.0; piperidinium chloride 112.6, 50.4; piperidinium picrate 106.8, 53.2; piperidinium trinitro-*m*-tolylloxide 104.8, 51.4. Measurement of the conductivity of very dilute solutions of hydrogen chloride in absolute and aqueous methyl and ethyl alcohols yields the values 0.25 and 0.06, respectively, for the equilibrium constant of the partition of the hydrogen ion between the alcohol and water; the difference of mobility of the alcoholated and hydrated hydrogen ion is in methyl alcohol 97.5 and in ethyl alcohol 40.3.

H. F. GILLBE.

Electrical conductivities of ammonia-water mixtures between 26 and 82% ammonia and from -30° to $+30^\circ$. M. DE K. THOMPSON and R. B. ATKINSON (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 19 pp.).—The electrical conductivities of ammonia-water mixtures were measured in a glass cell. For solutions of lower ammonia content (from 26%) the specific conductance increases regularly and rapidly with rise of temperature, but with the more concentrated solutions the increase is comparatively slow and irregularities are observed which are attributed to action on the glass. At $+30^\circ$ solutions containing more than 50% of ammonia attack glass to such an extent as to interfere with the measurements. With regard to the possibility of using the data for the determination of the composition of ammonia-water mixtures in different parts of the circulatory system of a refrigerator, it is concluded that above 15° the composition of pure mixtures containing up to 50% of ammonia could be determined to within 0.5%. At lower temperatures the accuracy becomes rapidly less and at -30° mixtures containing more than 32% of ammonia could not be analysed by this means.

H. J. T. ELLINGHAM.

High-frequency conductivity and dielectric constants of aqueous solutions of electrolytes. H. RIECKHOFF (Ann. Physik, 1929, [v], 2, 577–615).—The change in conductivity of an electrolyte in a high-frequency field can be measured by the damping action on another vibrating system. The method is a substitution process with potassium chloride as the standard electrolyte. A wave-length of 1 m. is used. Data for twenty electrolytes with various valency combinations and different concentrations are in satisfactory agreement with the Debye-Falkenhagen theory of the dispersion effect. The principal deviations occur with the ions of higher valency. The effect of temperature conforms with theoretical requirements. Investigation of dielectric constants shows that the introduction of a dispersion

correction produces changes in the values of Hellmann and Zahn, but that such changes are generally quite small. Anomalous data obtained by Walden's resonance method are ascribed to an error in the indicator coupling, and a satisfactory indicator system is described.

R. A. MORTON.

Dispersion of electrolytic conductivity. B. BRENDDEL, O. MITTELSTAEDT, and H. SACK (Physikal. Z., 1929, 30, 576—578).—Preliminary. A method for measuring the conductivity of an electrolyte with high frequencies is described. Results with magnesium sulphate in relation to potassium chloride are in moderately good agreement with the Debye theory.

R. A. MORTON.

Influence of pressure on the electrical conductivity of salt solutions. G. TAMMANN and A. ROHMANN (Z. anorg. Chem., 1929, 183, 1—29).—The percentage change of conductivity $\Delta\lambda$ with increase of pressure up to 3000 kg. per cm.² has been determined for aqueous solutions of sodium acetate, potassium cyanide, barium chloride, calcium chloride, mercuric chloride, ammonium cyanide, ammonium chloride, ammonium acetate, and hydrogen cyanide at 20—40°. The isothermal $\Delta\lambda/p$ curves for the strong electrolytes are all of the same type and exhibit maxima which with increase of concentration are displaced in the direction of higher pressure on account of the greater influence of pressure on the interionic friction at higher concentrations; with rise of temperature the maxima are displaced in the direction of lower pressures, and the curves become flatter. The isotherms for weak electrolytes are always concave to the pressure axis, and higher values are attained than for strong electrolytes; mercuric chloride is anomalous, since the isotherms for 0.1—0.3*N*-solutions resemble those for the weak electrolytes, for 0.01*N* are approximately linear, and for 0.001*N*-solutions become convex to the pressure axis. The variation of $\Delta\lambda$ with concentration at 500 kg. per cm.² approximates in general to that calculated from the influence of pressure on the volume and viscosity of the solution, the assumption being made that the influence of the interionic friction is equal to that on the viscosity of the solvent; at 300 kg. per cm.² the observed effect is greater than the calculated, although the curves are approximately parallel. The observed pressure effect affords evidence for the complete ionisation of strong electrolytes. The interionic friction of salt solutions, regarded as a function of pressure, passes through a minimum, the curves resembling that of the variation of the viscosity of water under pressure, but for acids the interionic friction diminishes continuously as the pressure rises. For the special case of zinc sulphate the variations with pressure of the interionic friction and the internal friction of the solution are very nearly equal on account of strong hydration. The influence of pressure on the hydrolysis of salts is discussed; although exact calculation of the effect is not possible, the experimental results are qualitatively in accord with theoretical requirements.

H. F. GILLBE.

Influence of pressure on the conductivity of solutions of acids. G. TAMMANN and W. TOFAUTE

(Z. anorg. Chem., 1929, 182, 353—381).—The influence of pressure on the conductivity of a number of solutions of weak and moderately strong electrolytes has been measured in relationship to the concentration and temperature. At constant temperature the percentage increase of conductivity, regarded as a function of concentration, reaches a maximum at a concentration which is the higher the greater is the dissociation constant of the acid. With ternary electrolytes the rate of increase of the influence of pressure on the dissociation constant with increase of concentration is less rapid, and lower maximum values are obtained, than for binary electrolytes. Increase of pressure causes an increase of interionic friction in all cases except that of the hydrogen and hydroxyl ions, for which the reverse holds true. The change of conductivity of water under pressure expressed as a function of the total ammonia and carbon dioxide concentration exhibits a well-defined minimum.

H. F. GILLBE.

Standard electrode potentials in methyl alcohol. P. S. BUCKLEY and (SIR) H. HARTLEY (Phil. Mag., 1929, [vii], 8, 320—341).—In view of numerous sources of error and divergent values in the work of previous investigators, a study was initially made of reference electrodes, liquid-junction potentials, and activity coefficients in methyl alcohol. Measurements were made of the standard electrode potentials of hydrogen, sodium, thallium, silver, cadmium, and copper, and the results have been used for determining the solubilities of silver chloride, bromide, iodide, and thiocyanate and of thallium chloride, and the dissociation constant of methyl alcohol. The standard electrode potentials of chlorine, bromine, and iodine were found from the solubility products of the corresponding silver halides. The quinhydrone electrode was studied in aqueous and alcoholic solutions.

N. M. BLIGH.

Quinhydrone electrode. A. E. BRODSKY and F. I. TRACHTENBERG (Z. physikal. Chem., 1929, 143, 287—300).—The general theory of the quinhydrone electrode is developed. The *E.M.F.* of the saturated quinhydrone electrode has been determined against that of the quinol electrode at various concentrations in water, and in absolute and aqueous methyl and ethyl alcohol solutions; the calculated solubilities agree with those determined analytically. The osmotic theory of electric cells is applicable to non-aqueous solutions.

H. F. GILLBE.

Acidity and ionic potentials. J. N. BRONSTED (Z. physikal. Chem., 1929, 143, 301—312).—In general ionic potentials and electric potentials in chemical systems cannot be determined on the basis of ordinary thermodynamic considerations on account of the theoretical and practical inapplicability of the thermodynamic functions when passing from the concept of unchanged molecules to that of ions. A method is described for dealing with such functions by consideration of an electrically neutral isolated homogeneous phase. The measurement of acidity in terms of hydrogen-ion concentration is particularly discussed.

H. F. GILLBE.

Electrode potentials of copper anodes and copper cathodes. E. F. KERN and R. W. ROWEN

(Amer. Electrochem. Soc., Sept., 1929. Advance copy, 14 pp.).—Measurements of the anodic polarisation at copper electrodes of various degrees of purity have been made in solutions of types used in copper refining, and of the cathodic polarisation during the deposition of copper from these solutions. All measurements were made at 1.6 amp./dm.² Agitation or circulation of the electrolyte decreased the polarisation, especially at the cathode, but the concentration of free acid in the electrolyte had no appreciable effect. Raising the temperature caused a slight decrease in anodic polarisation and a considerable fall in cathodic polarisation. The polarisation at the anode increased with increasing amounts of impurity in the copper. Addition of glue to the electrolyte produced a slight increase in anodic polarisation, but a considerable increase in cathodic polarisation, the latter actually increasing with rise in temperature. Addition of sulphite waste liquor residue ("goulao") caused a slight increase in polarisation at the anode, whereas that at the cathode was raised during only the first few minutes of electrolysis and then became normal. The effect of glue and goulao together was the sum of the separate effects. Equilibrium potentials were measured in all the above cases. These were slightly more positive for rolled than for cast anodes. The presence of glue made the equilibrium potential at the cathode slightly less positive.

H. J. T. ELLINGHAM.

Cathode potentials and electrode efficiencies of copper in copper cyanide-sodium cyanide solutions. G. M. SMITH and J. M. BRECKENRIDGE (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 8 pp.).—Solutions of copper cyanide in sodium cyanide solution were electrolysed at various constant current densities between copper electrodes for periods of 3 hrs. and the cathode potential at the end of the period and the cathodic and anodic current efficiencies over the period were measured. The cathode potential becomes more negative with increase in current density or dilution of the electrolyte, and the higher the molar ratio of copper to sodium cyanide the greater is the change of potential with increase in current density. The cathodic current efficiency decreases with increasing current density, with dilution of the electrolyte, and with decrease in the molar ratio of copper to sodium cyanide. If this ratio is less than 1:4 the efficiency is practically zero or even negative. The anodic current efficiency decreases with increasing current density and with increase in the molar ratio of copper to sodium cyanide.

H. J. T. ELLINGHAM.

E.M.F. of some molten salt cells. R. LORENZ and H. VELDE (Z. anorg. Chem., 1929, 183, 81—97).—The *E.M.F.* of lead, zinc, cadmium, and magnesium against their respective chlorides have been measured as functions of the temperature in the neighbourhood of 400—700°; for lead $E=1.2467-6.5 \times 10^{-4}(t-550^\circ)$, for cadmium $E=1.3421-6.29 \times 10^{-4}(t-599^\circ)$, and for magnesium $E=2.5112-6.73 \times 10^{-4}(t-700^\circ)$, whilst for zinc, which is peculiar in that the E/T curve is parabolic, $1.6050-4.6 \times 10^{-4}(t-427^\circ)-8.93 \times 10^{-7}(t-427^\circ)$. The *E.M.F.* of various combinations of the type $M|M'Cl|M''Cl|M''$

have been calculated on the assumption that there is no *P.D.* at the interface between the two chlorides, and in certain cases the results deviate considerably from those obtained experimentally. The theoretical significance of the results is discussed.

H. F. GILLBE.

Membrane potentials. J. M. ORT and W. G. FRANCE (J. Physical Chem., 1929, 33, 1374—1385).—A study of a modified form of Des Coudres' cell has shown the collodion membranes used to be specifically charged at zero pressure, the measured cell potentials differing from the values calculated by means of Des Coudres' equation; on the contrary, the potentials equal the algebraic sum of the specific charge and the calculated value. The effects of temperature, composition of electrolyte (mercurous nitrate in nitric acid), nature of the membrane, and time of exposure of the membrane to the electrolyte have been determined, and the origin of the specific charge is discussed.

L. S. THEOBALD.

Electrolysis with a mercury cathode. II. Explanation of the anomalies on the electro-capillary curves. J. HEYROVSKÝ and R. ŠIMŮNEK (Phil. Mag., 1929, [vii], 7, 951—970).—Current-voltage curves obtained with the dropping mercury cathode when solutions exposed to the air are polarised are found to show definite reproducible maxima due to the electro-reduction of dissolved atmospheric oxygen. These anomalies, first noted by Kucera, are most prominent in approximately 0.001*N*-solutions. The fall of the current at the maxima is associated with a sudden fall at the interfacial tension at the polarised mercury dropping cathode and a sharp increase of the cathodic potential. The presence of surface-active substance, active anions, or high concentrations of electrolytes eliminates the current maxima and the changes in interfacial tension; this may be explained on the basis of the preferential adsorption of the suppressing agencies. The discontinuous changes in current and interfacial tension are attributed to an effect of concentration polarisation which prevents the further adsorption of oxygen at the mercury-electrolyte interface.

A. E. MITCHELL.

Overpotential of bismuth in acid solutions. W. V. LLOYD (Trans. Faraday Soc., 1929, 25, 525—529).—The overpotential of bismuth in acid solutions has been measured and the results have been compared with those obtained (A., 1927, 317) with antimony. Both the direct and the commutator methods were used. A bismuth cathode must be polarised for a longer time in order to attain the maximum overpotential at a given current density. The overpotential of bismuth in acid solutions is approximately 0.1 volt greater than that of antimony. The incidence of maximum commutator potential of bismuth indicates a constant degree of supersaturation of the electrode with hydrogen, which is independent of the hydrogen-ion concentration, and the anion of the electrolyte.

F. J. WILKINS.

Theory of passivity. VI. Passivation of chromium at low current densities. W. J. MÜLLER and K. KONOPICKY (Monatsh., 1929, 52, 289—296).—Calculations based on the current

density-time curves of Müller and Noack (A., 1927, 942) show the applicability of the equation given by Müller and Konopicky for the rate of growth of the surface film, viz., $t-t_0=B(1/i^2-1/i_0^2)$, where i and i_0 are the current densities at times t and t_0 (this vol., 146). B is a function of the potential applied to the chromium and the potential at which $B=0$ is identical with the electrode potential of active chromium. The passivation of chromium at low current densities is therefore held to be due to a surface film. J. A. V. BUTLER.

Circuit transmission and interference of activation waves in living tissues and in passive iron. R. S. LILLIE (Science, 1929, 69, 305—308; cf. this vol., 272).—Circuit transmission has been obtained in passive iron by suspending "Armco" wire in a circular trough containing nitric acid (75—80% by volume). Interference has been observed after touching the wire with zinc at any point when two activation waves are set up and travel in opposite directions until they meet and extinguish each other. Contact with platinum stops such an activation wave started by zinc. These and similar experiments are compared with wave transmission in living tissues, which is also discussed, and explanations based on surface oxidation and reduction phenomena are advanced. L. S. THEOBALD.

Photo-voltaic cells with silver-silver bromide electrodes. II. S. E. SHEPPARD, W. VANSELOW, and V. C. HALL (J. Physical Chem., 1929, 33, 1403—1414; cf. this vol., 653).—Photographic records of the photo-potential changes which occur during the first second of illumination in cells with Ag|AgBr electrodes in various electrolytes have been obtained by means of a system containing an amplifier-oscillograph. The factors studied include the age of the electrode, the Svensson-Becquerel effect, halogen acceptors, electrolytes, and intermittent exposure to light. With potassium bromide solutions, saturated with silver bromide, as electrolyte, no photo-potentials are produced by exposure of this electrolyte to the quartz-mercury vapour arc. Small differences in potential were observed with electrodes of different age, but the maximum value is reached in all cases in approximately the same time, 0.06 second. In the presence of a halogen acceptor, such as acetone-semicarbazone, this time becomes greater and the negative potential is also increased. The maximum negative photo-potential also varies with the nature of the electrolyte. The results support the theory previously advanced (*loc. cit.*). L. S. THEOBALD.

Influence of temperature on photo-electric E.M.F. G. ATHANASIU (Compt. rend., 1929, 189, 460—462).—The electrodes of the cells investigated were: (a) Ag—AgI, (b) Ag—AgBr, (c) Ag—Ag₂S, (d) Cu—oxidised Cu, and (e) Hg—Hg₂I₂. No satisfactory results were obtained with (e). In (a), (b), and (c) the electrolyte was sulphuric acid, in (d) potassium chloride. One electrode was illuminated with monochromatic light from the region of the spectrum giving maximum photo-electric effect for that electrode. In all cases this effect increases as the temperature falls. The following results are given: (T =temperature limits; λ =wave-length; E =corre-

sponding E.M.F. in volts $\times 10^5$): (a) T 13—1°, λ 0.420 μ , E 43—81; (b) T 16—2°, λ 0.430 μ , E 38—47; (c) T 18.5—2.5°, λ 0.650 μ , E 46.7—125; λ 0.800 μ , E 97.0—256; λ 1.000 μ , E 170—480; (d) T 12—3°, λ 0.540 μ , E 17—38. The temperature coefficient of (c) is thus practically constant (1.60—1.68) for the wave-lengths used. These results support the author's conclusions (cf. this vol., 514) that the E.M.F. is the algebraic sum of E.M.F. due to (i) photochemical reaction but little affected by temperature, and (ii) thermal reaction favoured by rise in temperature. C. A. SILBERRAD.

Reduced equations in chemical kinetics. W. SWIENTOSLAWSKI and J. G. ZAWIDZKI (Bull. Acad. Polonaise, 1929, A, 295—315).—See this vol., 770.

Influence of indifferent gases on the thermal decomposition of ozone. E. H. RIESENFELD and E. WASSMUTH (Z. physikal. Chem., 1929, 143, 397—434).—The rate of decomposition of ozone at 90° and 100° has been measured by the static method in the presence of oxygen, nitrogen, carbon dioxide, helium, or argon, at different total pressures between 100 and 1000 mm. The decomposition proceeds in two ways simultaneously, viz., by a bimolecular reaction which is independent of the partial pressure of oxygen (cf. Riesenfeld and Bohnholtzer, A., 1928, 24), but is accelerated by the other gases named, and by a unimolecular reaction which is retarded by all the gases except helium. For the usual velocity coefficients of the unimolecular and bimolecular reactions must be substituted A_1+B_1p and A_2+B_2p , respectively, where A_1 and A_2 are constants independent of the nature of the indifferent gas, B_1 and B_2 are specific proportionality factors, and p is the partial pressure of the indifferent gas. To B_1 are assigned the values -6, -3, -10, 0, -6 for the different gases in the order named above, and to B_2 the values 0, 4, 10, 3, 3. The temperature coefficient of the unimolecular reaction between 90° and 100° is 1.8, that of the bimolecular 3.0, and neither is appreciably changed by admixture of the gases studied. The temperature coefficient of the unimolecular reaction corresponds with a heat of activation insufficient to account for a spontaneous change $O_3=O_2+O$, and it is therefore concluded that the primary reaction is initiated by traces of some foreign material in the gas or on the walls of the containing vessel, this substance being subsequently regenerated. The retarding effect of indifferent gases is due either to a specific action in breaking the ensuing "chain," or to their protecting the ozone against the action of the foreign material. The latter explanation receives support from the observation that the retarding effects are in the same order as the adsorbabilities. The bimolecular reaction is also to be regarded as a chain reaction, viz., (1) $O_3^*+O_3=3O_2^*$, (2) $O_2^*+O_3=O_3^*+O_2$, etc. The molecules of an indifferent gas act as energy carriers, and the differences observed are due to variations in the time of conservation of the energy carried, the latter being dissipated most rapidly by oxygen and least rapidly by carbon dioxide. F. L. USHER.

Ignition of phosphorus vapour in oxygen. A. KOWALSKY (Z. physikal. Chem., 1929, B, 4, 288—298).—Measurements have been made of the lower

and upper pressure limits, p_1 and p_2 , respectively, beyond which phosphorus vapour does not undergo oxidation in oxygen, and the relation between these two pressures and the partial pressure, p_F , of the phosphorus vapour has been determined. From Semenov's chain reaction theory of the oxidation of phosphorus vapour (cf. A., 1928, 483) the two expressions $p_1 p_F = k_1$ and $p_F/p_2 = k_2$ are derived. These are verified experimentally and the values 3.2×10^{-4} and 2.8×10^{-5} are found for k_1 and k_2 , respectively. From these constants the minimum partial pressure of phosphorus vapour below which reaction will not take place under any conditions can be calculated and is found to be 1.9×10^{-4} mm., in good agreement with the experimental result, which lies between 1.0 and 2.0×10^{-4} mm. Experimental support is therefore obtained for Semenov's theory. O. J. WALKER.

Quenching of flames in atmospheres of a certain composition and at the limits of explosion regions. W. P. JORISSEN and B. L. ONGKIEHONG (Rec. trav. chim., 1929, 48, 1069—1074).—From a comparison of the quenching of flames at the limits of explosion regions and the corresponding phenomena in a closed space or on plunging the flame into gas mixtures of various oxygen contents it is shown that a combustible gas or vapour will burn only in atmospheres with oxygen contents above a certain limit which is definite for each gas or vapour. The correspondence between the quenching of Bunsen flames and that of other flames is discussed from this point of view. Except with carbon dioxide the oxygen contents of atmospheres in which flames are quenched are in the same order as those of mixtures in which explosion limits have coincided.

F. G. TRYHORN.

Oxidation of phosphine at low pressures. R. H. DALTON and C. N. HINSHELWOOD (Proc. Roy. Soc., 1929, A, 125, 294—308).—It has long been known that mixtures of phosphine and oxygen explode when the pressure is reduced, and it is now found that, in addition to the higher pressure limit, there is also a lower pressure limit below which the rate of combination is negligible but above which explosion occurs. The nature of this limit has been investigated by compressing the gases at low pressure until explosion takes place. The phenomenon is explained by the theory that the oxidation is a chain reaction, the chains being broken only when they reach the walls of the vessel. The limiting pressure is that at which the rate of initiation of chains just begins to exceed the rate at which they are broken. The simple development of this theory leads to the following relation between the partial pressures of the various gases at the explosion point: $p_{O_2} \cdot p_{PH_3} \cdot d^2 [1 + p_{N_2}/(p_{O_2} + p_{PH_3})] = \text{constant}$, where d is the diameter of the containing tube and p_{N_2} the pressure of nitrogen or any other inert gas present. This formula is analogous to that used by Semenov for the oxidation of phosphorus vapour (this vol., 514). It describes the results qualitatively in that (a) there is an inverse relationship between the pressures of oxygen and phosphine at the explosion point, (b) the critical partial pressures are lowered by the presence of nitrogen or argon, and (c) in the absence

of inert gases the product $p_{O_2} \cdot p_{PH_3}$ is approximately inversely proportional to the square of the diameter of the tube. To obtain quantitative agreement the theory needs elaboration. In the absence of an inert gas, $p_{O_2} \cdot p_{PH_3}$ is not constant but passes through a maximum when $p_{O_2} = p_{PH_3}$. The effect of inert gases is smaller than that calculated, although the theory predicts the correct order of magnitude. Further, in wide tubes the product $p_{O_2} \cdot p_{PH_3} \cdot d^2$ tends to rise. These quantitative deviations are attributed to the fact that some of the chains may be broken in the gas and not solely at the walls of the reaction vessel.

L. L. BIRCHUMSHAW.

Kinetics of the oxidation of ethylene. H. W. THOMPSON and C. N. HINSHELWOOD (Proc. Roy. Soc., 1929, A, 125, 277—291).—The rate of reaction of oxygen with ethylene has been measured between 400° and 500° by the method previously described (A., 1928, 483). Although the rate of increase of pressure is not an exact measure of the rate of disappearance of the ethylene, it is sufficiently nearly so for the mixtures $C_2H_4 + O_2$, $C_2H_4 + 2O_2$, and $C_2H_4 + 3O_2$ to enable it to be used in an investigation of the effect on the reaction velocity of the total pressure, the temperature, and the relative proportions of the two gases. The influence of the total pressure on the rate is roughly that corresponding with a reaction of the third order, the effect depending much more on the partial pressure of the ethylene than on that of the oxygen. In certain regions of pressure the rate is proportional to about the third power of the ethylene concentration. The oxidation is assumed to take place by a chain mechanism, and it is suggested that the first stage in the reaction is the formation of an unstable peroxide, $C_2H_4 \cdot O_2$. If this collides with another ethylene molecule, two active hydroxylated molecules, e.g., $CH_3 \cdot CH \cdot OH$, are produced which continue the chain, but if the peroxide collides with oxygen it is either decomposed or oxidised to stable products. The reaction is considerably retarded by increasing the surface of the vessel exposed to the gas. A consideration of the temperature coefficient and the influence of nitrogen and argon on the velocity of reaction leads to the conclusion that the chains are comparatively short.

L. L. BIRCHUMSHAW.

Thermal decomposition of gaseous ethylene oxide. W. W. HECKERT and E. MACK, jun. (J. Amer. Chem. Soc., 1929, 51, 2706—2717).—The thermal decomposition of gaseous ethylene oxide in a pyrex vessel at 380—444° is a homogeneous unimolecular reaction: $\log_e k = 34.02 - 52000/RT$. There is a period of induction during which the velocity increases. In the later stages the velocity is diminished owing to the accumulation of reaction products, methane and carbon monoxide. Other indifferent gases have the same effect, but hydrogen behaves otherwise. A mechanism is suggested in which isomerisation to active acetaldehyde, with consequent interference with the formation of activating reaction chains (Christiansen and Kramers, A., 1924, ii, 28), is the first stage.

S. K. TWEEDY.

Irreversible transformations of organic compounds under high pressures. P. W. BRIDGMAN and J. B. CONANT (Proc. Nat. Acad. Sci., 1929, 15,

680—683).—Under a pressure of 10,000 atm. for 24 hrs. the following substances were not appreciably affected: amylene, pinacone, *tert.*-amyl alcohol, diacetone alcohol, aniline acetate dissolved in aniline, solid maleic acid, benzoquinone in isopropyl alcohol, and phenol in 20% aqueous formaldehyde. Under 9000 atm. for 24 hrs. isoprene, β -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene, styrene, and indene were partly polymerised; isobutaldehyde and *n*-butaldehyde under 12,000 atm. for 40 hrs. were converted into unknown polymerides which passed to a liquid in 24 hrs. The rate of polymerisation of isoprene was investigated at pressures up to 12,000 atm. Carboxyhaemoglobin under pressure gave a red precipitate resembling the "denatured" product obtained by the action of alcohol.

N. M. BLIGH.

Velocity of esterification of bromobenzoic acids in glycerol and ethyl alcohol solutions containing hydrochloric acid. A. KAILAN and K. HEXEL (Monatsh., 1929, 52, 260—288).—The velocities of esterification of *o*-, *m*-, and *p*-bromobenzoic acids have been determined at 25° in dry and moist ethyl alcohol and glycerol solutions, with hydrogen chloride as catalyst. In the dry media the unimolecular velocity coefficients are proportional to the catalyst concentration, but the addition of water causes a more rapid rise. The velocity coefficients in all cases except that of *p*-bromobenzoic acid in glycerol can be represented as functions of *c* and *w* (*c* being the concentration of hydrogen chloride, *w* that of water in g.-mol. per litre) by interpolation formulæ of the same type. The addition of water retards the reaction in glycerol much less than in alcohol solutions. The velocity coefficients of *o*-, *m*-, and *p*-bromobenzoic acids for $c=\frac{1}{2}$ and $w=0.03$ are in the ratio 0.29 : 0.69 : 0.54 in ethyl alcohol and 0.54 : 1.15 : 0.92 in glycerol solutions, the value for benzoic acid in a similar solution being taken as unity in each case. The solubilities of the bromobenzoic acids in ethyl alcohol and glycerol have been determined.

J. A. V. BUTLER.

Velocity of esterification of chloro- and fluoro-benzoic acids, ethyl hydrogen phthalate, and abietic acid in ethyl alcohol solutions containing hydrochloric acid. A. KAILAN and W. ANTROPP (Monatsh., 1929, 52, 297—338).—The velocities of esterification of *o*-, *m*-, and *p*-chloro- and -fluoro-benzoic acids, ethyl hydrogen phthalate, and abietic acid have been determined at 25° in dry and moist ethyl alcohol solutions, with hydrogen chloride as catalyst. The unimolecular velocity coefficients are proportional to the catalyst concentration in dry alcohol, but rise more rapidly in solutions containing water. They can be represented by interpolation formulæ similar to those previously employed (see preceding abstract). The velocity coefficients of *o*-, *m*-, and *p*-fluorobenzoic acids for $c=\frac{1}{2}$, $w=0.03$ are in the ratio 0.95 : 0.69 : 0.54 and those of the corresponding chlorobenzoic acids in the ratio 0.38 : 0.69 : 0.66, the value for benzoic acid in a similar solution being taken as unity. With the exception of anthranilic acid, the rate of esterification of abietic acid is smaller than that of any other organic acid investigated. The hydrolysis of the correspond-

ing neutral ester is apparent only in the case of ethyl hydrogen phthalate.

J. A. V. BUTLER.

Reactivity of atoms and groups in organic compounds. VIII. Relative reactivities of hydroxyl groups in certain alcohols. J. F. NORRIS (Rec. trav. chim., 1929, 48, 885—889; cf. A., 1925, i, 626; 1927, 1166).—A summary of results to be published later in more detail. The (second order) velocity coefficients for the reaction between hydrogen bromide (1 mol.) and various alcohols (25 mols.) at 100° and 60% conversion (appreciable quantities of ethers are formed towards the end of the reaction) are: methyl, 0.0056; ethyl, 0.0022; *n*-propyl, 0.0029; *n*-butyl, 0.0039; isopropyl, 0.0004; isobutyl, 0.001; *sec.*-butyl, 0.0017. Water has a marked effect on the velocity (particularly for secondary alcohols), and the change of velocity with changes in concentration of water and temperature has been studied. The temperature coefficients for the reactions are high. The data support the view that the mechanism of the reaction involves the direct addition of the two reactants and subsequent elimination of water.

H. BURTON.

Kinetics of the hydrolysis of certain glucosides. III. β -Methylglucoside, cellobiose, melibiose, and turanose. E. A. MOELWYN-HUGHES (Trans. Faraday Soc., 1929, 25, 503—520).—The critical increments for the acidic hydrolysis of β -methylglucoside, cellobiose, melibiose, and turanose, determined by following the reaction polarimetrically at 60° and 80°, are 33,730, 30,710, 38,590, and 23,450 g.-cal. per mol., respectively. From a survey of the velocity coefficient and critical increment data for seventeen glucosides, it is shown that the relative stability of the disaccharides towards acids is governed, not by the α - or β -nature of the biose linking, but by the position of attachment of the glucosidic monose unit to the second monose unit. Attachment of the oxygen atom of the biose linking at position 4 gives a biose less stable than when the junction involves position 6. The most stable type of disaccharide is that in which attachment of the monoses takes place through position 1.

Calculation of the number of degrees of freedom of the molecule which are associated with the critical increment, according to the method of Hinshelwood (A., 1927, 26), gives values of 45 for hydrolysis of glucosides by acids, 48 for the hydrolysis of galactosides by acids, 52 for the hydrolysis of sucrose by invertase, and 121 for the hydrolysis of starch by amylase.

F. J. WILKINS.

Effect of cohesion of medium on reaction velocity. Velocity of interaction of *N*-chloroacetanilide and hydrobromic acid in aqueous solutions. M. RICHARDSON and F. G. SOPER (J.C.S., 1929, 1873—1884).—The surface tension of a medium is taken as a measure of its cohesion, and it is shown from collected data that, in general, if the products of a reaction are substances of higher cohesion than the reactants, then the reaction is accelerated by solvents of high cohesion, and if the products are substances of lower cohesion than the reactants, the reaction is retarded by such solvents. When products and reactants have like cohesion, the solvent has

relatively little influence on reaction velocity. It is suggested that these results are connected with the influence which the solvent may exert on the critical complex of the two reactants.

The mechanism of the interaction of *N*-chloroacetanilide and hydrobromic acid has been investigated. The products have smaller cohesion than the reactants. The velocity of reaction was studied in various aqueous solutions, the relative cohesions of which are deduced by two independent methods.

The activities of the chloroamine and hydrogen bromide in the media were measured. The activity velocity coefficient was almost constant in sucrose solutions, where the surface tension is nearly the same as in water. In solutions of sodium and potassium nitrates the cohesion was increased and the activity velocity coefficient was decreased. The converse effects were observed in aqueous solutions of methyl and ethyl alcohols. The results agree with the theory.
J. G. A. GRIFFITHS.

Rate of corrosion of magnesium and ultra-light alloys. A. PORTEVIN and E. PRETET.—See B., 1929, 780.

Corrosion phenomena on aluminium sheet. R. WESENBERG.—See B., 1929, 779.

Theory of chemical reactions in concentrated solution of electrolytes. M. BOBELSKY (Z. anorg. Chem., 1929, 182, 93—96).—A discussion of catalysis and the neutral salt effect in the light of recent experimental work (cf. this vol., 1149).

H. F. GILLBE.

Acid and salt effects in catalysed reactions. XXI. Catalytic effects associated with oxalic acid in first and second stages of dissociation. H. M. DAWSON, C. R. HOSKINS, and J. E. SMITH (J.C.S., 1929, 1884—1895).—The catalytic effects of oxalic acid, in the first and second stages of dissociation, on the acetone-iodine reaction are in accord with the general relationships discovered by recent work with monobasic acids. The effective catalysts during the first stage are the hydrogen and hydrogen oxalate ions and the oxalic acid molecule. The respective catalytic constants are 465×10^{-6} , 13×10^{-6} , 210×10^{-6} . The coefficient for the hydrogen oxalate ion is much greater than is expected from results for anions of moderately strong monobasic acids and indicates its tendency to produce hydrogen ions by dissociation.

The action of oxalic acid is similar to that of other acids (cf. Dawson and others, this vol., 36), and it is suggested that the interionic force effect in salt-free solutions of such acids is relatively very small. Results with oxalic acid-potassium hydrogen oxalate solutions indicate an increase of ionisation constant K_1 with salt concentration, and observations with potassium chloride-oxalic acid solutions show that the inert salt effect is similar to that found for other acids (Dawson and Lowson, this vol., 889).

The catalytic action of oxalic acid in the second stage of dissociation has been studied by means of mixtures of normal and acid potassium oxalates. The results are due to the combined effects of the hydrogen, hydrogen oxalate, and oxalate (catalytic constant $= 1.0 \times 10^{-6}$) ions and undissociated oxalic acid.
J. G. A. GRIFFITHS.

Esterification of formic acid in ethyl alcohol solution. H. GOLDSCHMIDT, H. HAALAND, and R. S. MELBYE (Z. physikal. Chem., 1929, 143, 278—286).—A study of the catalysis by hydrogen chloride, picric acid, and trinitro-*m*-cresol of the esterification of formic acid with ethyl alcohol shows the velocity of the reaction to be proportional to the hydrogen-ion concentration; for the autocatalysis of the reaction by the formic acid hydrogen ions the same law is valid, but addition of a formate considerably retards the esterification velocity. Neutral salts at 0.025 to 0.25*N*-concentration cause retardation, but at higher concentrations acceleration is produced.

H. F. GILLBE.

Theory of heterogeneous catalytic reactions. Model of dehydrogenation catalysis. A. A. BALANDIN (J. Russ. Phys. Chem. Soc., 1929, 61, 909—937; cf. this vol., 772, 774).—The action of catalysts is ascribed to attachment of the substrate to groups of multiplets on their surface, the products of reaction being then removed by thermal impulses of the Boltzmann type taking place in the mass of the catalyst. The above conception explains the specificity of action of contact catalysts, the space lattice of which must possess dimensions and a configuration corresponding with those of the substrate. This conception is illustrated by the dehydrogenisation of *cyclohexane* in the presence of platinum catalyst. In this case, each multiplet consists of six atoms of the catalyst (platinum); three atoms adsorb and bind two atoms each of carbon, whilst the remaining three atoms each bind two atoms of hydrogen.

R. TRUSZKOWSKI.

Catalytic activity of carriers of platinum. I. E. ADADUROV and K. I. BRODOVITSCH (Ukraine Chem. J., 1929, 4, 123—127).—The authors have investigated a number of substances used, or entering into the composition of materials used, as platinum carriers in the catalysis of sulphur dioxide to sulphur trioxide as to their own catalytic effect in that reaction. Asbestos, under specified conditions of flow etc. and at 470°, had a catalytic effect of 47%, silica gel precipitated by nickelous chloride had an activity of 67%, the substance precipitated by ferrous chloride 64% at about 450°, whilst refractory material itself had an activity of 73%. When moistened with a mixture of 3 vols. of aluminium sulphate and 1 vol. of chromium sulphate it had at 454—470° an activity of between 91.4% and 100%.
A. FREIMAN.

Dissociating action of catalyst carriers. I. E. ADADUROV and K. I. BRODOVITSCH (Ukraine Chem. J., 1929, 4, 129—141).—Some of the substances investigated as catalyst carriers in the reaction $\text{SO}_2 \rightarrow \text{SO}_3$ had no dissociating effect, e.g., silica gel precipitated by nickelous chloride; others had only a very slight effect (0.06—0.22%), e.g., porcelain, glass spheres, aluminium oxide, etc., whilst some had a quite appreciable effect, e.g., magnesium oxide 0.67%, silica gel precipitated by ferrous chloride 4—3%, refractory material moistened by a mixture of 3 vols. of chromium sulphate and 1 vol. of aluminium sulphate 7—1.5%. It is concluded that there exists no direct or inverse proportionality between the catalytic activity of a material and its dissociating activity,

that a rise in temperature does not necessarily cause an increase in dissociation, and that for each substance there exists a separate maximum of its catalytic and dissociating activity in a given reaction. The catalytic and dissociating activities of the substances are attributed to light radiation emitted by the substance, and by applying Brodsky's equation (A., 1927, 705) giving the relation between the intensity of a spectral line and temperature, an attempt is made to explain the differing behaviour of the various substances.

A. FREIDMAN.

Catalytic dissolution of copper in sulphuric acid. J. B. EVTUSHENKO (J. Chem. Ind. Moscow, 1929, 6, 429—430).—The dissolution of copper in sulphuric acid is accelerated by the addition of a catalyst consisting of 1 part of chromic sulphate and 0.5 part of nitric acid per 100 parts of sulphuric acid. The product contains only a trace of chromium.

CHEMICAL ABSTRACTS.

Relative activation of a nitrogen-hydrogen mixture by electrons and by K^+ ions in the formation of ammonia. C. H. KUNSMAN (Physical Rev., 1928, [ii], 31, 307).—Without an applied *P.D.*, the iron-potassium catalyst used as the source of K^+ ions is much more active in synthesising ammonia from the nitrogen-hydrogen (1:3) mixture at pressures less than 1 mm. than is the tungsten filament used as the electron source. At electron speeds greater than 17 volts, however, a large increase is observed with tungsten whilst the rate with the K^+ ions remains unchanged up to 330 volts. L. S. THEOBALD.

Action of iron catalysts on mixtures of carbon monoxide and hydrogen. E. AUDIBERT and A. RAINEAU.—See B., 1929, 840.

Activation of halogens and carbon monoxide. N. C. JONES (J. Physical Chem., 1929, 33, 1415—1427).—The activation of chlorine, bromine, and carbon monoxide by charcoal and by hopcalite has been investigated. Chlorine and bromine, but not carbon monoxide, hydrogen, or oxygen, are activated by charcoal. Hydrobromic acid is formed when hydrogen containing bromine is passed over charcoal, the conversion of bromine into the acid being 13.2% at 100°, 49.1% at 150°, and 99.3% at 200°. In the synthesis of carbonyl chloride over charcoal, chlorine but not carbon monoxide is activated, since neither formaldehyde nor methyl alcohol could be synthesised from carbon monoxide and hydrogen, nor could carbon dioxide be formed from the monoxide and oxygen by passage over activated charcoal. Hopcalite activates oxygen, but not carbon monoxide or hydrogen, to such an extent that benzene vapour is completely oxidised at 78°. Carbon monoxide is shown to be a more powerful reducing agent than hydrogen, and is considered to be essentially electropositive in nature, since it reacts more readily with oxygen and chlorine than it does with hydrogen even when all three gases are activated. The above results support the theory of Fischer and Tropsch (B., 1926, 475) on the mechanism of the hydrogenation of carbon monoxide.

L. S. THEOBALD.

Platinised silica gels as catalysts for oxidation of sulphur dioxide. H. N. HOLMES, J. RAMSAY, and A. L. ELDER.—See B., 1929, 849.

Poisoning of the hydrogen electrode. A. H. W. ATEN and M. ZIEREN (Rec. trav. chim., 1929, 48, 944—948).—The effect of traces of arsonic trioxide on the potential of a platinum-black electrode (measured against a standard hydrogen electrode) immersed in various media and in contact with differing mixtures of hydrogen and oxygen has been determined. In 0.1N-sulphuric acid solution the potential of the platinum electrode is negligible until the gas mixture contains approximately 50 equiv.-% of oxygen. Then the potential suddenly increases to about 0.7 volt, after which with increasing oxygen the potential gradually rises to about 1.0 volt. The addition of small amounts of arsonic trioxide (up to 0.066%) causes the sudden increase in potential to occur at lower oxygen concentrations, but the maximum finally attained in pure oxygen is lower by about 0.3 volt. The results in 0.1N-sodium hydroxide solution are similar with the exception that the maximum potential finally attained is unaltered. The shift of the vertical portion of the potential-oxygen concentration curve is attributed to a retardation of the reaction $H_2 \rightarrow 2H$, and the lowering of the final potential to an inhibition of the reaction between atomic hydrogen and oxygen. It is suggested that the retardation of the reaction $H_2 \rightarrow 2H$ is due to the increase in the diffusion velocity of the electrolytic hydrogen into the electrode in the presence of the poison. These views are supported by the fact that addition of arsonic trioxide or mercuric chloride promotes the diffusion of electrolytic hydrogen in a thin polarised electrode of iron. F. G. TRYHORN.

Removal of gold from cathode metals in the glow discharge. T. ASADA and K. QUASEBARTH (Z. physikal. Chem., 1929, 143, 435—455; cf. Haber, Jaenicke, and Matthias, A., 1926, 699).—When a copper plate containing a small proportion (1 in 10^6 to 10^7) of gold is used as cathode in a glow discharge the metal is gradually deprived of gold. It is shown that the effect is not due to thermal evaporation, but that it depends on the disintegration of the cathode surface under bombardment by positive ions, the gold being sprayed away far more rapidly than the copper. The disintegration is about 25 times more rapid, and the loss of gold relatively greater, in mercury vapour than in air. When the surface of the cathode has been deprived of gold the resulting diffusion gradient becomes operative, and in the course of time the whole of the gold is brought to the active surface and there dissipated. From the initial and final gold content, assuming that the concentration of gold at the surface is constant and zero, the coefficient of diffusion of gold in copper is shown to be of the order 10^{-6} cm.²/day, at an estimated temperature of 200°. F. L. USHER.

Influence of the silent electric discharge on hydrogen sulphide. R. SCHWARZ and W. KUNZER (Z. anorg. Chem., 1929, 183, 287—295).—An apparatus in which the behaviour of hydrogen sulphide under the silent electrical discharge may be studied at different temperatures and compared with the simple thermal effect is described. With rise in temperature the amount of decomposition by the discharge diminishes, and above the b. p. of sulphur re-formation of the hydrogen sulphide from the products of thermal

decomposition takes place. This is ascribed to the activation of gaseous sulphur by the discharge as observed by Schwarz and Schenk (this vol., 1151).

M. S. BURR.

Electrolytic deposition of chromium from aqueous solutions of chromic acid. J. ROUDNICK (Bull. Soc. chim. Belg., 1929, 38, 276—294).—Oxidation and reduction during electrolysis of 20% chromic acid solutions containing 1% of sulphuric acid have been investigated, confirming the equation: Reduction %—oxidation % = yield ($\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{metal}}$) + yield ($\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{III}}$). The influence of the nature of the electrodes and of the concentration of chromic acid has been studied.

C. W. GIBBY.

Combination of alkali metals and nitrogen under the influence of electrical discharges. W. MOLDENHAUER [with H. MOTTIG] (Ber., 1929, 62, [B], 1954—1959).—Nitrogen, activated by exposure to the dark electric discharge, unites with the alkali metals with production of azides. In the cases of caesium, rubidium, and potassium, the products of the action contain small amounts of nitrides which result secondarily from the azides. Sodium does not appear to yield any nitride. With lithium, azide formation is not observed and nitride production to only a slight extent.

H. WREN.

Fibrous structure in metals deposited through difference in electrolytic solution pressures. II. S. TSUBOI (Mem. Coll. Sci. Kyoto, 1929, A, 12, 209—215; cf. A., 1928, 1175).—When lead is deposited by zinc from 2% and 5% solutions of lead acetate, dendritic crystals are obtained, of which the (111) planes are generally nearly parallel to the flat surface of the deposit. In the spongy deposit of cadmium similarly obtained from 1% and 3% solutions of cadmium sulphate, the (0001) plane of the hexagonal crystal is nearly parallel to the surface.

C. W. GIBBY.

Chemical action of electric discharge. I. Effect of nature of electrodes on production of nitric oxide in electric arc. E. BRINER and A. RIVIER (Helv. Chim. Acta, 1929, 12, 881—893).—In synthesising nitric oxide by the arc process, coating the electrodes with oxides of the alkaline-earth metals, particularly barium oxide, depresses the *P.D.* of the arc and at the same time increases the efficiency very considerably. The alkali silicates have a similar but much less marked effect. Beryllium, magnesium, zinc, and aluminium oxides are practically indifferent, and ferric oxide reduces the yield. Zirconium oxide slightly increases the *P.D.* and decreases the yield, whereas thorium oxide has the reverse effect. The rare-earth oxides distinctly reduce the *P.D.*, but have only a slight and variable effect on the yield. In general the results show that the effect of the various compounds on the yield runs parallel with their thermionic emissive power, suggesting that the activation of the reacting molecules is effected by electrons. In a particular group of oxides, the property of increasing the yield becomes more marked with increase in the atomic number of the metal.

R. CUTHILL.

Anodic relationships of aluminium. A. GUNTHER-SCHULZE (Z. physikal. Chem., 1929, 143, 62—

68).—The theory of Muller and Konopicky (this vol., 770) is regarded as untenable owing to errors in the experimental work.

H. F. GILLBE.

Oxidation of salts of monobasic fatty acids with potassium percarbonate and potassium persulphate. F. FICHTER and H. LAPIN (Helv. Chim. Acta, 1929, 12, 993—1002).—The mechanism of the action of inorganic salts in the electrolytic synthesis of alcohols by Hofer and Moest's method (A., 1902, i, 736) has been investigated. The action of carbonates is to be ascribed primarily, it would appear, to their alkaline reaction, although there may also be formation of percarbonates. Perchlorates certainly do not depend for their effect on the formation of ozone, for ozone does not produce methyl alcohol from acetates. Sulphates possibly owe their activity to the formation of persulphate, for potassium persulphate produces methyl alcohol from mixtures of acetate and carbonate, ethyl alcohol and ethylene from mixtures of propionate and carbonate, propylene from mixtures of butyrate and carbonate, and isobutylene and isobutyl isovalerate from mixtures of isovalerate and carbonate.

R. CUTHILL.

Peroxide theory of Kolbe's electrosynthesis. F. FICHTER (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 8 pp.).—Recent work on the oxidation of fatty acids by the action of fluorine or persulphates or by anodic treatment is reviewed and discussed, with special reference to evidence for the intermediate formation of per-acids (cf. preceding abstract).

H. J. T. ELLINGHAM.

Cathodic halogen: electrolysis of *N*-halogenoamides. H. R. L. STREIGHT and E. G. HALLONQUIST (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 9 pp.).—Solutions of a number of *N*-halogenated amides and imides in ethyl alcohol, nitromethane, acetonitrile, and pyridine have been electrolysed between silver electrodes. From pyridine solutions a deposit containing the halogen was always obtained at the cathode and the free halogen was detected in the catholyte in many cases, but with *N*-iodopropionamide and *N*-iodo-*n*-butyramide (m. p. 97°) anode deposits containing halogen were also obtained on prolonged electrolysis. From acetonitrile solutions several of the compounds give halogen at both electrodes, but from ethyl alcohol or nitromethane solutions the halogen is liberated only at the anode. Cathodic chlorine was obtained for the first time by electrolysis of pyridine solutions of *N*-chlorosuccinimide, *N*-dichlorocarbamide, and *N*-chlorophthalimide. It is concluded that the *N*-halogenoamides behave as electromerides, the halogen being negative in most solvents but entirely positive in pyridine (cf. A., 1928, 1197; this vol., 407).

H. J. T. ELLINGHAM.

Electrochemical preparation of phenylhydrazine. R. E. MCCLURE [with A. LOWY] (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 11 pp.).—The influence of various factors on the current efficiency of production of phenylhydrazine by the electrolytic reduction of aqueous solutions of certain benzenediazonium compounds has been studied. With benzenediazonium chloride the best current efficiency (36.5%) was obtained by electro-

lysis at 0–8° with 5.12 amp./dm.² at a mercury cathode and maintaining an excess of free hydrochloric acid in the solution. The current efficiency could not be increased by raising the temperature, since this caused decomposition of the diazonium salt. With potassium isodiazobenzenesulphonate, however, much higher temperatures could be used and the best current efficiency (47.6%) was obtained at 90–95° with 1.9 amp./dm.² at a mercury cathode, the solution containing acetic acid and sodium acetate during electrolysis, and afterwards being treated with hydrochloric acid and boiled. Some chemical reduction also occurred. It is observed that mercuric phenyl chloride is produced by stirring finely divided mercury with benzenediazonium chloride solution.

H. J. T. ELLINGHAM.

Chemical action of light. M. BODENSTEIN (Naturwiss., 1929, 17, 788–795).—A lecture.

A. J. MEE.

Action of ultra-violet radiation on inorganic compounds. II. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 708–709).—In the manner previously described (this vol., 1152) the action of ultra-violet radiation on thirty different salts has been examined qualitatively.

C. A. SILBERRAD.

Photosensitised decomposition of ozone. A. J. ALLMAND and J. W. T. SPINKS (Nature, 1929, 124, 651).—The transmission for the mercury line 3650 Å. of a mixture of ozone and chlorine containing a low concentration of chlorine increases appreciably during the early stages of the reaction. When gases dried with sulphuric acid are used a distinct mist is formed on insolation. Further, if chlorine dioxide, dried with phosphorus pentoxide, is mixed with dry ozone, a red liquid is produced; on admission of moist air a mist is formed and the liquid is hydrolysed with formation of chloric and perchloric acids. These observations suggest that the following processes take place: (1) production of chlorine atoms by light, (2) formation of ClO₃ groups by union of chlorine atoms and ozone molecules, (3) a short chain reaction, probably terminated by adsorption of intermediate atoms or groups on the walls, (4) union of some ClO₃ groups to form chlorine hexoxide, immediately hydrated in presence of water to chloric and perchloric acids, (5) formation from chlorine atoms and oxygen molecules of ClO₂ molecules, these reacting with ozone molecules to give ClO₃ groups and oxygen molecules.

A. A. ELDRIDGE.

Photochemical decomposition of iron pentacarbonyl. G. EYBER (Z. physikal. Chem., 1929, 144, 1–21; cf. Dewar and Jones, A., 1907, ii, 266).—Attempts to follow the course of the photochemical decomposition of iron pentacarbonyl dissolved in *n*-hexane proved unsatisfactory owing to the formation of by-products and to obstruction of the incident light by solid deposited on the walls of the vessel. The reaction has therefore been studied in the vapour phase at the ordinary temperature. The change is represented by the equation $2\text{Fe}(\text{CO})_5 = \text{Fe}_2(\text{CO})_9 + \text{CO}$, and the quantum yield at 20° for light of wave-length 400 μ is 2 mols. of pentacarbonyl. The velocity is directly proportional to the concentration of the vapour and to the light intensity. The reaction is

inhibited by admixture of hydrogen, and much less by carbon monoxide, carbon dioxide, nitrogen, or argon, and in such cases the velocity is equal to $k_1 I / (1 + k_2 [G] / k_3 [C])$, where *G* and *C* represent the foreign gas and the pentacarbonyl vapour, respectively, *I* is the light intensity absorbed per sec., and *k*₂ and *k*₃ are the respective velocity coefficients of reactions (2) and (3) in the following scheme: (1) $\text{Fe}(\text{CO})_5 + E = \text{Fe}(\text{CO})_5^*$; (2) $\text{Fe}(\text{CO})_5^* + \text{Fe}(\text{CO})_5 = \text{Fe}_2(\text{CO})_9 + \text{CO}$; (3) $\text{Fe}(\text{CO})_5^* + G = \text{Fe}(\text{CO})_5 + G^*$. In the presence of oxygen a different reaction occurs and ferric oxide is formed, and traces of air or of moisture give rise to a period of induction. The vapour pressures of the pentacarbonyl between –14° and +20° have also been determined and found to differ considerably from those given by Dewar and Jones.

F. L. USHER.

Photodichroism and photoanisotropy. IV. Colour selectivity of photochloride. F. WEIGERT and E. ELVEGARD (Z. physikal. Chem., 1929, B, 4, 239–257; cf. this vol., 871, 894).—The phenomenon of colour selectivity in the photochloride layer was investigated, using more accurate apparatus than had been used previously. The primary photodichroism was investigated with excitation with monochromatic light. Christiansen's universal filter was used, the incident light being purified by an ordinary monochromator. The existence of a selective effect of the dichroism in the excited layer varying with the wavelength of the light used was shown with certainty. The curves obtained for long wave-length light were quite different from those obtained with short wave-length light, whilst between the two ranges is an indifferent region in which the layer shows only very weak dichroism. This opposite action of short and long wave-length light is discussed from the point of view of micelle deformation.

A. J. MEE.

Photodichroism and photoanisotropy. V. Colour selectivity in dye systems. F. WEIGERT and M. NAKASHIMA (Z. physikal. Chem., 1929, B, 4, 258–276; cf. this vol., 871, 894).—By means of the method already described (cf. preceding abstract) different light-sensitive colour layers were investigated. The form of the dichroism curve for these systems shows that polarised light can effect two different actions. For weak excitation there is a very sharp colour selectivity. The special form of the extinction curve for any particular colouring matter does not influence the dichroism. For strong excitation this no longer holds. The extinction curve of the colouring matter is, in this case, important. For strong excitation, the spectral distribution of the optical changes is dependent on the form of the absorption spectrum of the colouring matter and independent of the colour of the exciting radiation. It must be concluded that in light-sensitive colouring matters, two quite different phenomena occur by the action of light; they can be separated from each other by the method of dichroism. The relationship between the new effects and previously known photochemical properties of colouring matters is discussed.

A. J. MEE.

Effect of X-rays on crystalline and dissolved sucrose. M. C. REINHARD and K. L. TUCKER (Radiol., 1929, 12, 151–153).—Sucrose crystals are

coloured reddish-brown by exposure to X-rays, measurable amounts of invert-sugar being formed. The amount of invert sugar formed by exposure of sucrose solutions to X-rays is, for a given quality of radiation, proportional to the time of exposure, but not to the concentration of sucrose.

CHEMICAL ABSTRACTS.

Uranyl oxalate method of daylight photometry and its photo-electric standardisation. W. R. G. ATKINS and H. H. POOLE (Sci. Proc. Roy. Dublin Soc., 1929, 19, 321—337).—The photo-sensitivity of uranyl oxalate solution has been used to study the intensity of daylight illumination along the coast and at sea. 10 C.c. samples of a solution containing 6.3 g. of crystalline oxalic acid and 4.27 g. of uranyl sulphate diluted to 1 litre were placed in quartz tubes 13 cm. long and 1.3 cm. in diameter. During the exposure the tubes were arranged either to swing about a mean vertical position or to rest slightly inclined from the horizontal in order to allow the gas to escape. The extent of the decomposition was determined by titration with 0.1N-permanganate solution, using 10 c.c. of the mixture, 10 c.c. of sulphuric acid (1 : 3), and 100 c.c. of boiling water. By deducing the mean illumination acting on the tubes from readings of a photometer containing a potassium vacuum cell, the rate of decomposition was found to be 0.225 c.c. of 0.1N-acid for an illumination of 1000 metre-candles. A comparison between glass and quartz tubes showed that the former required 1.14 times as long an exposure as quartz to produce equal amounts of decomposition. Figures are given for the mean horizontal and vertical illumination values at sea.

H. J. DOWDEN.

Antioxygenic action of cholesterol and ergosterol. IX. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 709—710).—The anti-oxygenic effect (Moureu's method) of the addition of 1% of ordinary and irradiated cholesterol and ergosterol to benzaldehyde, furfuraldehyde, and turpentine is shown to be practically the same and very slight in all cases. This is held to support the view that irradiation affects an impurity only in ergosterol. C. A. SILBERRAD.

Effect of X-rays on cholesterol. A. BACHEM and R. P. MACFATE (Strahlentherapie, 1927, 25, 476—478; Chem. Zentr., 1929, i, 1789).—If dissolved in chloroform or carbon tetrachloride, but not if dissolved in benzene, toluene, alcohol, acetone, butyl ether, or carbon disulphide, cholesterol is decomposed when exposed to X-radiation. Chloroform and carbon tetrachloride are themselves decomposed by X-rays. A. A. ELDRIDGE.

Action of high-speed cathode rays on acetylene. J. C. McLENNAN, M. W. PERRIN, and H. J. C. IRETON (Proc. Roy. Soc., 1929, A, 125, 246—262).—By means of an apparatus similar to that described by Coolidge (A., 1926, 989), the kinetics of the reaction taking place when acetylene is bombarded with high-speed electrons have been investigated in detail. During each experiment the voltage applied to the cathode-ray tube and the current through it were kept constant, and the pressure was read at different times. No change in pressure occurred during the bombardment until the voltage across the tube exceeded

85 kilovolts, when a slight mist formed throughout the reaction cell and a pale yellow amorphous solid (d_4^{20} 0.97, n_D^{20} 1.625) was deposited on the walls. This reaction was accompanied by a decrease in pressure. The product had no measurable vapour pressure and on bombarding it there was no increase of pressure. No X-ray spectrum could be obtained from it. The reaction is apparently unimolecular, the rate of change of pressure being proportional to the pressure for any given voltage, and the velocity coefficient increases directly as the voltage. A direct measure of the electron current outside the cathode-ray tube was made by collecting the electrons passing through the window in a Faraday cylinder placed close to the window and measuring the current with a microammeter. It is found by calculation that the number of molecules of acetylene reacting is of the same order as the number of ions formed by each electron passing through the window, and the observed facts are explained on the hypothesis that the reaction takes place between molecules of which some have been ionised by the cathode rays. L. L. BIRCHSHAW.

Salt-like compounds of sodium and their change into intermetallic phases. E. ZINTL (Naturwiss., 1929, 17, 782—783).—Compounds of sodium with a number of metallic and non-metallic elements were prepared and their decomposition was investigated. For following the changes quantitatively an electrometric titration method was used. All elements of the long periods of the periodic system occupying places 1—4 away from a rare gas, and forming liquid hydrides, will combine in liquid ammonia with sodium to give polysulphide-like compounds which have the characteristics of salts, and to which the name "polyanionic" salts is given. By treating sodium with lead iodide compounds of the type Na_4Pb_7 and Na_4Pb_9 can be obtained. Their constitution is probably of the form $\text{Na}^+[\text{Pb}^{4-}(\text{Pb})_3]$. These polyanionic salts are soluble in ammonia, the solutions being deeply coloured and capable of being electrolysed, the sodium going to the cathode, and other metals to the anode. Elements which occupy positions in the periodic table more than four places away from a rare gas will not form these polyanionic salts, but form instead typical intermetallic phases of another structural type, insoluble in liquid ammonia. Polyanionic salts may also be obtained by extracting alloys of the elements concerned with liquid ammonia. The solution contains negatively-charged sub-microns. The salts crystallise from ammonia in the form $[\text{Na}(\text{NH}_3)_y]_x^+[\text{X}^{n-}(\text{X})_z]$. X-Ray experiments show that $\text{Na}_4\text{Pb}_7, y\text{NH}_3$ and $\text{Na}_4\text{Pb}_9, y\text{NH}_3$ cannot exist in the polyanionic state in the ammonia-free form. The latter changes into an intermetallic phase with a cubic structure and four atoms in the elementary cell, of which the homogeneity range extends from 28% to 35% of sodium; it contains no chemical compound. The substance $\text{Na}_4\text{Pb}_7, y\text{NH}_3$ decomposes into two intermetallic phases. The introduction of a little sodium into the lead lattice causes a contraction, whereas an expansion would be expected; the contraction is due to the distorted symmetry of the charge distribution between neighbouring particles. A. J. MEE.

Double carbonates of alkalis and alkaline earths. W. EITEL and W. SKALIJS (*Z. anorg. Chem.*, 1929, **183**, 263—286).—By heating together the simple carbonates in a bomb, in which it was possible to obtain a pressure of 1200—1300 atm. at 800—900°, the following double carbonates have been prepared: $\text{Na}_2\text{Ca}(\text{CO}_3)_2$, m. p. 812°; $\text{K}_2\text{Ca}(\text{CO}_3)_2$, m. p. 813°; $\text{Na}_2\text{Mg}(\text{CO}_3)_2$, m. p. 677° ($p=1240$ kg./cm.²); $\text{K}_2\text{Mg}(\text{CO}_3)_2$; NaLiCO_3 , m. p. 514°; KLiCO_3 , m. p. 515°. When calcium and lithium carbonates are heated together in equimolecular proportions an eutectic mixture only is obtained. The magnesium salts had not previously been produced in the dry way, because of the high dissociation pressure of magnesium carbonate. The sodium lithium carbonate had not been prepared before. All the compounds are optically negative and belong to the hexagonal or trigonal crystal system. The potassium magnesium carbonate can be super-cooled and obtained in the vitreous form at the ordinary temperature, suggesting a relationship between carbon and silicon such as might be expected from their neighbouring positions in the periodic table. The refractive indices and specific volumes of the compounds are not additive. The following heats of formation from the simple carbonates are given: NaLiCO_3 , +0.54 kg.-cal. per mol.; $\text{Na}_2\text{Ca}(\text{CO}_3)_2$, -2.07 kg.-cal. per mol.; $\text{K}_2\text{Ca}(\text{CO}_3)_2$, +0.72 kg.-cal. per mol. The lattice structure of the sodium compounds and of the potassium calcium carbonate has been examined. Substitution of potassium for sodium in the calcium compound has a marked morphotropic effect in the direction to be expected from the respective ionic dimensions. M. S. BURR.

Preparation of pure cupric sulphide. K. FISCHBECK and O. DÖRNER (*Z. anorg. Chem.*, 1929, **182**, 228—234).—Pure cupric sulphide has been prepared by heating under pressure finely-divided copper, obtained by the reduction of copper oxalate with hydrogen at 220—260°, and sulphur precipitated from solution in carbon disulphide by means of light petroleum. The copper was covered with carbon disulphide, and then carbon disulphide containing sulphur in excess of that required to form the lower sulphide was added gradually with constant stirring. After transference to the bomb-tube, double the quantity of sulphur required to form the higher sulphide was added, and the tube was filled with carbon disulphide and heated, with rotation, in a current of steam for 4 hrs. The excess of carbon disulphide was removed and the product dried at 90—100° at a pressure of 0.1—1 mm. The dark blue cupric sulphide is soluble in potassium cyanide and is a good electrical conductor. The formation of a higher sulphide by this method is improbable. L. S. THEOBALD.

New antipyrine co-ordination compounds of metal perchlorates. E. WILKE-DORFUR and O. SCHLIEPHAKE (*Z. anorg. Chem.*, 1929, **183**, 301—310; cf. A., 1928, 494).—The general method of preparation of the antipyrine compounds of the metal perchlorates is to mix together, at the ordinary temperature, the corresponding metal salt solution, chloride, nitrate, or sulphate, and solutions of

antipyrine and pure ammonium perchlorate. In this way hexa-antipyrine perchlorates of magnesium, calcium, strontium, zinc, cadmium, lead, manganese, iron, cobalt, and nickel, of the general formula $[\text{M}(\text{COC}_{10}\text{H}_{12}\text{N}_2)_6](\text{ClO}_4)_2$, have been obtained. The barium salt can be obtained only by the use of barium perchlorate itself. Hexa-antipyrine perchlorates of aluminium, iron, and chromium, general formula $[\text{M}(\text{COC}_{10}\text{H}_{12}\text{N}_2)_6](\text{ClO}_4)_3$, and of quadrivalent thorium, as well as penta-antipyrine perchlorates of copper and uranyl, and silver tri-antipyrine perchlorate, have also been prepared. Solubilities, m. p., and densities are recorded in all cases, as well as the densities of the compounds previously obtained (*loc. cit.*). In every case the thermal stability of the perchlorate is increased by the introduction of antipyrine into the molecule. M. S. BURR.

Displacement of cadmium from its solutions by aluminium. P. G. POROV (*Ukraine Chem. J.*, 1929, **4**, 281—284).—Aluminium displaces cadmium from solutions of cadmium sulphate or nitrate also in the absence of cobalt or chromium nitrate, contrary to the observations of Goldschmidt (A., 1906, ii, 581). The solution requires, however, prolonged heating and the aluminium should preferably be in the form of a powder or dust. The reaction also proceeds with aluminium powder in presence of sodium or potassium hydroxide. A. FREIMAN.

Action of gaseous ammonia on mercuric bromide and mercuric chloride. M. FRANÇOIS (*Bull. Soc. chim.*, 1929, [iv], **45**, 616—621).—Contrary to statements by earlier experimenters, mercuric chloride and mercuric bromide combine with dry gaseous ammonia to give the compounds $\text{HgCl}_2 \cdot 2\text{NH}_3$ and $\text{HgBr}_2 \cdot 2\text{NH}_3$, respectively, and therefore behave similarly to mercuric iodide. The above two compounds appear to be additive compounds. They are fairly stable and do not lose ammonia appreciably at the ordinary temperature. O. J. WALKER.

Boron. I. Reaction of boron trifluoride with ammonia and alkylamines. C. A. KRAUS and E. H. BROWN (*J. Amer. Chem. Soc.*, 1929, **51**, 2690—2696).—Monoamminoboron trifluoride, $\text{BF}_3 \cdot \text{NH}_3$, is very conveniently prepared by saturating an ethereal solution of boron trifluoride with ammonia in the cold. It is a true compound and forms a white solid which fuses and sublimes in a vacuum at about 180° and is soluble in liquid ammonia, ethylamine, diethylamine, and triethylamine containing excess of ammonia, ammonolysis occurring in the first two liquids. Alkyl derivatives of the monoammino-compound may be prepared as white solids by treating a cooled ether solution of boron trifluoride with the corresponding alkylamine. Triethylaminoboron trifluoride, $\text{NEt}_3 \cdot \text{BF}_3$, m. p. 29.5°, becomes brown on keeping, is soluble in benzene and ether but insoluble in water. Diethylaminoboron trifluoride, $\text{NHEt}_2 \cdot \text{BF}_3$, m. p. 150—160°, is insoluble in benzene and ether but soluble in water. Ethylaminoboron trifluoride, $\text{NH}_2\text{Et} \cdot \text{BF}_3$, m. p. 89°, decomposes in air above its m. p., and is soluble in benzene and slightly soluble in ether. Other methods of preparing these compounds are given. S. K. TWEEDY.

Ultramarine. J. HOFFMANN (Z. anorg. Chem., 1929, 183, 37—76).—Methods of formation of ultramarine, and the reasons for the production of the colour and its variations, have been studied. The blue colour of boron ultramarines is primarily due to the presence of sulphur and is independent of the presence of water, but physical factors are at least as important as chemical. The colour is partly dependent on the nature of the alkali metal, and its production depends on a change of the borate beginning at the stage $R_2B_6O_{10} \rightarrow R_2B_{10}O_{16}$. Replacement by boron trisulphide of part of the boron trioxide which is in excess of that required for the presence of alkali tetraborate yields orange-red to brown substances, the blue colour appearing only when a sulphide of the alkali metal is present; thiosulphate is not necessarily present in the blue substances, but may be formed as an intermediate substance in certain types of ultramarine. The chemical and physical action of the sulphur is discussed. Since ultramarine is formed much more slowly when sulphur is heated with anhydrous borax than with alkali sulphide or polysulphide, the latter is probably formed as an intermediate. Conditions necessary for the formation of ultramarine are discussed, with particular reference to the part played by auxiliary valencies and the structure of the compounds formed. All the blue polysulphide ultramarines contain a structure analogous to diborates bridged by alkali monosulphide to the boric acid part of a higher borate which may range from tri- to octa-borate. The old idea that ultramarine synthesis depends on solubility phenomena is disproved. Ultramarines may be classified under five types: inorganic, including the ordinary ultramarines; organic, including a variety of organic dyes containing sulphur; inorganic-organic, including certain hydrocarbon ultramarines and compounds such as ethyl and butyl alumina ultramarine; temporary inorganic, such as phosphate and certain borate varieties; temporary organic, such as cyano-ultramarine. The formation in nature of the mineral ultramarines is discussed. H. F. GILLBE.

Behaviour of alkali fluoborates in tungsten-filament lamps. J. H. DE BOER (Rec. trav. chim., 1929, 48, 979—983).—Alkali fluoborates introduced into electric lamp bulbs can react with tungsten spattered from the filament during burning. In the case of the potassium salt a tungsten compound with a W : F atomic ratio of 1 : 3 is formed. The intensity of blackening of the bulb wall with the introduction of other alkali fluoborates shows that the amount of reaction is in the decreasing order caesium, rubidium, potassium. This is confirmed by the amount of tungsten extracted in these cases by sodium hydroxide and by hydrofluoric acid. Reaction is negligible with sodium fluoborate owing to the decomposition of this salt at temperatures above 320° during the evacuation of the lamp. F. G. TRYHORN.

Attack of aluminium by ammoniacal solutions. J. CALVET (Compt. rend., 1929, 189, 485—486).—The action of ammonia solutions of different concentrations on aluminium of different degrees of purity has been investigated. Very pure aluminium (99.96%) is attacked just as readily as less pure

specimens: Dilute solutions attack the metal to a greater extent than concentrated ones.

C. W. GIBBY.

Complex scandium oxalato-compounds. J. STERBA-BOHM and J. SKRAMOVSKY (Časopis Českoslov. Lek., 1928, 8, 211—215; Chem. Zentr., 1929, i, 2399).—Scandium oxalate crystallises $+6H_2O$. The compounds $HSc(C_2O_4)_2$, $H_4Sc_2(C_2O_4)_5$, and $H_3Sc(C_2O_4)_3$ have been prepared, and their relative stability has been observed.

A. A. ELDRIDGE.

Oxidisability of silicon as a function of its state of division. A. SANFOURCHE (Compt. rend., 1929, 189, 533—535).—A reply to Bedel's criticism (cf. this vol., 997, 1030). The author's experiments on pyrophoric silicon may be reproduced if the silicon is in a sufficiently fine state of division, e.g., if it is obtained from the aluminium-silicon alloy "alpax." The presence of impurities exerts only a secondary influence. J. GRANT.

Hydrates and hydrogels. XII. Mono- and di-silicic acids. R. WILLSTATTER, H. KRAUT, and K. LOBINGER (Ber., 1929, 62, [B], 2027—2034; cf. A., 1926, 36; this vol., 39).—By shortening the time of action and exercising greater precautions with regard to the optimal acidity (0.002N—0.001N) of the solution, it has been found possible to prepare monosilicic acid ($M=62$; calc. for SiO_2 , $M=60$) in greater purity. The stability of the acid and the subsequent members of the series depends greatly on the acidity of the solution. The mono- and di-acids are most stable in feebly acid solution and condense most rapidly in nearly neutral or incipiently alkaline solution. The variability of condensation with acidity causes silicic acids of mean mol. wt. 200—300 to vary irregularly in their properties, as shown by their behaviour towards egg-albumin. The gradual condensation of monosilicic acid in solutions of differing p_H is illustrated by a series of time-mol. wt. graphs, the most remarkable feature of which is the indication of the existence of a structural change in disilicic acid during the process without alteration of mol. wt. The condensation of silicic acid is delayed by addition of small amounts of ethylene glycol, glycerol, and other polyhydric alcohols, whereas ethyl alcohol is inactive.

The volatility of silicic acid during distillation of its solutions has been re-investigated, using monosilicic acid and the apparatus of Kraut, Lobinger, and Pollitzer (this vol., 1261). It has not been found possible to increase the mere trace of acid volatilised or to conduct the distillation without such volatilisation. Under the same conditions, distillation of a 0.4% solution of boric acid from 400 to 70 c.c. at 11° gave no trace of boric acid in the distillate.

H. WREN.

Action of the alkali carbonates on lead bromide, iodide, and nitrate in aqueous solutions. (MME.) N. DEMASSIEUX (Compt. rend., 1929, 189, 428—430).—These reactions have been followed by chemical analysis of the precipitates and by conductivity measurements. The bromide and iodide behave analogously to lead chloride (this vol., 1154), whilst the nitrate gives only lead carbonate.

J. GRANT.

Action of the alkali oxalates on the halogen salts of lead in aqueous solution. (MME.) N. DEMASSIEUX (Compt. rend., 1929, 189, 535—536).—Further experiments (cf. preceding abstract) have shown that analogous results are obtained by the use of the alkali oxalates. A lead chloro- or bromo-oxalate is first produced which is subsequently transformed by an excess of reagent into lead oxalate (cf. following abstract). J. GRANT.

X-Ray study of some halogen salts. MATHIEU (Compt. rend., 1929, 189, 536—537; cf. preceding abstract).—X-Ray measurements of the dimensions of the lattice confirm the conclusion that the salts obtained by Demassieux contain the PbCl or PbBr ion. In general, isomeric similarity between salts is much closer when the substituted element enters a complex group than when it plays an ionic role. J. GRANT.

Union of nitrogen and sulphur under the influence of electrical discharges. W. MOLDENHAUER [with A. ZIMMERMANN] (Ber., 1929, 62, [B], 2390—2392).—Under the influence of the dark electrical discharge, pure nitrogen at 10—1 mm. readily combines with sulphur at 80—100°, yielding a dark-coloured product from which extraction with ether and carbon disulphide yields nitrogen pentasulphide and nitrogen tetrasulphide. The residue left after treatment with these solvents is heated at 90—93°/vac. and then exhaustively treated with the same media, whereby the bluish-black *nitrogen disulphide*, (NS₂)_x, is isolated. The compound decomposes above 100° into nitrogen pentasulphide and tetrasulphide. It is decomposed by alkali hydroxide with evolution of ammonia and by concentrated hydrochloric acid into ammonium chloride and sulphur. H. WREN.

Constitution of nitrogen sulphide, N₄S₄. A. MEUWSEN (Ber., 1929, 62, [B], 1959—1969).—Nitrogen sulphide in benzene is converted by stannous chloride in 96% alcohol into the compound (HSN)₄ (cf. Wolbling, A., 1908, ii, 272), decomp. about 145° after becoming discoloured at about 100°. The product is moderately stable towards dilute acids, but completely hydrolysed by hot, concentrated alkali hydroxide mainly with formation of thiosulphate and complete evolution of nitrogen as ammonia, thus showing the absence of the N—N linking. The presence of the —SH group is indicated by the yellow colour which is observed when the colourless solution of (HSN)₄ in acetone is treated with neutral, alcoholic ethyl nitrite. Further, when the substance (HSN)₄ is dissolved in boiling formaldehyde, preferably in the presence of alkali, the compound (NS·CH₂·OH)₄ is obtained. It follows, therefore, that all the hydrogen atoms in (HSN)₄ are united to sulphur atoms, but they cannot be present as simple sulphdryl, SH, groups, since this would involve the presence of N—N linkings. It is therefore probable that the sulphur is quadrivalent, and this hypothesis is confirmed by the oxidative fission with bromine which requires 4×4 atoms of the halogen instead of 4×6 atoms required by the —SH group. The constitution is therefore deduced

and the compound is regarded as the inorganic analogue of hydrocyanic acid. Treatment of nitrogen sulphide with bromine shows that the four sulphur atoms exert twelve valencies towards nitrogen without indicating the number of valencies of the sulphur atoms to one another. Hydrolysis of nitrogen sulphide by alkali occurs almost quantitatively according to the scheme $S_4N_4 + 6NaOH + 3H_2O = Na_2S_2O_3 + 2Na_2SO_3 + 4NH_3$. The reaction thus closely resembles the hydrolysis of sodium hyposulphite, strengthening the conception that nitrogen sulphide is the cyclic nitrile of 2 mols. of hyposulphurous acid, $N \begin{smallmatrix} \diagup S \diagdown \\ \diagdown S \diagup \end{smallmatrix} N$. The constitution of the compounds PbN₂S₂NH₃ and HgN₂S₂NH₃, described by Ruff and Geisel (A., 1904, ii, 396), is discussed. H. WREN.

[Glow produced by] oxidation of phosphorus vapour. E. J. BOWEN and A. C. CAVELL (J.C.S., 1929, 1920—1926).—Intensity measurements are made by a photographic method incorporating special precautions. Within the range 60—380° and for oxygen pressures between 40 and 350 mm. the intensity of the glow does not vary appreciably. This is in agreement with the "chain" mechanism of oxidation (Backstrom, A., 1927, 1151). Ozone at low concentrations has no effect on the glow, but with more than 0.14% of ozone the intensity is increased linearly with concentration. Sulphur dioxide diminishes the glow and the effect is linear with respect to sulphur dioxide: oxygen ratio. Chlorine is a more efficient inhibitor and the intensity of glow decreases linearly with increase of chlorine: oxygen ratio over a large range, until the glow is less than one fifth of the maximum intensity. Further addition of chlorine has not the same quenching effect. It is suggested that chlorine can stimulate reaction chains involving oxygen. Ether vapour has no effect on the glow intensity even when present at a partial pressure fifty times that of the dry oxygen. J. G. A. GRIFFITHS.

Action of gaseous hydrogen chloride on phosphorus pentoxide. (MILE.) J. M. A. HOEF-LAKE (Rec. trav. chim., 1929, 48, 973—978).—The curve for the absorption by phosphorus pentoxide of hydrogen chloride dried by distillation at low temperatures is autocatalytic in type. The rapid absorption of further hydrogen chloride confirms the formation of a catalyst in the initial stages of the absorption. A comparison of the effects of the compounds HPO₃, POCl₃, and of mixtures of PO₂Cl and P₂O₅Cl₄ on the rate of absorption indicates that one or both of the latter intermediate chlorides is the catalyst. The initial period of delay in the reaction between hydrogen chloride and phosphorus pentoxide may be prolonged to 7 days by previously drying the gas with phosphorus pentoxide in two stages.

F. G. TRYHORN.

Dichlorophosphoric acid. H. MEERWEIN and K. BODENDORF (Ber., 1929, 62, [B], 1952—1953; cf. Lange, this vol., 662, 764).—If phosphoryl chloride or phosphorus pentachloride is treated with ice-water until dissolution is just complete the product requires almost exactly two or four equivalents of barium hydroxide for neutralisation in the presence of

thymolphthalein, thus showing the production of dichlorophosphoric acid as a recognisable intermediate. An oily product consisting mainly of dichlorophosphoric acid remains after treatment of phosphoryl chloride with the requisite quantity of water in ether; a crystalline ammonium or oxonium salt could not be prepared.

H. WREN.

Tantalum. V. SPITZIN and L. KASCHTANOV (*Z. anorg. Chem.*, 1926, **182**, 207—227).—Tantalum containing not more than 5% O as impurity has been prepared by the reduction of potassium fluotantalate with sodium in an atmosphere of hydrogen. The action of magnesium on tantalum pentoxide yields a product containing combined magnesium and having the formula Ta_2O_3Mg or Ta_2O_4Mg . The behaviour of the pure metal and some of its compounds on being heated in a stream of hydrogen chloride has also been investigated. The pure metal reacts at 700° , forming the pentachloride and hydrogen, whilst the metal containing some oxygen reacts at a slower rate, giving the pentachloride and possibly two oxychlorides, one of which has the formula Ta_2O_3Cl . The impure dioxide reacts at 850° with hydrogen chloride, forming hydrogen, a sublimate of the pentachloride, and a residue of the pentoxide and magnesium chloride. Above 500° , tantalum pentoxide is markedly volatile in hydrogen chloride and the reaction which takes place with the formation of water and the pentachloride is quantitatively reversed at lower temperatures. With a low concentration of water vapour, the black oxychloride, Ta_2O_3Cl , and a less stable, white substance, possibly of the composition $TaOCl_3$, can be obtained by hydrolysis of tantalum pentachloride at suitable temperatures. Sodium metatantalate when heated in hydrogen chloride is decomposed at 850° into sodium chloride, tantalum pentoxide, and water. L. S. THEOBALD.

Action of air on flowers of sulphur and ground sulphur. J. E. STEPHENSON and S. W. BRIDGE (*Analyst*, 1929, **54**, 590—591).—A known volume of air was passed over sulphur maintained at a constant temperature and then through standard iodine solution. At temperatures below 90° air had little or no action on ground sulphur (99.45% through 100-mesh), but appreciable and increasing quantities of sulphur compounds were evolved from flowers of sulphur from 17° and upwards. D. G. HEWER.

Preparation of hydrogen sulphide. H. GFELLER and K. SCHAEFER (*Schweiz. Apoth.-Ztg.*, 1929, **67**, 109—110; *Chem. Zentr.*, 1929, i, 1970).—A mixture of paraffin (25 g.), sulphur (15 g.), and asbestos fibre (5 g.) is heated. A. A. ELDRIDGE.

Action of hydrogen sulphide on solutions of nitric acid. H. B. DUNNCLIFF and S. MOHAMMAD (*J. Physical Chem.*, 1929, **33**, 1343—1362).—Solutions containing up to 5% of nitric acid are not attacked by hydrogen sulphide even if nitrogen peroxide be added. Solutions containing up to 40% of nitric acid are attacked after an interval of time. This interval is removed when nitrous fumes are added or when slight decomposition of the acid is produced by insolation. The addition of sulphuric acid lengthens the period of induction. The products of the reaction

are sulphuric and nitrous acids, ammonia, nitrous and nitric oxides, and nitrogen. The presence of sulphuric acid appears to influence the formation of the last-named, the evolution of which in the later stages of the reaction may be due to the formation of ammonia by secondary reactions and its subsequent decomposition. Sulphuric acid affects the course and the final products of the reaction, which ceases when the concentration of nitric acid falls to 23% and the total sulphuric acid content is 15%. A compound inert to the action of hydrogen sulphide is probably formed between the two acids. The mechanism of the formation of sulphuric acid and of the other products of the reaction is discussed.

L. S. THEOBALD.

Decomposition of thiosulphuric acid. J. SCHEFFER and F. BOHM (*Z. anorg. Chem.*, 1929, **183**, 151—188).—Earlier work on the mechanism of the reaction $H_2S_2O_3 \rightarrow H_2O + SO_2 + S$ is critically reviewed, and further study has been made of the reaction by nephelometric observation, measurement of the iodine titre, and the decolorisation of methylene-blue in the solution. At hydrogen-ion concentrations below 2.5×10^{-5} decomposition does not take place, the necessary condition for decomposition being the appearance of the labile HS_2O_3' ion; the ion SO_3'' and the non-ionised molecule are relatively stable. Decomposition of an acidified solution commences before cloudiness appears, as is evidenced by the increase of the iodine titre and the presence of pentathionic acid. On acidification of a thiosulphate solution containing methylene-blue rapid decolorisation ensues, but if methylene-blue be added to the solution 3 hrs. after acidification only partial decolorisation ensues; the dye is adsorbed readily by freshly-precipitated sulphur, but by the action of sulphur dioxide the sulphur loses this property.

H. F. GILLBE.

Preparation of pure uranium. E. BOTOLFSSEN (*Bull. Soc. chim.*, 1929, [iv], **45**, 626—627).—Uranium oxide is reduced by means of sublimed calcium by heating in an iron tube in a vacuum: $U_3O_8 + 8Ca = 3U + 8CaO$. The temperature is kept above the m. p. of calcium, the excess of which volatilises into the upper cold part of the tube. The uranium is separated through a sieve from most of the coarser calcium oxide, washed with 2% acetic acid solution and then with water, and finally dried with alcohol and ether. The powder obtained in this way contains 99.95% U. Uranium does not sublime in a high vacuum below its m. p. O. J. WALKER.

Reaction between ferric oxide and hydrogen sulphide at temperatures between 120° and 830° . L. A. SAYCE (*J.C.S.*, 1929, 2002—2006; cf. Pearson and Robinson, A., 1928, 606).—Pure ferric hydroxide was dried at 50° to constant composition and was then treated with hydrogen sulphide at various temperatures between 120° and 830° . Iron disulphide was the principal product between 120° and about 400° and was accompanied by gradually diminishing proportions of ferrous and ferric sulphides up to 250° . Above 400° the composition of the product was markedly different. The iron disulphide almost disappeared and at the same time the presence of

free sulphur was first noted. The product behaved as a mixture of ferrous and ferric sulphides.

J. G. A. GRIFFITHS.

Fluorides of group VIII of the periodic system.

O. RUFF and E. ASCHER (Z. anorg. Chem., 1929, 183, 193—213).—Pure cobalt trifluoride, CoF_3 , has been prepared by the action of fluorine on cobalt dichloride in a quartz tube at 150° . It is a light brown, crystalline, hygroscopic powder belonging to the hexagonal system; d (X-ray) 4.14; d (pycnometer) 3.88. By heating in a current of carbon dioxide it is completely decomposed to the difluoride at 350° . The previously known fluorides, FeF_3 and NiF_2 , may also be prepared by this method, whilst FeF_2 and CoF_2 may be obtained by the reduction of the higher fluorides at 400° and 200 — 300° , respectively. Rhodium trifluoride, RhF_3 , has been obtained by heating the metal in chlorine and then in fluorine at 500 — 600° . The product was not perfectly pure. It forms a red crystalline powder belonging to the rhombic system; d (X-ray) 5.67; d (pycnometer) 5.38. It is very stable towards water, acids, and bases. By heating the metal or the trifluoride in fluorine at 600° a red sublimate which may be either RhF_4 or RhF_5 is obtained. It is very reactive. Contrary to expectation, the compound obtained when palladium, or preferably the dichloride, is heated with fluorine is palladium trifluoride and not the difluoride. Sometimes brown crusts of the latter are obtained as the result of local heating. The trifluoride is a black, hygroscopic, crystalline powder belonging to the rhombic system, d (X-ray) 5.19; d (pycnometer) 5.06. Its chemical behaviour is similar to that of cobalt trifluoride. Impure palladium difluoride has been obtained by the action of reducing agents on the trifluoride or of hydrogen fluoride on the dichloride. Examined by the X-ray spectrograph it appears to be isomorphous with the other difluorides of the eighth group. The physical and chemical properties of all the fluorides mentioned have been tabulated.

M. S. BURR.

Cobalti-pentammines and a new case of isomerism. C. DUVAL and (MME.) DUVAL (Compt. rend., 1929, 189, 537—538).—The following new compounds were obtained by the action of freshly-prepared silver hydroxide on the compound $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$, the compound $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{OH})_3$ being formed as an intermediate product and decomposed at 70 — 100° by the appropriate acid or its alkali metal salt: boratopentamminecobaltic chloride, $[\text{CoBO}_2(\text{NH}_3)_5]\text{Cl}_2$; dichromatopentamminecobaltic chloride, $[\text{CoCr}_2\text{O}_7(\text{NH}_3)_5]\text{Cl}$; cobalt phosphatopentammine, $[\text{CoPO}_4(\text{NH}_3)_5]$; sodium cobaltipentamminopyrophosphate, $\text{Na}[\text{CoP}_2\text{O}_7(\text{NH}_3)_5]$; sodium cobaltipentamminobenzenepentacarboxylate, $\text{Na}_2[\text{CoC}_6\text{H}(\text{CO}_2)_5(\text{NH}_3)_5]$; sodium cobaltipentamminomellitate, $\text{Na}_3[\text{CoC}_6(\text{CO}_2)_5(\text{NH}_3)_5]$. The two following pairs of complexes have the same compositions but different electrolytic valencies (radical isomerism): cobalt persulphatopentamminecobaltic sulphate, $[\text{CoSO}_4(\text{NH}_3)_5]\text{SO}_4$ (orange); and sulphatopentamminecobaltic chloride, $[\text{CoSO}_4(\text{NH}_3)_5]\text{Cl}$ (rose); cobalt ferricyanopentammine, $[\text{Co}\{\text{Fe}(\text{CN})_6\}(\text{NH}_3)_5]$ (brown), and potassium cobaltiferrocyanide, $\text{K}[\text{Co}\{\text{Fe}(\text{CN})_6\}(\text{NH}_3)_5]$.

J. GRANT.

Ferrocyanomolybdates and analogous compounds of ruthenium and osmium. G. A. BARBIERI (Atti R. Accad. Lincei, 1929, [vi], 9, 1015—1019).—The canary-yellow, crystalline compound formed by the action of ammonium acetate on the reddish-brown, gelatinous precipitate obtained by the interaction of a molybdate and a ferrocyanide in acid solution (A., 1928, 160) is readily convertible into the corresponding silver compound, $\text{Ag}_4\text{Fe}(\text{CN})_6 \cdot 2\text{MoO}_3 \cdot \text{H}_2\text{O}$, the existence of the complex $[\text{Fe}(\text{CN})_6 \cdot 2\text{MoO}_3]$ being thus indicated. The ammonium compound probably has the structure $[\text{MoO}_3(\text{CN})_3\text{Fe}(\text{CN})_3\text{MoO}_3](\text{NH}_4)_4$. The corresponding ammonium ruthenocyanomolybdate, $(\text{NH}_4)_4\text{Ru}(\text{CN})_6 \cdot 2\text{MoO}_3 \cdot 3\text{H}_2\text{O}$, and osmiocyanomolybdate were also prepared.

T. H. POPE.

Modification of Glocker's method of quantitative analysis by means of X-ray absorption. N. H. MOXNES (Z. physikal. Chem., 1929, 144, 134—136; cf. A., 1925, ii, 270).—Preliminary. The original method of Glocker and Frohnmayer has been modified by substituting for a continuous X-ray spectrum a line spectrum as the basis of the absorption measurements.

F. L. USHER.

Simple sensitive method of spectrographic chemical analysis. E. VITERBO (Annali Chim. Appl., 1929, 19, 329—333).—A small drop of the solution to be examined is placed between the smooth, plane ends of two horizontal metal rods 2 mm. in diameter placed about 1 mm. apart. When the liquid has evaporated a condensed spark is passed between these electrodes, which may be of zinc, cadmium, or, better, magnesium. With a quartz spectrograph with a 0.01 mm. slit, the exposure used is a few seconds. The method is highly sensitive and permits of the detection, for example, of less than 6.4×10^{-10} g. of silver.

T. H. POPE.

Rapid qualitative analysis. II. Spot tests for the commoner cations and anions. G. GUTZEIT (Helv. Chim. Acta, 1929, 12, 829—850).—The use of the reactions previously described (this vol., 898) and of some supplementary reactions as spot tests is explained, and a scheme for systematic analysis in this way is given.

R. CUTHILL.

Photographic method for the determination of coloured solutions with special reference to the visual purple. R. J. LYTHGOE and K. TANSLEY (J. Physiol., 1929, 68, 45—48).—The photographic effect of light passing through the unknown solution is compared with that passing through a neutral tint wedge.

E. BOYLAND.

Theory of physical titration. E. N. GAPON (Ukraine Chem. J., 1929, 4, 149—153).—Physical titration is defined as titration in the course of which neither the titrated nor the titrating substance undergoes any change. Examples are the titration of a mixture of ethyl alcohol and water with benzene until separation into two layers occurs, and the titration of benzene with a mixture of ethyl alcohol and water until the whole becomes homogeneous. Using the data of Lincoln (A., 1900, ii, 392) and the formula of Bancroft (J. Physical Chem., 1897, 1, 786),

the physical method of titration is found to be quite satisfactory. A. FREIMAN.

Dilution in colorimetric hydrogen-ion measurements. I. Isohydric indicator methods for accurate determination of p_H in very dilute solutions. E. H. FAWCETT and S. F. ACREE (J. Bact., 1929, 17, 163—204).—Dilution curves reveal three types of variation from electrometric p_H values: buffer dilution effects, the effect of carbon dioxide and alkaline impurities in the water, and differences in p_H values of the indicator solutions. The incidence of these variations is examined. By the use of indicators adjusted at various p_H values the isohydric indicator method can be used at the usual and at extreme dilutions. CHEMICAL ABSTRACTS.

Determination of hydrogen-ion concentration in surgery. E. SIMENAUER (Arch. klin. Chir., 1928, 150, 193—201; Chem. Zentr., 1929, i, 1972).

Potentiometric titration of acids and bases. L. KAHLBERG and A. C. KRUEGER (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 11 pp.; cf. A., 1928, 1203).—An investigation has been made of the possibility of carrying out the potentiometric titration of hydrochloric acid with *N*-sodium hydroxide by using as electrodes two simple plates of dissimilar metals. The electrodes were merely immersed in the acid solution, which was mechanically stirred, and the variation in the *P.D.* between these plates during the addition of alkali was followed by means of a potentiometer. With the majority of pairs of metals used there was a marked inflexion of the titration curve at the end-point. Tungsten used in conjunction with most other metals gives a particularly sharp change of *P.D.* at the end-point and this change involves a reversal of polarity when the other electrode is nickel, cobalt, copper, silicon, chromium, or tin. In these latter cases the end-point can be determined to within about 0.1 c.c. by using only a voltmeter graduated in tenths of a volt to follow the change in *P.D.* In order to obtain the most rapid establishment of equilibrium it is recommended that copper, nickel, silicon, or cobalt should be used in conjunction with tungsten. H. J. T. ELLINGHAM.

Qualitative microanalysis of acids. F. FEIGL and P. KRUMHOLZ (Mikrochem., 1929, Pregl Fest., 77—86).—Small amounts of boric acid may be detected by the change in colour (violet to blue) which occurs on warming a 0.01% solution of quinalizarin in concentrated sulphuric acid with the substance dissolved in 1 c.c. of concentrated sulphuric acid. Nitrates, oxidising substances, and fluorides must be absent. Purpurin and alizarin-S may be used in place of quinalizarin, but the reaction is less sensitive. Traces of chromic acid may be detected by the reddish-violet colour given with diphenylcarbazide; mercuric salts and molybdates give similar colours, but the addition of sodium chloride in the former case and oxalic acid in the latter prevents interference by these metals. Traces of silica can be detected by warming a few drops of a slightly acid solution of the material with a drop of a nitric acid solution of ammonium molybdate, followed by addition of an acetic acid solution of benzidine and a saturated

solution of sodium acetate. A blue colour develops if only 0.0001 mg. of silica is present; arsenates and phosphates must be absent. The foregoing test can also be utilised for the detection of fluorine, the substance being warmed with concentrated sulphuric acid and quartz sand, the evolved silicon tetrafluoride being collected in a drop of water, and this solution tested for silica as above. The test may be used for the examination of mineral waters, and will detect 0.001 mg. of fluorine. Nitrates and halogens interfere, and should be previously removed.

H. F. HARWOOD.

Limits of applicability of indicators in simple p_H determinations. II. J. EISENBRAND (Pharm. Ztg., 1929, 74, 1287—1289; cf. this vol., 1157).—The application of indicators to p_H determinations in non-aqueous solutions on the basis of the mathematical equations previously given for aqueous solutions is not possible. Errors are caused by the alteration in the degree of dissociation of the indicator, and the absence of hydroxyl ions from many solvents. The presence in the solution of albumin and other substances of high mol. wt. also affects the p_H determination. The equations can be utilised only in the special case of a mixture of water with another solvent, the concentration of which varies within only narrow limits. Rapp's attempt to utilise p_H determinations as a means of affording a more accurate criterion of the degree of purity of various pharmaceutical products is adversely criticised, and the results are shown to be valueless for that purpose. The conclusion is reached that in the examination of pharmaceutical products the determination of the approximate limits of the p_H value by means of litmus paper is all that is necessary. H. F. HARWOOD.

Simple micro-analytical separation of chlorine and bromine. L. MOSER [with R. MIKSCHE] (Mikrochem., 1929, Pregl Fest., 293—295).—The greater thermal dissociation of hydrogen bromide and iodide as compared with hydrogen chloride has been utilised for an indirect determination of chlorine and bromine. The precipitate of silver chloride or bromide (about 5 mg.) is filtered on a micro-Munro crucible, dried at 150°, and weighed. Six times the quantity of pure dry ammonium bromide is added and the crucible heated at 250—300° until all ammonium salt has volatilised. A second treatment is usually sufficient to ensure complete conversion of the chloride into bromide. Silver bromide may be converted into silver iodide in a similar way by treatment with ammonium iodide. H. F. HARWOOD.

Determination of perchlorate. O. S. FEDOROVA (Z. anal. Chem., 1929, 78, 249—268).—The colorimetric method of Hahn (cf. B., 1926, 404) for the determination of perchlorate in saltpetre has been extended to the determination of small amounts in electrolytic baths containing chlorate, perchlorate, and chloride. Contrary to Hahn's statement, the presence of chlorates was found to have an appreciable effect on the colour of the methylene-blue reagent; hence it is necessary that the standard solutions used for comparison should contain an amount of chlorate approximately similar to that in the solution under examination. To 0.1—0.2 c.c. of the solution is

added 0.1 c.c. of 40% potassium nitrate solution, the whole is diluted to 0.3 c.c., and 5 c.c. of the zinc sulphate-methylene-blue reagent are added, the resulting liquid being matched against standards. Not more than 0.75% of potassium nitrate, 0.9% of chlorate, or 0.5% of chloride should be present in the final test solution, and under these conditions 0.0004% of perchlorate can be detected. Chromates if present must be previously removed by precipitation with lead acetate. The above method is considered more satisfactory for the determination of small quantities of perchlorate than the titanous chloride volumetric method of Spitalski and Jofa, which consumes considerable time. Attempts to utilise α -phenyl- β -diethylaminoethyl *p*-nitrobenzoate hydrochloride as a reagent for perchlorates yielded no satisfactory results.

H. F. HARWOOD.

Determination of iodine, especially in minute quantities [in organic substances]. J. SCHWABOLD (Z. anal. Chem., 1929, 78, 161—180).—Numerous published methods for the determination of iodine have been tested for their usefulness in determining minute amounts such as occur in soils, plants, and various other organic materials. Direct combustion of organic materials in oxygen combined with absorption of any iodine volatilised by potassium carbonate, heating the carbonate and the ash together until white, and extracting the residue with water yields a solution containing all the iodine as potassium iodide together with only small quantities of alkali salts. The iodine can be determined colorimetrically after extraction with chloroform; a modification of this method is described in detail. Alternatively, the iodide may be oxidised to iodate by boiling with chlorine water or with 0.1*N*-chloroamine solution; the iodate is then determined by addition of iodide and hydrochloric acid and titration of the liberated iodine. Periodate may be determined in the presence of iodate by treating the neutral solution with boric acid and iodide, whereby reduction to iodate is effected with liberation of iodine; after titration with thio-sulphate hydrochloric acid may be added and the total iodate determined by again titrating with thiosulphate.

A. R. POWELL.

Apparatus for micro-determination of sulphur dioxide in air. A. C. ROTTINGER (Mikrochem., 1929, Pregl Fest., 313—314).—An apparatus which permits of the determination of sulphur dioxide when using only 1—2 litres of air is described. The air is aspirated through 0.01*N*-iodine solution, which is subsequently titrated with 0.01*N*-thiosulphate.

H. F. HARWOOD.

Micro-determination of selenium and tellurium in organic compounds. H. D. K. DREW and C. R. PORTER.—See this vol., 1323.

Drop method for detection of nitrite ions in presence of other anions. N. M. RONSHINA (J. Russ. Phys. Chem. Soc., 1929, 61, 897—898).—0.004 Mg. of nitrite ion contained in 0.05 c.c. of solution can be detected by the use of test-papers dipped in solutions in acetic acid of benzidine, a rose-yellow to deep red coloration being obtained according to the concentration of nitrite. The solution examined should be made alkaline before applying the test.

Cations and other anions, with the exception of chromate, do not interfere with this test; in the presence of chromate, barium chloride should first be added in excess.

R. TRUSZKOWSKI.

Determination of nitrates in bismuth carbonate. G. J. W. FERRY.—See B., 1929, 850.

Availability of the isomeric aminonaphthol-sulphonic acids for the colorimetric determination of phosphorus. B. VASARHELYI (Mikrochem., 1929, Pregl Fest., 329—337).—The action of a number of different aminonaphthol-sulphonic acids and -disulphonic acids in reducing the complex phosphomolybdic acid to blue molybdenum oxides has been investigated, and compared with that of 1-amino- β -naphthol-4-sulphonic acid. With the latter acid the maximum blue colour develops more rapidly than when other isomeric acids are used, but some of the latter give a deeper colour. The rapidity of development of the blue colour with the different isomerides depends mainly on the relative positions of the sulphonic and amino-groups in the molecule, and to a smaller extent on the positions of the amino- and hydroxyl groups. The presence of large amounts of many salts, such as sodium chloride, ammonium sulphate, etc., hinders the reduction, and with 1-amino- β -naphthol-4-sulphonic acid silica (as potassium silicate) interferes.

H. F. HARWOOD.

Determination of degree of oxidation of some insoluble phosphates. A. COLANI (Bull. Soc. chim., 1929, [iv], 45, 621—623).—The amount of metallic oxide in uranous, molybdous, and ferrous phosphates is determined as follows. The phosphate is dissolved by heating at 200° in a sealed tube with a known volume of standard potassium dichromate solution (3—6 g. per litre) to which 4 vol.-% of sulphuric acid has been added. After complete dissolution the unreduced dichromate is titrated by one of the usual methods, the difference giving the amount of dichromate necessary for the oxidation of the metallic radical to the higher valency stage. In the case of uranous chlorophosphate, where the above procedure is inapplicable, the substance is melted in a vacuum with a large excess of sodium pyrophosphate, dissolved in water in an atmosphere of carbon dioxide, and the solution is then titrated with permanganate.

O. J. WALKER.

Accuracy of the Gutzeit method for [determining] arsenic. J. R. NELLER (J. Assoc. Off. Agric. Chem., 1929, 12, 332—341).—In a series of determinations of arsenic residues on fruit sprayed with lead arsenate, observations were made of the effects on the accuracy of such factors as size of the aliquot portion, absorption and evolution temperatures, method of preparing the mercuric bromide strips, and the point in the procedure at which the stannous chloride is added. The variations in the results were within the normal limits of accuracy of the method.

H. J. DOWDEN.

Polarographic studies with the dropping mercury cathode. V. Electro-reduction in acidic solutions of arsenious oxide. K. KAČÍŇKOVÁ (Coll. Czech. Chem. Comm., 1929, 1, 477—492).—A polarographic investigation with the dropping

mercury cathode of solutions of arsenious oxide in 0.1*N*- and *N*-hydrochloric acid has been made. The current-voltage curve exhibits four sudden rises and two maxima. The first rise in the curve is due to the electro-reduction of arsenious acid to arsenic, probably by the primarily deposited hydrogen, the second rise is due to the formation of arsine, the third increase, which is followed by a prominent maximum, is ascribed to the absorption of positively-charged dissociation products of arsenious acid, whilst the fourth rise is attributed to the evolution of hydrogen from hydrogen ions of the acid. Similar results were obtained with sulphuric and nitric acid of various concentrations, and the form of the curve was unchanged by the addition of 6*N*-calcium chloride and of 3*N*-potassium chloride. The addition of acetic acid and of propionic acid to a solution of arsenious oxide in *N*-hydrochloric acid resulted in a marked change in the shape of the curve, whilst the addition of 0.001*M*-solutions of methylene-blue and of fuchsin hydrochloride suppressed the dissociation of the arsenious acid as indicated by the practical disappearance of the second maximum.

A. I. VOGEL.

Potentiometric titrations with potassium ferricyanide in alkaline solution. I. Vanadium and hyposulphite. II. Arsenic, antimony, tin, and thallium. C. DEL FRESNO and L. VALDÉS (*Z. anorg. Chem.*, 1929, 183, 251—257, 258—262).—I. Vanadyl sulphate may be titrated potentiometrically with potassium ferricyanide in presence of sodium hydroxide at the ordinary temperature, but if ammonia, sodium carbonate, or borax is added a higher temperature (70°) must be used, or constant values of the potential will not be reached sufficiently quickly. An attempt has been made to determine vanadium and chromium in a mixture, but the first jump in the potential comes too soon. Potassium ferricyanide can be satisfactorily titrated with vanadyl sulphate if the ferricyanide is first warmed to 50—60° in a vacuum to remove dissolved air before making alkaline. Sodium hyposulphite may also be titrated by alkaline ferricyanide, but it must be kept in a current of nitrogen.

II. Solutions of stannous chloride, sodium arsenite, and antimony trichloride may be satisfactorily titrated in alkaline solution with potassium ferricyanide by the potentiometric method. The titration of stannous chloride must be carried out in an atmosphere of nitrogen. The titration of thallium gave results about 1% too low. With a high alkali content the potential reaches a constant value too slowly, and with a low one oxidation is incomplete.

M. S. BURR.

Micro-determination of carbon by Nicloux' method in dilute aqueous solutions. A. BORVIN (*Compt. rend. Soc. Biol.*, 1929, 100, 273—276; *Chem. Zentr.*, 1929, i, 1842).—Loss of carbon due to formation of carbon monoxide is avoided by dissolving the substance in water with sodium sulphate and drying in a vacuum to produce a large surface. Solutions poor in carbon are evaporated with sodium sulphate in a vacuum over sulphuric acid, and the residue is "washed" with dry sodium sulphate into Nicloux' apparatus.

A. A. ELDRIDGE.

Determination of carbon in iron and iron alloys. N. A. ZIEGLER.—See B., 1929, 854.

Determination of carbon dioxide in carbonates which may contain sulphides. R. CHANDELLE (*Bull. Soc. chim. Belg.*, 1929, 38, 248—254).—In a modification of the ordinary direct gravimetric method, the carbonate sample is dissolved by means of phosphoric acid containing potassium dichromate to oxidise any sulphide present. Accurate results are obtained even in presence of large amounts of sulphide.

O. J. WALKER.

Detection of alkali metal salts in mixtures of soluble salts and in silicates. N. A. TANANAEV (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 815—822).—A method for detecting alkali metals (sodium and potassium) in the presence of salts of tin, antimony, lead, silver, bismuth, cadmium, copper, aluminium, chromium, iron, cobalt, nickel, zinc, manganese, barium, strontium, calcium, and magnesium is described. If the salts are chlorides or nitrates their solutions are directly evaporated with an excess of oxalic acid, but if they are sulphates they are first converted into chlorides by treating with barium chloride. The solution is evaporated to dryness and ignited, when the metals remain either as carbonates or oxides or in the metallic state (Herschkovitsch, A., 1921, i, 495). On boiling with water the solution will be alkaline if either sodium or potassium is present. Potassium is detected by Cuttica's method and sodium by Kolthoff's method (A., 1927, 436). In the case of silicates the powdered silicate is first heated with hydrofluoric acid.

A. FREIMAN.

Detection of sodium with potassium antimonate. W. BORRGER (*Mikrochem.*, 1929, *Pregl Fest.*, 14—19).—Under the microscope 0.001 mg. of sodium can be detected by the reaction with potassium antimonate. For microchemical tests a solution of the reagent is best made by treating 0.05 g. with 5 c.c. of water at 50° for several minutes, and decantation of the solution from undissolved material. Large amounts of potassium salts do not affect the reaction, but magnesium salts interfere and must be removed before making the test.

H. F. HARWOOD.

Volumetric determination of silver in the presence of halides and cyanides. H. BAINES (*J.C.S.*, 1929, 2037—2041).—Previous methods are inapplicable to cases where silver halides are dissolved in the presence of unknown quantities of potassium cyanide. In this procedure iodine is added until a faint opalescence of silver iodide is produced and thus the potassium cyanide in excess of that necessary to keep the silver in solution is determined. The silver is determined by the further amount of iodine which has to be added to decompose the potassium argentocyanide into the metallic iodides and cyanogen iodide. Starch is used as indicator. The solution must be neutral or slightly alkaline and of a dilution at which the final end-point is not interfered with by cyanogen iodide. The method is shown to be accurate to within 0.14%.

J. G. A. GRIFFITHS.

Complex-chemical determination of silver. F. FEIGL and J. TAMCHYNA (*Ber.*, 1929, 62, [B],

1897—1901).—The solution of the silver salt is heated to boiling with 2% mercuric cyanide solution and 0.1*N*-sodium hydroxide is gradually added until phenolphthalein is rendered pink; after cooling, the silver cyanide is collected, washed with water and very dilute nitric acid, dried at 110°, and weighed. If lead is present, the silver and part of the lead are precipitated [as AgCN and Pb(OH)₂] by excess of alkali hydroxide; lead hydroxide is extracted from the filtered precipitate by 1% nitric acid. In neutral solution silver is determined volumetrically after addition of mercuric cyanide by titration with 0.1*N*-sodium hydroxide in presence of phenolphthalein or Congo-red. In acid solution preliminary neutralisation by barium carbonate is necessary. Alternatively, sodium hydroxide may be added to the solution at 70—80° until a slight permanent turbidity results and the titration may be completed as usual or the solution may be neutralised by sodium hydroxide in presence of methyl-red previous to addition of mercuric cyanide. The process is not complicated by the presence of thallium. Lead, if present in neutral solution, is precipitated by addition of sodium sulphate.

H. WREN.

Radiometric micro-analysis. R. EHRENBURG (Mikrochem., 1929, Pregl Fest., 61—68).—An account of the methods of determining small quantities of calcium, potassium, sodium, ammonium, sulphate, phosphate, and carbonate by the radiometric method, thorium-*B* being employed as the radioactive material.

H. F. HARWOOD.

Determination of calcium carbide in technical calcium cyanamide. D. STROHAL.—See B., 1929, 775.

Determination of strontium and barium. L. SZEBELLÉDY (Z. anal. Chem., 1929, 78, 198—206).—At 17°, 1 part of strontium bromide dissolves in 12.4 parts of anhydrous isobutyl alcohol, whereas 1 part of barium bromide requires 10,800 parts of the alcohol for complete dissolution. A method for separating the two elements is based on this difference in solubility; the solution containing about 0.5 g. of the two nitrates is evaporated to dryness with 50 c.c. of hydrobromic acid and the bromides are dried at 100° for 1 hr. The dried salts are ground with 2—3 c.c. of isobutyl alcohol, a further 10 c.c. of alcohol are added, the mixture is heated at 110° for 10 min., and, after settling, the clear liquor is decanted through a small filter. The filtrate is evaporated to dryness, the residue moistened with a few drops of water, about five times its weight of ammonium sulphate added, the mixture heated gently at first, then to bright redness, and the residue weighed as strontium sulphate. The barium bromide on the filter is dissolved in 25 c.c. of hot water, the solution evaporated to a syrup, treated with 2—3 c.c. of hydrobromic acid, and heated to obtain the dry bromide as before. The alcohol treatment is repeated and the weight of strontium sulphate added to that already obtained. The barium bromide residue is repeatedly treated as before until the weight of strontium sulphate obtained in an extraction is less than 5 mg. The barium salt is then dried at 180° and weighed. From the total weight of strontium sulphate obtained 0.5 mg. is

subtracted for every extraction made and added to the weight of barium bromide.

A. R. POWELL.

Detection and determination of minute amounts of magnesium. F. L. HAHN (Mikrochem., 1929, Pregl Fest., 127—139).—Small amounts of magnesium may be detected and determined colorimetrically by means of an alkaline solution of 1:2:5:8-tetrahydroxyanthraquinone, the colour changing from reddish-violet to cornflower-blue; 0.001 mg. of magnesium in 1 c.c. of solution can be detected by this reaction. In applying the method to the determination of magnesium in aluminium alloys the greater part of the aluminium must be removed by saturating the solution with hydrogen chloride at 0° after addition of ether before the magnesium is determined. Amounts of magnesium of the order of 0.000001 mg. may be detected by carrying out the reaction in capillary tubes, special precautions being necessary to ensure accuracy; details of the procedure are described.

H. F. HARWOOD.

Micro-determination of magnesium with 8-hydroxyquinoline, and its separation from calcium. R. STREIBINGER and W. REIF (Mikrochem., 1929, Pregl Fest., 319—322).—The ammoniacal solution of the magnesium salt containing ammonium chloride is heated at 70°, and an excess of a 1% alcoholic solution of the reagent added. After 20 min. the liquid is filtered through a Pregl filter tube, the precipitate washed with hot water containing ammonia, then with alcohol, dried at 105° for 20 min., and weighed as Mg(C₉H₆ON)₂·2H₂O. In the separation from calcium, the latter is first precipitated as oxalate in acetic acid solution, the filtrate neutralised with ammonia, ammonium chloride added, and the magnesium precipitated as above. When only minute amounts (0.04 mg.) of calcium are present with 5 mg. of magnesium, no precipitation of calcium oxalate takes place, even after the solution has been kept for several days.

H. F. HARWOOD.

Identification of lead in any form by means of three successive microcrystalline tests. G. DENIGÈS (Bull. Soc. chim., 1929, [iv], 45, 678—680; cf. A., 1919, ii, 523).—The lead compound is converted successively by means of potassium bromide and potassium iodide solutions into lead bromide, potassium lead iodide, and lead iodide. The crystals of these three substances can be identified microscopically. The method is applicable to all soluble and insoluble compounds of lead, except lead sulphate, which requires a modified procedure.

O. J. WALKER.

Determination of lead peroxide. A. V. PAMFILOV and others.—See B., 1929, 850.

Separation of lead and bismuth. H. BLUMENTHAL (Z. anal. Chem., 1929, 78, 206—213).—The nitrate solution of the two metals is treated with an excess of 10% sodium carbonate solution until a heavy precipitate of lead carbonate is obtained, nitric acid is added drop by drop until the solution is just acid to methyl-orange, and, after boiling to expel carbon dioxide, an emulsion of freshly-precipitated mercuric oxide is stirred in until a slight excess is present whereby all the bismuth is precipitated as

basic nitrate. The solution is diluted with 100 c.c. of cold water, set aside over-night, and filtered. The precipitate is washed with a cold 0.1% solution of potassium nitrate and dissolved in dilute nitric acid; the bismuth is precipitated as phosphate for weighing. For the determination of bismuth in impure lead the metal is dissolved in nitric acid, the solution rendered slightly alkaline with sodium carbonate, just reacidified with nitric acid, treated with 6 c.c. of 5% manganous nitrate solution, and boiled with 4 c.c. of *N*-permanganate. The precipitate of manganese dioxide contains all the antimony, arsenic, tin, and bismuth; it is dissolved in hydrochloric acid, the solution treated with hydrogen sulphide, the bismuth separated by digestion of the sulphides with sodium sulphide, dissolved in nitric acid, and separated from the remaining lead by the mercuric oxide method.

A. R. POWELL.

Detection of thallium. A. J. STEENHAUER (Mikrochem., 1929, Pregl Fest., 315—318).—Photomicrographs are given of the crystalline precipitates given by solutions of thallium salts with sodium thiosulphate, ammonium molybdate, picric acid, ammonium thiocyanate, ammonium dichromate, mercuric thiocyanate, and tartaric acid. Of the above, the last four are the most suitable for the detection of thallium.

H. F. HARWOOD.

Rapid microchemical determination of copper. G. SPACU and J. DICK (Z. anal. Chem., 1929, 78, 241—244).—An adaptation of the authors' previous method (cf. A., 1927, 746) to the determination of minute amounts of copper. The copper is precipitated as the compound $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2](\text{SCN})_2$, and weighed after drying for 10 min. in a vacuum at the ordinary temperature.

H. F. HARWOOD.

Electrometric determination of copper. I. Müller and Rudolph's method. II. Application of Volhard's method to electrometric analysis. M. E. PRING and J. F. SPENCER (Analyst, 1929, 54, 509—516, 576—581).—I. Müller and Rudolph's method (A., 1923, ii, 880) of reducing the solution of cupric salt by sodium hydrogen sulphite, heating at 70°, and titrating with potassium thiocyanate, using a copper electrode, is very sensitive to changes of temperature, concentration of hydrogen sulphite, and time taken for the operation; since no constant error was found no correcting factor could be used. The possibility of obtaining concordant results is regarded as remote. Sulphur dioxide was not satisfactory as a reducing agent, as reduction was incomplete even on boiling.

II. The copper solution (not more dilute than 0.04*N*) is saturated with sulphur dioxide, and 0.1*N*-potassium thiocyanate solution is added, whereby cuprous thiocyanate is precipitated, and the solution boiled to expel all sulphur dioxide. Water is added, and when cold a silver plate and a 0.1*N*-calomel electrode are inserted and the excess of thiocyanate is titrated with 0.1*N*-silver nitrate solution. To obtain a sharp end-point the rate of change of *E.M.F.* with changing amount of silver nitrate is plotted against the volume of silver nitrate added, and the titration is finished slowly. The presence of iron and zinc does not interfere with the accuracy of the titration,

and the experimental and calculated values agreed very closely.

D. G. HEWER.

Application of the thiocyanate method for the precipitation of copper in the confirmatory tests for cadmium and antimony [in Noyes' scheme of qualitative analysis]. A. F. DAGGETT (J. Amer. Chem. Soc., 1929, 51, 2758—2759).—The part of the ammoniacal solution remaining after confirming copper is slightly acidified and 5 c.c. of *N*-potassium thiocyanate solution are added; the solution is boiled, then 0.5 g. of sodium sulphite is added, and the cuprous thiocyanate precipitate, coagulated by further boiling, is filtered off and the filtrate examined for cadmium by means of hydrogen sulphide. A similar procedure may be used to prevent copper interfering with the test for antimony. S. K. TWEEDY.

Rapid microchemical determination of mercury. G. SPACU and G. SUCIU (Z. anal. Chem., 1929, 78, 244—247).—The method previously described (this vol., 901) for the precipitation and weighing of mercury in the form of its compound $(\text{HgI}_2)(\text{Cu en}_2)$, has been applied to the determination of minute amounts of the metal. It offers the advantage that the determination can be carried out directly in solutions containing aqua regia after neutralisation with ammonia and ethylenediamine.

H. F. HARWOOD.

Electrometric titration of iodomercures. L. MARICQ (Bull. Soc. chim. Belg., 1929, 38, 259—264).—The iodomercure ion can be accurately determined by electrometric titration with mercuric chloride, in the presence or absence of iodides, the reaction being $\text{HgI}_4'' + \text{Hg}^{++} \longrightarrow 2\text{HgI}_2$.

C. W. GIBBY.

Use of Nessler's reaction for the rapid characterisation of mercury oxycyanide and its detection in mercuric cyanide. J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1928, 66, 209—211; Chem. Zentr., 1929, i, 2088).—A 1% solution of the substance (2 c.c.) is treated with 5% potassium iodide solution (5 c.c.), ammonia solution (1 c.c.), and sodium hydroxide solution (1 c.c.), when a brown precipitate is obtained owing to the intermediate formation of potassium mercuri-iodide: $\text{HgO} + 4\text{KI} + \text{H}_2\text{O} = \text{K}_2\text{HgI}_4 + 2\text{KOH}$.

A. A. ELDRIDGE.

Use of potassium iodide for the rapid detection of mercury [ions] in mercuric cyanide. J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1928, 66, 206—209; Chem. Zentr., 1929, i, 2087).—In presence of sulphuric acid, potassium iodide is a satisfactory reagent for concentrated solutions of mercuric cyanide; for dilute solutions antipyrine is added to produce a precipitate or an opalescence in the potassium mercuri-iodide solution.

A. A. ELDRIDGE.

Gravimetric analysis with Kuhlmann's microbalance. [Determination of aluminium.] A. BENEDETTI-PICHLER (Mikrochem., 1929, Pregl Fest., 6—13).—Aluminium may be determined by precipitation with 8-hydroxyquinoline in the presence of ammonium acetate. The precipitate is washed with cold water and dried in a current of air for 5 min. at 140°. A special form of drying tube for use with this and other micro-precipitates is described.

H. F. HARWOOD.

Use of 8-hydroxyquinoline in separations of aluminium. G. E. F. LUNDELL and H. B. KNOWLES (*Bur. Stand. J. Res.*, 1929, 3, 91—96).—Aluminium alone is precipitated by 8-hydroxyquinoline from ammoniacal solutions containing in addition phosphorus, arsenic, fluorine, and boron; from ammoniacal solutions (to which hydrogen peroxide has been added) containing in addition vanadium, tantalum, niobium, titanium, and molybdenum; and from ammonium carbonate solutions containing in addition uranium. For separation from beryllium, Kolthoff and Sandell (*A.*, 1928, 981) precipitate in acetic acid solution with 8-hydroxyquinoline. The precipitate in each case has the formula $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$, and may be weighed as such after drying at 110° (Berg, *A.*, 1927, 436, 639, 674, 745, 847, 848; 1928, 39; this vol., 286), but it is preferable to destroy the organic matter with nitric and sulphuric acids and precipitate the aluminium with ammonia as usual. C. HOLLINS.

Quantitative analysis of gallium. III. A. BRUKL (*Monatsh.*, 1929, 52, 253—259; cf. this vol., 670).—Methods, depending on the precipitation of gallium by "cupferron" after the removal of interfering metals, for the quantitative separation of gallium from titanium, zirconium, thorium, vanadium, molybdenum, tungsten, and the rare-earth metals are described. J. A. V. BUTLER.

Microchemical permanganate determinations. J. MIKA (*Z. anal. Chem.*, 1929, 78, 268—297).—In microchemical titrations with permanganate a correction for the excess of solution used is always necessary. This may be obtained by titrating in all cases to a definite tint, a solution of cobalt ammonium sulphate being utilised as a comparison liquid, and subtracting the amount of a similar titration carried out on pure water. The 0.01*N*-permanganate used can be directly standardised microchemically against sodium oxalate; the factor so obtained is about 0.3% less than that given by the macrochemical standardisation with either sodium oxalate or sodium thiosulphate, hence special care must be taken that all the materials used are free from reducing substances. If the permanganate be standardised against 0.01*N*-thiosulphate the results agree, whether obtained in the microchemical or macrochemical way. The microchemical determination of manganese by the Fischer-Volhard method requires the titration to be carried out in the presence of zinc acetate and acetic acid, preferably in a solution of p_H 5.0. The excess of permanganate used must be determined by centrifuging the solution after titration, and withdrawing a portion of the clear liquid, which is then titrated with 0.01*N*-thiosulphate after addition of potassium iodide. Details are given of a form of micro-weight-burette which is also suitable for the titration of hot solutions, and of a device for effecting the removal of a known amount of the clear solution after titration.

H. F. HARWOOD.

Determination of manganese and iron by successive titrations with permanganate. J. TELETOV and (MME.) N. ANDRONIKOV (*Bull. Soc. chim.*, 1929, [iv], 45, 674—677).—Ferric hydroxide and hydrated manganese dioxide are precipitated from the solution containing ferrous and manganous

salts by means of sodium hydroxide and hydrogen peroxide. The precipitate is collected and well washed, and the manganese is determined by treatment with oxalic acid in presence of sulphuric acid and titration of the excess oxalic acid with permanganate solution in the usual way. The iron is then reduced to the ferrous state by filtering the solution slowly through a layer of electrolytic cadmium, and is titrated in turn with permanganate solution. O. J. WALKER.

Iodometric determination of [ferric] iron. E. H. SWIFT (*J. Amer. Chem. Soc.*, 1929, 51, 2682—2689).—The conditions essential for the accurate (0.2%) determination of ferric iron by addition of potassium iodide and acid and titration with thio-sulphate are elucidated experimentally. Sulphuric acid is less suitable than hydrochloric acid. The accuracy of the method is only apparent, however, since the reaction is incomplete and this is compensated by an oxygen error. S. K. TWEEDY.

Potentiometric determination of iron with permanganate solution. T. HECZKO (*Z. anal. Chem.*, 1929, 78, 247—249).—A suitable comparison electrode (which permits of the end-point being marked by a reversal of the direction of the current) for use in the potentiometric titration of ferrous salts by permanganate consists of a 0.5% solution of vanadium pentoxide in dilute phosphoric acid containing a few drops of 0.1*N*-ferrous sulphate. The solution is employed in an Emich filter tube in the manner previously described (*A.*, 1928, 1345).

H. F. HARWOOD.

Two new reversible oxidimetric indicators, and their use with permanganate. J. KNOP (*Chem. Listy*, 1929, 23, 366—375).—See this vol., 670.

Volumetric determination of iron, using potassium permanganate in the presence of the oxidimetric indicators erioglaucin A and erio-green B. J. KNOP and (MLE.) O. KUBELKOVÁ (*Chem. Listy*, 1929, 23, 399—402).—See this vol., 670.

Oxamide, a reagent for nickel. J. LISKA (*Chem. Listy*, 1929, 23, 402—403).—The presence of 0.1 mg. of nickel in 1 c.c. of solution can be demonstrated by the addition of crystalline oxamide, after which the solution is heated to boiling and 20% sodium hydroxide solution added, when an intense yellow coloration is obtained. This reaction, which is less delicate than that of Tschugaev, is not adapted to the determination of nickel. R. TRUSZKOWSKI.

Identification of vanadium and cerium, using hydrogen peroxide. J. LUKAS and A. JILEK (*Chem. Listy*, 1929, 23, 417—419).—30% Hydrogen peroxide solution produces a brown coloration on addition to solutions of vanadium in dilute sulphuric acid. A yellowish-green coloration, discharged by boric acid, is given under these conditions by solutions containing molybdenum. Neutral solutions of cerium salts give a yellow or orange coloration in the presence of 30% hydrogen peroxide solution and of quinine hydrochloride. R. TRUSZKOWSKI.

Quinhydrone electrode. G. E. CULLEN (*J. Biol. Chem.*, 1929, 83, 535—538).—A modification of the electrode of Cullen and Billmann (*A.*, 1925, i,

1201) which eliminates errors due to loss of carbon dioxide is described. C. R. HARRINGTON.

Apparatus for continuous purification of mercury. E. BOTOLFSSEN (Bull. Soc. chim., 1929, [iv], 45, 782—784).—The mercury is drawn by a water pump up a long tube standing in a reservoir; an inlet tube drawn to a fine point admits air at the bottom of this tube so as to break up the column of mercury into small portions. The tube is bent twice at right angles, thus delivering the mercury into a funnel with narrow end through which it passes in a finely-divided state into a column of purifying liquid, at the bottom of which it collects and is thence passed back into the reservoir. A diagram and dimensions are given. C. A. SILBERRAD.

Graduated burette with calibrated globe attached for accurate volumetry. A. TIAN (Bull. Soc. chim., 1929, [iv], 45, 778—782).—For very accurate volumetric work, e.g., when the result depends on the difference between two much larger measurements, a burette with very open scale (20 cm. for 10 c.c.) is surmounted by a calibrated globe containing 40 c.c. It is shown that for maximum accuracy (i) 5 min. should elapse before reading; (ii) the precision of reading is considerably increased by such a scale; but (iii) correction for dilatation must be made if the temperature of reading differs from that of calibration by more than 0.5°.

C. A. SILBERRAD.

Improved stopcock for gas analysis burettes. W. E. KUENTZEL (J. Amer. Chem. Soc., 1929, 51, 2759—2760).—The improved four-way cock has provision for connecting the absorption pipette to the under-side of the barrel. S. K. TWEEDY.

Laboratory ozoniser. A. L. HENNE (J. Amer. Chem. Soc., 1929, 51, 2676—2677).—An inexpensive, efficient ozoniser which is a simplified form of that described by Smith (A., 1925, ii, 896) is described.

S. K. TWEEDY.

Measurement of vacuum during distillation under reduced pressure. P. WALTHER (Pharm. Ztg., 1929, 74, 1289—1290).—Attention is directed to the error involved in the preparation of a manometer by filling with mercury a tube previously evacuated by means of a water-pump, and a number of manometers suitable for use in vacuum distillations are described.

H. F. HARWOOD.

Apparatus for the distillation of sensitive solutions in a vacuum. H. KRAUT, K. LOBINGER, and F. POLLITZER (Ber., 1929, 62, [B], 1939—1941).—An apparatus is figured and described in which local superheating of the solution is avoided by causing a circulation of the liquid by the bubbles of vapour. Its application to the concentration of enzyme solutions is discussed. H. WREN.

Distillation under highly reduced pressures. B. STEMPEL (Arch. Pharm., 1929, 267, 484—486).—A simple vacuum distillation apparatus is set up and fitted with a porcelain test-tube in direct communication with the receiver. The air in the apparatus is then removed and replaced by hydrogen or carbon dioxide, and the whole evacuated with a water pump. The apparatus is then closed and the porcelain tube,

which contains a few grams of metallic calcium (or magnesium when carbon dioxide is used), is heated at about 800°. The gases are completely absorbed and a pressure of 0.05 mm. may be obtained.

S. COFFEY.

Apparatus for distillation at very low pressures. H. I. WATERMAN and E. B. ELSBACH (Chem. Weekblad, 1929, 26, 469).—An apparatus in which 1-bromonaphthalene may be distilled at the ordinary temperature, and dibromoisosafrole may be distilled without decomposition, is described. S. I. LEVY.

Still heads and laboratory rectification columns. V. LONGINOV and A. PRIANISCHNIKOV (Trans. Inst. Pure Chem. Reagents, Moscow, 1929, No. 7, 54 pp.).—A study of the effect of height, diameter, isolation, rate of distillation, reflux ratio, and the nature of the filling material on the efficiency of the Hempel column. CHEMICAL ABSTRACTS.

Centrifuge tube with detachable bottom. A. FRIEDRICH (Mikrochem., 1929, Pregl. Fest., 103—105).—A new form of tube, the lower portion of which consists of a small glass cap with ground joint, is described; the cap can be removed after centrifuging together with the precipitate it contains.

H. F. HARWOOD.

Apparatus for determination of m. p. under the microscope. G. KLEIN (Mikrochem., 1929, Pregl. Fest., 192—203).—An improved form of apparatus for the determination of the m. p. of substances under the microscope has been devised. The apparatus is heated electrically, and is available for temperatures between 50° and 350°. The m. p. temperature is read directly on a thermometer, no correction being necessary. H. F. HARWOOD.

Pump for circulating gas of various kinds through a closed system. M. DOLCH and K. GIESELER (Chem. Apparatur, 1928, 15, 229—231, 268—269; Chem. Zentr., 1929, i, 1722).

Removal of dissolved gases from liquids by vacuum sublimation. J. H. HIBBEN (Bur. Stand. J. Res., 1929, 3, 97—104).—The liquid is introduced by means of a pipette through a side-tube (which is then sealed) into the space between the walls of a Dewar vessel, the space being connected through a liquid-air trap to a McLeod gauge and mercury-vapour pump, drying tubes, and oil-pump. The space is then evacuated and the liquid frozen. The inner walls are then cooled by solid carbon dioxide and ether and the frozen liquid sublimates on to the cooled under-surface, the released gases being removed by the evacuating pump. At the end of the operation the inner wall is warmed and the melted sublimate falls back to its original position at the bottom of the space between the walls, the last traces being transferred by reversing the sublimation. During the operation the frozen liquid may be warmed to accelerate sublimation; for water a jacket at 50—80° may be used without melting the ice, so rapid is the sublimation. The temperature gradient, the temperature of the cooling surface, and the pressure in the space must be adjusted so that (a) the vapour pressure of the sublimate at the temperature of the inner wall is negligible, (b) there is direct condensation

to solid without liquid phase, (c) the vapour pressure of each gas in the sublimate must be greater than its partial pressure in the evacuated space. The application of the method to water containing ammonia, hydrogen chloride, carbon dioxide, or oxygen is described. For hydrogen chloride condition (c) is not fulfilled; part of the sublimed ice melts and dissolves hydrogen chloride, and there is no removal of the dissolved gas. Oxygen and carbon dioxide are completely removed by one sublimation; for ammonia several repetitions are required. C. HOLLINS.

Apparatus for the analysis of small samples of gas. H. R. AMBLER (Analyst, 1929, 54, 517—522).—The apparatus, which can conveniently deal with samples of gas from 1 to 15 c.c., consists of two three-way taps connected with a glass, water-jacketed measuring bulb (C), absorption bulb (B) fitted with platinum electrodes and spark gap, or a platinum spiral, or both. The sample is introduced into B, then transferred to C for measuring, by observing the pressure at which the constant volume of bulb (or bulbs) is filled on a mercury manometer attached to a scale, C being sealed against any leak by running mercury to a marked point. After introducing the absorbent solution into B, the gas is returned, and after absorption again passed to C and measured.

D. G. HEWER.

Cæsium-magnesium photo-cell. V. ZWORYKIN and E. D. WILSON (J. Opt. Soc. Amer., 1929, 19, 81—89).—Cæsium is retained on the surface of freshly-distilled magnesium without any change in photo-electric properties. Colour-sensitivity curves are given for vacuum cells, and for cells containing argon, helium, and neon. The behaviour of the cells is practically independent of temperature.

C. W. GIBBY.

Photo-electric smoke recorder. E. H. VEDDER (Elec. J., 1929, 26, 199—201).

CHEMICAL ABSTRACTS.

Use of photo-electric cells for polarimetric measurements. G. TODESCO (Nuovo Cim., 1928, 5, 376—390; Chem. Zentr., 1929, i, 2084).

Thermionic valve potentiometer for the determination of p_H with the glass electrode. W. C. STADIE (J. Biol. Chem., 1929, 83, 477—492).—A null method for the measurement of the potential of glass electrodes by a valve potentiometer is described. The grid, filament, and plate circuits of two valves are connected in parallel, the plate circuits being arranged as a Wheatstone bridge which may be balanced by variable resistances permitting a high-sensitivity galvanometer to be inserted in the plate circuit. The potential of a glass electrode in the grid circuit of one valve may then be measured to within 0.001 volt. The apparatus is very steady in action and is free from electrostatic disturbances. Its sensitivity in measuring potentials through resistances of from 20 to 600 megohms is 1—4 mm. of deflexion per millivolt. F. G. TRYHORN.

Electrically conductive antimony mirrors on glass. S. MILLER (J. Opt. Soc. Amer., 1929, 19,

101—102).—Electrically conducting mirrors of antimony may be prepared by the thermal decomposition of stibine. They are stable in air, and do not sublime in a vacuum at 300°, but do so below the softening point of pyrex glass. C. W. GIBBY.

Pressure-controlled McLeod gauge. N. UNDERWOOD (J. Opt. Soc. Amer., 1929, 19, 78).—The mercury in a McLeod gauge is caused to rise by pressure applied to it in the reservoir by means of an atomiser bulb. Releasing the pressure brings the mercury back to its normal position.

C. W. GIBBY.

Voltage regulator for gas discharge X-ray tubes. F. E. HAWORTH (J. Opt. Soc. Amer., 1929, 19, 79—80).—An improvement on the regulator described by Bozorth (A., 1927, 502).

C. W. GIBBY.

Universal stand for electrolysis with rotating electrode. A. I. GUNDER (Ukraine Chem. J., 1929, 4, 293—295).

A. FREIMAN.

Scopometer. W. G. EXTON (J. Amer. Med. Assoc., 1929, 92, 708—712).—A simple apparatus for the measurement of turbidity and colour is described.

CHEMICAL ABSTRACTS.

Sources of error and calculation in the measurement of surface tension by the ring method and micro-balance. G. ORBÁN and L. REINER (Biochem. Z., 1929, 211, 487—490).—In the determination of surface tension by the ring method, the weight required to detach the ring depends, not only on the surface tension and radius of the ring, but also on the ratio of radius (r) to square root of specific cohesion (a). This cannot be neglected when r is small. When $r/a > 3$, $F(r/a)$ is unity.

J. H. BIRKINSHAW.

Micro-polarimeter tubes with matt inner surface. H. NAUMANN (Biochem. Z., 1929, 211, 239—243).—By the action of hydrofluoric acid a matt inner surface is produced in black glass micro-polarimeter tubes. Errors in polarimetric readings due to reflexion from the inner surface of the tubes are thus avoided. The tubes can be cleaned without difficulty.

W. MCCARTNEY.

Measurement of vapour pressures at high temperatures by a transference method. K. JELLINEK and G. A. ROSNER (Z. physikal. Chem., 1929, 143, 51—54).—A convenient apparatus is described for measuring the vapour pressure of solids at high temperatures by determination of the quantity of vapour carried over when a current of inert gas is passed over the material, which is contained in an electrically heated porcelain tube.

H. F. GILLBE.

Nomography. O. LIESCHE (Chem. Fabrik, 1929, 437—438).—A diagram is given by which analytical results may be read, the weight of material taken, the final weight, the appropriate factor, and the percentage determined being each read on a separate vertical axis.

S. I. LEVY.

Geochemistry.

Atmospheric ozone. G. M. B. DOBSON (J. Phys. Radium, 1929, [vi], 10, 241—246).—Observations made during 1920—1928 on the distribution of ozone in the atmosphere in different parts of the world show certain regularities. At a height of 50 km. there is a layer in which the concentration of ozone is equivalent to 2 mm. thickness at atmospheric pressure. The height of this layer is nearly constant, but the concentration varies. It is greater to the west of a cyclone and less to the east, the distribution being reversed for an anticyclone. Whilst the concentration of ozone at 50 km. is related to the meteorological conditions, that near the earth's surface appears to be unrelated. There is a marked variation of concentration in the 50 km. layer with latitude, the value being least at the equator and greatest at the poles. The polar concentration is greatest in the spring and least in the autumn. Atmospheric ozone cannot therefore be formed by solar radiation, but probably results from magnetic disturbances like the aurora.

C. J. SMITHELLS.

Height of the ozone in the upper atmosphere. II. F. W. P. GOTZ and G. M. B. DOBSON (Proc. Roy. Soc., 1929, A, 125, 292—294).—Measurements made previously (A., 1928, 1209) have been corrected, and the average thickness of the ozone layer over Arosa is now found to be about 50 km., in good agreement with the values obtained by other investigators. There are indications that the height is greater in spring than at other times of the year and is also greater when there is much ozone present than when there is little.

L. L. BIRCHUMSHAW.

Origin of helium-rich natural gas. R. C. WELLS (J. Wash. Acad. Sci., 1929, 19, 321—327).—Measurements have been made of the rate of separation of hydrogen from carbon dioxide by fractional diffusion through a plug of ball clay and it is shown to be possible to obtain a product containing 90% H₂ from one containing only 2.6% H₂ in seven stages. The bearing of these results on the accumulation of helium in natural gas deposits is discussed briefly and a programme of further work to establish the value of this theory is outlined.

A. R. POWELL.

Hydro-chemistry of the upper Kama and its tributaries. A. TRIFONOV (Bull. inst. res. biol. univ. Perm, 1927, 5, 147—156).—A study of the water of the R. Kama between Perm and the mouth of the Wischera and at the mouths of seven tributaries supports the theory of universal chemical heterogeneity in the cross-section of a flowing stream.

CHEMICAL ABSTRACTS.

Thermal water of the military station at Acqui. S. CORTASSA (Annali Chim. Appl., 1929, 19, 297—306).—The composition of the slightly radioactive water, which contains sulphide, sodium chloride, lithium, bromide, iodide, and borate, is recorded.

T. H. POPE.

Precipitation of limestone by submarine vents, fumaroles, and lava flows. J. E. A. KANIA (Amer. J. Sci., 1929, [v], 18, 347—359).—A possible explanation is given for the occurrence of non-

fossiliferous limestone beds intercalated between submarine lava flows. Limestone is precipitated on account of the removal of carbon dioxide from seawater by the heating and agitating action of submarine lava flows. The occurrence of limestone beds is often associated with times of great volcanic activity.

C. W. GIBBY.

Application of X-rays in the classification of fibrous silicate minerals commonly termed asbestos. H. V. ANDERSON and G. L. CLARK (Ind. Eng. Chem., 1929, 21, 924—933).—The effects of acid and heat treatment on thirty samples of "asbestos" are described. X-Ray diffraction patterns are given and discussed: they constitute a rigorous method of specification.

C. W. GIBBY.

Alkaline character of lavas from volcanoes at Antiparos (Cyclades). C. A. KATENAS (Compt. rend., 1929, 189, 489—491).—Analyses of lavas from Antiparos are given. With one exception they all contain an excess of potassium over sodium.

C. W. GIBBY.

Constitution of mica. V. Pegmatitic muscovite. VI. Non-pegmatitic muscovite. J. JAKOB (Z. Krist., 1929, 69, 403—410, 511—515; Chem. Zentr., 1929, i, 2295).—Analyses are recorded and considered.

A. A. ELDRIDGE.

Chemical relationships of rock-forming pyroxenes and amphiboles to one another and to the matrix. F. ANGEL (Z. Krist., 1929, 69, 455—475; Chem. Zentr., 1929, i, 2296).

Fahl ore. V. V. NIKITIN (Z. Krist., 1929, 69, 482—502; Chem. Zentr., 1929, i, 2296).—The formula (Cu^I₂, Ag₂, Zn, Fe, Hg)₃(As, Sb, Bi)₂S₈ is suggested.

A. A. ELDRIDGE.

Ore-lead and rock-lead and the origin of certain ore deposits. A. HOLMES (Nature, 1929, 124, 477—478).—Although the average lead produced and accumulated in rocks during the earth's geological history cannot have an at. wt. higher than 206.9, the at. wt. of ore-lead never differs significantly from 207.2. Hence no appreciable part of ordinary lead can have been derived from the radioactive elements during their terrestrial history, and the hypothesis that within the earth the proportions of uranium and thorium diminish and become negligible is supported. Rock-lead, being a mixture in approximately equal parts of ore-lead and lead generated within the rocks, should have at. wt. 207.05, a mean value obtained by Piutti and Migliacci (A., 1924, ii, 181, 859) for lead from the Vesuvian sublimate cotunnite.

A. A. ELDRIDGE.

Meteoric stone of Lake Brown, Western Australia. G. T. PRIOR (Min. Mag., 1929, 22, 155—158).—This stone, found in 1919 and weighing 21½ lb., is an intermediate hypersthene-chondrite of the Baroti type. Separate analyses of the magnetic portion and of the unattracted portion (also of the part insoluble in hydrochloric acid) give the bulk composition: Fe 6.10, Ni 1.08, Co 0.06, Fe 3.98, S 2.28, SiO₂ 39.43, TiO₂ 0.35, Al₂O₃ 2.00, Cr₂O₃ 0.18,

Fe_2O_3 3.65, FeO 11.99, MnO 0.25, NiO 0.32, MgO 25.15, CaO 1.88, Na_2O 0.81, K_2O 0.10, $\text{H}_2\text{O}(+110^\circ)$ 0.50, $\text{H}_2\text{O}(-110^\circ)$ 0.08, P_2O_5 0.31, total 100.50. This corresponds approximately with the mineral composition: nickel-iron 7, troilite 6, olivine 36, pyroxene 38, feldspar 8, ferric oxide, water, etc. 5%. The ratio $\text{Fe}:\text{Ni}$ in the nickel-iron is about 5.5 and in conformity with this the ratio $\text{MgO}:\text{FeO}$ in the ferro-magnesian silicates is about 3.5. The composition is very close to that of the Warbreccan (Queensland) stone (A., 1916, ii, 633). L. J. SPENNER.

Analysis of allanite from Hagata-Mura, Iyo Province. Y. MINAMI (Japan. J. Chem., 1929, 4, 1—5).—Analyses of allanite lead to the formula $4\text{R}^{\text{II}}\text{O}, 3\text{R}^{\text{III}}_2\text{O}_3, 6\text{SiO}_2, \text{H}_2\text{O}$, where R^{II} may be Ca, Mn, Fe, and R^{III} Al, Fe, Ce, Y. The arc spectrum and the absorption spectrum of a solution of the rare earths extracted from allanite have been measured. C. W. GIBBY.

Geological age of ishikawaite from Iwaki Province. Y. UZUMASA (Japan. J. Chem., 1929, 4, 11—14).—Ishikawaite from Iwaki contains 0.069% Pb and 19.289% U, whence its age is calculated to be about 3×10^7 years (cf. Sasaki, A., 1927, 225). C. W. GIBBY.

Manganese diaspore and manganophyll from Postmasburg, Griqualand West. K. CHUDOBÄ (Zentr. Min. Geol., 1929, A, 11—18; Chem. Zentr., 1929, i, 1914).—Manganese diaspore, $d^{20} 3.328$, $n_\alpha 1.7023$, $n_\beta 1.7219$, $n_\gamma 1.7502$, having the composition SiO_2 0.11, Al_2O_3 78.58, Fe_2O_3 1.96, Mn_2O_3 4.32, Mo (spectr.), CaO trace, H_2O 14.65%, is described. A. A. ELDRIDGE.

X-Ray study of the domeykite group. L. S. RAMSDELL (Amer. Min., 1929, 14, 188—196).—The copper-arsenic system contains only Cu_3As and copper-arsenic solid solutions. Whitneyite, Cu_3As , is a mixture of algodonite and copper-arsenic solid solution; algodonite, Cu_3As , a definite compound, breaks down at the m. p. into Cu_3As (domeykite) and the solid solution. Near the m. p., domeykite is converted into a form corresponding with the artificial compound. CHEMICAL ABSTRACTS.

Mooreite, a new mineral, and fluoborite from Sterling Hill, N.J. L. H. BAUER and H. BERMAN (Amer. Min., 1929, 14, 165—172).—Mooreite, $7\text{R}(\text{OH})_2, \text{RSO}_4, 4\text{H}_2\text{O}$, where $\text{R}=\text{Mg}:\text{Mn}:\text{Zn}$ (4:1:2), monoclinic, has d 2.470, H 3, α 1.533, β 1.545, γ 1.547. δ -Mooreite, $6\text{R}(\text{OH})_2, \text{RSO}_4, 4\text{H}_2\text{O}$, where $\text{R}=\text{Mg}:\text{Mn}:\text{Zn}$ (5:3:4), granular, has d 2.665, H 3, α 1.570, β 1.584, γ 1.585. Fluoborite, $6\text{MgO}, \text{B}_2\text{O}_3, 3(\text{F}, \text{H}_2\text{O})$, with $\text{H}_2\text{O}:\text{F}=2:3$, hexagonal has d 2.88. CHEMICAL ABSTRACTS.

Loseyite, a new Franklin mineral. L. H. BAUER and H. BERMAN (Amer. Min., 1929, 14, 150—153).—Loseyite, $2\text{RCO}_3, 5\text{R}(\text{OH})_2$, where $\text{R}=\text{Mn}:\text{Zn}:\text{Mg}$ (5:4:1), monoclinic, has d 3.27, H 3, α 1.637, β 1.648, γ 1.676. CHEMICAL ABSTRACTS.

Hydrophilite. C. B. SLAWSON (Amer. Min., 1929, 14, 160—161).—Artificial hydrophilite is probably orthorhombic with pseudo-tetragonal development; α 1.600, β 1.605, γ 1.613 (± 0.003). CHEMICAL ABSTRACTS.

Radioactivity of the coals and anthracites of the Donetz coal basin. E. S. BURKSER, M. J. SCHAPIRO, and K. G. BRONSTEIN (Ukraine Chem. J. [Tech.], 1929, 4, 95—100).—The radioactivity of samples of different Donetz coals and anthracites was measured by determining their ionising activity by means of an Engler-Siebecking apparatus, whilst their α -ray activity was measured by means of an α -ray electroscope. The emanation formation was measured under reduced pressure. The samples were then burnt and the ash was submitted to the same tests; the ash was next fused with sodium or potassium hydroxide, treated with hydrochloric acid, and the acid and alkali solutions were tested for emanation. The potassium content of the ash was determined by Berzelius' method. Anthracites were also examined for their β - and γ -ray activity. Only the upper layers covering the coals and the middle coal layers have a high radioactivity, much higher than that observed by Joly for granites (2.7×10^{-12} g. Ra per g.). Other coals and anthracites have a radium content characteristic of limestones (according to Joly and Fletcher 0.5×10^{-12} g. per g.). A. FREIDMAN.

Organic Chemistry.

Chemical effects of semi-corona discharge in gaseous hydrocarbons. S. C. LIND and G. GLOCKLER (J. Amer. Chem. Soc., 1929, 51, 2811—2822).—Methane, ethane, propane, butane, and ethylene condense to liquid and solid hydrocarbons in the semi-corona discharge (central aluminium rod in pyrex glass cylinder) (cf. A., 1928, 988). With the saturated hydrocarbons condensation is brought about by elimination of hydrogen and some methane; the reactions have the same general character as those produced in the same gases by α -radiation. The liquid products from different hydrocarbons (or from the same hydrocarbon in different tubes) have similar physical properties when obtained at the same trap temperature. The physical properties of these products can be varied by changing the temperatures of the discharge region and traps. H. BURTON.

Action of oxygen atoms on hydrocarbons. P. HARTECK and U. KORSCH (Naturwiss., 1929, 17, 727).—With the exception of methane, which is inert, hydrocarbons react with oxygen atoms, a bluish-violet flame being noticed in the zone of the reaction. The colour is ascribed to CH bands, and the OH bands are also found to be emitted strongly, so that the formation in the flame of the hydroxyl radical is proved. The relative intensities of the CH and OH bands, using benzene and ethylene, exhibit marked differences corresponding with different carbon contents. Carbonic acid is found among the products of the reaction. R. A. MORTON.

Action of high-speed cathode rays on acetylene. J. C. McLENNAN, M. W. PERRIN, and H. J. C. IRETON.—See this vol., 1249.

Use of substituted epidibromohydrins for the preparation of acetylenic hydrocarbons. Δ^7 -Hexene and Δ^7 -hexinene. R. LESPIEAU and WIEMANN (Bull. Soc. chim., 1929, [iv], 45, 627—635).—With bromine at 0° in absence of solvent α -bromo- Δ^8 -pentene (Bouis, A., 1928, 1112) yields, in addition to $\alpha\beta\gamma$ -tribromopentane, m. p. 2.5—3°, d^{20} 2.0682, n_D 1.5583, a little $\alpha\beta\delta$ -tetrabromopentane, m. p. 114°, b. p. 152°/115 mm., and $\alpha\gamma$ -dibromopentane, b. p. 73—75°/14 mm., d^{25} 1.681, n_D 1.509, also obtained by addition of hydrogen bromide to α -bromo- Δ^8 -pentene, a reaction which, together with its b. p., indicates its $\alpha\gamma$ -structure. With zinc dust and alcohol $\alpha\gamma$ -dibromopentane yields a hydrocarbon, b. p. 35.8—36°, d^{20} 0.866, n_D 1.377, either ethyltrimethylene or dimethyltrimethylene. Under atmospheric pressure $\alpha\beta\gamma$ -tribromopentane yields with potassium two fractions, b. p. 72.5—73.5°/13 mm., d^{19} 1.745, n_D 1.53079, and b. p. 75—76°/13 mm., d 1.7475, n_D 1.5329, of Bouis' epidibromohydrin, which from a comparison of its b. p. with that of $\alpha\beta$ -dibromopentane, b. p. 68°/14 mm., and the formation of the bromides $\text{CH}_2\text{Br}\cdot\text{CH}\cdot\text{CHR}$ by the action of phosphorus tribromide on the alcohols $\text{CH}_2\cdot\text{CH}\cdot\text{CHR}\cdot\text{OH}$, is regarded as $\alpha\beta$ -dibromo- Δ^8 -pentene and not $\beta\gamma$ -dibromo- Δ^8 -pentene. The latter, b. p. 56°/11 mm., 1.711, n_D 1.5182, is obtained when $\alpha\beta\gamma$ -tribromopentane is treated with potassium under reduced pressure. Zinc dust and alcohol convert it into ethylallene, b. p. 43—45°, whilst on repeated distillations a fraction, b. p. 72°/11 mm., is always obtained, indicating the progressive isomerisation of the $\beta\gamma$ - into $\alpha\beta$ -dibromo- Δ^8 -pentene. $\beta\gamma$ -Dibromo- Δ^8 -pentene is also obtained by addition of bromine to ethylallene and in smaller amounts from potassium and $\alpha\beta\gamma$ -tribromopentane under normal pressure. With magnesium methyl bromide $\alpha\beta$ -dibromo- Δ^8 -pentene is converted into γ -bromo- Δ^7 -hexene, b. p. 34°/16 mm., d^{21} 1.197, n_D 1.459, yielding with cold bromine in absence of solvent mainly $\beta\gamma\gamma$ -tribromohexane, b. p. 105—106°/9 mm., d^{20} 1.9434, n_D 1.5508, together with $\beta\gamma$ -dibromohexane, b. p. 73—74°/10 mm., d^{20} 1.5995, n_D 1.5042, giving with zinc dust Δ^7 -hexene, b. p. 64°/753 mm., d^{19} 0.6807, n_D 1.394, and a tetrabromohexane, b. p. 151°/12 mm., d 2.225, n_D 1.586. $\beta\gamma\gamma$ -Tribromohexane is converted by sodium ethoxide into $\gamma\delta$ -dibromo- Δ^7 -hexene, b. p. 60—61°/9 mm., d^{20} 1.6128, n_D 1.514, which with zinc dust in alcohol yields Δ^7 -hexinene b. p. 79—80°/770 mm., m. p. —51°, 0.724, n_D 1.4115, together with a fraction, b. p. 65—70°/770 mm., yielding a silver salt, probably γ -methyl- Δ^8 -pentinene, and possibly due to the presence of $\beta\gamma$ -dibromo- Δ^8 -pentene in the $\alpha\beta$ -isomeride. As in the case of the heptinenes and octinenes, the b. p. of the Δ^7 -hexinenes lies between those of the Δ^8 - and Δ^9 -isomerides.

Magnesium ethyl bromide and $\alpha\beta$ -dibromo- Δ^8 -pentene similarly yield propyllallene and δ -bromo- Δ^8 -heptene, b. p. 53.5°/25 mm., 44.5—45°/12 mm., d^{23} 1.1742, n_D 1.463, which with alcoholic potassium hydroxide gives a little γ -ethyl- Δ^8 -pentinene, b. p. 87—88.5°, d^{20} 0.7246, n_D 1.4043 (cf. Prévost, this vol., 46), and, chiefly, Δ^7 -heptinene, b. p. 105—106°, d^{25} 0.7337, n_D 1.415. α -Bromo- Δ^8 -butane with bromine yields $\alpha\beta\gamma$ -tribromobutane, b. p. 101—101.5°/13 mm., m. p. —19°, converted by potassium into $\alpha\beta$ -dibromo-

Δ^8 -butene, b. p. 58.5—59.5°/12 mm., d^{25} 1.88, n_D 1.5392, and $\beta\gamma$ -dibromo- Δ^8 -butene, b. p. 50—52°/17 mm., d^{21} 1.8698, 1.536. The latter, which is also obtained by addition of bromine to methylallene, is slowly transformed into the $\alpha\beta$ -isomeride even at the ordinary temperature.

R. BRIGHTMAN.

Pseudohalogens. IV. Hydrolysis constants of bromotricyanomethane and of chloro-, bromo-, and iodo-trinitromethanes. L. BIRCKENBACH and K. HUTTNER (Ber., 1929, 62, [B], 2065—2075; cf. this vol., 302).—An extension of the nomenclature proposed previously (*loc. cit.*) is advocated to chlorotritromethane etc., which is therefore designated chlorotritromethyl. The chemical properties of chloro-, bromo-, and iodo-trinitromethane are in complete harmony with those of bromotricyanomethane. In chlorotritromethane the trinitromethyl group is the more electronegative component; the decomposition potential of potassium trinitromethyl in 0.1*N*-aqueous solution is about 2.0 volts, thus approximating closely to that of 0.1*N*-potassium chloride. Hydrolysis of the compounds is represented by the equation $K = [\text{H}^+] \times [\text{pseudohal.}] \times [\text{hal.}\cdot\text{OH}] / [\text{hal.}\cdot\text{pseudohal.}]$ and is determined by conductivity measurements. Among halogenotritromethane compounds, the iodo-compound is most completely hydrolysed, thus resembling iodine monochloride. In extent of hydrolysis, bromotricyanomethane shows a similarity to bromine which is not observed with bromotritromethane. In general, the relationships observed during hydrolysis support the similarity of the halogenotritro- and halogenotricyano-methane compounds with the halogens, but exceptions exist, since the chlorine in chlorotritromethane is much less labile than in the chlorine molecule itself.

H. WREN.

Spectrochemistry of aliphatic nitro-compounds. K. VON AUWERS and L. HARRES (Ber., 1929, 62, [B], 2287—2297).—Spectroscopical examination of the compounds CHCl_3 , CCl_4 , CHBr_3 , CBr_4 , $\text{CH}(\text{CO}_2\text{Et})_3$, $(\text{CO}_2\text{Me})_2\text{C}(\text{CO}_2\text{Et})_2$, $\text{C}(\text{CO}_2\text{Et})_4$, and $(\text{CO}_2\text{Et})_3\text{C}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ does not give a perfectly uniform picture, but shows that, in general, accumulation of negative substituents at a carbon atom does not cause marked deviations from the normal spectrochemical behaviour, although small local irregularities are observed. With aliphatic polynitro-compounds, spectrochemistry has not a firm basis. All mononitro-derivatives investigated are spectrochemically normal, but deviations occur as the nitro-groups accumulate, and it is doubtful whether these are due to structural changes or are to be regarded as optical anomalies. On spectrochemical grounds there is no support for the three-ring formula. If it is assumed that, since the spectrochemical behaviour of polynitro-compounds does not correspond with the hypothesis of pure nitro-forms, these compounds must contain groups of another kind, it is probable that the isomerisation of the true nitro-compounds occurs according to a definite general scheme leading either to nitrites or nitrones; the balance of the evidence is in favour of the nitron formulation, since irregularities are observed for the nitrite structure for which there appear to be no adequate reasons. The case of

tetranitromethane is discussed in detail. The following data, amongst others, are recorded: carbon tetrachloride, d_4^{20} 1.5933, n_D^{20} 1.45881; bromoform, d_4^{20} 2.8833, n_D^{20} 1.59632; carbon tetrabromide, d_4^{20} 2.9609, n_D^{20} 1.59998; bromopicrin, d_4^{20} 2.7922, 1.58009; ethyl bromonitromalonate, d_4^{20} 1.4835, n_D^{20} 1.45500; dichlorodinitromethane, d_4^{20} 1.6606, n_D^{20} 1.45871; nitroform, d_4^{20} 1.5967, n_D^{20} 1.44511; trinitroethane, d_4^{20} 1.4223, 1.42005; chlorotrinitromethane, d_4^{20} 1.6810, n_D^{20} 1.45050; bromotrinitromethane, d_4^{20} 2.0443, 1.48175; tetranitromethane, d_4^{20} 1.6377, n_D^{20} 1.43766; ethyl nitroacetate, b. p. 94°/11 mm., d_4^{20} 1.2115, n_D^{20} 1.42692; ethyl acinitroacetate ethyl ether, b. p. 88°/3.5 mm., d_4^{20} 1.1680, n_D^{20} 1.45799. H. WREN.

Thermal decomposition of primary aliphatic alcohols. K. KASHIMA (Bull. Chem. Soc. Japan, 1929, 4, 177—190).—The relative amounts of ethers and olefines produced when methyl, ethyl, propyl, butyl, and amyl alcohols are being dehydrated over Japanese acid clay at 200—400° are recorded. The amounts of ether formed decrease with increase of mol. wt. of the alcohol and also with higher reaction temperatures, being almost zero at 400°. Above 300° almost quantitative decomposition into the olefine takes place. Butyl alcohol gives a mixture of Δ^1 - and Δ^2 -butene, the latter being formed from the former by movement of the double linking under the catalytic influence of the clay. Methyl alcohol gave small amounts of hexamethylbenzene in addition to the main products. From considerations of the heats of formation it is concluded that ethers are first formed and are further decomposed by the action of the catalyst. A. A. GOLDBERG.

Determination of ethyl alcohol by chromic oxidation. L. SEMICHON and M. FLANZY (Ann. Falsif., 1929, 22, 414—415; cf. B., 1929, 449).—Boidin's method is considered to be longer, less sensitive, and to require greater attention to avoid loss of aldehyde than the method recommended by the authors (*loc. cit.*). H. J. DOWDEN.

Configurative relationships of heptan- γ -ol and octan- δ -ol to lactic acid. Effect of unsaturation on optical activity. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, 83, 579—589).— Δ^2 -Octen- δ -ol, from crotonaldehyde and magnesium butyl bromide, has b. p. 78±1.5°/20 mm.; the *l*-carbinol (hydrogen phthalate, $[\alpha]_D^{20}$ -7.7° in alcohol, the resolution being made with cinchonidine) has $[\alpha]_D^{20}$ -3.0° without solvent, and is dextrorotatory in ethereal solution. When reduced with hydrogen and palladium it gave *d*-octan- δ -ol, b. p. 79°/20 mm., $[\alpha]_D^{20}$ +0.27° in alcohol (laevorotatory in ether). With ozone it yielded *d*- α -hydroxyhexaldehyde, b. p. 60—64°/1 mm., $[\alpha]_D^{20}$ +19.9° in alcohol, reduced with sodium amalgam to *d*-hexane- $\alpha\beta$ -diol, b. p. 85—90°/1.5 mm., $[\alpha]_D^{20}$ +5.7° in alcohol (naphthylcarbamate, m. p. 165—168°, $[\alpha]_D^{20}$ -7.1° in acetic acid). Δ^1 -Hepten- γ -ol (hydrogen phthalate, m. p. 66—67°, was resolved with strychnine; from the insoluble salt was obtained the *l*-carbinol, b. p. 65°/20 mm., $[\alpha]_D^{20}$ -22.2° without solvent, which, on reduction, gave *d*-heptan- γ -ol, b. p. 66—67°/20 mm., $[\alpha]_D^{20}$ +6.7° without solvent, n_D^{20} 1.4198, and, with ozone, yielded *l*- α -hydroxyhexalde-

hyde, $[\alpha]_D^{20}$ -28.8° in alcohol. *l*- Δ^1 -Hexen- γ -ol was treated with ozone, and the crude α -hydroxyvaleraldehyde, $[\alpha]_D^{20}$ +23.0°, was reduced to *d*-pentane- $\alpha\beta$ -diol, b. p. 88—90°/2 mm., $[\alpha]_D^{20}$ +16.8° in alcohol (phenylcarbamate, m. p. 108—110°, $[\alpha]_D^{20}$ +16.2° in alcohol). *d*-Octan- δ -ol and *d*-heptan- γ -ol are therefore related to one another and to *l*- α -hydroxy-*n*-hexoic acid; further, *d*-hexan- γ -ol is related to *l*- α -hydroxy-*n*-valeric acid. The optical relationships here observed between corresponding saturated and unsaturated carbinols are in disagreement with those recorded by Kenyon and Snellgrove (A., 1925, i, 771). The effect of introduction of a double linking on the optical activity of a carbinol depends both on its distance from the asymmetric carbon atom and on whether it is situated in the lighter or heavier radical.

C. R. HARRINGTON.

Secondary citronellol [$\beta\zeta$ -dimethyl- Δ^8 -octen- η -ol]. J. DEUVRE (Bull. Soc. chim., 1929, [iv], 45, 710—715).—Magnesium methylheptenyl bromide (this vol., 907) and acetaldehyde yield a fraction, b. p. 119—120°/760 mm., containing a mixture of hydrocarbons, C_8H_{16} and C_8H_{14} (this vol., 1038), a methyl ketone, b. p. 84—87°/13 mm., probably $\beta\zeta$ -dimethyl- Δ^8 -octen- η -one, by reaction of the secondary magnesium derivative, $CMe_2CH[CH_2]_2[CHMe]_2OMgBr$, with excess of aldehyde, and, mainly, secondary citronellol ($\beta\zeta$ -dimethyl- Δ^8 -octen- η -ol), b. p. 101—103°/13 mm., d_4^{20} 0.857, n_D^{20} 1.4570, which on quantitative ozonisation (this vol., 542) affords 7% of formaldehyde, 13% of formic acid, and 78% of acetone, indicating that the *sec*-citronellol is a mixture of 20% of the α (methylenic) form ($\beta\zeta$ -dimethyl- Δ^8 -octen- η -ol) and 78% of the β -form. The original methylheptenyl bromide contained 22% of the α - and 76% of the β -form. Similarly, the *sec*-citronellol, b. p. 106—108°/19 mm., d_4^{20} 0.858, n_D^{20} 1.4557, obtained from natural methylheptenone, by conversion into its glycidic ester, b. p. 143—145°/18 mm., d_4^{20} 0.978, n_D^{20} 1.454 (Verley, A., 1924, i, 865), hydrolysis with alcoholic potassium hydroxide to $\beta\zeta$ -dimethyl- Δ^8 -hepten- η -al (yield 30%), b. p. 80°/19 mm., d_4^{20} 0.853, n_D^{20} 1.4447 (together with products of b. p. above 145°/19 mm.), and condensation of the aldehyde with magnesium methyl iodide (yield 60%), is probably a mixture of the α - and β -forms essentially in the proportion in which they are present in the natural methylheptenone. On dehydrogenation at 250°/15 mm. in presence of reduced copper catalyst, *sec*-citronellol is converted (yield 50%) into *dimethyl- Δ^8 -octen- η -one*, b. p. 87°/13 mm., d_4^{20} 0.851, 1.4461, probably a mixture of the α - and β -forms. *Dimethyl- Δ^8 -nonen- η -ol*, from magnesium methylheptenyl bromide and propaldehyde, has b. p. 114—116°/16 mm., d_4^{20} 0.856, n_D^{20} 1.4543.

R. BRIGHTMAN.

Action of potassium mercuri-iodide in alkaline medium on polyhydric alcohols and related substances. Analytical applications. P. FLEURY and J. MARQUE (J. Pharm. Chim., 1929, [viii], 10, 241—258).—Various polyhydric alcohols, mannitol, dulcitol, inositol, erythritol, glycerol, and glycol, and related polysaccharides, both reducing and non-reducing, dextrose, sucrose, raffinose, stachyose, and glycogen, are oxidised by potassium mercuri-iodide in alkaline solution at 100°, and the effect of con-

centration and time of heating on the course of the reaction has been studied. The amount of oxidation, measured by the quantity of the reagent which is reduced, increases, towards a limit, with increasing concentration of alkali, with increasing concentration of mercuri-iodide if this is also accompanied by a corresponding increase in the volume of sodium hydroxide added, and with time; but after 30–40 min. for a given concentration of mercuri-iodide it is almost independent of time and is fixed at various limits depending on the alkalinity. Under the conditions given below the maximum quantity of oxygen taken up by the polyhydric alcohols studied slightly exceeds 1 atom for each atom of carbon. Similar results are obtained with the polysaccharides, but these are more resistance to attack the greater is their mol. wt. On the other hand, various hydroxy-acids, glycollic, lactic, gluconic, malic, tartaric, saccharic, mucic, citric, and salicylic, are unattacked or only very slightly attacked, the protective influence of the carboxyl group being evident in the greater resistance of dibasic than of monobasic acids. On the basis of these results the method has been applied to the determination of the alcohols mannitol, dulcitol, inositol (anhydrous), and glycol, the iodometric method of Baudouin and Lewin (A., 1927, 476) and of Rupp (A., 1905, ii, 484) being followed, but with the addition of 8–10 c.c. of a 10% aqueous suspension of precipitated barium sulphate. This absorbs the precipitated mercury and keeps it in a fine state of division so that it is readily soluble in the known volume of standard iodine solution which is added. The excess of the latter is titrated, after a few minutes, with standard sodium thiosulphate solution. Under these conditions (described in detail in the original) 10 mg. of the above alcohols are equivalent, respectively, to 7.31, 6.86, 7.34, and 7.15 c.c. of 0.1N-iodine solution.

J. W. BAKER.

Action of hydrogen bromide and bromine on a glycol of the ethylenic series. J. SALKIND and S. SABOJEV (Ber., 1929, 62, [B], 2169–2176; cf. A., 1927, 443).—Treatment of β -dimethyl- Δ^x -hexene- β -diol (β -variety) with saturated, aqueous hydrobromic acid at the atmospheric temperature affords 2 : 2 : 5 : 5-tetramethyl-2 : 5-dihydrofuran, b. p. 102–103°, and a very unstable, liquid dibromide, $C_8H_{14}Br_2$, b. p. 117–120°/18 mm., which is completely resinified in 2–3 days. If the diol is added very gradually to the well-cooled hydrobromic acid and the product is worked up after $\frac{1}{2}$ hr., an isomeric dibromide, m. p. 55–57°, stable in anhydrous ether, but very easily resinified if exposed to air, is obtained. The liquid compound is converted by cold 10% potassium hydroxide into 2 : 2 : 5 : 5-tetramethyl-2 : 5-dihydrofuran, whereas the solid substance regenerates the original glycol. They are regarded as the cis- and trans- β -dibromo- β -dimethyl- Δ^x -hexenes. They add bromine in chloroform solution, giving tetrabromodimethylhexane, m. p. 101°, and unstable γ -tribromo- β -dimethyl- Δ^x -hexene. When the diol is treated with hydrobromic acid at 40–50°, 3-bromo-2 : 2 : 5 : 5-tetramethyltetrahydrofuran, b. p. 115–120°/14 mm., is produced. Addition of the diol to hydrogen bromide in glacial acetic acid leads to the formation of the

stable β -tribromo- β -dimethylhexane, b. p. 135–140°/13 mm., hydrolysed with difficulty to 3-bromo-2 : 2 : 5 : 5-tetramethyltetrahydrofuran (cf. supra), and a product of m. p. 52–55°. Tetramethyldihydrofuran is transformed by bromine in chloroform into 3 : 4-dibromo-2 : 2 : 5 : 5-tetramethyltetrahydrofuran, b. p. 100–101°/15 mm., m. p. 32–33°. Tetramethylbutenediol and bromine in ether afford γ -dibromo- β -dimethylhexane- β -diol, m. p. 98.5–99.5°, and a heavy oil which could not be purified, but passes when treated with steam into a resin and 3 : 4-dibromo-2 : 2 : 5 : 5-tetramethyltetrahydrofuran. The dibromo-glycol is hydrolysed by potassium carbonate to the dioxide, $\left(\begin{smallmatrix} \text{CMe}_2 \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{CH}_2 \right)_2$,

b. p. 73–74°/20 mm., 172–173°/atm. press., d_4^{20} 0.9506, n_D^{20} 1.42632, converted by hot water into β -dimethylhexane- β - γ -tetraol, m. p. 153–154°, and by hydrobromic acid into β -dibromo- β -dimethylhexane- γ -diol, m. p. 119–120°. H. WREN.

Action of chlorosulphonic acid on aldehydes. K. FUCHS and E. E. KATSCHER (Ber., 1929, 62, [B], 2381–2386; cf. A., 1928, 43).—Acetaldehyde and paracetaldehyde react vigorously with chlorosulphonic acid, yielding dark products which are soluble in water and not analogous to those derived from formaldehyde. Trichloroacetaldehyde yields up to 65% of octachlorodiethyl ether, $(CCl_3 \cdot CHCl)_2O$, b. p. 130–131°/11 mm., m. p. 47°, which separates when the reaction mixture is cooled to –50°; hydrogen chloride and traces of carbonyl chloride are evolved. The filtrate from the ether yields chloralide, m. p. 114–115°, after long preservation. Tetrachloroethyl hydrogen sulphate appears to be the primary product of the action, since water-soluble compounds are initially obtained which are hydrolysed to chloral hydrate, sulphuric and hydrochloric acids. Similar results are obtained with metachloral and chloral hydrate. Fluorosulphonic acid and polymeric formaldehyde even at 90° yield compounds soluble in water and possibly containing fluoromethyl alcohol. Chloral and fluorosulphonic acid afford octachlorodiethyl ether in 20–25% yield.

Octachlorodiethyl ether reacts with aromatic and aliphatic Grignard reagents, but the isolation thereby of α -alkylated or -arylated hexachlorodiethyl ethers has not been effected. H. WREN.

Highly-polymerised compounds. XX. Polyethylene oxides. H. STAUDINGER and O. SCHWEITZER (Ber., 1929, 62, [B], 2395–2405).—Polymerisation of ethylene oxide in the presence of tertiary amines, alkali metals, or stannic chloride gives ether-like compounds, $[\text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}]_n$. Polymerisation occurs somewhat irregularly and is sometimes autocatalytically accelerated so as to give rise to violent explosions, thus indicating a possible danger in the technical use of ethylene oxide compressed in steel flasks. Sunlight, ultra-violet light, and Florida earth do not induce the change. Gaseous ethylene oxide and stannic chloride vapour give a solid polymeride and dioxan.

The polyethylene oxides are more stable than the polyoxymethylenes, but are decomposed above 300°, not into monomeric ethylene oxide, but into unsatur-

ated products of higher b. p. and readily volatile materials containing acetaldehyde and acraldehyde. They dissolve readily in water, alcohol, benzene, and chloroform, but not in light petroleum or ether.

The polyethylene oxides can be separated by addition of ether to the benzene solution into a series of polymeric homologues, the m. p. and viscosity in water and benzene of the individual fractions increasing with increase in mean mol. wt. The relative viscosity is greater in water than in benzene, so that the viscosity of solutions of highly polymerised compounds depends, not only on the length of the molecules, but also on the solvent.

When cooled, the molten polyethylene oxides crystallise, the process commencing at individual nuclei and spreading concentrically in all directions. The operation thus resembles that in paraffin wax. The polyethylene oxides, like the polyoxymethylenes and the paraffins, are rontgenographically well crystallised. It is therefore established that the power to crystallise is not confined to completely homogeneous substances, but is also possible with molecules of unequal length but similar mode of structure. The crystallisation of cellulose derivatives, for example cellulose acetates, is not a proof that the product is composed of small, homogeneous molecules, but thread molecules of cellulose acetates can separate from a solution in such a manner that lattice-like arrangement of the molecules results. Similarly, the crystallisation of caoutchouc is not evidence of its structure from uniform, small fundamental molecules.

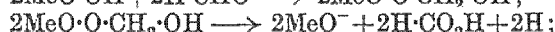
H. WREN.

Determination of organic peroxides. S. MARKS and R. S. MORRELL (*Analyst*, 1929, 54, 503—508).—A quantitative result is obtained by adding potassium iodide (2 c.c. of concentrated solution or 2 g. of powder) to 0.2 g. of the peroxide dissolved in 25 c.c. of glacial acetic acid, and after a few minutes, diluting with about 100 c.c. of water and titrating with 0.1*N*-sodium thiosulphate solution. The result of a blank test is deducted. The method is applicable to straight-chain compounds. In the case of oxidised oils 1 g. is dissolved in 25 c.c. of acetic acid, and 1 c.c. of 50% sulphuric acid and 2 c.c. of cold saturated potassium iodide solution are added; after keeping in the dark for 24 hrs. in a closed vessel the mixture is diluted and titrated as before, a benzoyl peroxide control and two blanks being made.

D. G. HEWER.

Alkyl peroxides. III. Methyl hydrogen peroxide. A. RIECHE and F. HIRTZ (*Ber.*, 1929, 62, [B], 2458—2474; cf. A., 1928, 734; this vol., 292).—Dilute solutions of methyl hydrogen peroxide may be prepared by the action of methyl sulphate and potassium hydroxide on 10% hydrogen peroxide followed by distillation of the acidified solution. For the preparation of the homogeneous compound, b. p. 38—40°/65 mm., d_4^{15} 0.9967, n_D^{15} 1.36408, the aqueous distillate is exhaustively extracted with ether and the extract is dried for a protracted period over anhydrous copper sulphate and distilled over sodium sulphate. Methyl hydrogen peroxide is a colourless liquid with an intensely unpleasant odour. It explodes violently when heated, and is very sensitive to shock when hot.

The oxidising action of methyl hydrogen peroxide exceeds that of the dialkyl peroxides, but is inferior to that of hydrogen peroxide. With hydrogen iodide reaction is complete only after some hours, and does not lead to the quantitative production of methyl alcohol. It reacts rapidly but incompletely with titanium trichloride or sulphurous acid. It does not react with acid permanganate. With excess of hot, strongly alkaline permanganate the peroxide is completely transformed into carbon dioxide and the residual permanganate can be titrated, but elementary analysis is the most certain criterion of homogeneity. In freezing benzene the peroxide is associated, but normal values for the mol. wt. are obtained in water. Aqueous solutions freely dissolve barium and calcium hydroxides, giving readily soluble salts. In alkaline solution, methyl hydrogen peroxide vigorously evolves hydrogen mixed with a little oxygen and leaves mainly formate. Since the change is greatly accelerated by addition of formaldehyde, monohydroxydimethyl peroxide, $\text{MeO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{OH}$, is regarded as an intermediate product, and since hydrogen is liberated in the atomic state, the change is represented by the scheme: $2\text{MeO} \cdot \text{OH} \longrightarrow 2\text{H} \cdot \text{CHO} + 2\text{H}_2\text{O}$;



$2\text{MeO}^- \longrightarrow \text{MeOH} + \text{H} \cdot \text{CHO} \xrightarrow{+\text{MeO} \cdot \text{OH}} \text{MeO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{OH}$, etc. Ethyl hydrogen peroxide decomposes when warmed in alkaline solution, evolving very little hydrogen. After addition of formaldehyde to the concentrated solution almost explosive evolution of hydrogen is observed. Ethyl alcohol is formed in rather more than the calculated amount, and the production of acetaldehyde is betrayed by the brown colour of the solution; the presence of acetic acid can be detected. In presence of spongy platinum methyl hydrogen peroxide decomposes vigorously, mainly into carbon dioxide and methyl alcohol; formaldehyde and formic acid are produced in minor amount. Methylene-blue is decolorised by methyl hydrogen peroxide in alkaline solution in presence or absence of formaldehyde. Dinaphthylene dioxide 4:4'-quinone is reduced by methyl or ethyl hydrogen peroxide, alkali, and formaldehyde, but not by methyl hydrogen peroxide and alkali. Indigotin and anthraquinone are not reduced by methyl hydrogen peroxide and formaldehyde, although ethyl hydrogen peroxide reacts with anthraquinone in presence of formaldehyde and alkali. In very weakly alkaline solution at the ordinary temperature leucomethylene-blue immediately becomes coloured by methyl or ethyl hydrogen peroxide in presence or absence of formaldehyde; the last-named compound does not function as activator. If an alkaline solution of potassium ferricyanide is added to an ethereal solution of methyl hydrogen peroxide, potassium ferrocyanide is formed and a peroxide can be extracted from the aqueous solution, which contains nearly the whole of the active oxygen originally present in the methyl hydrogen peroxide.

Monohydroxydimethyl peroxide, which does not boil below 50°/20 mm., is a colourless, fairly mobile liquid of unpleasant odour which explodes violently when heated. It is associated in benzene. It evolves

hydrogen when treated with alkali at the ordinary temperature.

Ethyl hydrogen peroxide, b. p. 41–42°/55 mm., d_4^{25} 0.955, n_D^{20} 1.3833, is obtained analogously to methyl hydrogen peroxide. Constancy of d and n are the most trustworthy criteria of homogeneity, since the determinations with titanium trichloride or iodometrically are untrustworthy and combustion in a stream of nitrogen gives results about 1.7% low for carbon.

H. WREN.

β -Chloroethyl carbonate and sulphate. V. NEKRASSOV and J. F. KOMISSAROV (J. pr. Chem., 1929, [ii], 123, 160–168).—Treatment of anhydrous ethylene chlorohydrin with carbonyl chloride at 0° affords β -chloroethyl chloroformate (I), b. p. 152.5°/752 mm., d_4^{25} 1.3825, n_D^{20} 1.4465, also obtained in presence of water and calcium carbonate. When I is treated with ethylene chlorohydrin at 130–150° β -chloroethyl carbonate, b. p. 240–241°, 115°/8 mm., m. p. 8–5°, d_4^{25} 1.3506, n_D^{20} 1.4610, is obtained. The same ester is formed by the action of ethylene chlorohydrin on trichloromethyl chloroformate (II), and also when I is boiled with β -chloroethyl nitrite (III). Carbonyl chloride and III at 65° yield I, whilst II and III give I and a small amount of the carbonate.

Ethylene chlorohydrin and sulphuryl chloride at 165° afford β -chloroethyl sulphate, b. p. 150–152°/7 mm., m. p. 11°, d_4^{25} 1.4801, n_D^{20} 1.4622, also formed from sulphuryl chloride and III. Appreciable amounts of di- β -chloroethyl ether are formed during these reactions.

H. BURTON.

Synthesis of mixed fatty and amino-acid glycerides. M. WEIZMANN, L. HASKELBERG, and S. MALKOWA (Z. physiol. Chem., 1929, 184, 241–245).—*Allylphthalimide*, m. p. 65–65.5°, is brominated in chloroform solution to $\beta\gamma$ -dibromopropylphthalimide, m. p. 107–108°, which is hydrolysed by 48% hydrobromic acid to $\beta\gamma$ -dibromo- α -aminopropane hydrobromide, m. p. 164°. Resolution of the base and successive conversion into the d -dibromohydrin and epibromohydrin is effected by Abderhalden and Eichwald's method (A., 1914, i, 801). d -Glycerol α -monobromohydrin (obtained by hydrolysis of the epibromohydrin with cold hydrochloric acid) gives with palmityl chloride in presence of pyridine and chloroform the 1- $\beta\gamma$ -dipalmitate, m. p. 62–63°, [α] –32.5° in 95% alcohol. An inactive α -leucyl- $\beta\gamma$ -dipalmitylglyceride, m. p. 216°, is obtained in 32% yield when the dry sodium salt of leucine is heated with the d -dipalmitate at 150–160°. H. BURTON.

Conversion of alkyl sulphites into chlorosulphonates and normal sulphates. R. LEVAILLANT (Compt. rend., 1929, 189, 465–467).—Chlorine acts on alkyl sulphites, in a freezing mixture, to give good yields of the corresponding alkyl chlorosulphonate: $R_2SO_3 + Cl_2 \rightarrow RCl + RO \cdot SO_2Cl$, and thus are prepared methyl (90% yield), ethyl (87%), and n -propyl chlorosulphonates. By the action of thionyl chloride on ethylene chlorohydrin first at 0° and finally at 100°, a 75% yield of β -chloroethyl sulphite, b. p. 133°/12 mm., d_4^{25} 1.422, 1.481, is obtained, similarly converted by the action of chlorine into β -chloroethyl chlorosulphonate, b. p. 92°/14.5 mm., d_4^{25} 1.580, n_D^{20} 1.4578, in 87% yield. By the action of

alkyl sulphites on alkyl chlorosulphonates at 120–190°, alkyl sulphates are obtained: $RO \cdot SO_2Cl + R_2SO_3 \rightarrow RCl + SO_2 + R_2SO_4$, and hence these are the main products of the action of chlorine on alkyl sulphites at 120–140°.

J. W. BAKER.

Interaction of alkyl sulphides and mercury salts. W. F. FARAGHER, J. C. MORRELL, and S. COMAY (J. Amer. Chem. Soc., 1929, 51, 2774–2781).—When finely-divided mercurous nitrate (or its aqueous solution) is treated with methyl, ethyl, n -propyl, n - and *iso*-butyl, and *iso*amyl sulphides, mercury is precipitated and the additive compound $R_2S \cdot Hg(NO_3)_2$ formed. Mercurous chloride is not acted on except by methyl sulphide in presence of water. With mercurous acetate and the above sulphides mercury is formed in presence of water; methyl sulphide causes precipitation in absence of water. Mercury is formed from mercurous sulphate or iodide and the above sulphides even in absence of water. The compound $Et_2S \cdot Hg(NO_3)_2$ has m. p. 63°. Thiophen reacts with mercurous nitrate only in presence of water. Each of the above sulphides furnishes two of the three following types of mercuric chloride additive compounds: $(R_2S)_2 \cdot HgCl_2$, $R_2S \cdot HgCl_2$, and $R_2S \cdot 2HgCl_2$. The following are described: $Et_2S \cdot HgCl_2$, m. p. 76.5–77°; $Et_2S \cdot 2HgCl_2$, m. p. 119–119.5°; $Pr^i_2S \cdot HgCl_2$ (I), m. p. 87.5–88°; $Pr^i_2S \cdot 2HgCl_2$ (II), m. p. 121–122°; $Bu^i_2S \cdot HgCl_2$ (III), m. p. 116°; $Bu^i_2S \cdot 2HgCl_2$ (IV), m. p. 131°; $Bu^i_2S \cdot 2HgCl_2$, m. p. 112–113°; $(Bu^i_2S)_2 \cdot HgCl_2$, an oil; $(iso-C_5H_{11})_2S \cdot 2HgCl_2$, and $[(iso-C_5H_{11})_2S]_2 \cdot HgCl_2$, an oil. Various factors (molecular proportions, crystallisation solvent) decide the type formed and the various discrepancies in m. p. recorded in the literature are readily explained. The interconversions I, II and III, IV are brought about by crystallisation. The additive compounds from the sulphides and mercuric salts of oxy-acids are soluble in water.

H. BURTON.

Action of chloropicrin on mercaptans. V. NEKRASSOV and N. N. MELNIKOV (Ber., 1929, 62, [B], 2091–2094; cf. Ray and others, J.C.S., 1919, 115, 1308; 1922, 121, 323).—Chloropicrin behaves as an oxidising agent towards the simple mercaptans, thus converting potassium ethyl sulphide into ethyl disulphide, b. p. 151.5–153°/745 mm., d_4^{25} 1.9982, n_D^{20} 1.5030, potassium phenyl sulphide into phenyl disulphide, m. p. 60°, and potassium p -tolyl sulphide into p -tolyl disulphide, m. p. 46°. Reaction is accompanied by considerable evolution of gas, mainly carbon dioxide and nitrogen with smaller, approximately equal, quantities of nitric oxide and carbon monoxide, thus indicating the following changes: $2(SR)_3C \cdot NO_2 = 3RS \cdot SR + 2CO_2 + N_2$ (and $+2CO + 2NO$). The production of phenyl disulphide from potassium phenyl sulphide and chloropicrin in aqueous solution is a very sensitive test for the nitrohalide. Chloropicrin reacts very slowly with free mercaptans.

H. WREN.

β - n -Butyl sulphide. O. HINSBERG (Ber., 1929, 62, [B], 2166–2168; cf. this vol., 310).— n -Butyl sulphide (now termed " α -variety") is slowly converted by warm 70% perchloric acid into β - n -butyl sulphide perchlorate, $[Bu_2S]_2 \cdot HClO_4 \cdot H_2O$, decomposed

by potassium hydroxide or potassium acetate into β -*n*-butyl sulphide, b. p. 190—230° (slight decomp.). Physically, it closely resembles the α -sulphide, from which it is distinguished by its immediate conversion by perchloric acid into the perchlorate described above and by yielding a yellow solution in concentrated sulphuric acid, in which the α -variety is colourless. Oxidation of either sulphide by hydrogen peroxide affords α -*n*-butyl sulphone, m. p. 44°.

H. WREN.

Diethyl triselenide, sulphodiselenide, and disulphoselenide. G. R. LEVI and A. BARONI (Atti R. Accad. Lincei, 1929, [vi], 9, 1019—1024; cf. this vol., 1039).—*Diethyl triselenide*, Et_2Se_3 , b. p. 100°/26 mm., d_4^{25} 1.7805, n_D^{25} 1.60919, is formed by the action of selenium oxychloride on selenomercaptan or by that of selenium on diethyl diselenide; *diethyl sulphodiselenide*, Et_2SSe_2 , b. p. 98°/26 mm., d_4^{25} 1.7070, n_D^{25} 1.60244, by the action of selenomercaptan on thionyl chloride or that of sulphur on the diselenide; and *diethyl disulphoselenide*, $\text{Et}_2\text{S}_2\text{Se}$, b. p. 94°/26 mm., d_4^{25} 1.4094, n_D^{25} 1.57914, from either mercaptan and selenium oxychloride, or mercaptan and selenium chloride, or diethyl disulphide and selenium.

T. H. POPE.

Preparation of fatty acids from their higher homologues. F. ROCHUSSEN (Ber. Schimmel, 1929, 179—186).— α -Halogeno-fatty acids (or their esters) may be degraded directly to saturated fatty acids containing two atoms of carbon less by fusion with potassium hydroxide. After the first vigorous reaction is over the mixture is heated to 300—350° until gas evolution ceases. Acids containing C_{n-1} and C_{n-3} are sometimes obtained as by-products, the quantity of the former produced increasing as the series of fatty acids is descended and depending on the period of heating. Their formation is explained

by the scheme $2\text{CHRBr}\cdot\text{CO}_2\text{K} \xrightarrow{-2\text{KBr}} \text{O} \begin{array}{c} \text{CHR}\cdot\text{CO} \\ \text{CO}\cdot\text{CHR} \end{array} \text{O} \xrightarrow{-2\text{O}} 2\text{R}\cdot\text{CHO} \xrightarrow{2\text{KOH}} 2\text{R}\cdot\text{CO}_2\text{K} + \text{H}_2$. Thus ethyl α -bromomyristate gives a 77% yield of lauric acid. Ethyl α -bromolaurate is similarly degraded (72% total yield) to equal quantities of decoic and undecic acids, whilst the α -chloro-ester gives (72.8%) a mixture containing 34.5 and 65.5%, respectively, of these two acids. Only poor yields are obtained when free α -bromolauric acid is used. Methyl α -chloro-undecate gives a mixture (69.7%) containing octoic (23.7), nonoic (35.3), and decoic (41%) acids. Ethyl α -bromo-octate gives (80.4%) a mixture of hexoic (29.7) and heptoic (70.3%) acids when heating is continued for 1.5 hrs. at 340—350°, but with short heating the proportion of the products is 15.6 and 84.4%, respectively (total yield 84.4%).

J. W. BAKER.

Catalytic action of cupric salts in promoting oxidation of fatty acids by hydrogen peroxide. M. A. BATTIE and I. SMEDLEY-MACLEAN (Biochem. J., 1929, 23, 593—599).—Oleic acid is sometimes but not always rapidly attacked by hydrogen peroxide in the presence of ferrous iron with the formation of carbonic, formic, acetic, and succinic acids. The addition of small amounts of nickel, manganese, or zinc does not influence the reaction, but that of copper salts does. The addition of cupric salts to succinic acid catalyses

the degradation of the acid in acid but not in alkaline solution. After the mixture has been kept for $\frac{1}{2}$ hr. at 60° about 75% of the succinic acid has been decomposed into carbon dioxide, formic acid, and acetic acids. Neither in acid nor in alkaline media did ferrous salts influence the oxidation of succinic acid, whilst cupric chloride, cuprous chloride, or cupric sulphate did. Cuprous salts are more effective in decomposing hydrogen peroxide, but cupric salts are more active in catalysing the oxidation of the aliphatic acids by hydrogen peroxide. The effect of the above oxidising agent on some acids which might possibly occur as oxidation products of succinic acid was investigated. Dihydroxymaleic acid is much less readily oxidised to carbon dioxide than is tartaric acid, although the former acid is the first product of oxidation when the latter is oxidised by means of hydrogen peroxide in the presence of ferrous iron. Pyruvic and dihydroxymaleic acids were oxidised by hydrogen peroxide in the absence of the cupric salt. Alcohol, acetone, and glycol were not oxidised by the above reagents.

S. S. ZILVA.

Organic molecular compounds with co-ordination centres. II. Co-ordination numbers of alkyl esters of fatty acids in cholic acids.—See this vol., 1293.

Preparation of acid chlorides. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1929, 9, 523—531).—Yields of 80—90% of acid chlorides are obtained by the reaction $\text{R}\cdot\text{CCl}_3 + \text{R}'\cdot\text{CO}_2\text{H} \rightarrow \text{R}\cdot\text{COCl} + \text{R}'\cdot\text{COCl} + \text{HCl}$, where R represents an aromatic and R' an aliphatic radical. The reaction proceeds at 70—80°, and is catalysed by zinc chloride. Aliphatic acid anhydrides may also be used in place of acids.

R. TRUSZKOWSKI.

Differing behaviour of α - and β -chlorobutyric acids during catalytic hydrogenation. C. PAAL and H. SCHIEDEWITZ (Ber., 1929, 62, [B], 1935—1939; cf. A., 1927, 646).—*r*- α -Chloro- and *r*- β -chlorobutyric acids in alcoholic solution are only slightly attacked by hydrogen in the presence of palladised barium sulphate and reaction soon ceases owing to the liberated hydrogen chloride. Under similar conditions, calcium α -chlorobutyrate (+2H₂O) is almost quantitatively transformed into calcium butyrate, whereas with the generally more unstable calcium β -chlorobutyrate very little hydrogen is absorbed. Silver α -chlorobutyrate and the unstable silver β -chlorobutyrate are incidentally described.

H. WREN.

Modes of addition to conjugated unsaturated systems. II. Reduction of conjugated unsaturated acids by metals dissolving in aqueous media. H. BURTON and C. K. INGOLD (J.C.S., 1929, 2022—2037; cf. A., 1928, 634).—A study has been made of the reduction products of vinylacrylic, sorbic, β -methylsorbic, and $\beta\delta$ -dimethylsorbic acids, dealing with the relative proportions of the 1:2- and 1:4-dihydro-isomerides produced in each case. Three cases of conjugative addition are discussed: (a) in which both parts are stable as anions, (b) in which one part is stable as an anion and the other as a cation, (c) in which both parts are stable as cations. The experimental work relates to the last case.

It is assumed that the reduction takes place in three

stages: (i) the unsaturated molecule, polarised in the electric field at the surface of the metal, extracts a proton from the aqueous solution; this proton becomes attached to that atom (C_α) which most readily tolerates the negative polarisation charge developed

prior to co-ordination $C_\beta \rightleftharpoons C_\alpha \rightarrow X + H^+$ —

$C_\beta-CH-X$; (ii) the cation possesses an electron sextet at C_β and its electron affinity exerted in the region of the metallic surface locally breaks down, the electrostatic potential barrier inhibiting the escape of the metallic electrons. The successive absorption of the two electrons necessary to complete the octet converts the cation into an anion, $C_\beta^{\ominus}-C_\alpha H-X$. (iii) The anion extracts a second proton from the solution, giving $C_\beta H \cdot C_\alpha H \cdot X$. The theory shows that in the cases investigated 1:2 and 1:4 reduction products should be formed, and the proportion in which these appear will depend on the distribution of the charge in the electromeric anion, as determined by the relative degrees of electron absorption of the groups terminating the system. The results obtained are in general agreement with the theory given.

New methods are given for the preparation of vinyl-acrylic, β -methylsorbic, and β -methyl- Δ^7 -hexenoic acids.

J. W. PORTER.

Lower olefinic acids. I. n -Hexenoic acids. E. N. ECCOTT and R. P. LINSTAD (J.C.S., 1929, 2153—2165).—"Hydrosorbic acid" (the acid mixture obtained by the reduction of sorbic acid) is shown to contain $\beta\gamma$ - and $\gamma\delta$ -hexenoic acids; these have also been prepared synthetically.

A mixture of $\alpha\beta$ - and $\beta\gamma$ -hexenoic acids was prepared by equilibration of Δ^6 -hexenoic acid by means of 40% potassium hydroxide at 100°. The mixture of the isomerides when distilled under reduced pressure, and the distillate cooled in ice, yields a liquid richer in the $\beta\gamma$ -isomeride, which is completely freed from the $\alpha\beta$ -isomeride by repeated controlled esterifications with cold alcoholic hydrogen chloride. The $\beta\gamma$ -isomeride (purity determined by iodometric analysis) had b. p. 105°/13 mm., m. p. 4—5°, d_4^{25} 0.9626, n_D^{25} 1.4397 (anilide, m. p. 75°).

The $\gamma\delta$ -isomeride was synthesised from crotonaldehyde, which was reduced to the alcohol, and this converted into the bromide, which by the action of ethyl malonate furnished ethyl Δ^8 -butenylmalonate. The corresponding acid when heated at 140° is converted into $\gamma\delta$ -hexenoic acid. This synthesis leaves no doubt of the position of the double linking, and gives a pure product, which is shown to be the β -form of Δ^7 - n -hexenoic acid, b. p. 111—112°/20 mm., d_4^{25} 0.9584, n_D^{25} 1.4367. This differs from the α -form described by Fichter (A., 1904, i, 547) in b. p., density, and refractivity, but gives a similar anilide, toluidide, and cadmium salt.

J. W. PORTER.

Mechanism of the degradation of fatty acids by mould fungi. III. H. B. STENT, V. SUBRAMANIAM, and T. K. WALKER (J.C.S., 1929, 1987—1993; cf. A., 1928, 804).—Acetone is one of the products of the growth of *Aspergillus niger* in calcium n -butyrate solution. The non-volatile products consist of succinic acid which is further degraded to a mixture

of *dl*- and *l*-malic acids. When the mould is grown in *dl*-malic acid, the *l*-acid is converted into fumaric acid, thus rendering the solution dextrorotatory. It is postulated that the acetone is produced from n -butyric acid by β -oxidation, and that the acetone is oxidised to succinic acid by a process comparable with the production of the latter from acetone by the action of hydrogen peroxide.

J. W. PORTER.

Acidity measurements of the higher fatty acids by the iodometric method. W. RUCZKA (J. pr. Chem., 1929, [ii], 123, 61—73).—Koltzoff's method for determining the acidity of weak acids can be employed in the case of the higher fatty acids, using emulsions of these. It is necessary to use an initial excess of thiosulphate, and to keep the experimental conditions constant; the values so obtained are inversely proportional to the number of carbon atoms present, but are independent of the degree of unsaturation. Acids containing hydroxyl groups yield higher values, dependent on the number of such groups present.

H. F. HARWOOD.

Separation of glycerides. VI. Linseed oil, soya-bean oil, and whale oil. VII. Herring oil. VIII. Cod-oil. IX. Sardine oil. X. Sand-eel oil. XI. Oil from *Theragra chalcogramma*. XII. Cuttle-fish oil. XIII. Red salmon oil. XIV. Shark-liver oil. B. SUZUKI. XV. Two new fatty acids from fish oils. B. SUZUKI and Y. YOKOYAMA (Proc. Imp. Acad. Tokyo, 1929, 5, 265—271, 272—273).—VI. Bromination in light petroleum and separation of the soluble bromo-glycerides by fractional precipitation with alcoholic calcium chloride solutions of increasing concentration affords the following bromides in addition to those previously described (A., 1928, 152, 736). Linseed oil: bromides of *linoleo-diolein* (I), f. p. 5°, of an isomeric *linoleo-diolein*, f. p. —2°, *stearo-linoleo-olein* (II), f. p. —4°, and of *stearo-linolen-olein*, f. p. —7°; soya-bean oil: I, and *oleo-dilinolenin bromide*, f. p. 6°; whale oil: bromides of *stearo-dizoomarin*, f. p. 1°, *stearo-linoleo-zoomarin*, f. p. —3°, *stearo-linolen-zoomarin* (III), f. p. —6°, and of *palmito-stearidono-gadolein*, f. p. —3°, and a substance (IV), f. p. —4°, which is either *tri-erucen* or *tricitolein bromide*.

VII. Bromination of herring oil by the method previously described (A., 1928, 152) gives *zoomaro-stearidono-arachidonin bromide*, m. p. 148°, *zoomaro-arachidon-chupanodonin bromide*, m. p. 150° (decomp.), *gadoleo-diarachidonin bromide*, m. p. 180°, and two compounds derived from a new acid, $C_{22}H_{36}O_2$ (see below), *gadoleo- $C_{22}H_{35}O$ -linolenin bromide*, m. p. 104°, and *zoomaro- $C_{22}H_{35}O$ -stearidonin bromide*, m. p. 150°; *linoleo-digadolein bromide* (VI), m. p. 6°, *linoleo-dizoomarin bromide* (V), m. p. 2°, III, *dieruco- or dicetoleo-gadolein bromide*, m. p. 5°, and IV, are also obtained by the precipitation method described above.

VIII. The oil is a mixture of oils from various organs other than the liver of cod. The following are obtained: *zoomaro-linolen-chupanodonin bromide*, m. p. 131°, *zoomaro-linoleo-arachidonin bromide*, m. p. 255° (decomp.), V, *linolen-dizoomarin bromide*, m. p. —2°, *stearidono-dizoomarin bromide*, m. p. —4°, and *dieruco- or dicetoleo-stearin bromide*, m. p. —7°.

IX. By application of the foregoing methods,

sardine oil affords the following, some of which are derived from the new acids $C_{18}H_{28}O_2$ and $C_{22}H_{36}O_2$ (see later): bromides of *di*- $C_{22}H_{36}O$ -*arachidonin*, m. p. 85° , of *zoomaro*- $C_{22}H_{36}O$ -*stearidonin*, m. p. 120° , of *di*- $C_{18}H_{27}O$ -*arachidonin* (VII), m. p. 110° , of *stearidono*- $C_{18}H_{27}O$ -*zoomarin*, m. p. 135° , of *tri**arachidonin* (VIII), m. p. 205° (decomp.), of *triolein*, m. p. 6° , VI, of *dieruceo*- or *dicetoleo*-olein, m. p. -2° , II, and of *dieruceo*- or *dicetoleo*-*arachidonin*, m. p. -3° .

X. Sand-eel oil yields the following: IV, V, VII, bromides of *di*- $C_{18}H_{27}O$ -*clupanodonin*, m. p. 124° , of *linoleo*- $C_{18}H_{27}O$ -*arachidonin*, m. p. 153° , of *arachidono*- $C_{18}H_{27}O$ -*clupanodonin*, m. p. 230° , of *dieruceo*- or *dicetoleo*-*clupanodonin*, of *dilinoleo*-*zoomarin*, of *dioleo*-*zoomarin*, and of *palmito*-*zoomarin*.

XI. The oil yields the bromides of *diclupanodono*-*arachidonin*, m. p. 95° , of *stearidono*-*diclupanodonin*, m. p. 125° , of *diclupanodono*-*linolenin*, m. p. 165° (decomp.), VIII, of *arachidono*-*dizoomarin*, and of *zoomaro*-*linoleo*-*stearin*.

XII. The oil affords VIII, the bromides of $(C_{18}H_{27}O)_3$, m. p. 74° , of $(C_{18}H_{27}O)_2$ -*linolenin*, m. p. 81° , of $C_{18}H_{27}O$ -*distearidonin*, m. p. 125° , of *linoleo*-*dizoomarin*, and of *trizoomarin* (IX).

XIII. Red salmon oil yields the bromides IV, V, IX, and *dilinoleo*-*arachidonin*, m. p. 103° , and *linoleo*-*diarachidonin*, m. p. 115° , bromides.

XIV. Shark-liver oil yields the bromides VIII, IX, and those of *arachidono*-*diclupanodonin*, m. p. 110° (cf. above), *clupanodono*-*diarachidonin*, m. p. 140° and 112° , *clupanodono*-*arachidono*-*linolenin*, m. p. 117° , *digadoleo*-*linolenin*, *dizoomaro*-*linolenin*, *palmito*-*diolein*, and of *triolein*.

XV. The acid $C_{22}H_{36}O_2$, obtained as the octabromide, m. p. 96° , by hydrolysis of the bromoglyceride (cf. above) with 20% hydrochloric acid, by debromination in acetic acid suspension with zinc dust and catalytic hydrogenation of the product with platinum-black in amyl-alcoholic solution furnishes behenic acid. The acid, $C_{18}H_{28}O_2$, isolated as the octabromide, m. p. 104 – 105° , isomeric with stearidonic acid octabromide, m. p. 200° (decomp.), by debromination and hydrogenation in a similar manner yields stearic acid, and is probably an isomeride of stearidonic acid. C. W. SHOPPEE.

Preparation of α -ketonic acids. V. TSCHELIN-CEV and W. SCHMIDT (Ber., 1929, 62, [B], 2210–2214).—Acyl cyanides are obtained in 58–80% yield by heating a mixture of 1 mol. of acyl bromide with 1 mol. of cuprous cyanide on the water-bath for $1\frac{1}{2}$ –2 hrs. and distilling the cyanide. The following compounds have been prepared: acetyl cyanide, b. p. 93° , d^{20}_D 0.9745, n^{20}_D 1.3743, and thence pyruvic acid in 73.2% yield by hydrolysis with concentrated hydrochloric acid; propionyl cyanide, b. p. 108 – 110° , n^{20}_D 1.3225, and thence propionylformic acid, b. p. 74 – 78° /25 mm., n^{20}_D 1.3972; isobutyryl cyanide, b. p. 116 – 118° , d^{20}_D 0.9860, and the very unstable isobutyrylformic acid, d^{20}_D 0.9968, 1.3790; isovaleryl cyanide, b. p. 145 – 149° , from which the corresponding acid could not be obtained. H. WREN.

Reaction of bromine with aliphatic acids. III. [Keto-enol tautomerism in] α - and γ -ketonic acids. E. D. HUGHES and H. B. WATSON

(J.C.S., 1929, 1945–1954).—Evidence of the existence of keto-enol tautomerism in α - and γ -ketonic acids, corresponding with that in β -diketones and β -diketonic acids, is given in the cases of pyruvic and lævulic acids. A study of the kinetics of the bromination of these acids in aqueous solution shows that the speed of the reaction is constant throughout, and independent of the initial concentration of the halogen. The absence of an enolide in appreciable quantities in pure pyruvic acid is demonstrated by the fact that in none of the experiments has a measurable quantity of bromine been found to be absorbed instantaneously. The results show clearly that the bromination is preceded by a change of the acid to its enolic form, which reacts readily with the halogen.

In chloroform solution the bromination commences only after a latent period of variable duration, which is compared with the arrest of mutarotation observed by Lowry and Richards (A., 1925, i, 886). The mechanism of the enolisation is discussed in terms of the electronic theory of valency. J. W. PORTER.

Configurative relationships of α -, β -, and γ -chloro- and -hydroxy-aliphatic acids. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, 83, 591–600).— Δ^a -Hexen- γ -ol was resolved by the phthalate method, yielding an *l*-carbinol, b. p. 133 – 134° , $[\alpha]^{25}_D$ -23.4° without solvent; with phosphorus trichloride this gave *d*- γ -chloro- Δ^a -hexene, $[\alpha]^{25}_D$ $+17.85^\circ$ without solvent, which, with ozone, furnished *l*-chloro-*n*-valeric acid, b. p. 80 – 84° /1 mm., $[\alpha]^{25}_D$ -11.6° in ether (sodium salt, $[\alpha]^{25}_D$ -3.0°). When reduced with hydrogen and palladium the above hexenol gave *d*-hexan- γ -ol, b. p. 130 – 132° , $[\alpha]^{25}_D$ $+2.75^\circ$ without solvent. *l*- Δ^a -Hepten- γ -ol, $[\alpha]^{25}_D$ -22.2° without solvent, gave *d*- γ -chloro- Δ^a -heptene, $[\alpha]^{25}_D$ $+14.60^\circ$ without solvent, which yielded *l*- α -chloro-*n*-hexoic acid, b. p. 80 – 95° /1 mm., $[\alpha]^{25}_D$ -2.1° in ether. *d*- Δ^a -Hexen- β -ol (cf. Levene and Haller, A., 1928, 1353) gave *l*- δ -chloro- Δ^a -hexene, b. p. 119 – 122° , $[\alpha]^{25}_D$ -38.75° without solvent, which yielded *l*- γ -chloro-*n*-valeric acid, b. p. 95 – 100° /1 mm., $[\alpha]^{25}_D$ -40.9° in ether (sodium salt, $[\alpha]^{25}_D$ -27.4°). *l*- γ -Chloro-*n*-valeric acid is thus related to *d*- γ -hydroxy-*n*-valeric acid, since the latter has already (*loc. cit.*) been related to the *d*-hexenol; this conclusion is contrary to that previously reached, and it is now thought that the rule of the change of direction of rotation on passing from the non-ionised to the ionised state is generally applicable as a guide to configuration only among the α -substituted acids; in β - and γ -substituted acids the rule is applicable only when the substituent is the hydroxyl group. C. R. HARRINGTON.

Formation of lactic acid from sucrose under pressure. H. WOLF (Biochem. Z., 1929, 210, 458–465).—By the action of lime under pressure on sucrose 73%, and on invert-sugar only 38% is obtained as lactic acid. The amounts of formic acid obtained are inversely. It is suggested that the labile modification of lævulose present in sucrose breaks down almost quantitatively into lactic acid.

P. W. CLUTTERBUCK.

Preparation of the enolic form of ethyl acetate. G. MINGASSON (Bull. Soc. chim., 1929, [iv], 45, 716–718).—The sodium derivative obtained

in the usual way by condensation of ethyl acetate in presence of sodium ethoxide is decomposed with acetyl chloride in ether, and the enolic acetate, b. p. 90—91°/10 mm., d_{4}^{17} 1.0989, n_D^{17} 1.46906, when hydrolysed with boiling 1% oxalic acid for $\frac{1}{2}$ hr., furnishes the pure enol, d_{4}^{17} 1.0379, n_D^{17} 1.444, which yields ethane quantitatively with magnesium ethyl bromide (cf. Rumeau, A., 1924, i, 939; Grossmann, *ibid.*, 834).

R. BRIGHTMAN.

Walden inversion. P. NEBBELING (Chem. Weekblad, 1929, 26, 462—469).—The various theories postulated to explain the mechanism of the conversion of *d*- into *l*-malic acid by the successive actions of phosphorus pentachloride and moist silver oxide are discussed, and inconsistencies between the arguments pointed out. No one theory can be said effectively to explain the inversion. S. I. LEVY.

Hydroxydialkylsuccinic anhydrides. P. CORDIER (Compt. rend., 1929, 189, 538—543; cf. Bougault, A., 1925, i, 921, 1152; 1926, 725).—Treatment of α -methoxybenzylidene- β -phenylethylsuccinic acid with acetic anhydride at 100° for short periods yields the normal anhydride, m. p. 155°, which is also obtained by heating the acid at 160°. Prolonged treatment, however, with boiling acetic anhydride yields α -hydroxy- α -methoxybenzyl- β -phenylethylsuccinic anhydride, m. p. 70° (corresponding methyl ether, m. p. 46°). A. A. GOLDBERG.

Keto-lactol tautomerism. III. Influence of bulky substituents on the tautomerism of α -carboxy- γ -acetyl- β -methyl- β -ethyl- and - β -diethyl-butyric acids. M. QUDRAT-I-KHODA (J.C.S., 1929, 1913—1920; cf. this vol., 295, 698).—The above acids have been prepared and found to yield dilactones and keto-monobasic acids when heated a few degrees above their m. p. In the case of the former acid the dilactone conversion amounts to 32%, whilst in the latter it amounts to 45%. The conversion into dilactones also takes place when the acids are heated in benzene solution, the latter acid changing the more readily. The acids give normal keto-esters on esterification, and react in the lactol form in the presence of dehydrating agents or concentrated hydrochloric acid.

Methyl β -methyl- Δ^{β} -butenyl ketone condenses with cyanoacetamide to give 6-hydroxy-2-keto-3-cyano-4:6-dimethyl-4-ethylpiperidine, m. p. 240°, which on alkaline hydrolysis yields α -carboxy- γ -acetyl- β -methyl- β -ethylbutyric acid, m. p. 89° (semicarbazone, m. p. 166°; diethyl ester, b. p. 154°/10 mm., d_{4}^{18} 1.0414, n_D^{18} 1.44873, and its semicarbazone, m. p. 89°). The acid when heated gives the dilactone, m. p. 82°, and γ -acetyl- β -methyl- β -ethylbutyric acid, b. p. 150°/10 mm., d_{4}^{18} 1.0425, n_D^{18} 1.45773 (semicarbazone, m. p. 152°, ethyl ester, b. p. 112°/10 mm., d_{4}^{18} 0.967526, n_D^{18} 1.43899, and its semicarbazone, m. p. 94°). The substituted butyric ester when treated with sodium and absolute alcohol gives 5-methyl-5-ethyl-dihydroresorcinol, m. p. 106°.

Methyl β -ethyl- Δ^{α} -butenyl ketone condenses with cyanoacetamide to give 6-hydroxy-2-keto-3-cyano-6-methyl-4:4-diethylpiperidine, m. p. 251°, which by alkaline hydrolysis yields α -carboxy- γ -acetyl- β -diethyl-

butyric acid, m. p. 97° (semicarbazone, m. p. 158°; ethyl ester, b. p. 167°/12 mm., d_{4}^{18} 1.0405, n_D^{18} 1.4553, and its semicarbazone, m. p. 88°). The acid when heated gives the dilactone, m. p. 113°, and γ -acetyl- β -diethyl-butyric acid, b. p. 158°/10 mm., d_{4}^{18} 1.04214, n_D^{18} 1.46639 (semicarbazone, m. p. 155°; ethyl ester, b. p. 125°/11 mm., d_{4}^{18} 0.966424, n_D^{18} 1.44392, and its semicarbazone, m. p. 93°).

The lactones of δ -hydroxy- β -methyl- β -ethyl- Δ^{γ} -hexenoic acid, b. p. 90°/10 mm., d_{4}^{18} 0.991443, n_D^{18} 1.4622, and δ -hydroxy- β -diethyl- Δ^{γ} -hexenoic acid, b. p. 106°/10 mm., d_{4}^{17} 0.996021, n_D^{17} 1.46867, are also described. J. W. PORTER.

Double citrates of bismuth and quinine. H. LENORMAND (J. Pharm. Chim., 1929, [viii], 10, 162—168).—The preparation and properties of the following compounds are described:

$C_6H_6O_7, BiOH, 2(C_6H_5O_7, C_{20}H_{24}O_{12}N_2), 2H_2O$;
 $C_6H_6O_7, BiOH, C_6H_8O_7, C_{20}H_{24}O_{12}N_2$;
 $(C_6H_6O_7, BiOH)_2, C_6H_8O_7, C_{20}H_{24}O_{12}N_2$;
 $C_6H_6O_7, BiOH, (C_{20}H_{24}O_{12}N_2)_2$;
 $C_6H_6O_7, BiOH, C_{20}H_{24}O_{12}N_2$. They are micro-crystalline powders insoluble in the usual organic solvents.

E. H. SHARPLES.

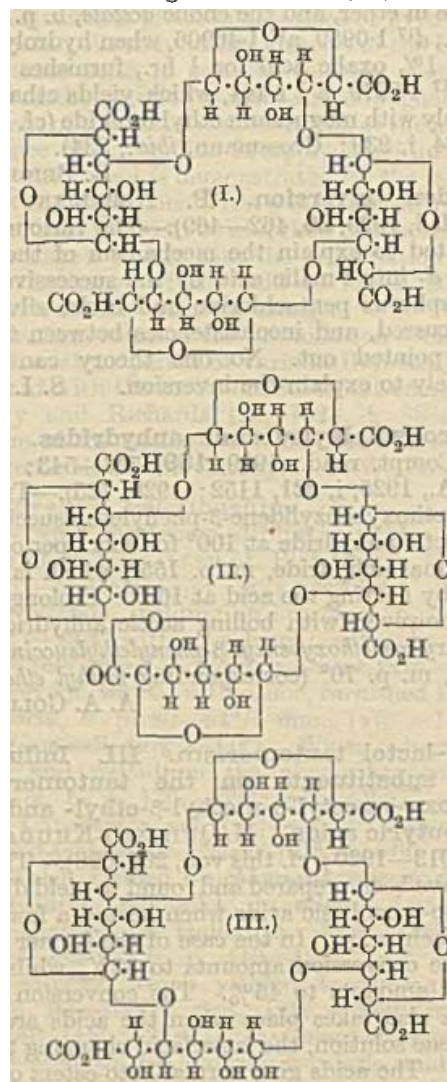
Pectin substances. Tetragalacturonic acids and *d*-galacturonic acid from the pectin of the sugar beet. F. EHRLICH and F. SCHUBERT (Ber., 1929, 62, [B], 1974—2027).—The pectin of sugar beet (*Beta vulgaris*) is present in the root in a form insoluble in water and forms about 50% of the residue left after extraction of the shavings with cold water, alcohol, and ether. The genuine pectin (urpectin, protopectin) cannot be isolated as such, since treatment with warm water causes more or less extensive hydrolysis to water-soluble hydratopectin, obtained in gelatin-like sheets by evaporation of the solution, and separated by 70% alcohol into araban and the calcium magnesium salts of pectic acid. Since the araban cannot be extracted directly from the shavings by 70% alcohol, it does not exist uncombined therein; it is a mixture of anhydrides of *l*-arabinose, from which almost quantitative yields of arabinose are obtained by the aid of boiling, dilute acids. Pectic acid, isolated from the calcium magnesium salt, appears to be a homogeneous product, $C_{41}H_{60}O_{36}$, formed by loss of 9 mols. of water from 4 mols. of galacturonic acid, 1 mol. of arabinose, 1 mol. of galactose, 2 mols. of acetic acid, and 2 mols. of methyl alcohol. It is identical with the pectic acid derived from other sources and, except for greater homogeneity, with the pectin of other investigators. It exists probably in different states of hydration, since $[\alpha]_D$ varies from +110° to +160° for different preparations and can reach +220° if solutions in dilute hydrochloric acid are preserved. It is an acid ester in which two carboxyl groups are esterified with methyl alcohol. Its main component is galacturonic acid, present to the extent of 68.70%, according to the Tollens-Lefèvre method. Treatment of pectic acid with 2—5% hydrochloric acid on the water-bath causes the separation of tetragalacturonic acid A, which can also be prepared in about 15% yield directly from hydratopectin. It is a white, amorphous powder which absorbs 10—15% of water from

the air without apparent change. In acid, neutral, or slightly alkaline solution it has $[\alpha]_D^{20} +275^\circ$. With salts of the heavy metals or alkaline earths it gives gelatinous precipitates, but not with magnesium salts. It reduces Fehling's solution slightly, strongly after hydrolysis. Analyses of the acid and its salts and determinations of mol. wt. show that it is a tetra-anhydrotetragalacturonic acid, $C_{24}H_{32}O_{24}$, with four free carboxyl groups. With 12% hydrochloric acid it affords furfuraldehyde and carbon dioxide quantitatively: $C_{20}H_{28}O_{16}(CO_2H)_4 = 4C_5H_4O_3 + 4CO_2 + 8H_2O$. It is oxidised by protracted action of 5% hydrochloric acid and bromine at 75° to mucic acid (yield 60.5%) and oxalic acid; under these conditions mucic acid is considerably oxidised to oxalic acid and other products.

The mother-liquors from the preparation of tetragalacturonic acid from pectic acid or hydratopectin contain *tetragalacturonic acid B*, isolated by precipitation with alcohol. The yield of the acid increases with increasing duration of hydrolysis, whereas that of the *A* acid diminishes, so that the former is a degradation product of the latter, as confirmed by the direct conversion in presence of dilute acid or water, preferably under pressure. The acid *B* is an amorphous powder closely resembling the acid *A*. It has $[\alpha]_D$ about $+250^\circ$ in water. Its alkali salts are soluble in water (sodium salt $+H_2O$, $[\alpha]_D^{20} +217.7^\circ$ in water) and the solutions give granular or slimy but not gelatinous precipitates, which are partly soluble in excess of precipitant, particularly in the cases of the alkaline-earth salts. The acid reduces hot Fehling's solution. Analyses and determinations of mol. wt. indicate the composition $C_{24}H_{32}O_{24}$. Three carboxyl groups are directly titratable, the fourth only after hydrolysis with excess of alkali hydroxide. The compound is therefore regarded as trianhydrotetragalacturonomonolactone. With hydrochloric acid it evolves furfuraldehyde and carbon dioxide in amount exactly corresponding with its galacturonic acid content. With hydrochloric acid and bromine it yields mucic acid (yield 68.2%) and oxalic acid.

Tetragalacturonic acid C is obtained by the alkaline hydrolysis of pectic acid and is invariably produced by the acid hydrolysis of pectic acids of higher optical activity ($[\alpha]_D +170^\circ$ to $+220^\circ$) which have received preliminary treatment with cold hydrochloric acid. It can be obtained as transformation product of acid *A*, which it resembles in physical and chemical properties. It has $[\alpha]_D +285^\circ$. It contains 1 mol. of water more than the *A* acid, which is not lost at 100° vac., and hence it is regarded as monohydratetetra-anhydrotetragalacturonic acid. It has four titratable carboxyl groups and gives a sodium salt identical with that derived from the *A* acid, from which hydrochloric acid invariably liberates the *C* acid, thus giving a ready transformation from *A* to *C*. Protracted ebullition of *A* or *C* with water or dilute mineral acids, particularly under pressure, results in conversion into *B*. The *A* acid when treated with an excess of sodium or potassium hydroxide immediately yields an intensely yellow solution, which, after a time, suddenly becomes turbid and slowly colourless with separation of the alkali salt. Under similar conditions, acid *C* becomes only faintly yellow and rapidly colourless

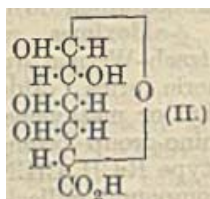
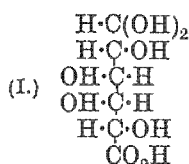
again with separation of the salt. The constitutions I, II, and III are assigned to acids *A*, *B*, and *C*.



The presence of the free aldehydic group in acid *B* appears to be established by its oxidation by hypiodite in amount corresponding with one $\cdot CHO$ group, whereas the acids *A* and *C* are not oxidised by this reagent.

The three tetragalacturonic acids are converted by prolonged acid hydrolysis into *D*-galacturonic acid, which is best prepared by heating a suspension of acid *A* in 1% sulphuric acid for 10–20 min. under 4–5 atm. Sulphuric acid is precipitated with a minimal excess of barium hydroxide, the filtrate is evaporated in a vacuum, the residue extracted with alcohol, and the extract allowed to evaporate (yield 35%). Crystalline α -*D*-galacturonic acid has m. p. 156 – 159° (decomp.) after softening at 110° , becoming red at 130 – 140° and brown at 150° . It gives the orcinol and naphtharesorcinol reactions. It is converted by hydrochloric acid into furfuraldehyde and carbon dioxide. It reduces Fehling's solution strongly when heated, but not when cold. With nitric acid and cold bromine water, respectively, it gives 76%

and quantitative yields of mucic acid. With hypiodite it absorbs the oxygen required for one $\cdot\text{CHO}$ group. Its carboxyl group can be titrated directly with alkali. Attempts to obtain crystalline galacturone from it were unsuccessful. α -*d*-Galacturonic acid, $\text{C}_6\text{H}_{10}\text{O}_7\cdot\text{H}_2\text{O}$, has $[\alpha]_D^{20} +97.9^\circ$ to $+50.9^\circ$ in aqueous solution ($+107.0^\circ$ to $+55.6^\circ$ for the anhydrous substance). β -*d*-Galacturonic acid, $\text{C}_6\text{H}_{10}\text{O}_7$, crystallises anhydrous and has $[\alpha]_D^{20} +27.0^\circ$ to $+55.3^\circ$ in water (time 2 hrs.). In the preparation of *d*-galacturonic acid from pectin substances, the α - and β -modifications are obtained in varying proportion, depending on the degree of concentration of the syrups and the concentration of the alcohol used for extraction and crystallisation. Evaporation of hot aqueous or dilute alcoholic solutions invariably yields only the α -variety, whereas the β -modification, m. p. 160° , is obtained from the α -form by ebullition with a large excess of absolute alcohol and rapid evaporation of the solution. The reverse transformation takes place in warm, aqueous solution, from which the α -variety is isolated by evaporation. The water in the α -acid is very firmly retained, but it appears possible, although difficult, to effect its removal by desiccation with consequent production of the β -acid. Aqueous solutions of the α -acid give a violet colour with magenta-sulphurous acid after $\frac{1}{2}$ min., whereas the colour develops only slowly in solutions of the β -acid, indicating the presence of the aldehydic group in the α - but not in the β -acid. The constitutions (I) and (II) are assigned to the α - and β -acids.



The following salts of *d*-galacturonic acid are described: *sodium*, $\text{C}_6\text{H}_9\text{O}_7\cdot\text{Na}$, $[\alpha]_D^{20} +36.02^\circ$ in water (non-mutarotatory); *cinchonine*, $\text{C}_6\text{H}_{10}\text{O}_7\cdot\text{C}_{19}\text{H}_{22}\text{ON}_2\cdot\text{H}_2\text{O}$, m. p. 178° (decomp.) after darkening at 176° , $[\alpha]_D^{20} +139.0^\circ$ in water; *brucine*, $\text{C}_6\text{H}_{10}\text{O}_7\cdot\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2$, m. p. 180° after darkening above 170° , $[\alpha]_D^{20} -7.70^\circ$ in water; anhydrous *morphine* salt, m. p. 162 – 163° (decomp.) after darkening at 158° and softening at 160° , $[\alpha]_D^{20} -56.6^\circ$ in water.

H. WREN.

Humic acids. W. FUCHS (Kolloid-Z., 1929, 49, 47).—A discussion of the methods of investigating the constitution of humic acid. E. S. HEDGES.

Solubility of humic acids in phenol. M. SOUM and F. PODBREZNÍK (Bull. Inst. Pin, 1929, 61–64; Chem. Zentr., 1929, i, 2194).—The humic acids can be dissolved in phenol in presence of a small quantity of hydrochloric acid; certain more highly condensed humin substances are also soluble in phenol. The solubility can be employed in the determination of humin substances in fossil fuels. A. A. ELDRIDGE.

Humic acids in coal and lignite. F. PODBREZNÍK (Bull. Inst. Pin, 1928, 193–196, 209–214, 237–238; Chem. Zentr., 1929, i, 1701).—Humic acids from Siorac-de-Belves (Dordogne) lignite, by repeated

treatment with sodium hydroxide followed by hydrochloric acid, were obtained as a brownish-black powder; extraction with alcohol afforded hymatomelanic acid, which can also be obtained by treatment of coal with acetone. The calcium and barium salts are amorphous. The mol. wt. of humic acid is about 1120, and that of hymatomelanic acid (if tetrabasic) about 720. Two samples of coal contained 38.32 and 48.72%, respectively, of humic acids. The composition of humic acid corresponds with the formula $\text{C}_{51}\text{H}_{58}\text{O}_{26}$. The relation of the humic acids to the age and coking properties of the coal is discussed. A. A. ELDRIDGE.

Condensation of aliphatic aldehydes with malonic acid and formation of new $\alpha\beta$ -unsaturated fatty acids. B. ZAAR (Ber. Schimmel, 1929, 297–308).—Condensation of aliphatic aldehydes with malonic acid in the presence of primary and secondary bases (Knoevenagel's method) yields only $\beta\gamma$ -unsaturated acids, whilst the use of tertiary bases as condensing agents (Harding and Weizmann, J.C.S., 1910, 97, 299) gives mainly $\alpha\beta$ -unsaturated acids together with 5–10% of the $\beta\gamma$ -compound. The presence of the latter is due to small amounts of primary and secondary bases in the pyridine used as a condensing agent and not to migration of the double linking under the influence of sulphuric acid during the conversion of the $\beta\gamma$ -acid into the lactone. Thus condensation of *n*-heptaldehyde with malonic acid in the presence of piperidine or diphenylamine gives Δ^8 -octenoic acid, b. p. 114 – $115^\circ/2$ mm., d_4^{20} 0.929, n_D^{20} 1.44842, solidification point -4.4° (chloride, b. p. 80 – $81^\circ/4.5$ mm., d_4^{20} 0.9550; amide, m. p. 74.5 – 75°), which is converted by 85% sulphuric acid at 80° into the corresponding lactone, b. p. 113 – $114^\circ/4$ mm. With pyridine as a condensing agent the product is Δ^9 -octenoic acid (86.24% yield), b. p. 130 – $132^\circ/2$ mm., d_4^{20} 0.9316, n_D^{20} 1.45942, solidification point -0.9° , together with only 5% of the Δ^8 -acid (determined as the lactone). Similarly, from the appropriate aldehyde are obtained Δ^9 -nonenoic acid, b. p. 148 – $149^\circ/4.5$ mm., d_4^{20} 0.9280, n_D^{20} 1.46161, solidification point 8.5° (chloride, b. p. 95 – $97^\circ/2.5$ mm., d_4^{20} 0.9640; amide, m. p. 122 – 122.5°), and a small yield of the Δ^8 -acid isolated as the corresponding lactone, b. p. 125 – $127^\circ/3.5$ mm.; Δ^9 -undecenoic acid, b. p. 164 – $165^\circ/2$ mm., d_4^{20} 0.9130, n_D^{20} 1.46390, solidification point 18° (chloride, b. p. 122 – $124^\circ/2.5$ mm., d_4^{20} 0.9430; amide, m. p. 113.5 – 114.5°); and Δ^9 -dodecenoic acid, b. p. 169 – $171^\circ/2$ mm., d_4^{20} 0.8995, n_D^{20} 1.46121, solidification point 27.9° (chloride, b. p. $131^\circ/3$ mm., d_4^{20} 0.9380; amide, m. p. 116°).

J. W. BAKER.

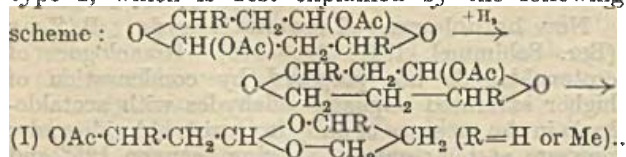
New homologues of crotonaldehyde. B. ZAAR (Ber. Schimmel, 1929, 309–316).—Homologues of crotonaldehyde are prepared by condensation of higher saturated aliphatic aldehydes with acetaldehyde in the presence of anhydrous zinc chloride under pressure at temperatures varying between 125° and 190° . Thus *n*-heptaldehyde furnishes α -ethylidene-*n*-heptaldehyde (20–25% yield), b. p. 57 – $59^\circ/3$ mm., d_4^{20} 0.8584, n_D^{20} 1.45362, purified through its semicarbazone, m. p. 168 – 168.5° (oily oxime; p-bromophenylhydrazone, m. p. 63 – 64° ; p-nitrophenylhydr-

azone, m. p. 102—103°, and is oxidised by silver oxide to α -ethylidene-*n*-heptioic acid, b. p. 118—124°/3.5 mm. (amide, m. p. 100°), and reduced with zinc and acetic acid to the acetate, b. p. 74.5—77°/2.5 mm. of α -ethylidene-*n*-heptyl alcohol, b. p. 82.5°/4.5 mm., Similarly from the appropriate aldehyde are obtained: α -ethylidene-*n*-butaldehyde, b. p. 34—38°/14 mm., d^{15}_4 0.8723, n^{20}_D 1.44762 (semicarbazone, m. p. 194—195°; *p*-nitrophenylhydrazone, m. p. 154.5—155.5°; *m*-nitrobenzhydrazone, m. p. 144—145°); α -ethylidene-*n*-octaldehyde, b. p. 70—75°/2.5 mm., d^{15}_4 0.8630, n^{20}_D 1.45412 (semicarbazone, m. p. 162—163°); α -ethylidene-*n*-decaldehyde, b. p. 99—103°/3 mm., d^{15}_4 0.8640, n^{20}_D 1.45712 (semicarbazone, m. p. 163—163.5°). J. W. BAKER.

Magnesium compounds derived from propargyl acetal. J. GRARD (Compt. rend., 1929, 189, 541—543).—The action of magnesium methyl bromide on propargyl acetal gave magnesium $\gamma\gamma$ -diethoxy- Δ^a -propinenyl bromide (I) and magnesium γ -ethoxy- Δ^a -butinenyl bromide (II). Interaction of I with acetaldehyde gave β -hydroxy- $\alpha\alpha$ -diethoxy- Δ^a -pentinene, d^{20}_4 0.995, n^{20}_D 1.446, which reacted with urethane to give the compound $\text{OH}\cdot\text{CHMe}\cdot\text{C}\cdot\text{C}\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})_2$, m. p. 168—168.5°. With iodine I yielded α -iodo- $\gamma\gamma$ -diethoxy- Δ^a -propinene, m. p. 7—8°, d 1.533, n^{22}_D 1.502, which when heated with alcoholic iodine yielded $\alpha\beta$ -tri-iodoacetaldehyde, m. p. 129—130°. $\alpha\alpha\delta\delta$ -Tetraethoxy- Δ^b -butinene, b. p. 102—105°/3 mm., m. p. 18°, d^{20}_4 0.9526, n^{20}_D 1.431, which with urethane yielded a product, m. p. 300°, is described. The action of water on II gave γ -ethoxy- Δ^a -butinene, b. p. 87—88°, d^{20}_4 0.8075, n^{20}_D 1.402, which with ammoniacal silver nitrate yielded a monosilver derivative (III) and with iodine $\alpha\alpha\beta$ -tri-iodo- γ -ethoxy- Δ^a -butene, m. p. 47—48°. With carbon dioxide II gave γ -ethoxy- Δ^a -pentinenoic acid, b. p. 107—108°/4 mm., d^{20}_4 1.0514, n^{20}_D 1.458, the potassium salt of which, when treated with silver nitrate, loses carbon dioxide to give III. Treatment of the potassium salt with aqueous copper sulphate gave a dicuprous derivative of β -hydroxy- γ -ethoxy- Δ^a -butene and carbon dioxide. Sodium γ -ethoxy- Δ^a -pentinenoate reacted with ethyl iodide to give ethyl γ -ethoxy- Δ^a -pentinenoate, b. p. 68—70°/3 mm., d^{20}_4 0.842, n^{20}_D 1.444, which was also obtained by treatment of II with ethyl carbonate.

A. A. GOLDBERG.

Structure of bimolecular lactolides. M. BERGMANN and A. MIEKELEY (Ber., 1929, 62, [B], 2297—2303).—Chemical evidence in favour of the main valency conception of certain bimolecular lactolides is afforded by the catalytic hydrogenation of lactol acetates of β -lactaldehyde and aldol to acetals of the type I, which is best explained by the following



Further, Bergmann and Weil (unpublished work) have prepared a methyl-lactolide of benzoin, m. p. 297°, and a transformation product therefrom, the production of which is most readily explained on the basis of the bimolecular, main valency structure,

$\text{CHPh} \begin{array}{c} \text{Ph}(\text{OMe})\cdot\text{O} \\ \text{O}\cdot\text{CPh}(\text{OMe}) \end{array} \text{CHPh}$. A fundamental error has been discovered in the proof of unimolecular structure based on measurements of vapour density. The use of porcelain fragments, asbestos, or silver vessel in the Bleier-Kohn apparatus leads to the catalytic decomposition of the small amounts of lactolide, thus giving a far too low mol. wt. This decomposition is not observed in control experiments in which larger amounts of lactolide are heated in glass vessels for considerable periods at the temperature of the determination, frequently even if asbestos is present. In the case of acetomethyl-lactolide the decomposition leads to methyl alcohol and a substance, $\text{C}_7\text{H}_{12}\text{O}_3$, m. p. 60—61°/15 mm. Analogously, methyl alcohol is obtained from the methyl-lactolide of oxycyclohexanone and acetic acid from the lactol acetate of acetaldo. If the determinations of the vapour densities of lactolides are made in the absence of catalysts which cause rapid decomposition and at a sufficiently low temperature, values are obtained for the lactolides of glycollaldehyde, acetol, β -lactaldehyde, aldol, and oxycyclohexanone which indicate the bimolecular form. The methyl- and ethyl-lactolides of salicylaldehyde appear unique, since they are unimolecular in phenol.

H. WREN.

Determination of the configuration of oximes. T. P. RAIKOWA (Ber., 1929, 62, [B], 2142—2149; cf. this vol., 911).—The "nitrile method" for the determination of configuration is applicable only to those aldioximes which do not pass by desmotropic change into ψ -aldioximes, and hence, according to the Hantzsch-Werner hypothesis, exist in two stereoisomeric forms. Aldioximes which do not contain a methyl or methylene group in juxtaposition to the oximino-group belong to this class. Aldioximes of the type $\text{R}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ (in which R is any simple or compound radical) which can isomerise to ψ -aldioximes and therefore, contrary to the Hantzsch-Werner theory, exist only in one form, cannot be examined by the nitrile method. The "Beckmann transformation" method can be applied to the determination of the configuration of ketoximes which cannot undergo desmotropic change and therefore exist in two stereoisomeric forms, but not to those in which desmotropic change is possible and of which only one form exists. There is no method of determining the configuration of aldioximes and of ketimines which, contrary to the Hantzsch-Werner theory, exist in only one modification.

H. WREN.

Electrolytic reduction of acetone at a mercury cathode. C. J. HAGGERTY (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 5 pp.).—By the electrolysis of acetone dissolved in 40% sulphuric acid solution using a mercury cathode, varying amounts of mercury diisopropyl were obtained and very little isopropyl alcohol seemed to be formed (cf. Tafel, A., 1902, ii, 442; 1906, i, 941).

H. J. T. ELLINGHAM.

Reduction of acetone by magnesium in presence of anhydrous aluminium chloride. M. I. USCHAKOV (Z. anorg. Chem., 1929, 183, 140—150).—By treatment of an ethereal solution of anhydrous

aluminium chloride with dry acetone the compound $\text{Al}_3\text{Cl}_9 \cdot 5\text{COMe}_2$, m. p. 110–114°, has been prepared. Dilute solutions of anhydrous aluminium chloride in acetone contain the ions Cl' and AlAc_6''' and exhibit a conductivity maximum at about 10 mol.-% of aluminium chloride; the chlorine ion may be quantitatively precipitated by sodium iodide solution, and from the resulting solution the compound $\text{AlI}_3 \cdot \text{COMe}_2$ has been prepared. In dilute acetone solutions of aluminium chloride magnesium reduces the $[\text{Al}(\text{COMe}_2)_6]'''$ ion, but in more concentrated solutions (25 mol.-% of aluminium chloride) the ion $[\text{Al}_2(\text{COMe}_2)_6\text{Cl}_2]'''$ is reduced; by treatment of the reaction products with water pinacol is obtained.

H. F. GILLBE.

Ketals of hydroxyketones. V. V. EVLAMPYEV (Ber., 1929, 62, [B], 2386–2389).—The action of ethyl orthoformate on acetol in presence of hydrogen chloride gives the corresponding crystalline ethyl-lactolide, $(\text{OEt} \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{O})_n$, m. p. 73.2–73.5°, whereas in presence of sulphuric acid a compound, $\text{C}_5\text{H}_{10}\text{O}_2$, was obtained, the molecular constitution of which could not be established by observations in freezing benzene. Chloroacetone, ethyl orthoformate, ethyl alcohol, and a little sulphuric acid yield α -chloro- $\beta\beta$ -diethoxypropane, b. p. 52–53°/14 mm.; α -bromo- $\beta\beta$ -diethoxypropane, d_4^{20} 1.1075, is similarly obtained, whereas in the preparation of α -iodo- $\beta\beta$ -diethoxypropane, b. p. 69°, the addition of moist silver oxide is advisable. Attempts to replace the halogen atoms of these compounds by $\cdot\text{OH}$ or $\cdot\text{OAc}$ were unsuccessful, since reaction either could not be caused to occur or proceeded with rupture of the molecule. β -Ketopropyl acetate is converted by ethyl orthoformate, ethyl alcohol, and a trace of sulphuric acid into $\beta\beta$ -diethoxypropyl acetate, b. p. 78.5–79.5°(corr.)/8 mm., d_4^{20} 0.9990, hydrolysed by aqueous calcium hydroxide at 80–90° to $\beta\beta$ -diethoxypropyl alcohol (acetol ethylketal), b. p. 68–68.5°(corr.)/9 mm., d_4^{20} 0.9828, mol. wt. 138.0 in freezing benzene; acetic anhydride in ether re-converts the alcohol into its acetate. The ketal is stable in neutral and alkaline aqueous solution, but is readily hydrolysed by traces of acid.

H. WREN.

Form and size of highly complex molecules by spreading of unimolecular layers on a water surface. II. Comparison of polysaccharides and degraded polysaccharides. J. R. KATZ and P. J. P. SAMWEL (Annalen, 1929, 474, 296–300; cf. A., 1928, 937).—The observation of Bergmann, Herzog, and Jancke (A., 1928, 822) that biosan and alkali-soluble cellulose have the same X-ray spectra is confirmed. Although the work of Hess and Friese (A., 1927, 861) indicates that biosan is the anhydride of a disaccharide, complete agreement is found between the figures for area per $\text{C}_6\text{H}_{10}\text{O}_5$ unit and the thickness of unimolecular films given by derivatives of biosan and cellulose. Inulin acetate degraded by heating in tetrahydronaphthalene, normal inulin acetate, and the acetate of a cellulose degradation product described by Pringsheim (A., 1928, 1226) which cryoscopically appears to consist of a single $\text{C}_6\text{H}_{10}\text{O}_5$ unit, give the same values for area

per $\text{C}_6\text{H}_{10}\text{O}_5$ unit, thickness, compressibility, and resistance to fracture, which are similar to those obtained for cellulose triacetate. It appears that the space occupied by a $\text{C}_6\text{H}_{10}\text{O}_5$ unit and its side-chains in a unimolecular layer is largely unaffected, whether the $\text{C}_6\text{H}_{10}\text{O}_5$ units are united in large molecules by polymerisation or association, or whether they are present (in the unimolecular layer) as freely mobile individuals. The agreement found between the foregoing properties and the forms of the compressibility curves of biosan derivatives and maximally degraded polysaccharides is unexpected, and it is suggested that the latter are not degraded to the degree indicated by their cryoscopic behaviour.

C. W. SHOPPEE.

Oxidation of carbohydrates, fats, and nitrogenous substances by hydrogen peroxide and ferric salts. S. N. CHAKRABARTI and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 617–626).—Oxidation of a 1% solution of potassium stearate, oleate, and palmitate, dextrose, starch, alanine, and lactic acid with 12% hydrogen peroxide in presence of a small amount of ferric sulphate at 37° gives in all cases some reducing substances. Determinations of the volatile acetone-like products formed during similar oxidation of seven sugars, dextrin, inulin, glycogen, egg-white and -yolk, butter, and cholesterol, by titration with iodine show that varying amounts are produced from all the substances quoted. Oxidation of carbohydrates in presence of nitrogenous compounds or fats, fats in presence of nitrogenous substances, and a mixture of fats, carbohydrates, and nitrogenous compounds causes a decrease in the amount of reducing substances formed. The oxidation of a group of compounds is, therefore, retarded by the addition of a second group of substances. The amounts of acetone-like substances produced during the oxidation of mixtures of fats and carbohydrates are decreased further with increase in the added carbohydrate; retardation of the oxidation is greatest with starch and sucrose.

The disappearance of the acetone substances from the body after injection of insulin is considered to be due to a more complete oxidation of fats following the primary oxidation of the dextrose. H. BURTON.

Degradation of l-arabinose. V. DEULOFEU and R. J. SELVA (Anal. Asoc. Quim. Argentina, 1929, 17, 13–24).—See this vol., 427.

Deoxyribose and deoxyxylose and their bearing on thyminose. P. A. LEVENE and T. MORI (J. Biol. Chem., 1929, 83, 803–816).—The deoxypentose obtained by hydrolysis of the thymonucleosides is designated thyminose. Although this compound titrates as a β -deoxyaldopentose and yields lævulic acid when heated with dilute sulphuric acid it is not identical with deoxyribose or with deoxyxylose. Thyminose (cf. this vol., 590) has m. p. 150° after softening at 78°, $[\alpha]_D^{20}$ –90.6° to –40.0° in pyridine, –60.0° to –50.0° in water (as. *phenylbenzylhydrazone*, m. p. 128°, $[\alpha]_D^{25}$ –17.5°). Acetobromoxylose yielded, with zinc and acetic acid, d-diacetylxyloal, b. p. 103–107°/1.5–1.8 mm., m. p. 40°, $[\alpha]_D^{25}$ –314.7° in chloroform, which was hydrolysed with barium hydroxide to d-xylal, b. p. 109—

112°/1.2 mm., m. p. 49—50°, $[\alpha]_D^{25}$ —254.5° in water; with dilute sulphuric acid this yielded d- β -deoxyxylose, m. p. 92—96°, $[\alpha]_D^{25}$ —40.25° to +50.75° in pyridine, —22.5° to —2.0° in water (as. *phenylbenzylhydrazone*, m. p. 116—118°, $[\alpha]_D^{25}$ +13.5° in pyridine). Similarly from acetobromoarabinose there was obtained 1- β -deoxyribose, m. p. 80.5—90°, $[\alpha]_D^{25}$ +2.75° to +2.13° in pyridine, +2.88° to 2.13° in water (as. *phenylbenzylhydrazone*, m. p. 115—117°, $[\alpha]_D^{25}$ +7.8° in pyridine).

C. R. HARRINGTON.

Determination of pentosans. C. KULLGREN and H. TYDÉN (Handl. Ing. Vetenskaps-Akad. Stockholm, 1929, No. 94, 62 pp.).—A very detailed investigation of the Tollens method of determining pentoses and pentosans by conversion into furfuraldehyde is recorded. The 12% hydrochloric acid used in the older method is open to objection, since as the distillation proceeds the composition tends to approach the azeotropic mixture, 20.2%. It is replaced by 13.15% hydrochloric acid saturated with sodium chloride, a mixture of constant b. p. This change leads also to a quicker distillation of the furfuraldehyde, since the distillation factor (ratio of furfuraldehyde in the vapour to that in the liquid phase) rises from 6.0 to 14.7. Under these conditions 96.9% of the furfuraldehyde formed can be distilled. Precipitation of the distillate with phloroglucinol or barbituric acid is replaced by the much quicker titration with potassium bromate-bromide mixture. The excess of bromate is titrated by thiosulphate after the addition of potassium iodide (cf. Powell and Whittaker, A., 1924, ii, 354). In a solution with a slight excess of acid each molecule of furfuraldehyde is initially equivalent to 2 atoms of bromine, but this value rises to 4.5 atoms within 4 days. This is interpreted as a rapid initial oxidation of the aldehydic group followed by a slow general oxidation (cf. Pervier and Gortner, A., 1924, ii, 71). Using a catalyst of ammonium molybdate to hasten the liberation of bromine from the bromide-bromate mixture, bromine absorption-time curves are given for various concentrations of free acid. In a solution containing 0.5—1% of acid theoretical bromine absorption occurs in about 4 min. The amount of bromate in excess is of small importance. Contrary to the results of Pervier and Gortner (A., 1923, ii, 884), the use of steam during the distillation does not lead to any increased yield of furfuraldehyde. The formation of humic substances, responsible for the lack of theoretical yield of furfuraldehyde, proceeds from the pentose and not from the furfuraldehyde.

By working under completely standardised conditions reproducible results may be obtained. The original communication should be consulted for details.

T. H. MORTON.

Conversion of methylpentoses into methylfurfuraldehyde. E. VOTOCER and F. RÁC (Coll. Czech. Chem. Comm., 1929, 1, 516—520).—The formation of methylfurfuraldehyde by the action of mineral acids on sugars is not limited to aldehydic methylpentoses, but is also given by the keto-compounds. 2-Ketorhamnose, prepared by boiling rhamnose-phenylosazone with benzaldehyde in the presence of a large excess of water, concentrating the aqueous

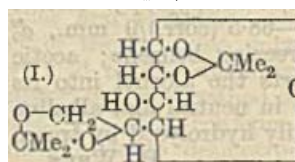
solution in a vacuum, and treating the resultant product with zinc and acetic acid, gives a 20% yield of methylfurfuraldehyde when distilled with 12% hydrochloric acid. 2-Ketorhamnose yields a violet and rhamnose a yellowish-brown coloration with carbazole.

A. I. VOGEL.

Synthetic hexosephosphates and their phenylhydrazine derivatives. A. L. RAYMOND and P. A. LEVENE (J. Biol. Chem., 1929, 83, 619—630).—Dextrose and laevulose were phosphorylated directly by treatment with phosphoryl chloride and pyridine; diisopropylidene-glucose and α - and β -diisopropylidene-fructose were phosphorylated as above and the isopropylidene residues removed by graduated hydrolysis with hydrochloric acid; the resulting phosphoric esters were treated with phenylhydrazine. The ester from dextrose gave no crystalline products; the ester from diisopropylidene-glucose gave an *anhydrohexosazone*, m. p. 156—159°, $[\alpha]_D^{25}$ —146°, apparently identical with the compound prepared by Levene and others (this vol., 683) from α -diisopropylidene-fructose through the phosphate; the ester from laevulose gave glucosazone; the ester from α -diisopropylidene-fructose yielded a *diphenylhydrazine* salt of a *phosphohydrazone*, $C_{24}H_{35}O_8N_6P$, m. p. 96—98°, decomp. 123—125°, $[\alpha]_D^{25}$ —50.6° to —35.0° in pyridine-methyl alcohol, and the anhydrohexosazone mentioned above; the ester from β -diisopropylidene-fructose gave a *phenylhydrazine* salt of a *phosphohydrazone*, $C_{18}H_{27}O_8N_4P$, which darkened at 107—110° after sintering at 96—97°, $[\alpha]_D^{25}$ —15.0° to —33.6° in pyridine-methyl alcohol, and glucosazone.

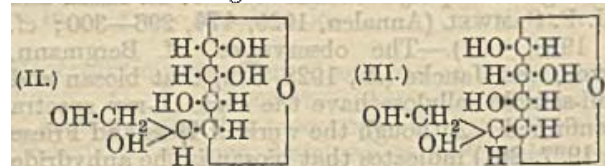
C. R. HARRINGTON.

Transformation reactions in the carbohydrate group. II. Configuration of the furoid γ -glucose and its isopropylidene derivatives. K. JOSEPHSON (Ber., 1929, 62, [B], 1913—1916).—A theoretical paper in which arguments are adduced in



favour of the structure I for furoid glucose diisopropylidene ether. The ready migration of the acetyl group in 3-acetylglucose isopropylidene ether from position 3 to 6

and the easy formation of Fischer's anhydroglucose from derivatives of isopropylidene-glucose are simply explained. To α - and β -glucofuranose the structures II and III are assigned.

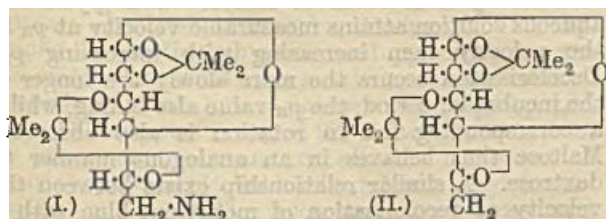


H. WREN.

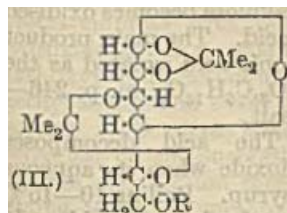
Acetone [isopropylidene] compounds of the sugars and their derivatives. XIV. isoDiisopropylidene-glucose. H. OHLE and L. VON VARGHA (Ber., 1929, 62, [B], 2425—2434; cf. A., 1928, 871).—*p*-Toluenesulphonylglucose isopropylidene ether, m. p. 108°, is hydrolysed to the non-crystalline *p*-toluenesulphonylglucose, which, when treated with acetic anhydride and pyridine, gives a mixture of 6-*p*-

toluenesulphonyl-1 : 2 : 3 : 4-tetra-acetyl- β -glucopyranose, m. p. 200°, $[\alpha]_D^{20} +23.97^\circ$ in chloroform, and (1) 6-*p*-toluenesulphonyl-1 : 2 : 3 : 4-tetra-acetyl- α -glucopyranose (+H₂O), m. p. 129—130°, $[\alpha]_D^{20} +105.7^\circ$ in chloroform. The *p*-toluenesulphonyl group in the isopropylidene sugar must therefore be in position 6.

The position of the *p*-toluenesulphonyl group in *p*-toluenesulphonylisoglucose diisopropylidene ether, prepared from 6-*p*-toluenesulphonylglucose isopropylidene ether, m. p. 108° (see above), is established as follows: (1) The diisopropylidene compound is converted in poor yield by hydrogen bromide and glacial acetic acid into a non-crystalline bromo-derivative, transformed by methyl alcohol and silver carbonate into 6-*p*-toluenesulphonyl-2 : 3 : 4-triacetyl- β -methylglucoside (cf. Helferich and others, A., 1927, 1174); (2) partial hydrolysis of the diisopropylidene compound by 80% acetic acid (optically controlled) affords 6-*p*-toluenesulphonylglucose isopropylidene ether; (3) hydrolysis of 6-*p*-toluenesulphonylisoglucose diisopropylidene ether by alcoholic ammonia at 100° affords a mixture of isoglucosyl-6-amine diisopropylidene ether (I) (*p*-toluenesulphonate, m. p. 172.5°, $[\alpha]_D^{20} +30.96^\circ$ in water), diisoglucosyl-6-imine diisopropylidene ether, $[\alpha]_D +41.4^\circ$ in chloroform [*p*-toluenesulphonate, m. p. 183° (decomp.), $[\alpha]_D^{20} +20.1^\circ$ in chloroform], and glucoseen (5 : 6)-diisopropylidene ether (II), $[\alpha]_D^{20} +33.2^\circ$ in chloroform; the amine is hydrolysed by



acids to the known glucosyl-6-amine, identified as the *p*-toluenesulphonate of its hydrazone. (4) Direct hydrolysis of *p*-toluenesulphonylisoglucose diisopropylidene ether by alcoholic sodium hydroxide or methoxide yields a mixture of isoglucose diisopropylidene ether and glucoseen diisopropylidene ether which cannot be separated into its components. On the other hand, isoglucose diisopropylidene ether is readily obtained by deamination of isoglucosyl-6-amine diisopropylidene ether and is converted by *p*-toluenesulphonyl chloride into the initial *p*-toluenesulphonylisoglucose diisopropylidene ether. The acetate, b. p. 140°/0.4 mm., $[\alpha]_D^{20} +32.8^\circ$ in chloroform, and benzoate, b. p. 200° (bath temp.)/0.6 mm., $[\alpha]_D^{20} +29.5^\circ$ in chloroform, of isoglucose diisopropylidene ether are non-crystalline. The methyl ether (III, R=Me), b. p. 105°/0.1 mm., $[\alpha]_D^{20} +15.3^\circ$ in chloroform, is hydrolysed to

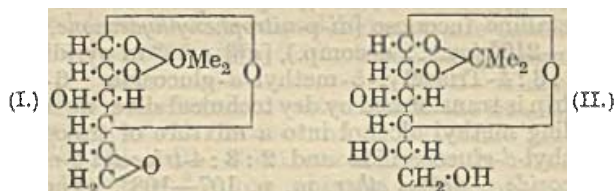


identified by its osazone. The constitution III (R=H) is thus established for isoglucose diisopropylidene ether.

isoglucose diisopropylidene ether is transformed by methyl iodide and silver carbonate into the corre-

sponding methyl carbonate, C₁₄H₂₂O₈, m. p. 111°, $[\alpha]_D^{20} +38.4^\circ$ in chloroform. H. WREN.

Acetone [isopropylidene] compounds of the sugars and their derivatives. XV. 5 : 6-Anhydroglucose isopropylidene ether and the 5-methyl ether of glucofuranose. H. OHLE and L. VON VARGHA (Ber., 1929, 62, [B], 2435—2444; cf. preceding abstract).—Hydrolysis of 6-*p*-toluenesulphonylglucose isopropylidene ether by sodium methoxide affords 5 : 6-anhydroglucose isopropylidene ether (I), m. p. 133.5°, $[\alpha]_D^{20} -26.5^\circ$ in water, identical with the compound described by Freudenberg and others (A., 1928, 1223). It is characterised by unusual instability, being hydrolysed to dextrose by 80% acetic acid at the ordinary temperature. It is converted by sodium hydroxide into glucose isopropylidene ether, m. p. 157°, and other products derived from mono- and di-hexoses, from which *d*-idose isopropylidene ether is isolated in a non-homogeneous condition. Treatment with acetic acid and pyridine transforms the crude ether into non-homogeneous triacetyl-*d*-idose isopropylidene ether, b. p. 130—135°/0.5 mm., $[\alpha]_D^{20} +58.3^\circ$ in chloroform, converted by successive treatment with sodium hydroxide and dilute sulphuric acid into *d*-idose, identified as the phenylosazone, m. p. 168°. Slightly impure trimethyl-*d*-idose isopropylidene ether, b. p. 92—93°/0.007 mm., $[\alpha]_D^{20} +66.2^\circ$ in methyl alcohol, is described. The production of idose isopropylidene ether (II) affords further proof of the constitution of the original material, since, under the conditions adopted, only a 5 : 6-anhydroglucose isopropylidene ether could undergo epimerisation to an idose derivative.



Ammonia appears to open the ethylene oxide ring of 5 : 6-anhydroglucose isopropylidene ether almost entirely in one direction, giving isopropylidene-glucosyl-6-amine, characterised by hydrolysis and conversion into the *p*-toluenesulphonate of glucosyl-6-aminephenylhydrazone. Addition of sodium methoxide appears to lead exclusively to isopropylidene-glucofuranose 5-methyl ether, m. p. 71—72°, $[\alpha]_D^{20} -6.42^\circ$ in chloroform, identified by conversion into isopropylideneglucose trimethyl ether, b. p. 138—140°/12 mm., $[\alpha]_D^{20} -27.1^\circ$ in methyl alcohol, and thence into glucofuranose 2 : 3 : 5 : 6-tetramethyl ether, b. p. 120°/0.03 mm., $[\alpha]_D^{20} -7.28^\circ$ in water (cf. Irvine and Scott, J.C.S., 1913, 103, 574). Hydrolysis of isopropylideneglucose methyl ether affords *d*-glucofuranose 5-methyl ether, m. p. 143—144°, $[\alpha]_D^{20} +101.2^\circ$ to $+59.92^\circ$ in water in 3 hrs. [phenylosazone, m. p. 180° (decomp.), $[\alpha]_D^{20} -101.9^\circ$ to -86.6° (incomplete) in pyridine]. It reduces Fehling's and ammoniacal silver solution powerfully when heated, but does not react with sulphurous acid-magenta. The possible existence of glucofuranose forms in the

equilibrium mixtures derived from dextrose is suggested.

Zemplen's method of hydrolysis appears applicable only to such compounds as contain the *p*-toluenesulphonyl group very loosely united. 5:6-Di-*p*-toluenesulphonylglucose isopropylidene ether is smoothly converted into 5-*p*-toluenesulphonyl-3:6-anhydroglucose isopropylidene ether. 3-*p*-Toluenesulphonylglucose diisopropylidene ether, 6-*p*-toluenesulphonylglucose diisopropylidene ether, 3:5:6-tri-*p*-toluenesulphonylglucose isopropylidene ether, and 5-*p*-toluenesulphonyl-3:6-anhydroglucose isopropylidene ether are unaffected. H. WREN.

New dicarbonyl sugars. B. HELFERICH and E. HIMMEN (Ber., 1929, 62, [B], 2136—2141; cf. A., 1928, 1221).—The preparation of triacetyl- β -methyl-*d*-glucosene is more advantageously effected from triacetyl- β -methyl-*d*-glucoside 6-bromohydrin than from the corresponding iodohydrin (cf. *loc. cit.*). β -Methyl-*d*-glucosene is hydrolysed by cold 0.1*N*-sulphuric acid to the compound (I), which, by reason of its analogy to Fischer's *d*-isorhamnose, is termed *isorhamnose*. It has m. p. 125.5—126° (corr.), $[\alpha]_D^{20} -15.2^\circ$ —33.6° in water. It reduces Fehling's solution very strongly when heated gradually at the ordinary temperature. It immediately yields a *di-p*-nitrophenylhydrazone, m. p. 120.5° (corr.; decomp.), $[\alpha]_D^{20} -83.5^\circ$ in pyridine. Similarly, diisopropylidene-galactose ζ -iodohydrin is transformed by silver fluoride and pyridine into diisopropylidene-*d*-galactosene, m. p. 86—87° (corr.), $[\alpha]_D^{20} -136^\circ$ in *s*-tetrachloroethane, $[\alpha]_D^{20} -142.6^\circ$ in chloroform (cf. Freudenberg and Raschig, this vol., 427), hydrolysed to the non-crystalline fuconose [*di-p*-nitrophenylhydrazone, m. p. 209—210° (corr.; decomp.), $[\alpha]_D^{20} +59^\circ$ in pyridine].

2:3:4-Triacetyl- β -methyl-*d*-glucoside 6-iodohydrin is transformed by dry technical silver fluoride in boiling methyl alcohol into a mixture of triacetyl- β -methyl-*d*-glucosene and 2:3:4-triacetyl- β -methylglucoside 6-methyl ether, m. p. 107—108°. The last-named compound is transformed by methyl-alcoholic ammonia into β -methyl-*d*-glucoside 6-methyl ether, m. p. 133—135° (corr.), $[\alpha]_D^{20} -27.0^\circ$ in water, which is not hydrolysed by emulsin. H. WREN.

Rotatory power and structure in sugar group. XX. Two isomeric crystalline compounds of *d*-mannose with calcium chloride. J. K. DALE (J. Amer. Chem. Soc., 1929, 51, 2788—2795).—When β -*d*-mannose is mixed with a concentrated aqueous solution of calcium chloride at the ordinary temperature the compound (I), $C_6H_{12}O_6 \cdot CaCl_2 \cdot 4H_2O$, m. p. 101—102° (corr.), crystallises. Evaporation of an alcoholic solution of I on the water-bath gives the compound (II), β - $C_6H_{12}O_6 \cdot CaCl_2 \cdot 2H_2O$, m. p. 159—160° (corr.; decomp.). Conversion of II into I is effected by the addition of water to an alcoholic solution of II and subsequent evaporation at the ordinary temperature. Details are also given for the preparation of I and II from vegetable ivory. Acetylation of II with acetic anhydride and pyridine affords β -mannose penta-acetate. Mutarotation of II in water, $[\alpha]_D^{20} -7.7^\circ$ after 2 min. $\rightarrow +6.73^\circ$ at

∞ , is normal, but I shows an unusual course, $[\alpha]_D^{20} -23.68^\circ$ after 0.75 min. $\rightarrow +11.35^\circ$ after 23 min. $\rightarrow +6.5^\circ$ at ∞ . Extrapolation of the mutarotation curve to zero time indicates an initial rotation for the mannose constituent of $[\alpha]_D^{20}$ about -60° , and it is presumed that the sugar residue of I is the β -form of the 1:5-ring form of mannose (cf. Hudson, A., 1926, 714). H. BURTON.

Crystalline difructose anhydride from hydrolysed inulin. R. F. JACKSON and S. M. GOERGEN (Bur. Stand. J. Res., 1929, 3, 27—38).—Although inulin consists solely of lævulose residues, hydrolysis gives only 91.8% of lævulose. The remainder contains 3% of another reducing sugar and 5.2% of an unfermentable mixture of disaccharides which is hydrolysed by 0.4*N*-sulphuric acid at 100° to lævulose exclusively. Acetylation of the disaccharides yields a crystalline *hexa-acetate*, m. p. 137°, $[\alpha]_D^{20} +0.54^\circ$ (in chloroform), from which on hydrolysis with barium hydroxide a crystalline *dilævulose anhydride-I*, $[\alpha]_D^{20} +27^\circ$ (in water), is obtained. The acetylation mother-liquors contain one or more unisolated hexaacetates, mean $[\alpha]_D^{20} +31^\circ$. C. HOLLINS.

Reaction between sugars and amino-acids. V. H. VON EULER, G. RENGMAN, and E. BRUNIUS (Svensk Kem. Tidskr., 1929, 41, 203—209; cf. this vol., 175).—Decolorisation of a methylene-blue solution by a mixture of maltose and glycine in aqueous solution attains measurable velocity at p_H 8, the velocity then increasing with increasing p_H . Decolorisation occurs the more slowly the longer is the incubation period, the p_H value also falling, whilst a corresponding fall in rotation is also observed. Maltose thus behaves in an analogous manner to dextrose. A similar relationship exists between the velocity of decolorisation of methylene-blue with a mixture of galactose and glycine in aqueous solution and the p_H value, but, in this case, the maximum decrease in the rotation occurs after 1.5 hrs. The specificity of enzyme action is discussed.

J. W. BAKER.

Influence of hydrogen sulphite solutions on sugars at higher temperatures. II. E. HAGG-LUND and H. URBAN (Ber., 1929, 62, [B], 2046—2051; cf. this vol., 428).—Mannose is converted by heating with solutions of calcium hydrogen sulphite and sulphurous acid into mannonic acid; a reversion to polymeric sugars is not observed. Possibly, unstable sulphonc acids are formed as intermediate products.

Under certain conditions, lævulose becomes oxidised to α - β -trihydroxy-*n*-butyric acid. The main product is apparently a fructosesulphonic acid isolated as the *brucine* salt, $C_{23}H_{26}O_4N_2 \cdot H_2SO_3 \cdot C_6H_{12}O_6$, m. p. 246—247° (decomp.), and *barium* salt, $(C_6H_{12}O_6 \cdot H_2SO_3)_2Ba \cdot 2H_2O$. The acid decomposes with evolution of sulphur dioxide when its aqueous solution is concentrated to a syrup. Boiling 10—15% sulphuric acid causes slow loss of sulphur dioxide. It is stable toward cold 2*N*-sodium hydroxide, slowly decomposed by the hot reagent. The acid and its salts slowly reduce Fehling's solution. The formation of sulphurous but not sulphuric acid as product of acid hydrolysis suggests that the sulphonc group is

attached to a carbon atom united to a hydroxyl group. Its stability indicates that the acid is not a simple hydrogen sulphite derivative of lævulose.

H. WREN.

Effect of X-rays on sucrose. M. C. REINHARD and K. L. TUCKER.—See this vol., 1248.

Alizaringlucoside and alizarinbiosides. G. ZEMPLÉN and A. MÜLLER (Ber., 1929, 62, [B], 2107—2118).—Alizarintetra-acetylglucoside, $C_{11}H_{16}O_2(OH) \cdot O \cdot C_6H_7O_5Ac_4$, m. p. 205° after softening at 201°, is prepared by the action of silver oxide on a mixture of alizarin and acetobromoglucose in quinoline. Alizarintetrazobenzoylglucoside, m. p. 232°, is obtained analogously. By the action of methyl-alcoholic ammonia, the tetra-acetyl and tetrabenzoyl derivatives and alizaringlucoside become transformed into the supposed diglucoside,

$C_6H_4 \left\langle \begin{array}{c} C(OH)(NH_2) \\ C(OH)(NH_2) \end{array} \right\rangle C_6H_2(O \cdot C_6H_{11}O_5)_2$, of Glaser and Kahler (A., 1927, 752). The compound does not contain acetyl or methoxyl groups. The analytical composition could not be determined exactly, but the compound is certainly a monoglucoside closely allied to alizaringlucoside; it is possibly an ammonium salt. Alizaringlucoside, m. p. 235—236°, is prepared by acid hydrolysis of the ammonia compound or by alkaline treatment of the tetra-acetyl or tetrabenzoyl glucoside.

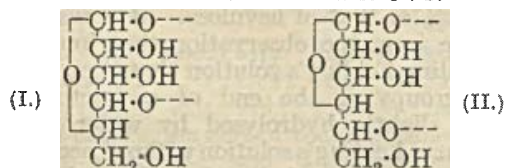
Alizarinhepta-acetylcellobioside, m. p. 249°, is prepared from alizarin and acetobromocellobiose in presence of silver oxide and quinoline. It is transformed by acetic anhydride and pyridine into the octa-acetyl compound, m. p. 219°, and by methyl-alcoholic ammonia into the compound (?) $C_{26}H_{31}O_{14}N$, m. p. 230° after softening at 220°. Acid hydrolysis of the ammonia compound or alkaline treatment of alizarinhepta-acetylcellobioside affords alizarincellobioside, m. p. 256°. Acetobromogentiobiose and alizarin give alizarinhepta-acetylgentiobioside, m. p. 258°, which yields the octa-acetyl derivative, m. p. 232°, ammonia derivative, $C_{26}H_{31}O_{14}N$, m. p. 199—200°, and alizaringentiobioside, m. p. 178—180°. Experiments with acetobromomaltose did not lead to crystalline compounds.

Ruberythric acid is certainly not identical with alizarin gentiobioside. With alizarincellobioside it has a close analogy in the m. p. of the free substance and of the octa-acetyl derivative, but the identity of the compounds is not maintained.

H. WREN.

Methylation of α -tetra-amylose. [Sir] J. C. IRVINE, H. PRINGSHEIM, and A. F. SKINNER (Ber., 1929, 62, [B], 2372—2378).—Repeated treatment of α -tetra-amylose with methyl sulphate and sodium hydroxide gives a product containing 36—37% of methoxyl as a maximum. Further treatment with methyl iodide and silver oxide does not cause further increase. The methylated tetra-amylose is, however, converted by the successive action of boiling thionyl chloride and sodium methoxide into a product containing 40.8% of methoxyl (maximum). Fractional extraction of a material with 37.1% or 36.1% of methoxyl with (a) boiling light petroleum, b. p. 40—60°, and (b) cold ether gave three portions which, in spite of their differing solubilities, had the same analytical composition and the same optical activity

and appeared to contain tri- and di-methylglucosan residues in the ratio 1:1, 1:2, or 1:3. Hydrolysis of methylated tetra-amylose (OMe=37.1%) by boiling 1% methyl-alcoholic hydrogen chloride affords 2:3:6-trimethyl- β -methylglucoside, m. p. 57° (whence 2:3:6-trimethylglucose, m. p. 110—112°), and a dimethylmethylglucoside, n_D 1.4738, in apparently equimolecular proportion. Hydrolysis of the dimethylmethylglucoside gives a syrupy dimethylglucose containing 7% of a monomethylglucose. It yields a laevorotatory γ -methylglucoside, but does not form a phenylosazone; attempts to condense it with acetone yield ill-defined products. Fission of methylated tetra-amylose (OMe=40.8%) gives trimethylmethylglucoside and dimethylmethylglucoside. The yields are almost exactly in the ratio 3:1.



It appears established that three of the four glucosan residues of α -tetra-amylose are symmetrical and have the constitution I or II, either of which is in harmony with the formation of 2:3:6-trimethylglucose by methylation and subsequent hydrolysis. The structure of the fourth glucosan residue which resists complete methylation is not definitely elucidated.

The formation of 2:3:6-trimethylglucose from polyamyloses indicates the possible existence in them and other polysaccharides of γ -glucose residues. In support it is found that 2:3:6-trimethyl- γ -methylglucoside and 2:3:6-trimethyl- β -methylglucoside prepared from 2:3:6-trimethylglucose are similarly hydrolysed to crystalline 2:3:6-trimethylglucose.

H. WREN.

Solubility of starch in water below the swelling temperature. M. SAMEC and N. TOMAZO (Ber., 1929, 62, [B], 2076—2078).—Contrary to the observation of Hess and Smith (this vol., 914), prolonged extraction of potato starch with water at 55° removes only 0.59% as water-soluble substance; the phosphorus content and microscopic appearance of the residue is identical with that of the original material. The earlier results are possibly due to unusual amounts of free acid or to diastatic enzymes present in the material which cause enrichment of the residue in phosphorus as observed by Hess and Smith. Treatment of the residue left after extraction at 55° with water at 75—80° causes dissolution of 39.4% of the material, which includes a considerable proportion of phosphatic substances.

H. WREN.

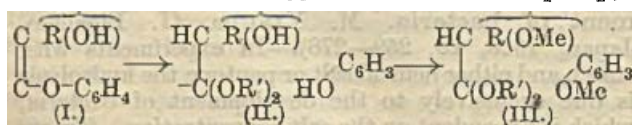
Nature of salt hydrolysis of starch considered in the light of the influence of salt on the development of bacteria. M. YASUDA (J. Biochem. Japan, 1929, 10, 259—276).—In experiments with starch and either neutral salt or peptone the hydrolysis is due exclusively to the development of bacteria, which is dependent on the salt concentration. Traces of multivalent cations have a considerable influence, and exercise a favourable effect on the transfer of oxygen to the bacteria.

CHEMICAL ABSTRACTS.

Inulin. VIII. H. PRINGSHEIM, J. REILLY, and P. P. DONOVAN (Ber., 1929, 62, [B], 2378—2381; cf. A., 1928, 1225).—Inulin is soluble in molten acetamide and, in concentration up to 2.5%, has in it the mol. wt. required by the formula $(C_6H_{10}O_5)_2$. The carbohydrate, precipitated by alcohol from acetamide, is unchanged in elementary composition and specific rotation, but has undergone disaggregation. More prolonged action of molten acetamide transforms inulin into *inulan*, which, when freshly prepared, is freely soluble in cold water, in which it has the composition $(C_6H_{10}O_5)_2$. When preserved, it gradually becomes as insoluble in water as inulin, from which it can no longer be distinguished.

Inulin and inulan can be boiled with water in glass or quartz flasks for 5 hrs. without the reducing power attaining 1% of that of *lævulose*. It is inadmissible to conclude from the observation that inulin feebly reduces boiling Fehling's solution that it contains free carbonyl groups at the end of a fructose chain. Sucrose is slightly hydrolysed by water and very faintly reduces Fehling's solution without necessitating the assumption of a chain of sugar residues with terminal carbonylated groups. H. WREN.

Lignin. XI. Degradation of lignin with methylglycolic [β -methoxyethyl-alcoholic] hydrogen chloride. W. FUCHS (Ber., 1929, 62, [B], 2125—2132; cf. this vol., 1046).—Hydrochloric acid pine lignin swells rapidly in boiling 0.1*N*- β -methoxyethyl-alcoholic hydrogen chloride and, after 30 min., is mainly dissolved to a dark, viscous, difficultly filterable solution which is relatively easily filtered after boiling for a few hrs. Acetyl- and methyl-lignin, from Willstätter lignin, dissolve equally readily in the reagent in which the lignin in ordinary or methylated pine wood is almost as readily soluble. Acetylated pine wood is less easily attacked and cellulose is scarcely affected. If the solution obtained from hydrochloric acid lignin is treated with excess of water, a product is obtained (75% yield) soluble in dilute alkali hydroxide and containing 21% of methoxyl. The methylglycol derivative with diazomethane gives a product insoluble in alkali hydroxide and containing 26.5% of methoxyl. Each entering methylglycol molecule therefore corresponds with one free phenolic group, and the minimal mol. wt. of lignin is about 400. Monomethyl-lignin dissolves in β -methoxyethyl-alcoholic hydrogen chloride, giving a product containing 22.8% of methoxyl, which is soluble in alkali hydroxide. Hence, during the degradation one free hydroxyl group must be developed for every two entering methylglycol residues. This product when treated with diazomethane gives a material insoluble in alkali and containing 25.8% of methoxyl; it is very similar to the methyl ether of the methylglycol derivative of lignin. The following scheme is therefore suggested ($R' = OMe \cdot CH_2 \cdot CH_2 \cdot$),



Treatment of II with boiling methyl alcohol results in partial displacement of the β -methoxyethyl group.

Present work, coupled with a review of the literature,

suggest the mol. wt. 802 ($\pm 5\%$) as most probable for lignin.

The possibility of the rupture and reunion of components during dissolution and precipitation respectively of complex natural products is favourably discussed. The author adopts the view that large molecular compounds disintegrate into "reactals" just as a salt forms ions. A reactal is defined as a bivalent atomic group which is distinguished from the molecule by its unsaturated character and from the ion by its electrical neutrality. H. WREN.

Willstätter-lignin. B. RASSOW and P. ZICKMANN (J. pr. Chem., 1929, [ii], 123, 189—234).—In investigations into the constitution of lignin it is essential that extraction should be effected with indifferent reagents which do not alter its structure. Attempted extraction with a large number of neutral organic solvents was found to be impossible, whilst many of the methods used by previous investigators are not free from the above objection. Owing to the resistance of lignin to hydrolysis the methods most free from objection are extraction (a) with 72% sulphuric acid, (b) with 1% hydrochloric acid under pressure, and (c) by Willstätter and Zechmeister's method (A., 1913, i, 955) with 43% hydrochloric acid at the ordinary temperature for 1 day, the last-named most nearly approaching the required conditions. Extraction of pine wood which had the composition: water 12.65; ash 0.56; pentosans 4.43; cellulose 54.7; lignin (ash-free) 30.6% by process (c) yielded a product (C, 64.2; H, 5.4%) which is acetyl-free, has 14.65% OMe ($C_{20}H_{20}O$ requires OMe 16.64%), and contains no pentosans, whilst the shortened process of Hagglund yields a product which still contains pentosans. The dark colour of the product is removed by washing with water and is due to the formation of an oxonium salt which is decomposed slowly by cold and instantly by hot water, the regenerated lignin being unaltered in composition. Most of the various colour reactions of the original wood with phenols and amines are not given by the lignin so prepared, but Klason's, Cross and Bevan's, and Maule's are typical for lignin. Lignin is unaltered by attempted reduction with active aluminium, zinc, and hydrochloric or acetic acid, and, contrary to Schwalbe's conclusion ("Die Chemie der Cellulose," 1910, 447), but in agreement with König's (cf. B., 1922, 9), is therefore saturated. Oxidation with permanganate gives only a small yield of oxalic acid, whilst concentrated nitric acid gives 80% of oxalic acid and 1% of picric acid. Chlorination of lignin gives no evidence concerning its structure, the products being soluble but of complex reaction, and no simple derivative could be obtained. By the action of chlorine for 15 hrs. and repeated precipitation of the product from alcoholic solution with water an intermediate product containing 32.8% Cl is obtained, whilst the final product contains 38.22% Cl. With aqua regia the final product contains 36.26% Cl, and only traces of chloroquinone are obtained. The yield of the latter never exceeds 1% and is found only when much oxidation occurs and most of the lignin is completely destroyed. Similarly, no trace of "mairagallol" or "leucogallol" obtained by Cross, Bevan, and Beadle from jute

lignin (A., 1894, i, 63) could be detected. Bromination in various solvents gives a product containing 30-60% Br, an equivalent quantity of hydrogen bromide being liberated and deep-seated alteration in the structure taking place. Dry distillation of lignin in a vacuum yields a distillate (16% at 12 mm.; 11.8% in a high vacuum) in which small quantities of acetic and formic acids, formaldehyde, and methyl alcohol can be detected, and 9% of a tar containing higher phenols and in which eugenol can be detected. Fusion of lignin with potassium hydroxide under varying conditions gives a maximum yield of 3% of protocatechuic acid, but by addition of zinc dust (at 250°) to prevent oxidation, 15% of the crystalline acid can be isolated (cf. Heuser and Winsvold, A., 1923, i, 541). The various structures proposed for lignin are criticised on the basis of these results and it is concluded that lignin must contain an aromatic nucleus and a pyrone ring and contain the skeleton of 2-phenylflavone. The structure best in agreement with this is that of Klason (A., 1922, i, 324) and a scheme representing the formation of various degradation products on this basis is given.

J. W. BAKER.

Action of nitrous acid on amino-compounds.
III. Dimethylamine, *n*-propylamine, and glycine ethyl ester. T. W. J. TAYLOR and L. S. PRICE (J.C.S., 1929, 2052—2059; cf. A., 1928, 993).—The action of nitrous acid on the above amino-compounds has been investigated, a different type of product being produced in each case, namely, a nitrosoamine, an alcohol, and an aliphatic diazo-compound, respectively. In each case it is shown that the reaction velocity varies as the product $[RNH_3]^+[NO_2]^-/[HNO_2]$. The action of nitrous acid on *n*-propylamine is remarkable in that the product consists of 42% of *n*- and 58% of *iso*-propyl alcohol, but the experimental work offers no explanation of the formation of these two products. In the case of glycine ethyl ester a formula for the reaction velocity has been derived which conforms with the experimental results.

J. W. PORTER.

New thiocholine bromide. T. HARADA (Bull. Chem. Soc. Japan, 1929, 4, 171—176).—The action of 2-thiouracil or 4-methyl-2-thiouracil on bromocholine bromide gave *thiocholine bromide*, slow decomp. above 220°, isoelectric point 7.0°, which when oxidised with hydrobromic acid yielded *bromocholine disulphide*. Treatment of thiocholine bromide with silver oxide and hydrobromic acid gave a *silver derivative*, $C_5H_{13}NSBr_2Ag_2$, decomp. 214°. A. A. GOLDBERG.

Action of nitrosyl bromide on amino-acids. G. ZEMPLEN and Z. CSUROS (Ber., 1929, 62, [B], 2118—2125).—The action of nitrosyl bromide on amino-acids leads smoothly to the production of bromo-acids only in the case of α -compounds. β -Aminopropionic acid can be transformed into β -bromopropionic acid, m. p. 60—61°, at about 20°, but similar change is not observed when the amino-group is more remote from the carboxyl group. If γ -amino-*n*-butyric acid is repeatedly treated with nitrosyl bromide at the atmospheric temperature, 68%, it can be recovered as γ -benzamido-*n*-butyric acid, m. p. 78—79°. δ -Amino-*n*-valeric acid does not give δ -bromo-*n*-valeric acid. Similarly, ϵ -amino-*n*-hexoic

acid is not attacked (ϵ -benzamido-*n*-hexoic acid, m. p. 80°). ϵ -Benzamidoamyl iodide and ethyl sodiummalonate in alcohol yield ethyl ϵ -benzamidoamylmalonate, hydrolysed by alkali hydroxide to ϵ -benzamidoamylmalonic acid, m. p. 115° after softening at 112°, from which ζ -benzamido-*n*-heptoic acid, m. p. 80—81°, is derived. ζ -Amino-*n*-heptoic acid, m. p. 186°, obtained by boiling its benzoyl derivative or ϵ -benzamidoamylmalonic acid with fuming hydrochloric acid, is unchanged by nitrosyl bromide.

H. WREN.

New crystalline form of tyrosine. J. C. ANDREWS (J. Biol. Chem., 1929, 83, 353—355).—By partial neutralisation with 4*N*-sodium hydroxide of a saturated solution of *l*-tyrosine in concentrated hydrochloric acid the amino-acid is obtained in blunt prisms.

C. R. HARRINGTON.

Synthesis of optically active, substituted asparagines. II. O. LUTZ (Ber., 1929, 62, [B], 1916—1921; cf. this vol., 1048).—The rotation graphs of *l*-asparagine and of the *d*-anilino-, *d*-*m*-toluidino-, *d*-*p*-toluidino-, and *d*-*p*-phenetidino-succinmonoamides derived from it have been determined. In any series the concentration of the organic component is maintained constant and the effect of gradual increase of acid or alkali hydroxide on the specific rotation is observed. In every case the derivative is found to belong to the series opposite to the original material.

H. WREN.

Trimethyl- α -glutarobetaine. H. D. DAKIN and R. WEST (J. Biol. Chem., 1929, 83, 773—776).—Glutamic acid was treated with methyl sulphate and sodium hydroxide; the product, isolated by precipitation with phosphotungstic acid, proved to be trimethyl- α -glutarobetaine, $CO_2H \cdot [CH_2]_2 \cdot CH(NMe_3 \cdot OH) \cdot CO_2H$, m. p. 211—213°, $[\alpha]_D +12.0^\circ$ in water [chloroaurate, m. p. (anhydrous) 139—140°; chloroplatinate, m. p. 204—205°]. The compound was stable towards concentrated potassium hydroxide.

C. R. HARRINGTON.

Transformations of peptide-like substances.
XXVII. Structure of clupeine. Autoracemisation of anhydrides of amino-acids containing arginine. M. BERGMANN, L. ZERVAS, and H. KOSTER (Ber., 1929, 62, [B], 1901—1905).—*d*-Phenylalanyl-*d*-arginine anhydride undergoes rapid racemisation in aqueous solution at 21°, the reaction being unimolecular. If the solution is treated with hydrochloric acid immediately after completion of racemisation, phenylalanylarginine anhydride hydrochloride monohydrate, m. p. about 170° and 241—243° (corr. decomp.) after resolidification, is obtained, in which both amino-acids are present in inactive form. If, however, the solution is preserved, dipeptide formation ensues as a consequence of autohydrolysis. *d*-Phenylalanyl-*d*-arginine is optically stable under these conditions. *d*- α -Diguano-*n*-valeric anhydride similarly suffers rapid autoracemisation in aqueous solution at 20°, probably owing to intermediate tautomerisation of $\cdot CHR \cdot CO \cdot$ to $\cdot CR \cdot C(OH) \cdot$ under the influence of the basicity of the free guanido-group. The comparatively very slow racemisation of clupeine in aqueous solution excludes the possibility of the presence in it of arginine in the form of simple anhydride.

H. WREN.

Transformations of peptide-like substances.
XXVIII. Syntheses of peptides containing arginine; *d*-tyrosyl-*d*-arginine and its anhydride. M. BERGMANN, L. ZERVAS, and V. DU VIGNEAUD (Ber., 1929, 62, [B], 1905—1909).—Condensation of *d*-arginine with the azlactone of α -acetamido-*p*-acetoxy-cinnamic acid followed by hydrogenation of the product in the presence of palladium-black affords *diacetyl-d-tyrosyl-d-arginine* ($+CH_3 \cdot CO_2H$), m. p. 196° (corr.), $[\alpha]_D^{25} -19.5^\circ$ in water. Treatment with hydrochloric acid yields *d-tyrosyl-d-arginine*, m. p. $200-202^\circ$ (corr.; decomp.) when rapidly heated, $[\alpha]_D^{25} -105.7^\circ$ in 0.2*N*-hydrochloric acid [*salicylidene* derivative, yellow needles, m. p. $192-194^\circ$ (corr.) after softening, or almost colourless, hexagonal leaflets, m. p. $252-254^\circ$ (corr.)]. *d-Tyrosyl-d-arginine anhydride hydrochloride* had m. p. about 220° (corr. decomp.) after softening at 165° , $[\alpha]_D^{25} -40.4^\circ$ in water. H. WREN.

Transformations of peptide-like substances.
XXIX. Acyl migrations and hydrolytic processes with diketopiperazines. M. BERGMANN, V. DU VIGNEAUD, and L. ZERVAS (Ber., 1929, 62, [B], 1909—1913).—Glycine reacts with diacetylglycine anhydride in the presence of aqueous sodium hydroxide, yielding glycine anhydride and aceturic acid. Diacetyldiketopiperazine and *d*-arginine in water and chloroform afford diketopiperazine and acetyl-*d*-arginine, $[\alpha]_D^{25} +9.07^\circ$ in water. In presence of ethyl alcohol, diacetyldiketopiperazine undergoes alcoholysis under the catalytic influence of arginine, yielding primarily *NN'*-*diacetylglycylglycine ethyl ester*, $NHAc \cdot CH_2 \cdot CO \cdot NAc \cdot CH_2 \cdot CO_2Et$, m. p. $74-76^\circ$, which readily loses an acetyl group under the influence of bases, giving acetylglycylglycine ethyl ester, m. p. 153° (corr.). The presence of the second acetyl group also facilitates remarkably the separation of the glycyl residues from one another. H. WREN.

Influence of structure of polypeptides and derivatives on their fission by *N*-alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1929, 11, 45—63).—The hydrolysis of a series of polypeptides and their derivatives (prepared by the usual methods) with *N*-sodium hydroxide, trypsin-kinase (p_H 7.8 and 8.4), and erepsin (none of the compounds used is hydrolysed by this enzyme) at 37° has been studied. The *benzoyl*, m. p. $205-207^\circ$ (not sharp), *p-nitrobenzoyl*, m. p. 213° with darkening, and *p-chlorobenzoyl*, m. p. 189° , derivatives of *dl*-leucylglycyl-*dl*-leucine (I) are all hydrolysed more readily by alkali than is I; the *naphthalene-2-sulphonyl*, m. p. 200° with darkening, *benzyl*, m. p. 226° (decomp.), and *methyl*, m. p. 253° (decomp.), derivatives undergo fission less readily than I, but a primary acceleration is observed with the benzyl derivative. All the above compounds and chloroacetyl-*dl*-leucylglycyl-*dl*-leucine are attacked (to various extents) by trypsin-kinase at both p_H values. *Glycyl-dl-leucylaniline*, m. p. $115-117^\circ$ after sintering at 94° (from *chloroacetyl-dl-leucylaniline*, m. p. 168°), *dl*-leucylglycyl-*dl*-leucylaniline (II), m. p. about 150° with darkening (from *dl*- α -bromoisohexoylglycyl-*dl*-leucylaniline, m. p. 176°), and the *methyl* derivative, m. p. $160-161^\circ$, of II are all hydrolysed

by alkali; *di*(*naphthalene-2-sulphonyl*)glycyl-*dl*-tyrosine is unaffected by alkali, but is hydrolysed by trypsin-kinase at p_H 8.4. Trypsin-kinase has no action on II or its methyl derivative (cf. Abderhalden and Brockmann, this vol., 180). H. BURTON.

Sulphur in proteins. IV. Effect of alkalis on cystine. R. A. GORTNER and W. B. SINCLAIR (J. Biol. Chem., 1929, 83, 681—696).—The following experiments were conducted in duplicate with *l*-cystine and inactive cystine (A., 1927, 1212), no differences being observed in the behaviour of the two forms of the amino-acid. Boiling with 1 or 5% sodium carbonate causes destruction of about 50% of the cystine in 24 hrs. in each case, although, with the 5% alkali, more sulphur is obtained as sulphide. Boiling with 6.5% barium hydroxide (hydrate) causes 50% destruction in 1 hr.; strontium and calcium hydroxides also cause extensive deamination of cystine, whilst with 20% sodium or potassium hydroxide the deamination is much less, although the sulphur is rapidly liberated; deamination of cystine in alkaline solution appears to be associated with an oxidation-reduction system requiring the integrity of the group containing sulphur. The action of lead in promoting decomposition of cystine in alkaline solution is not specific as has been claimed by Andrews (this vol., 85). The products obtained by boiling cystine for 24 hrs. with 6.5% barium hydroxide consist of an ether-soluble fraction and an alcohol-soluble fraction, both of which give positive tests for labile sulphur, and a water-soluble fraction in which the amino-nitrogen:sulphur ratio corresponds with that of cystine. C. R. HARRINGTON.

Oxidation-reduction systems of biological significance. V. Composition of oxidised cobalt-cysteine complex; micro-determination of cobalt. L. MICHAELIS and S. YAMAGUCHI (J. Biol. Chem., 1929, 83, 367—373).—On addition of cysteine to a solution of cobalt sulphate, proportionate increase in colour development occurs until the ratio of 1 atom of cobalt to 3 mols. of cysteine is reached, when the colour is at maximum intensity. This confirms the previously suggested structure (this vol., 1011) of the cobalt-cysteine complex, which is formulated $Co[S \cdot CH_2 \cdot CH(NH_2) \cdot CO_2]_3H_2$. The formation of this coloured complex is made the basis of a micro-method for the colorimetric determination of cobalt. C. R. HARRINGTON.

Acylation of cystine. Y. INOUE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 647—651).—Acetylation of cystine ester in pyridine solution and subsequent hydrolysis gave acetylcystine. The following were prepared: *diacetyl-l-cystine*, m. p. 75° ; *diacetyl-l-cystine dipropyl ester*, m. p. $117-118^\circ$; *diacetyl-l-cystine diamyl ester*, m. p. $128-129^\circ$; *diacetyl-l-cystine dibenzyl ester*, m. p. $126-128^\circ$; *di-p-nitrobenzoyl-l-cystine*, m. p. $193-194^\circ$; and *dinaphthalyl-l-cystine*, m. p. $194-195^\circ$. The cystine esters of the lower alcohols are hygroscopic and unstable.

A. A. GOLDBERG.

Thiocyanopropionic acids. A. FREDGA (J. pr. Chem., 1929, [iii], 123, 110—128).—Treatment of a fairly concentrated solution of potassium α -bromopropionate with solid potassium thiocyanate, sub-

sequent evaporation to dryness, and extraction with alcohol affords the potassium salt (I) of α -thiocyanopropionic acid (II), m. p. 49.5—51°, k 3.62×10^{-3} (sodium and calcium $[+2H_2O]$ salts). From *l*- and *d*- α -bromopropionic acids are obtained similarly potassium (—)- α -thiocyanopropionate, $[\alpha]_D^{25} -58.2^\circ$ in water [free acid (III), m. p. 51—53°, $[\alpha]_D^{25} -55^\circ$ in alcohol], and potassium (+)- α -thiocyanopropionate, $[\alpha]_D^{25} +58.3^\circ$ in water [free acid (IV), m. p. 50—53°, $[\alpha]_D^{25} +54.2^\circ$ in alcohol], respectively. When an aqueous solution of II is treated with a small amount of hydrochloric acid at the ordinary temperature α -carbamylthiopropionic acid, m. p. 125° with evolution of gas, k 3.26×10^{-4} (the anilide, m. p. 117°; *o*-toluidide, m. p. 135—137°; *p*-toluidide, m. p. 114—115°; α -naphthylamide, m. p. 161—162°, and β -naphthylamide, m. p. 154—156°, are prepared by the action of the requisite arylamine hydrochloride on an aqueous solution of I, or directly from α -bromopropionic acid, potassium thiocyanate, and the amine), is obtained. Similarly, III and IV furnish (+)- α -carbamylthiopropionic acid, m. p. 117° (decomp.), $[\alpha]_D^{25} +94.7^\circ$ in water, and (—)- α -carbamylthiopropionic acid, m. p. 117° (decomp.), $[\alpha]_D^{25} -94^\circ$ in water, respectively. Hydration of III with water, hydrochloric acid, and hydrochloric acid and potassium chloride solution is followed polarimetrically; the unimolecular velocity coefficient increases with increase in the concentration of the acid, but is lowered by the addition of potassium chloride. Racemisation of III or IV occurs by the addition of potassium thiocyanate, and the velocity coefficient is a linear function of the thiocyanate-ion concentration. Prolonged action of concentrated hydrochloric acid on the above carbamyl derivatives yields 2:4-diketeto-5-methyltetrahydrothiazole, m. p. 48—50° (lit. 46—47°), also formed by the action of hydrogen chloride on I in ether suspension. β -Thiocyanopropionic acid, m. p. 7.5—8.5°, k 1.32×10^{-4} (sodium salt), is converted by treatment with 4*N*-hydrochloric acid into β -carbamylthiopropionic acid.

Thiocyanoacetic acid, m. p. 35—40°, is obtained solid by inoculation of the oily acid with selenocyanoacetic acid.

H. BURTON.

Selenocyanopropionic acid. II. α -Selenocyanobutyric acids. A. FREDGA (J. pr. Chem., 1929, [ii], 123, 129—145; cf. this vol., 426) — (—)- α -Selenocyanopropionic acid (I), m. p. 90—91°, $[\alpha]_D^{25} -58.1^\circ$ in alcohol (potassium salt, $[\alpha]_D^{25} -67.1^\circ$ in water), is obtained by the method previously described (*loc. cit.*) from *l*- α -bromopropionic acid. Prolonged treatment of I with 4*N*-hydrochloric acid affords (+)-diselenodi- α -propionic acid (II), m. p. 43—45°, $[\alpha]_D^{25} +251.2^\circ$ in water. When II is treated with diselenodiacetic acid, m. p. 99—100° (by the action of hydrochloric acid on selenocyanoacetic acid, k 1.79×10^{-3}), the initial activity of the mixture is lowered to the extent of 19—23% after 3—5 days. Solutions of II alone do not alter in rotatory power and it is suggested that radical formation ($R\cdot Se\cdot Se\cdot R \rightarrow 2R\cdot Se\cdot$) and subsequent recombination ($R\cdot Se\cdot + R'\cdot Se\cdot \rightarrow R\cdot Se\cdot Se\cdot R'$) may occur. Diselenodi- β -propionic acid, m. p. 137°, is prepared by the action of hot hydrochloric acid on β -selenocyano-

propionic acid (*loc. cit.*). α -Selenocyanobutyric acid, m. p. 50—51°, k 2.7×10^{-3} (potassium salt), and α -selenocyanoisobutyric acid, m. p. 79—80°, k 6.1×10^{-3} (potassium salt), are obtained by the general method and converted into diselenodi- α -butyric acid, m. p. 80—81°, and diselenodi- α -isobutyric acid, m. p. about 185° (decomp.), respectively, by treatment with hydrochloric acid. Oxidation of the above diselenides with iodine in sodium hydrogen carbonate solution proceeds quantitatively thus: $(R\cdot Se\cdot)_2 + 3I_2 + 4H_2O \rightarrow 2R\cdot SeO\cdot OH + 6HI$. The same oxidative fission also occurs when oxidation is effected with hydrogen peroxide in aqueous or acetone solution. There are thus prepared α -seleninopropionic acid, m. p. 83° (decomp.; lead and silver salts), α -seleninoisobutyric acid, m. p. 122° (decomp.), and seleninoacetic acid, m. p. 99° (decomp.).

H. BURTON.

Pseudohalogens. V. Mixed halogen, bromo-oxycyanogen. L. BIRCKENBACH and M. LINHARD (Ber., 1929, 62, [B], 2261—2277; cf. this vol., 1265). —Oxycyanogen, $(OCN)_2$, does not appear to be produced by the action of bromine or iodine on silver cyanate in organic liquids at low temperatures and in absence of moisture; the action of chlorine is not completely elucidated. If silver cyanate is added to a solution of bromine in ethyl chloride at -20° , silver bromide and bromo-oxycyanogen, $OCN\cdot Br$, are rapidly and quantitatively produced. Conversely, bromo-oxycyanogen does not liberate bromine from silver bromide and does not react with silver cyanate in presence of ethyl chloride. Bromo-oxycyanogen forms pale yellow needles, m. p. 72°. At 80—90° sudden polymerisation and partial decomposition occur. It reacts with the more readily attacked organic solvents. It is permanent in absence of light and moisture and becomes polymerised only when heated in the dark, moderately rapidly at the atmospheric temperature if exposed to sunlight. With aqueous potassium iodide, bromo-oxycyanogen reacts according to the equation $OCN\cdot Br + 2KI = I_2 + K\cdot OCN + KBr$, whereby a method of determining bromo-oxycyanogen is afforded. With aqueous sulphurous acid, bromo-oxycyanogen, after hydrolysis, is quantitatively and immediately reduced to cyanic acid and hydrogen bromide. The mixed halogen is hydrolysed by atmospheric moisture. If ice water is cautiously added to its solution or suspension in indifferent organic media, reaction occurs slowly in accordance with the scheme $6OCN\cdot Br + 4H_2O = 3Br_2 + N_2 + 4CO_2 + 2CO(NH_2)_2$; the rate of reaction is controlled by the intermediate change $2HOCN + H_2O = CO(NH_2)_2 + CO_2$ or $CO(NH_2)_2 + 3Br\cdot OH = 3HBr + CO_2 + N_2 + 2H_2O$. In alkaline solution the total reaction may be expressed: $3OCN\cdot Br + 8KOH = 3KBr + N_2 + 2K_2CO_3 + KOCN + 4H_2O$. Alcohol reacts violently with bromo-oxycyanogen. If the reaction is carried out in presence of ethyl chloride at -80° , ethyl *N*-bromoallophanate, m. p. 117°, separates. The product is hydrolysed by hot water to hypobromous acid and ethyl allophanate, m. p. 193°. When treated with dilute sulphurous acid, the bromine is quantitatively converted into hydrogen bromide; 1 mol. of ethyl *N*-bromoallophanate liberates 2 atoms of iodine from

acid potassium iodide. Determination of the mol. wt. of bromo-oxycyanogen in phosphoryl chloride gives values nearly double those required for $\text{OCN}\cdot\text{Br}$. The formation of ethyl bromoalphanate by alcoholysis in ethyl chloride and determinations of mol. wt. in phosphoryl chloride show that the solutions contain dimeric bromo-oxycyanogen. The occurrence of by-products during alcoholysis and a deficit in the mol. wt. values indicate an equilibrium, $2\text{OCN}\cdot\text{Br} \rightleftharpoons (\text{OCN}\cdot\text{Br})_2$, the constants of which depend on the solvent. This view is supported by the observation that the analogous iodo-oxycyanogen is converted by ethylene in ether into *N*- β -iodoethyl-*N'*-phenylcarbamide, m. p. 152°, in addition to other products, thus indicating the presence of monomeric iodo-oxycyanogen. Bromo-oxycyanogen in ether or ethyl chloride slowly adds ethylene, yielding an unstable crystalline product, analysis of which establishes the presence in it of the components in the ratio 1 : 1. H. WREN.

Action of sodium hypochlorite on acid amides. V. I. J. RINKES.—See this vol., 1296.

Action of activated hydrogen and nitrogen on carbon monoxide. G. B. CRIPPA and M. GALLOTTI (Gazzetta, 1929, 59, 507—509).—Minute crystals of carbamide have been obtained by the interaction for several hours at 115—120° of carbon monoxide and hydrogen and nitrogen activated by the silent discharge.

F. G. TRYHORN.

Preparation of dichloromethylarsine. E. V. ZAPPI and V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1929, 17, 59—62).—See this vol., 178.

Optimum concentration of the organic halide for initiating some Grignard reactions. H. GILMAN and R. J. VANDERWAL (Bull. Soc. chim., 1929, [iv], 45, 641—644).—The colour reaction previously described (A., 1925, ii, 1011; this vol., 303) has been used to determine the optimum concentration of the organic halide for starting Grignard reactions. With benzyl chloride and bromobenzene a concentration of 25—30% by volume gives the most rapid reaction; higher concentrations retard the reaction. Thus with 70% ethereal benzyl chloride no reaction takes place in several months. Similarly, with *n*-butyl bromide (in presence of iodine) and *n*-butyl chloride the optimum concentrations are 55% and 70%, respectively, and even in presence of iodine as catalyst the reaction at a concentration of 93—97% of butyl chloride is greatly retarded. Where a concentration of 30—40% of halide in ether cannot be obtained the use of a mixture of ether and benzene is recommended in spite of the negative catalytic effect of the latter (cf. this vol., 800).

R. BRIGHTMAN.

Preparation of Grignard's reagent for the micro-determination of hydroxyl groups by Tschugaev and Zerevitinov's method. B. FLASCHENTRAGER (Mikrochem., 1929, Pregl Fest., 87—88).—An improved method of preparation from magnesium, isoamyl ether, and methyl iodide is described. The reagent so prepared will keep good for several months in air-tight bottles.

H. F. HARWOOD.

Reaction between esters and magnesium phenyl bromide. Mobility of alkyl groups in

esters. H. GILMAN and J. D. ROBINSON (Bull. Soc. chim., 1929, [iv], 45, 636—641).—Since with methyl ethylsulphonate magnesium phenyl bromide yields 21% of toluene ($\text{R}\cdot\text{SO}_2\cdot\text{OAlk} + \text{R}'\cdot\text{MgX} \longrightarrow \text{R}'\cdot\text{Alk} + \text{R}\cdot\text{SO}_2\cdot\text{OMgX}$) and 14% of phenyl ethyl sulphone ($\text{R}\cdot\text{SO}_2\cdot\text{OAlk} + \text{R}'\cdot\text{MgX} \longrightarrow \text{R}\cdot\text{SO}_2\cdot\text{R}' + \text{aryl}\cdot\text{OMgX}$) (cf. Ferns and Lapworth, J.C.S., 1912, 101, 273; Strecker, A., 1910, i, 532), alkyl alkylsulphonates differ from alkyl arylsulphonates only in the relative extent to which the two reactions occur, arylsulphonates giving smaller amounts of sulphone (cf. A., 1928, 1124; this vol., 545). Since phenyl ethylsulphonate yields 74% of phenyl ethyl sulphone and 85% of phenol, it is probable that aryl esters of all sulphonic acids yield sulphones and phenols unless the presence of substituents modifies the properties of the aryl group. Methyl benzenesulphonate yields 63% of diphenyl sulphide, together with methyl alcohol, the small amount of diphenyl sulphoxide also observed (cf. A., 1926, 1239) being due to the presence of a little methyl benzenesulphonate, methyl benzenesulphonate itself affording 65% of diphenyl sulphoxide, a little methyl alcohol, but no toluene or diphenyl sulphide. In accordance with previous results obtained for the mobility of organic radicals, allyl benzoate yields 86% of triphenylcarbinol and allylbenzene, and benzyl benzoate gives 86% of benzyl alcohol, 69.7% of phenyldibenzylcarbinol, and 6.6% of dibenzyl (cf. Gilman and Kirby, this vol., 801). Since no alkylation products are obtained in the action of magnesium phenyl bromide on alkyl esters of strong carboxylic acids the behaviour of the alkyl esters of the sulphonic acids cannot be attributed to the high dissociation constants of the sulphonic acids. Thus ethyl tribromoacetate gives bromobenzene and a little diphenyl, ethyl trinitrobenzoate 35% of phenol and 7.25% of diphenyl (cf. Gilman and McCracken, this vol., 546), and ethyl acetylenedicarboxylate 14% of diphenyl, no ethylbenzene being formed in any of these cases or with ethyl nitroacetate or triphenylacetate.

R. BRIGHTMAN.

Possible interchange of radicals on heating a mixture of $\text{R}'\cdot\text{X}$ and $\text{R}\cdot\text{MgX}$ compounds. H. GILMAN and H. L. JONES (J. Amer. Chem. Soc., 1929, 51, 2480—2483).—Magnesium aryl or aralkyl halides do not react with aryl or aralkyl halides thus: $\text{R}\cdot\text{MgX} + \text{R}'\cdot\text{X} \longrightarrow \text{R}\cdot\text{X} + \text{R}'\cdot\text{MgX}$, since decomposition of the reaction product with carbon dioxide furnishes only the acid $\text{R}\cdot\text{CO}_2\text{H}$. A secondary reaction (formation of $\text{R}\cdot\text{R}'$) takes place to varying extents according to the reactivity of the halide ($\text{R}'\cdot\text{X}$) used. Magnesium phenyl bromide and triphenylmethyl chloride afford a small amount (0.63%) of tetraphenylmethane and 47.4% of diphenyldiphenylmethane, m. p. 111°.

H. BURTON.

1 : 2-Dimethylcyclopropanes. J. BAUDRENGHIEN (Bull. Soc. chim. Belg., 1929, 38, 172—193).—See this vol., 801.

1 : 2-Dimethyl-3-isopropylcyclopentane. B. KASANSKI (Ber., 1929, 62, [B], 2205—2210; cf. Godchot and Taboury, A., 1913, i, 348; Zelinski and Kasanski, A., 1927, 670).—Dihydrocamphorone, b. p. 181—183°/748.5 mm., d_4^{25} 0.8899, n_D^{25} 1.4412, is transformed by ethereal magnesium methyl iodide into the

corresponding tertiary alcohol, which could not be obtained quite homogeneous, but is dehydrated by oxalic acid at 130° and then reduced in presence of nickel at 160–170° to 1:2-dimethyl-3-isopropylcyclopentane, b. p. 159–161°/757 mm., d_4^{25} 0.7883, n_D^{25} 1.4319. Thujamenthone, b. p. 206–208°/749 mm., d_4^{25} 0.8894, n_D^{25} 1.4484, is transformed into the hydrazone, converted by distillation in presence of solid potassium hydroxide and platinised earthenware into 1:2-dimethyl-3-isopropylcyclopentane, b. p. 159–160.5°/757.6 mm., d_4^{25} 0.7877, n_D^{25} 1.4328. The divergence of the constants of Godchot's compound is probably due to degradation of the isopropyl group owing to the relatively high temperature of the treatment with nickel. 1-Methyl-2-isopropylcyclopentane, obtained from dihydrocamphorone by the hydrazine method, has b. p. 140–142.5°/764.8 mm., d_4^{25} 0.7750, n_D^{25} 1.4257. H. WREN.

spirocycloDecane and its contact isomerisation. N. D. ZELINSKI and N. I. SCHUIKIN (Ber., 1929, 62, [B], 2180–2186).—Adipic acid, prepared in 91% yield by oxidation of cyclohexanol with permanganate in cold, very dilute alkaline solution, is converted into cyclopentanone, b. p. 130–131° (yield 76.5% in presence of barium hydroxide or 90% in presence of thorium oxide hydrate). Reduction of the ketone in aqueous-etheral solution at +5° in a current of carbon dioxide yields mainly cyclopentanol and 2-cyclopentylcyclopentanol, b. p. 117–118°/12 mm., d_4^{20} 0.9802, n_D^{20} 1.4885; the *pinacol*,

$\begin{bmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{bmatrix} > \text{C}(\text{OH}) \cdot$, m. p. 107–108°, is obtained in 3% yield. The last-named compound is converted by hot dilute sulphuric acid into 2:2-tetramethylenecyclohexanone, b. p. 98–100°/13 mm., d_4^{20} 0.9898, n_D^{20} 1.4848 (*semicarbazone*, m. p. 191–192°). The ketone is transformed into its *hydrazone*, which, when decomposed in presence of platinum and potassium hydroxide, passes into 1:1-tetramethylenecyclohexane (spirocyclodecane),

$\begin{bmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{bmatrix} > \text{C} < \begin{bmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{bmatrix} > \text{CH}_2$, b. p. 185–186°/745 mm., d_4^{20} 0.8877, n_D^{20} 1.4748. The hydrocarbon slowly decolorises dilute permanganate and with bromine yields a *tetrabromide*, m. p. 130–132° (decomp.). *spirocycloDecane* is isomerised in presence of platinised charcoal and hydrogen at 190° to a compound, $\text{C}_{10}\text{H}_{18}$, b. p. 185.5–186.5°/750 mm., d_4^{20} 0.8730, n_D^{20} 1.4683; isomerisation occurs more slowly in an atmosphere of carbon dioxide. The product reacts slowly with permanganate. It does not become dehydrogenated in presence of palladised asbestos or platinised charcoal at 300°. H. WREN.

Meaning of action constants in substitution reactions in the benzene nucleus. W. HUCKEL and H. HAVEKOS (Ber., 1929, 62, [B], 2041–2043; cf. A., 1928, 987).—Examination of Holleman's data for the replacement of chlorine in chloronitro- and chlorodinitro-benzenes under the action of diethylamine and sodium methoxide shows that variations in the action constants may occur which cannot be foretold from probabilities of steric hindrance or furtherance. A theoretical basis of the relationship between constitution and action constants cannot be given. Present theories, for example that of induced

alternate polarities, do not take this into consideration and, for further progress, it is necessary to recognise the influence of action constants on velocity coefficients and to separate their part from that of activation energy. H. WREN.

Benzene and mobility of the iodoxy-group. D. VORLÄNDER (Rec. trav. chim., 1929, 48, 912–918).—Substitution in the benzene nucleus is discussed briefly (cf. A., 1919, i, 319). Oxidation of 1-iodo-2:4-dinitrobenzene with hypochlorous acid in acetic acid solution gives 1-iodoxy-2:4-dinitrobenzene (I), explodes between 140° and 160°, according to rate of heating. The mobility of the iodoxy-group in I is great (cf. A., 1925, i, 1055). Thus, treatment of I with silver nitrate gives silver iodate and *m*-dinitrobenzene, sodium nitrite in the cold converts I into 1:2:4-trinitrobenzene, and the action of aqueous sodium azide yields 2:4-dinitroazidobenzene. These results are explicable on the author's theory of alternating charges. H. BURTON.

Highly-polymerised compounds. XXI. Reduction of polystyrene. H. STAUDINGER and V. WIEDERSHEIM (Ber., 1929, 62, [B], 2406–2411; cf. this vol., 910).—Hemicolloidal polystyrenes (mean mol. wt., 1800–5000) which, according to Heuer (unpublished work), are not essentially degraded when heated in solution at 200°, are not reduced in cold solution in presence of Willstätter's platinum, platinum oxide, or nickel, but are completely hydrogenated in decahydronaphthalene at 200° in presence of Kelber's nickel to hexahydropolystyrenes, in which the absence of non-hydrogenated, aromatic nuclei is established by their inability to react with concentrated nitric acid or tetranitromethane. Reduction of a preparation of mean mol. wt. 1800 gave a product of unchanged mean mol. wt. and identical viscosity in solution. More complex products are cracked in some degree by a similar treatment, but in the main are reduced without decomposition if the process is effected rapidly in the presence of a sufficient amount of active catalyst. The smaller fragments are removed by re-precipitation, leaving mixtures of approximately the same viscosity and mean mol. wt. as the initial materials. Complex polymerisation products can therefore be subjected to chemical change without alteration of the mean mol. wt. In the solution the compound exists as molecules and not as associations and the mean mol. wt. of the products is truly determined. Mol. wts. of hydrocarbons of this order of magnitude can be accurately determined, and erroneous values are not obtained due to solvation or micelle formation. The viscosity of the solutions depends on the size of the long thread molecules, which hinder the normal movement of the liquid molecules and thus cause viscosity in the solutions. H. WREN.

Preparation of *p*-tolylacetylene. A. WILLEMART (Bull. Soc. chim., 1929, [iv], 45, 644–645).—*p*-Tolyl methyl ketone is treated with phosphorus pentachloride and the monochloro-compound, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CCl} \cdot \text{CH}_2$, b. p. 86–96°/12 mm. (Auwers and Keil, A., 1903, i, 620), is converted into *p*-tolylacetylene, m. p. 23°, b. p. 53–56°/11–12 mm., with 2.2 mols. of sodamide in presence of vaseline oil (cf.

Meunier and Desparmet, A., 1924, i, 701; Bourguet, A., 1925, i, 770).

R. BRIGHTMAN.

Homologues of diphenyl. E. BOEDTKER [with B. WIGER and R. KERLOR] (Bull. Soc. chim., 1929, [iv], 45, 645—650).—A residual specimen of Bert's *pp'*-diisopropyldiphenyl (A., 1923, i, 1005) on re-examination had m. p. 49°, but contained some crystals, m. p. 65—66°. *p*-Cumyl iodide, b. p. 236—238°, with commercial copper powder yielded only Schreiner's *pp'*-diisopropyldiphenyl, m. p. 49° (A., 1910, i, 367). Since, however, a second experiment gave only the substance, m. p. 65—66°, either Bert's or Schreiner's product is probably *p*-isopropylphenylphenyldimethylmethane, $\text{Pr} \cdot \text{C}_6\text{H}_4 \cdot \text{CPhMe}$, (cf. Weiler, A., 1896, 237, 242), and although the *pp'*-di-*tert*-butyldiphenyl obtained by Schreiner's method or from *p*-iodo-*tert*-butylbenzene by Tschitschibabin's method (A., 1928, 404) had m. p. 122°, this product also is regarded as probably a mixture of two similar isomerides. *n*-Butylbenzene, b. p. 180°, d_4^{20} 0.8679, n_D^{20} 1.4942 (yield 71% from *n*-butyl bromide, bromobenzene, and sodium), is converted by Klages and Storp's method (A., 1902, i, 670) into *p*-iodo-*n*-butylbenzene, b. p. 144°/20 mm., d_4^{20} 1.4616, n_D^{20} 1.5693, yielding, with copper powder, *pp'*-di-*n*-butyldiphenyl, m. p. 58—59°, b. p. 228—230°/14 mm., d_4^{20} 0.9499, n_D^{20} 1.5503. Similarly, sec.-butylbenzene, b. p. 171.3—172.3°, d_4^{20} 0.8612, n_D^{20} 1.4914, yields *p*-iodo-sec.-butylbenzene, b. p. 129—130°/16 mm., d_4^{20} 1.4701, n_D^{20} 1.5731, and *pp'*-di-sec.-butyldiphenyl, b. p. 222—224°/20 mm., d_4^{20} 0.9530, n_D^{20} 1.5577, and *tert*-amylbenzene, b. p. 189—190°, gives *p*-iodo-*tert*-amylbenzene, b. p. 139°/15 mm., d_4^{20} 1.4226, n_D^{20} 1.5669, and *pp'*-di-*tert*-amylidiphenyl, b. p. 224°/16 mm., d_4^{20} 1.5503, n_D^{20} 1.5570, which after some months deposits traces of a crystalline substance volatilising above 200°. R. BRIGHTMAN.

Mononitro- and monoamino-derivatives of 1-methylnaphthalene. V. VESELY, F. STURSA, H. OLEJNÍČEK, and E. REIN (Coll. Czech. Chem. Comm., 1929, 4, 493—515).—Nitration of 1-methylnaphthalene in acetic anhydride with excess of nitric acid (d 1.52) below 15° yielded 4-nitro-1-methylnaphthalene, m. p. 68—69°, together with a liquid which, contrary to Lesser (A., 1914, i, 33), furnished only the 4-amino-compound (isolated as the acetyl derivative, m. p. 166—167°) on partial reduction by hydrogen and platinum-black. 2:4-Dinitro-1-methylnaphthalene was reduced by platinum-black and hydrogen or by ammonium hydrogen sulphide to 2-nitro-4-amino-1-methylnaphthalene, m. p. 131—132°, and the latter converted into 2-nitro-1-methylnaphthalene, m. p. 58—59°. Reduction of the last-named with zinc dust and acetic acid afforded 2-amino-1-methylnaphthalene, m. p. 49—50° (acetyl derivative, m. p. 188—189°; benzoyl derivative, m. p. 222°), which was identical with the substance obtained from 1-methyl-2-naphthol. 3-Nitro-4-acetamido-1-methylnaphthalene, m. p. 224—225°, obtained from 4-acetamido-1-methylnaphthalene in acetic anhydride and nitric acid (d 1.52), was converted into 3-nitro-4-amino-1-methylnaphthalene, m. p. 179.5°, by warming with alcoholic hydrochloric acid, from which 3-nitro-1-methylnaphthalene (I), m. p. 81—82°, was prepared. The following compounds are described: 3-amino-1-

methylnaphthalene, m. p. 68° (acetyl derivative, m. p. 172—173°); 3-hydroxy-1-methylnaphthalene, m. p. 80—81°. 3:4-Diamino-1-methylnaphthalene, m. p. 91°, was produced by the reduction of 2-nitro-4-methyl- α -naphthylamine with stannous chloride. Treatment of 1-methylnaphthalene in carbon tetrachloride solution at 0° with chlorosulphonic acid furnished chiefly the 4-sulphonic acid, which was converted into 1-methylnaphthalene-4-sulphonyl chloride (II), m. p. 78—80°. When II is nitrated with nitric acid (d 1.475) at -5° to 3° the 5-nitro-, m. p. 161—161.5°, together with the 8-nitro-, m. p. 115—116°, 1-methylnaphthalene-4-sulphonyl chlorides are obtained, and separated by means of ether. The 5-nitro-sulphonyl chloride yielded 5-nitro-1-methylnaphthalene-4-sulphinic acid with sodium sulphite and sodium hydrogen carbonate, converted by warming with 60% sulphuric acid or 80% phosphoric acid into 5-nitro-1-methylnaphthalene, m. p. 82—83°. 5-Amino-1-methylnaphthalene, m. p. 77—78° (acetyl derivative, m. p. 194—195°; benzoyl derivative, m. p. 173—174°); 5-hydroxy-1-methylnaphthalene, m. p. 97—98°, was obtained by the hydrolysis of 5-nitro-1-methylnaphthalene-4-sulphonyl chloride with alkali, reduction of the resultant sodium nitro-sulphinate with iron and dilute acetic acid, and treatment of the sodium amino-sulphonate with sodium amalgam. 5-Acetamido-1-methylnaphthalene in acetic anhydride and nitric acid (d 1.525) at 15—20° afforded a mixture of two mononitro-compounds, separated by fractional crystallisation from ethyl acetate into 6-nitro-5-acetamido-1-methylnaphthalene (III), m. p. 245—246°, and 8-nitro-5-acetamido-1-methylnaphthalene (IV), m. p. 197—198°. Hydrolysis of III with alcoholic hydrochloric acid furnished 6-nitro-5-amino-1-methylnaphthalene, m. p. 178—179° (8-nitro-5-amino-1-methylnaphthalene similarly prepared from IV has m. p. 163—164°), which was converted into 6-nitro-1-methylnaphthalene, m. p. 76—77° [6-amino-1-methylnaphthalene, m. p. 63—64° (acetyl derivative, m. p. 123—124°; benzoyl derivative, m. p. 155—156°)]. The orientation of 6-nitro-5-amino-1-methylnaphthalene was confirmed by reduction with stannous chloride to 5:6-diamino-1-methylnaphthalene, m. p. 151—152°, which condensed with phenanthraquinone in glacial acetic acid to give 1-methylnaphthalene-5:6-phenanthrazine, m. p. 254—256°. 8-Nitro-1-methylnaphthalene-4-sulphonic acid was prepared from the sulphonyl chloride and converted by heating with 60% sulphuric acid into 8-nitro-1-methylnaphthalene, m. p. 63—64°. 8-Amino-1-methylnaphthalene, m. p. 67—68° (acetyl derivative, m. p. 183—184°; benzoyl derivative, m. p. 195—196°), was obtained from 8-amino-1-methylnaphthalene-4-sulphonic acid in the manner described above. Attempts to prepare 8-hydroxy-1-methylnaphthalene from the amino-compound were unsuccessful. Nitration of 8-acetamido-1-methylnaphthalene in acetic anhydride with nitric acid (d 1.525) and acetic anhydride afforded a mixture of mononitro-compounds, which was separated by ethyl acetate into 5-nitro-8-acetamido-1-methylnaphthalene, m. p. 193—194°, and a eutectic mixture. Partial hydrolysis of the latter with alcoholic potassium hydroxide yielded 5-nitro-1-methyl-8-naphthylamine, m. p. 162—163° (converted by elimination of

the amino-group into 5-nitro-1-methylnaphthalene, m. p. 83–84°, and 7-nitro-8-acetamido-1-methylnaphthalene (V), m. p. 186–187°. 7-Nitro-1-methyl-8-naphthylamine, m. p. 150–152°, obtained from V and alcoholic hydrochloric acid, was converted into 7-nitro-1-methylnaphthalene, m. p. 98–99° (7-acetamido-1-methylnaphthalene, m. p. 158.5–160°).

The constitution of 8-nitro-5-amino-1-methylnaphthalene was established by reduction with stannous chloride to the 5:8-diamine, followed by oxidation of the latter in anhydrous acetic acid with ferric chloride, when 1-methyl-5:8-naphthaquinone, m. p. 121–122°, was obtained. The same quinone was produced from 5-nitro-8-amino-1-methylnaphthalene.

A. I. VOGEL.

Catalytic transference of hydrogen between organic compounds. S. AKABORI and T. SUZUKI (Bull. Chem. Soc. Japan, 1929, 4, 198–202).—See this vol., 1170.

ms-Dialkylanthracenes and "transannular tautomerism." VI. E. DE B. BARNETT and J. L. WILTSHIRE (Ber., 1929, 62, [B], 1969–1973; cf. this vol., 1171).—1:4-Dichloroanthrone, m. p. 148°, is prepared by reduction of 1:4-dichloroanthraquinone in boiling glacial acetic acid with tin and hydrochloric acid or in cold concentrated sulphuric acid with aluminium powder. 1:4-Dichloroanthryl acetate has m. p. 174°. Treatment of 1:4-dichloroanthrone with magnesium ethyl bromide or magnesium benzyl chloride affords, respectively, 1:4-dichloro-9-ethylanthracene, m. p. 103°, and 1:4-dichloro-9-benzylanthracene, m. p. 113°. Bromine in carbon disulphide transforms the last-named compound into 1:4-dichloro-10-bromo-9-benzylidene-9:10-dihydroanthracene, m. p. 206°, from which the corresponding -10-piperidino-, m. p. 200°, -10-methoxy-, m. p. 185°, and -10-ethoxy-, m. p. 158°, compounds are derived by means of piperidine or the requisite alcohol in presence of calcium carbonate. 1:4-Dichloro-10-bromo-9-benzylidene-9:10-dihydroanthracene is converted by potassium acetate in acetic acid followed by boiling glacial acetic acid into 1:4-dichloro-9- α -acetoxybenzylanthracene, m. p. 208°. 1:4-Dichloro-10-methoxy-9-benzylidene-9:10-dihydroanthracene is transformed by methyl alcohol containing a little hydrochloric acid into 1:4-dichloro-9- α -methoxybenzylanthracene, m. p. 118°. 1:4-Dichloro-9- α -ethoxybenzylanthracene, m. p. 135°, is prepared similarly.

H. WREN.

Aromatic substitution from the viewpoint of electronic theory of valency. C. K. INGOLD (Rec. trav. chim., 1929, 48, 797–812).—A resume of the investigations on aromatic substitution carried out by the author and his co-workers during the last 4 years.

H. BURTON.

Theories of aromatic substitution. B. FLURSCHEIM (Rec. trav. chim., 1929, 48, 817–820).—The electrostatic and non-electrostatic theories are discussed briefly and the former criticised.

H. BURTON.

Orienting power of substituents in the benzene nucleus. F. SWARTS (Rec. trav. chim., 1929, 48, 1025–1028).—The effect of substituents on refraction is discussed. There appears to be no relationship

between refraction and orienting power. The variation of thermal energy involved in the introduction of groups into a substituted benzene nucleus is commented on.

H. BURTON.

Synthesis of aniline. M. SMIAŁOWSKI (Przemysł Chem., 1929, 13, 397–401).—Mixtures of chlorobenzene vapour and ammonia are passed through tubes heated at 250–400° and containing a catalyst consisting of 10% of nickel or cobalt intimately mixed with various carriers such as sodium or calcium carbonate, calcium oxide, pumice, lead, lead chromate, chromic oxide, and the products are analysed. Small quantities of aniline (0–1%) are found, together with ammonium carbonate, benzene, diphenyl, and carbazole, as well as traces of diphenylamine in those cases where lead is present. The presence of carbon monoxide in the reaction mixture slightly depresses the yields of aniline. The low yields of aniline obtained are due, not to inactivation of the catalyst, but probably to side reactions and to the reversal of the reaction, as mixtures of aniline and chlorobenzene vapours exhibit after passage through the tube a diminished aniline content.

R. TRUSZKOWSKI.

Nitration of esters of phenylmethylcarbamic acid. P. VAN ROMBURGH (Rec. trav. chim., 1929, 48, 922–925).—A modified account of work already published (A., 1901, i, 201). Jaeger's observation (A., 1906, i, 500) that methyl 2:4:6-trinitrophenylmethylcarbamate exists in two modifications, m. p. 107° and 118°, is confirmed. Treatment of this ester with a mixture of nitric (*d* 1.5) and sulphuric acids gives methyl 2:4:6-trinitrophenylcarbamate.

H. BURTON.

Nitration of aromatic compounds in alcoholic solution. F. REVERDIN (Rec. trav. chim., 1929, 48, 838–842; cf. this vol., 310).—Nitration of *p*-methoxybenzanilide (I), *p*-anisylurethane (II), and *p*-toluenesulphonamidophenetole with nitric acid (*d* 1.185) in boiling alcoholic solution affords the corresponding 3-nitro-4-acylamido-derivatives; *p*-ethoxyacetanilide (III) undergoes hydrolysis only. With nitric acid (*d* 1.4) *p*-toluenesulphon- and 2-nitro-*p*-toluenesulphon-amidophenetoles yield the corresponding 3:5-dinitro-derivatives; III furnishes 3-nitro-4-acetamidophenetole under regulated conditions, whilst I and II afford mainly the mononitro-derivatives. Acyl groups other than acetyl are not hydrolysed during nitration.

H. BURTON.

Phenoxyethylaniline and related compounds. D. H. PEACOCK, M. BHATTACHARYA, and B. L. RAO (J.C.S., 1929, 1926–1927).—The following compounds have been prepared by heating phenoxyethyl *p*-toluenesulphonate (Peacock and Tha, A., 1928, 1115) and the corresponding amine in the presence of rather more than the calculated amount of aqueous sodium carbonate: β -phenoxyethyl-*o*-toluidine, m. p. 64°; -*m*-toluidine, b. p. 220°/13 mm.; -*p*-toluidine, m. p. 52°; -ethylaniline; -diethylaniline, b. p. 212–213°/17 mm.; -*p*-chloroaniline, b. p. 228°/11 mm.; - α -naphthylamine, m. p. 106°.

R. K. CALLOW.

Electrochemical preparation of phenylhydrazine. R. E. MCCLURE and A. LOWY.—See this vol., 1247.

Stereoisomerism of diazo-compounds. W. SWIENTOSLAWSKI (Ber., 1929, 62, [B], 2034—2040; cf. A., 1920, i, 336).—A reply to Hantzsch (this vol., 805). H. WREN.

Reduction of normal diazohydrates. A. ANGELI and Z. JOLLES (Ber., 1929, 62, [B], 2099—2100).—Benzoylphenylhydrazine is produced when a solution of benzenediazonium chloride is rendered alkaline and treated with a solution of sodium stannite containing alcohol and benzaldehyde. Support is thus afforded to the author's theory (A., 1926, 947) of the intermediate production of phenyldi-imide during the reduction of normal diazohydrates: $\text{O:NPh:NH} + \text{H}_2 = \text{H}_2\text{O} + \text{NPh:NH}$. The production of ammonia and azoimide by reduction of potassium azodicarboxylate is explained by the intermediate formation of di-imide and the formation of the compound $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{O}) \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ from nitrosodimethylaniline and semicarbazide by the intermediate occurrence of $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \cdot \text{NH}$. Di-imide also appears to be intermediately formed during the production of diazonium salts from quinones and benzenesulphonylhydrazine or azodicarboxylic acid. The oxygen atom in normal diazohydrates appears present as oxide and not as hydroxyl. H. WREN.

Constitution and reactions of diazohydrates. A. ANGELI (Atti R. Accad. Lincei, 1929, [vi], 9, 933—940, and Ber., 1929, [B], 62, 1924—1928).—A refutation of Hantzsch's criticism (this vol., 805) of the author's views (A., 1928, 1129), in support of which Swientoslawski's thermochemical data (A., 1925, ii, 1044) are quoted. T. H. POPE.

Reactions of diazohydrates. D. BIGIARI (Ber., 1929, 62, [B], 2101—2102).—Whereas isodiazohydrates do not react with the sodium salt of nitrohydroxylamine, the normal diazohydrates give temporary, violet-blue colorations, marked gas evolution, resinification, and production of nitrosobenzene. The change is probably due to intermediately formed nitroxyl: $\text{O:NPh:NH} + \text{N} \cdot \text{OH} \longrightarrow \text{O:NPh} + \text{N}_2 + \text{H}_2\text{O}$. H. WREN.

Optically active diazo-compounds. IV. **Stable alicyclic diazo-amine.** C. W. BENNETT and W. A. NOYES (Rec. trav. chim., 1929, 48, 895—898).—When 2-aminofluoronehydrazone, m. p. 209° [prepared by Gerhardt's method (A., 1920, i, 766)], is suspended in 95% alcohol in which a small amount of sodium has been dissolved and then treated with mercury acetamide, 2-amino-9-diazofluorene, m. p. 137° with evolution of nitrogen, is obtained. This is stable at the ordinary temperature, but becomes brown on long exposure to light. Resolution is not effected by *d*-camphorsulphonic acid. Improved methods of preparation of 2-nitrofluorene and 2-nitro- and 2-amino-fluorenone are given. H. BURTON.

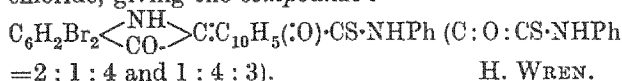
cis-trans-Isomerism and steric hindrance. IX. **Propylcyclopentanols.** G. VAVON and J. FLURER (Bull. Soc. chim., 1929, [iv], 45, 754—762).—1-Propylcyclopentan-2-one, b. p. 67°/8 mm., d_4^{20} 0.9111, n_D^{20} 1.4470 [semicarbazone, m. p. 212—213°, yielding when hydrogenated in aqueous hydrochloric acid the hydrochloride of 1-propylcyclopentyl-2-semicarbazide (m. p. 151—152°); oxime, b. p. 109—111°/9 mm.,

hydrogen oxalate, m. p. 149—150°], with sodium and alcohol gives 70% of a mixture, b. p. 80°/10 mm., of 1-propylcyclopentan-2-ols rich in the *trans*-isomeride. *trans*-1-Propylcyclopentan-2-ol isolated through the hydrogen phthalate has b. p. 78—79°/10 mm., d_4^{20} 0.9018, n_D^{20} 1.4565 (hydrogen phthalate, m. p. 68°; hydrogen succinate, d_4^{20} 1.0686, n_D^{20} 1.4605; 3:5-dinitrobenzoate, m. p. 30—31°; phenylurethane, m. p. 61—62°). *cis*-1-Propylcyclopentan-2-ol, b. p. 79—80°/12 mm., d_4^{20} 0.9165, n_D^{20} 1.4600 (3:5-dinitrobenzoate, m. p. 70—71°; hydrogen phthalate, m. p. 95—96°; hydrogen succinate, m. p. 27—28°; phenylurethane, m. p. 83—84°), is obtained by hydrogenation of the ketone in presence of platinum-black in acetic acid containing hydrochloric acid and purification of the dinitrobenzoate. A mixture richer in the *trans*-isomeride is obtained in absence of hydrochloric acid (cf. A., 1928, 1000). The *cis-trans*-configurations are assigned for similar reasons to those given in the case of the propyl-, isopropyl-, and cyclohexyl-cyclohexanols (A., 1927, 455, 761; 1928, 166, 516). The *cis*-1-propylcyclopentan-2-ol is converted into the *trans*-isomeride by heating its sodium derivative at 180—190° for 12 hrs. in an atmosphere of nitrogen. The *cis*-hydrogen phthalate is much less soluble in organic solvents than the *trans*-isomeride. *cis*-2-Propylcyclopentan-1-ol is esterified more rapidly than the *trans*-isomeride with acetic acid at 100°, in the absence of a catalyst, but in presence of a catalyst esterification is more rapid with the *trans*-isomeride at 0° and at 39°. The *trans*-hydrogen phthalates and succinates are hydrolysed more rapidly than the *cis*-isomerides, the ratio of the velocity coefficients for the *trans/cis*-hydrogen phthalates in water being 4.3 at 39° and 5.5 at 0°, and in 75% alcohol, 2 at 39° and 2.5 at 68°. Similarly for the hydrogen succinates, the ratio of the velocity coefficients in 75% alcohol at 0° is 2.4 and at 39°, 2.7. Comparison of these ratios with those previously obtained for the esters of the 1-isopropylcyclopentan-2-ols (A., 1928, 100) shows that the steric effect of the propyl group in hydrolysis is less than that of the isopropyl, the propylcyclopentyl esters having greater velocity coefficients but smaller *trans/cis*-ratios than the corresponding isopropyl derivatives.

1-Propylcyclopentan-2-one is obtained by hydrogenation of 1-propylidenecyclopentan-2-one, b. p. 80°/10 mm., d_4^{20} 0.9559, n_D^{20} 1.4855 (semicarbazone, m. p. 224—225°), in ether in presence of platinum-black. The latter is obtained in 65% yield by dehydration of the ketol, b. p. 100—105°/8—9 mm., prepared from propaldehyde and cyclopentanone in presence of sodium (yield 40—45%) under 40—50 mm. in presence of 2% of oxalic acid. R. BRIGHTMAN.

Action of phenylthiocarbimide on phenols. F. MAYER and A. MOMBOUR (Ber., 1929, 62, [B], 1921—1924; cf. Karrer and Weiss, this vol., 697).—Condensation is effected (i) with aid of aluminium chloride in carbon disulphide and (ii) by means of zinc chloride and hydrogen chloride in ether. Phenol and phenylthiocarbimide, by either method, afford *p*-hydroxythiobenzanilide, m. p. 164°, converted by sodium carbonate solution at 160° into hydrogen sulphide, aniline, phenol, and *p*-hydroxybenzanilide. Similarly, resorcinol affords 2:4-dihydroxythiobenzanilide, m. p.

182° (Karrer and Weiss, m. p. 176°). α -Naphthol by the second method yields 4-hydroxythionaphthanilide, m. p. 207—208°, whereas by the first method it gives 1-hydroxy-2-thionaphthanilide, m. p. 183—184°. The thionaphthanilides condense with 5 : 7-dibromoisatin chloride, giving the compounds :



H. WREN.

Acyl derivatives of *o*-aminophenol. V. R. E. NELSON and H. S. ROTHROCK (J. Amer. Chem. Soc., 1929, 51, 2761—2764).—Schotten-Baumann treatment of *o*-benzamidophenol with *n*-butyl chloroformate or of *n*-butyl *o*-hydroxycarbanilate with benzoyl chloride affords *o*-carbo-*n*-butoxyaminophenyl benzoate, m. p. 62·5°, hydrolysed to *n*-butyl *o*-hydroxycarbanilate. Similarly, *o*-carboisobutoxyaminophenyl benzoate, m. p. 85·5—85·8°, is obtained from the corresponding isobutyl derivatives as above. In both these cases acylation of *o*-benzamidophenol causes migration of the benzoyl group from nitrogen to oxygen. *o*-Benzamidophenol and *n*-valeric anhydride afford *o*-benzamidophenyl *n*-valerate, m. p. 103·5—104·5°, whilst *o*-valeramidophenol, m. p. 79°, and benzoyl chloride yield *o*-valeramidophenyl benzoate, m. p. 73—74°. Both the diacyl derivatives are hydrolysed to *o*-benzamidophenol, migration of the benzoyl group from oxygen to nitrogen taking place with the benzoate. Hydrolysis of *o*-isovaleramidophenyl benzoate, m. p. 96—97·5° (from *o*-isovaleramidophenol, m. p. 100·5—102°), gives a small amount of the starting material in addition to *o*-benzamidophenol. *o*-Benzamidophenyl isovalerate has m. p. 113·5—117°.

Benzoylation of methyl *o*-hydroxycarbanilate, m. p. 122—123°, or treatment of *o*-benzamidophenol with methyl chloroformate affords *o*-benzamidophenyl methyl carbonate, m. p. 128°, hydrolysed mainly to *o*-benzamidophenol. In the first of these acylations migration of the carbomethoxy-group from nitrogen to oxygen occurs, but in most of the cases studied (cf. A., 1928, 168, 517) the carboalkoxy-group is able to displace the benzoyl group attached to the nitrogen atom.

H. BURTON.

Electrolytic preparation of 2 : 4-diaminophenol. W. E. BRADT and O. W. BROWN (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 14 pp.).—The effect of varying conditions on the yield and current efficiency of production of 2 : 4-diaminophenol by electrolytic reduction of the corresponding nitro-compound has been investigated. The best cathode material was found to be a copper gauze electrolytically coated with copper sponge. Using a catholyte of 2 : 4-dinitrophenol dissolved in an aqueous sodium carbonate or hydroxide solution gave poor yields, whilst in sulphuric acid solutions low solubility and volatilisation losses limited the yield. The use of a closed cell with vigorous agitation, raising the temperature, and addition of alcohol to the catholyte improved the yield. The best conditions are : catholyte consisting of 5 g. of the nitro-compound in 200 c.c. of sulphuric acid (*d* 1·66) and 100 c.c. of 95% alcohol vigorously stirred at 118°, with 5 amp./dm.² at the cathode. The yield and current efficiency were then 94·4%.

H. J. T. ELLINGHAM.

Action of normal sulphites on 3-chloro- β -naphthol and on 1 : 3-dichloro- β -naphthol. A new case of intramolecular transposition. C. MARSHALK (Bull. Soc. chim., 1929, [iv], 45, 651—662).—When heated with dilute sodium or potassium sulphite under reflux, or in an autoclave at 120°, 3-chloro- β -naphthol yields β -naphthol and β -naphthol-4-sulphonic acid, the formation of β -naphthol being greater in an autoclave. The formation of the β -naphthol-4-sulphonic acid is attributed to direct addition of the sulphite followed by elimination of sodium chloride. The absorption spectrum of 1-benzeneazo- β -naphthol-4-sulphonic acid shows bands in aqueous solution at 530 and 499, in sulphuric acid at 559 and 523. Similarly, 1 : 3-dichloro- β -naphthol with dilute (1·25%) potassium sulphite at 120° yields 3-chloro- β -naphthol-1-sulphonic acid, hydrolysed by 45—50% sulphuric acid to 3-chloro- β -naphthol, and by 10% potassium sulphite at 170° to β -naphthol-1- and -4-sulphonic acids, and a little β -naphthol. Since 1 : 2-aminonaphthol is converted into 1-amino- β -naphthol-4-sulphonic acid by sodium sulphite solution in presence of a current of air, air should be excluded in the above operations. β -Naphthol-4-sulphonic acid is readily prepared by reduction of 1-diazo- β -naphthol-4-sulphonic acid with sodium sulphide. When treated with nitrous acid and heated with hydrochloric and acetic acids, 3-chloro- β -naphthol is converted successively into 3-chloro-1-nitroso- β -naphthol and 3-chloro-2-hydroxy- α -naphthaquinone, m. p. 214—215°.

R. BRIGHTMAN.

Derivatives of 2-hydroxyfluorene. II. C. RUÍZ (Anal. Asoc. Quím. Argentina, 1928, 16, 225—233; cf. this vol., 1063).—It has not been found possible to methylate I (or 3)-nitro-2-hydroxyfluorene. 3-Nitro-2-methoxyfluorene (I) (Ecker and Langecker, A., 1928, 521) is reduced to 3-amino-2-methoxyfluorene, m. p. 187°, which, when diazotised and the solution run into boiling dilute sulphuric acid, yields 3-hydroxy-2-methoxyfluorene (II), m. p. 185°. The constitution of these compounds is demonstrated by the formation of 3-nitro-2-aminofluorene when I is heated with ammonia in a sealed tube, and by the failure of II to form an indophenol, indamine, or phthalein, although it reacts with ferric chloride, nitrous acid, and diazonium salts. R. K. CALLOW.

Nitroveratroles. H. VERMEULEN (Rec. trav. chim., 1929, 48, 969—972).—The 4-nitroveratrole of Pschorr and Silberbach (A., 1904, i, 581) is a mixture (compound?) of 4 parts of the 4-nitro- (I), m. p. 96°, and 5 parts of the 4 : 5-dinitro- (II), m. p. 130—131°, derivatives, and is obtained by the action of nitric acid (*d* 1·43) on I. Nitration of 4-acetamidoveratrole, m. p. 130° (lit. 136°), with nitric acid (*d* 1·4) in acetic acid gives 5-nitro-4-acetamidoveratrole, prepared also by acetylating the product obtained by the partial reduction of II with stannous chloride and 2·3*N*-alcoholic hydrochloric acid. Nitration of I with cold nitric acid (*d* 1·5) gives II; at the ordinary temperature 3 : 4 : 5-trinitroveratrole (III) results, whilst 3-nitroveratrole affords III, 3 : 4- and 3 : 5-dinitroveratroles. 3-Acetamidoveratrole is converted by nitric acid (*d* 1·45) at the ordinary temperature into 5-nitro-3-acetamidoveratrole, m. p. 173°, and the 4 : 5-dinitro-derivative, m. p. 240° (decomp.). H. BURTON.

Aromatic allyl and propenyl compounds. III. isoSafrole dibromide. H. I. WATERMAN and R. PRIESTER (Rec. trav. chim., 1929, 48, 941—943).—Bromination of crude *isosafrole* in carbon disulphide solution affords a product which, contrary to the results of Nagai (A., 1921, i, 857), is optically inactive. *isoSafrole*, purified through the picric acid additive compound, yields a dibromide, m. p. 52—53°, d_4^{20} 1.7682, n_D^{20} 1.6095, which is distillable in a cathode vacuum at a temperature not above 60°.

H. BURTON.

Compounds of aldehydes with dimethyldihydroresorcinol (aldimethone compounds). G. KLEIN and H. LINSE (Mikrochem., 1929, Pregl Fest., 204—234).—The compounds formed with dimethyldihydroresorcinol (aldimethones) by the following aldehydes occurring in plant products have been prepared and studied: formaldehyde, m. p. of dimethone 187°, anhydride, m. p. 171°; acetaldehyde, m. p. 139°, anhydride, 173°; propaldehyde, m. p. 155°, anhydride, 148°; butaldehyde, m. p. 142°, anhydride, 141°; isobutaldehyde, m. p. 154°, anhydride, 144°; isovaleraldehyde, m. p. 137°, anhydride, 168°; heptaldehyde, m. p. 135°, anhydride, 110°; acraldehyde, m. p. 135°, anhydride, 170—188°; glyoxal, m. p. 228°, anhydride, 170°; glyoxylic acid, m. p. 239°, anhydride, 245°; aldol, m. p. 184—186°, anhydride, 126°; crotonaldehyde, m. p. 180—183°, anhydride, 120°. The anhydrides are best prepared by boiling the aldimethones with 40% sulphuric acid for 2 hrs., removing the free acid with powdered barium hydroxide, and extracting the resulting mass with light petroleum. The anhydride is obtained by evaporation of the extract. No general quantitative method for the separation of mixtures of the above compounds could be found, but in a number of cases separation can be effected by fractional sublimation or extraction with various solvents. Glyoxylic acid may be separated from the remaining aldehydes by conversion into its lead salt before forming the aldimethones. A table giving the solubilities of the above compounds in a number of solvents and illustrations of the characteristic crystalline forms of the sublimates obtained from them accompany the paper.

H. F. HARWOOD.

Action of cinnamic acid on cholesterol. A new isomeride of cholesterol. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 771).—When heated with 2 mols. of cinnamic acid at 200° for $\frac{1}{2}$ hr., cholesterol is partly converted into cholesteryl cinnamate, m. p. 157—158°, but the alcoholic mother-liquors from the crystallisation of the cinnamate deposit an isomeride of cholesterol, m. p. 137—137.5°, $[\alpha]_D$ —19° (bromide, m. p. 76°; acetate, m. p. 103°; benzoate, m. p. 131—132°), which gives the Liebermann reaction more slowly than cholesterol, and is converted into the latter by alcoholic potassium hydroxide. R. BRIGHTMAN.

Steryl phosphates. H. VON EULER, A. WOLF, and H. HELLSTROM (Ber., 1929, 62, [B], 2451—2456; cf. A., 1927, 1066).—Addition of cholesterol in chloroform to a solution of phosphoryl chloride in acetone yields the *dichloride of moncholesteryl phosphate*, $C_{27}H_{45}O_2Cl_2P$, m. p. 122° (decomp.), hydrolysed by boiling water to moncholesteryl

phosphate, m. p. 193°. The *chloride of dicholesteryl phosphate*, $C_{54}H_{90}O_2ClP$, m. p. 171°, is obtained under certain conditions during the preparation of dicholesteryl phosphate, m. p. 204°. β -Chloroethyl-phosphoryl chloride and cholesterol in pyridine afford *dicholesteryl β -chloroethyl phosphate*, $C_{56}H_{96}O_4ClP$, m. p. 158°. *Diergosteryl β -chloroethyl phosphate*, m. p. 165—167°, is described.

The absorption curves of ergosterol and diergosteryl phosphate before and after irradiation are given; those of the irradiated materials differ much more markedly from one another than do those of the untreated materials. H. WREN.

Decomposition of cholesterylene and of cholesteryl ether by aluminium chloride. N. D. ZELINSKI and N. N. SEMIGANOVSKI (Ber., 1929, 62, [B], 2199—2202; cf. A., 1928, 731, 865).—Thermal decomposition of cholesterylene in presence of aluminium chloride, under atmospheric or 16 mm. pressure, affords optically inactive, almost non-fluorescent hydrocarbons with very small iodine values. Under like conditions (at 16 mm.), cholesterol gives dextrorotatory products of markedly unsaturated character. Cholesteryl ether gives products similar to those from cholesterylene. H. WREN.

Irradiated sterols. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 771—776).—Pure commercial cholesterol, $[\alpha]_D$ —33.57°, and ergosterol, $[\alpha]_D$ —117°, when recrystallised three times from 95% alcohol yield material, $[\alpha]_D$ —38.28° and —119°, respectively, which after exposure to ultra-violet light does not affect a sensitised plate, and it is concluded that activation of cholesterol and ergosterol is due to the presence of traces of isomerides which are eliminated by successive crystallisations. Since the irradiation process is unaffected by temperature and the irradiated material is free from traces of ketones which should accompany a secondary alcohol, it is improbable that the activated constituent is produced by oxidation or migration of a double linking. The transformation of ergosterol into irradiated ergosterol is a reversible process, the irradiated ergosterol rapidly losing its power of affecting a sensitised plate, even when kept in the dark, an observation which is also inconsistent with an oxidation process of activation. Cholesterol from different sources contained no lecithin or fat, and accordingly these cannot be the source of the activated material (cf. Rosenheim and Webster, A., 1927, 381, 487; Schultz, Ziegler, and Morse, A., 1927, 703). The reaction of vitamin-D or irradiated ergosterol with fuchsin (Steigmann, A., 1928, 926) could not be confirmed and was not obtained with cholesterol or ergosterol. The reducing action of vitamin-D with silver oxide is attributed to the presence of double linkings. R. BRIGHTMAN.

Destruction of cholesterol by X-rays *in vitro*. A. H. ROFFO and L. M. CORREA (Forsch. Röntgenstr., 1929, 39, 882—889).—Contrary to the assertion of Schreuss and Schulze (*ibid.*, 37, 212) that X-rays are incapable of decomposing cholesterol, it is confirmed that irradiation of 0.2% solutions in chloroform causes decomposition to the extent of 35%. A claim for priority as to the oxidative nature of the decom-

position process brought about by irradiation is made.

C. W. SHOPPEE.

Effect of X-rays on cholesterol. A. BACHEM and R. P. MACFATE.—See this vol., 1249.

Heteropolar carbon compounds. VIII. Methoxytriphenylcarbenium salts. W. DILTHEY and W. ALFUSZ (Ber., 1929, 62, [B], 2078—2081; cf. this vol., 1067).—The perchlorates of *mono-* (m. p. 192°), *di-* (m. p. 212°), and *tri-* (m. p. 192—193°) methoxytriphenylcarbinol have been prepared. Titration of their solutions in anhydrous acetone with aqueous alcohol (*d* 0.8665) until colourless shows that hydrolysis commences and is complete more rapidly with the *di-* than with the *tri-anisyl* compound. A slowly progressive hydrolysis cannot be doubted, since the direction of change is reversed by increase of temperature or concentration or by addition of perchlorate ions and the solution develops increasing acidity. In apparently anhydrous solution the colour is more slowly but ultimately discharged by dilution. It is doubtful whether colourless carbonium ions are present in solutions which have suffered hydrolysis (alcoholysis, acetonolysis), but, until the contrary is established, salt formation and occurrence of colour must be considered to go hand in hand and the titration hydrolysis must be regarded as giving a relatively accurate picture of the increase of basicity caused by the introduction of methoxy-groups into cations of this type.

H. WREN.

Organic molecular compounds with co-ordination centres. II. Co-ordination numbers of alkyl esters of fatty acids in choleic acids. H. RHEINBOLDT, O. KONIG, and R. OTTEN (Annalen, 1929, 473, 249—259).—Co-ordination compounds similar to those previously described (A., 1927, 242) are obtained from deoxycholic acid and alkyl esters of fatty acids. The co-ordination numbers of the esters (other than formates) are usually less than the values for the fatty acids of the same molecular composition. For a series of esters $R \cdot CO_2Alk$, where the number of carbon atoms in Alk is greater than in $R \cdot CO_2$, the co-ordination numbers of the esters are greater than the values for the acids $R \cdot CO_2H$ and the same as those for the alcohols $Alk \cdot OH$ (values assumed from acids of same carbon content). The co-ordination numbers of the octyl esters of formic to heptioic acids are all 6, whilst octoic acid has a value of 4 (*loc. cit.*). Octyl octoate and octyl alcohol also give the value 6. It is concluded that the heptyl group shows the value 4, and the octyl group 6. The increase in the co-ordination number from 4 to 6 is, therefore, between C_7 and C_8 and not C_9 and C_{10} (cf. *loc. cit.*). The same result is obtained by a comparison of several pairs of esters, $R \cdot CO_2Me$ and $Me \cdot CO_2R$, which show the same co-ordination numbers. The increases in the co-ordination numbers from 3 to 4 and 6 to 8 are between C_2 and C_3 , and C_{13} and C_{14} , respectively (cf. *loc. cit.*). The values for the acids $R \cdot CO_2H$ and the formates $H \cdot CO_2R$ are identical; both carboxyl and formate groups have no influence on the co-ordination number. The esters, $R \cdot CO_2R$, show the next higher co-ordination number than the group R . *Choleic acids* are obtained from the following compounds and deoxycholic acid (the number of mols. of the latter is

given, followed by the m. p. of the choleic acid in parentheses): *n*-hexyl formate, 4 (167.5°); *n*-heptyl formate, 4 (168—169°); *n*-octyl formate, 6 (170.5—171°); *n*-dodecyl formate, b. p. 145—146°/15 mm., 6 (179°); *n*-tetradecyl formate, b. p. 166°/17 mm., 8 (185°); *n*-hexadecyl formate, b. p. 188°/17 mm., 8 (187.5°); methyl acetate, 3 (about 145° [decomp.]); *n*-propyl acetate, 4 (142—146° [decomp.]); ethyl acetate, 3 (140—145° [decomp.]); *n*-hexyl acetate, 4 (168—169°); *n*-heptyl acetate, 4 (169°); *n*-octyl acetate, 6 (172—173°); *n*-dodecyl acetate, 6 (180.5°); *n*-tetradecyl acetate, 8 (185.5—186°); *n*-hexadecyl acetate, 8 (189°); methyl propionate, 3 (144—148° [decomp.]); ethyl propionate, 4 (145—149° [decomp.]); *n*-heptyl propionate, 4 (170—171°); *n*-octyl propionate, 6 (173.5—174.5°); *n*-dodecyl propionate, b. p. 166—168°/20 mm., 6 (182°); *n*-hexadecyl propionate, b. p. 211—212°/18 mm., 8 (187°); methyl butyrate, 4 (about 148—152° [decomp.]); *n*-octyl butyrate, 6 (176—176.5°); *n*-dodecyl butyrate, b. p. 177—178°/19 mm., 6 (183.5°); *n*-hexadecyl butyrate, 8 (189°); *n*-butyl *n*-valerate, 6 (169—170°); *n*-octyl valerate, 6 (176—177°); *n*-amyl *n*-hexoate, 6 (173.5°); *n*-octyl hexoate, 6 (181—181.5°); methyl *n*-heptoate, 4 (169—170°); *n*-hexyl heptoate, b. p. 137°/19 mm., 6 (177—177.5°); *n*-octyl heptoate, 6 (182°); methyl octoate, 4 (169—170°); *n*-heptyl octoate, 6 (180.5—181°); *n*-octyl octoate, 6 (181—181.5°); methyl nonoate, 6 (174—175°); *n*-heptyl nonoate, b. p. 210°/75 mm., 6 (182.5—183°); *n*-octyl nonoate, b. p. 183°/21 mm., 8 (185°); *n*-nonyl decaoate, b. p. 210.5—211.5°/20 mm., 8 (186.5—187°); methyl dodecoate, 6 (180°); ethyl dodecoate, 6 (182°); *n*-propyl dodecoate, b. p. 155—156°/18 mm., 6 (183.5—184°); *n*-butyl dodecoate, b. p. 180°/18 mm., 6 (184—184.5°); *n*-hexyl dodecoate, b. p. 199°/19 mm., 6 (185.5°); *n*-octyl dodecoate, b. p. 204—205°/17 mm., 6 (186°); methyl tetradecoate, 6 (181.5—182°); ethyl tetradecoate, 6 (183.5°); *n*-butyl tetradecoate, b. p. 195°/18 mm., 6 (186°); *n*-hexyl tetradecoate, b. p. 215°/17 mm., 6 (188°); *n*-tetradecyl tetradecoate, m. p. 43°, 8 (194.5—195.5°); *n*-hexadecyl tetradecoate, m. p. 47°, 8 (197—198°); methyl pentadecoate, 8 (184.5—185°); *n*-octyl alcohol, 6 (169.5—170°); *n*-tetradecyl alcohol, 8 (183.5—184.5°). The *choleic acid*, m. p. 187—188°, from *n*-hexadecyl acetate and apocholeic acid contains 8 mols. of the latter.

H. BURTON.

Optical activity of the hydrocarbons obtained by the decomposition of resin acids by aluminium chloride. N. D. ZELINSKI and N. N. SEMIGANOVSKI (Ber., 1929, 62, [B], 2202—2205).—The primary products of the decomposition of optically inactive resin acids by aluminium chloride are optically active, dextrorotatory hydrocarbons. It is probable that the optical inactivity of the acids is an accidental result of the compensation of the dextrorotatory acids with those of opposite sign. The active hydrocarbons are markedly unsaturated. The more volatile fractions of the primary product are rich in aromatic compounds. Treatment of the active fractions with aluminium chloride causes production of optically inactive hydrocarbons with very low iodine numbers. The possibility that resin acids have played a part in the formation of mineral oils is discussed. H. WREN.

Chemistry of the three-carbon system. XXII. Preparation and interconversion of isomeric unsaturated nitriles. A. KANDIAH and R. P. LINSTEAD (J.C.S., 1929, 2139—2153).—Anomalies in the chemistry of certain $\alpha\beta$ - and $\beta\gamma$ -unsaturated nitriles (Birch and Kon, *ibid.*, 1923, 123, 2440) have led to their re-investigation. A study of the interconversion of eight pairs of nitriles by sodium ethoxide at 25° is described. The mobility is high, decreasing with increased size of the α -group, and the equilibrium is far on the side of the $\alpha\beta$ -phase, all the equilibria examined showing a predominance of $\alpha\beta$ -amounting to 90—99%. The high activity and the position of equilibrium are attributed to the powerful effect of the terminal nitrile group. A general method for the preparation of the nitriles from amides is by treatment with a solution of phosphorus pentachloride in phosphorus oxychloride.

Δ^1 -cyclohexenylacetamide, m. p. 152°, yields Δ^1 -cyclohexenylacetonitrile, b. p. 105°/22 mm., d_4^{20} 0.9533, n_D^{20} 1.4843, $[R_L]_D$ 36.30, isomeric with cyclohexenylacetonitrile, b. p. 107—108°/22 mm., d_4^{20} 0.9483, 1.4928, $[R_L]_D$ 37.1, from cyclohexylidenacetamide, m. p. 147°. α -cyclohexylidenepropionamide, m. p. 120°, gives α -cyclohexylidenepropionitrile, b. p. 102—103°/13 mm., d_4^{20} 0.9366, n_D^{20} 1.4941, $[R_L]_D$ 42.0, isomeric with α - Δ^1 -cyclohexenylpropionitrile, b. p. 113°/13 mm., d_4^{20} 0.9382, n_D^{20} 1.4761, $[R_L]_D$ 40.7, from α - Δ^1 -cyclohexenylpropionic acid, m. p. 38°, b. p. 144°/14 mm. (anilide, m. p. 56°), by way of the amide, m. p. 90°. α -cyclohexylidenebutryonitrile, b. p. 114°/11 mm., d_4^{20} 0.9225, n_D^{20} 1.4887, $[R_L]_D$ 46.53, is isomeric with α - Δ^1 -cyclohexenylbutryonitrile, b. p. 112°/12 mm., d_4^{20} 0.9263, n_D^{20} 1.4794, $[R_L]_D$ 45.68, from α - Δ^1 -cyclohexenylbutyramide, m. p. 115—116°. cycloPentylidenacetone, b. p. 97—98°/24 mm., d_4^{20} 0.9427, n_D^{20} 1.4805, $[R_L]_D$ 32.30, in 55% yield from cyclopentylidenacetamide, m. p. 138°, is isomeric with Δ^1 -cyclopentenylacetonitrile, b. p. 91—92°/19 mm., d_4^{20} 0.9395, n_D^{20} 1.4683, $[R_L]_D$ 31.7. β -Methyl- Δ^6 -pentenonitrile has b. p. 63°/20 mm., d_4^{20} 0.8432, n_D^{20} 1.4447, $[R_L]_D$ 30.0, and β -methyl- Δ^8 -pentenonitrile, b. p. 60°/19 mm., d_4^{20} 0.8478, n_D^{20} 1.4367, $[R_L]_D$ 29.36, from β -methyl- Δ^8 -pentenamide, m. p. 124—125°. 2-Methyl- Δ^{10} -cyclohexenyl-1-acetonitrile, b. p. 101°/14 mm., d_4^{20} 0.9384, n_D^{20} 1.47621, $[R_L]_D$ 40.4 (piperonylidene derivative, m. p. 122°), is obtained from α -cyano-1-methylcyclohexylidene-2-acetic acid, m. p. 106—107°, by distillation. 3-Methyl- Δ^1 -cyclohexenyl-1-acetonitrile, b. p. 113°/20 mm., d_4^{20} 0.9239, n_D^{20} 1.4732, $[R_L]_D$ 41.3 (piperonylidene derivative, m. p. 84°), gives an imino-compound when condensed with cyanoacetamide, hydrolysed to the ω -imide of α -cyano-3-methylcyclohexane-1:1-diacetic acid, m. p. 225°. 4-Methyl- Δ^1 -cyclohexenyl-1-acetonitrile has b. p. 109°/16 mm., d_4^{20} 0.9232, n_D^{20} 1.4726, $[R_L]_D$ 41.0 (ω -imide of α -cyano-4-methylcyclohexane-1:1-diacetic acid, m. p. 230°; piperonylidene derivative, m. p. 132°).

D. W. HILL.

Replacement of halogen in o-bromobenzoic acid. W. R. H. HURTLEY (J.C.S., 1929, 1870—1873).—Salicylic acid is readily formed by boiling sodium o-bromobenzoate with sodium and copper acetates in aqueous solution. In boiling alcoholic sodium ethoxide solution in presence of copper-

bronze o-bromobenzoic acid reacts with acetylacetone to give phenylacetylacetone-o-carboxylic acid, m. p. 142°. Similarly, ethyl malonate yields ethyl o-carboxyphenylmalonate, m. p. 102°. Ethyl hydrogen homophthalate alone is obtained with ethyl acetoacetate or ethyl acetonedicarboxylate, and β -deoxybenzoic-o-carboxylic acid, m. p. 168° (sintering 145°) (lit. 162—163°; 140°), with benzoylacetone. With resorcinol, either when boiled in sodium hydroxide solution and a little copper sulphate solution added, or when fused, the lactone of 2':4'-dihydroxydiphenyl-2-carboxylic acid, m. p. 232°, is formed. Methylation of the lactone with methyl sulphate and alkali gives in the cold the lactone of 2'-hydroxy-4'-methoxydiphenyl-2-carboxylic acid, m. p. 141°, or, at 100°, 2':4'-dimethoxydiphenyl-2-carboxylic acid, m. p. 150°. At 160°, o-bromobenzoic acid and copper-bronze yield cuprous bromide and cuprous benzoate. In boiling water benzoic acid and 7% of diphenic acid are formed. Diphenic acid is obtained in 43% yield by heating potassium o-bromobenzoate and copper-bronze at 100° and stirring in a little water. Ethyl o-bromobenzoate, p-bromobenzoic acid, and o-bromonitrobenzene do not undergo these reactions.

R. K. CALLOW.

Dynamic isomerism involving mobile hydrocarbon radicals. I. The triarylbenzenylamidines. A. W. CHAPMAN (J.C.S., 1929, 2133—2138).—Dynamic isomerism as known in the cases of mobile hydrogen, anions, or valency linkings extends also to mobile hydrocarbon radicals, more drastic conditions being necessary to induce migration. *N*-Diphenyl-*N'*-p-tolylbenzamidine, $\text{NPh}_2\text{CPh:N}\cdot\text{C}_7\text{H}_7$, and *NN'*-diphenyl-*N*-p-tolylbenzamidine, $\text{NPh:CPh:NPh}\cdot\text{C}_7\text{H}_7$, are converted into an equilibrium mixture containing 60—65% of the latter by heating at 322—323° for about 4 hrs.

D. W. HILL.

X-Ray investigations of optically active compounds. I. Proof of molecular asymmetry in optically active α -aminophenylacetic acid. G. L. CLARK and G. R. YOHE (J. Amer. Chem. Soc., 1929, 51, 2796—2807).—X-Ray examinations of *d*-, *l*-, and *dl*- α -aminophenylacetic acids have been made by the rotation and powder diffraction methods. Crystal structure analysis was possible by the rotation method, although no crystallographic or optical data were available. The *d*- and *l*-acids crystallise in the orthorhombic system, space-group and the unit cell contains four molecules and has the dimensions *a* 15.2, *b* 5.05, *c* 9.66 Å. No molecular symmetry is possible. Whilst the crystal form of the *dl*-acid differs from that of the *d*- and *l*-acids, it is not possible to distinguish between *d*- and *l*-forms by X-ray diffraction methods.

l- α -Aminophenylacetic acid, sublimes at 245—248° (lit. 227—310°), $[\alpha]_D^{20}$ -149° in 0.14*N*-hydrochloric acid, and *d*- α -aminophenylacetic acid, m. p. 242—244°, $[\alpha]_D^{20}$ +147° in 0.105*N*-hydrochloric acid, are obtained by resolution of the *dl*-acid with *d*-camphorsulphonic acid.

H. BURTON.

2-Bromo-3-hydroxybenzoic acid. P. H. BEJER (Rec. trav. chim., 1929, 48, 1010—1011).—Nitration of *m*-acetamidobenzoic acid by Kaiser's method (A., 1886, 149), separation of the 2-nitro-derivative through

its barium salt, and subsequent boiling with potassium hydroxide solution affords 2-nitro-3-hydroxybenzoic acid, reduced by alkaline sodium sulphide to the corresponding 2-amino-derivative. This is converted by the usual method into 2-bromo-3-hydroxybenzoic acid, m. p. 160—161°.

H. BURTON.

Derivatives of 6-amino-3-hydroxybenzoic acid. E. PUXEDDU and G. SANNA (Gazzetta, 1929, 59, 489—495).—The methyl ester, m. p. 158° (hydrochloride, m. p. 223°), and ethyl ester, m. p. 140° (hydrochloride, m. p. 214°), of 6-amino-3-hydroxybenzoic acid (cf. this vol., 555) have been prepared. Condensation of the acid with chloroacetyl chloride yields 6-chloroacetamido-3-hydroxybenzoic acid (+0.5H₂O), m. p. 222°. This could not be esterified directly, but the methyl ester, m. p. 187°, was obtained from the amino-ester, and yielded, when treated with dimethylamine, methyl 6-dimethylaminacetamido-3-hydroxybenzoate, m. p. 149°. The preparation of the carbamido-derivative and the ureide from 6-amino-3-hydroxybenzoic acid described by Froelicher and Cohen (J.C.S., 1921, 119, 1425) is confirmed. The acid condenses with ethyl acetoacetate.

R. K. CALLOW.

Elimination of carbon dioxide from organic compounds. VII. Pyrogenic degradation of cyclic hydroxy-acids. Salicylic, protocatechuic, gallic, o-hydroxycinnamic, 3:4-dihydroxycinnamic, and cyclogallipharic acids and their derivatives alone and in presence of phloroglucinol, aniline, and pyridine. H. KUNZ-KRAUSE and P. MANICKE (Arch. Pharm., 1929, 267, 555—571; cf. A., 1920, i, 312).—Salicylic acid does not decompose smoothly into phenol and carbon dioxide when heated at 250°. After 1 hr. only 17.56% of carbon dioxide is evolved; phenyl salicylate and a small amount of phenol are also obtained. Increased evolution of carbon dioxide occurs when the heating is carried out in presence of phloroglucinol at 250°, pyridine at 180°, or aniline at 175—180°; in the last case 1 mol. of carbon dioxide is eliminated from 1 mol. of the acid after 135 min. heating. With acetyl-salicylic acid at 250° only a small amount of carbon dioxide is evolved; acetic anhydride, salicylosalicylic and trisalicylosalicylic acids are formed also. Protocatechuic acid evolves 1 mol. of carbon dioxide in presence of phloroglucinol at 218—225°, but the residue has properties corresponding with a tannoid (cf. loc. cit.); in presence of aniline or pyridine evolution of carbon dioxide occurs at 180° or 150°, respectively. Decomposition of gallic acid (cf. loc. cit.) takes place at 170° in presence of aniline, and at 110—120° in presence of pyridine. It is necessary to raise the temperature for evolution of 1 mol. of carbon dioxide. o-Hydroxy- and 3:4-dihydroxycinnamic acids decompose readily at about 200° into carbon dioxide and the corresponding styrene; in presence of aniline or pyridine a lower temperature is required. cyclo-Gallipharic acid (Kunz-Krause and Manicke, A., 1911, i, 130) is decomposed by heating with aniline at 160° into carbon dioxide and cyclogallipharol. Coumarin, umbelliferone, and daphnetin do not eliminate carbon dioxide at 220—250°.

H. BURTON.

Phthalide derivatives. F. MAYER, W. SCHAFER, and J. ROSENBAACH (Arch. Pharm., 1929, 267, 571—

584).—Magnesium ethyl bromide converts α -naphthaldehyde-8-carboxylic acid into the lactone, m. p. 68°, of 1- α -hydroxypropylnaphthalene-8-carboxylic acid. Bromination of 2-methyl- α -naphthoyl chloride (I) at 155—160°, subsequent conversion of the product formed into ethyl 2-bromomethyl- α -naphthoate, and elimination of ethyl bromide from this by heating gives the lactone, m. p. 152—153°, of 2-hydroxymethyl- α -naphthoic acid. Chlorination of I at 150—170° under the influence of arc-lamp irradiation and hydrolysis of the product formed with water and calcium carbonate affords β -naphthaldehyde-1-carboxylic acid, m. p. 176° (oxime, m. p. 215°, not sharp). 1-Bromo-2-methyl-5:6:7:8-tetrahydronaphthalene, b. p. 140—155°/11—12 mm., is converted by the usual Grignard method into 2-methyl-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid, m. p. 172—173° (chloride, b. p. 170—175°/26 mm.; ethyl ester, b. p. 194—196°/21 mm.), oxidised by nitric acid to mellophanic acid. Treatment of the sodium hydrogen sulphite compound of 2-methoxy- α -naphthaldehyde with aqueous potassium cyanide gives the corresponding cyanohydrin, m. p. 112°, reduced and hydrolysed by boiling hydriodic (d 1.99) and acetic acids to 2-hydroxynaphthylacetic acid, m. p. 147° (lactone, m. p. 103—104°). Magnesium methyl iodide reacts with the anhydride of naphthalene-2:3-dicarboxylic acid, yielding the lactone, m. p. 127°, of 2- α -hydroxyisopropylnaphthalene-3-carboxylic acid.

Oximinoaceto-5:6:7:8-tetrahydro- α - (II), m. p. 179°, and β -naphthylamides (III), m. p. 168°, are prepared by Sandmeyer's method (A., 1919, i, 318). When II is heated with slightly diluted sulphuric acid (cf. loc. cit.) conversion into the corresponding isatin, m. p. 230°, occurs. The mixture of 4- and 6-methylisatin, m. p. 187° (lit. 169°), obtained similarly from oximinoaceto-*m*-toluidide (cf. A., 1925, i, 1315) is converted by treatment with sodium hydroxide and hydrogen peroxide into a mixture of 2-amino-*p*-toluic and 6-amino-*o*-toluic acids, m. p. 118° (lit. 125°). The mixture of isatins formed from III yields by similar treatment 2-amino-5:6:7:8-tetrahydronaphthalene-1-, m. p. 137° (3 parts), and -3-carboxylic acids, m. p. 179° (1 part) (methyl ester, m. p. 69°), separable by partial esterification. Electrolytic reduction of a series of aminobenzoic acids (obtained by oxidation of the requisite isatin), using lead electrodes and 20% sulphuric acid, gives usually good yields of the corresponding aminobenzyl alcohols. The following are described: 2-amino-3-methyl-, m. p. 71°; 2-amino-5-methyl-, b. p. 145—150°/13 mm., m. p. 123°; 2-amino-6-methyl-, m. p. 85°; 2-amino-4-methyl-, m. p. 141°; 2-amino-3:5-dimethyl-, m. p. 73°, and 2-amino-3:6-dimethyl-benzyl alcohols, m. p. 106°. 2-Amino-1-hydroxymethyl-, m. p. 87°, and 2-amino-3-hydroxymethyl-5:6:7:8-tetrahydronaphthalenes, m. p. 158°, are obtained similarly; 1-amino-5:6:7:8-tetrahydronaphthalene-2-carboxylic acid furnishes a compound, m. p. 215°, and a small amount of a substance, m. p. 108°. 2-Amino-3-hydroxymethylnaphthalene (diacetyl derivative, m. p. 149°) has m. p. 183°. The amino-alcohols are converted by the usual method into the cyanobenzyl alcohols, which on hydrolysis with sodium hydroxide solution afford the corresponding phthalides. The following are described: o-cyano-

benzyl alcohol, b. p. 170—175°/30 mm., hydrolysed to phthalide; *2-cyano-5-methylbenzyl alcohol*, m. p. 110—112°, yielding 4-methyl-1:2-phthalide, m. p. 118° (cf. Perkin and Stone, A., 1926, 64); *2-cyano-3:5-dimethylbenzyl alcohol*, m. p. 85°, hydrolysed to 4:6-dimethyl-1:2-phthalide, m. p. 100°, and *2-cyano-3-hydroxymethylnaphthalene*, m. p. 130° (corresponding phthalide, m. p. 206°). H. BURTON.

Action of sodium hypochlorite on amides. V. I. RINKES (Rec. trav. chim., 1929, 48, 960—964).—Treatment of benzoylformamide with sodium hypochlorite at -5° gives benzoic acid; in presence of methyl alcohol at -10° methyl benzoate results, and treatment of the residue with hydrazine acetate and then with acetic acid affords hydrazodicarbonamide. Δ^{α} -Pentenoamide is converted in methyl-alcoholic solution at -5° into methyl Δ^{α} -butenylcarbamate, m. p. 25—26°, hydrolysed by 15% sulphuric acid to *n*-butaldehyde. *o*-Nitrophenylpropionamide, m. p. 159° (from the chloride and ammonia in benzene solution), is converted by aqueous sodium hypochlorite into the *N*-chloro-derivative, m. p. 127.5° (cf. A., 1921, i, 27). When maleamide is heated with zinc chloride a small amount of maleimide is obtained. Treatment of methyl styrylcarbamate (A., 1927, 652) with ozonised air in ethyl acetate solution, and decomposition of the oily ozonide by boiling with water and calcium carbonate affords benzaldehyde and *N*-carbomethoxyformamide, b. p. 94°/10 mm., m. p. 91°. H. BURTON.

Compounds of bivalent carbon. III. Acetals of dicarbonic oxide and their decomposition into carbonic oxide acetals. H. SCHEIBLER and E. BAUMANN (Ber., 1929, 62, [B], 2057—2065; cf. A., 1926, 711).—The solid reaction product from ethyl diphenoxyacetate and sodium ethoxide, suspended in light petroleum, is decomposed by addition of cold water or by the successive action of phosphoryl chloride, hydrogen chloride, and excess of sodium ethoxide into diphenoxyacetic acid and α -diethoxy- $\beta\beta$ -diphenoxyethylene, b. p. 140—145°/0.8 mm. The constitution of the last-named compound is deduced from its transformation by aqueous-alcoholic hydrochloric acid into ethyl diphenoxyacetate and thence into diphenoxyacetic acid. Attempts to prepare diphenoxyketen from diphenoxyacetyl chloride, b. p. 148—150°/0.7 mm., were unsuccessful, since it appears to yield ketenium bases with pyridine and trimethylamine, whereas diphenoxybromoacetyl bromide does not react with zinc. Diphenoxyacetyl chloride is converted by bromine in chloroform into dibromophenoxymethyl bromide, m. p. 63°. Ethyl di-*p*-tolylloxycetate, b. p. 186—187°/6 mm., is prepared from dichloroacetic acid and *p*-cresol followed by esterification of the product. Ethyl di-*p*-tolyloxymalonate, b. p. 203—205°/0.8 mm., m. p. 62—63°, derived from ethyl dibromomalonate and sodium *p*-tolylloxide, is hydrolysed to di-*p*-tolyloxymalonic acid, m. p. 160° (decomp.), converted by thionyl chloride into carbon dioxide and di-*p*-tolylloxycetyl chloride. Ethyl di-*z*-naphthoxyacetate has m. p. 73°. Diphenyldithiolacetic acid, m. p. 104°, may be prepared from dichloroacetic acid and thiophenol. H. WREN.

Syntheses in the hydroaromatic series. V. Δ^4 -Tetrahydro-*o*-phthalic acid. O. DIELS and

K. ALDER (Ber., 1929, 62, [B], 2087—2090; cf. this vol., 1297).—Mainly a reply to Farmer and Warren (this vol., 812). The hypothesis that the product of the condensation of maleic anhydride and butadiene is *cis*- Δ^4 -tetrahydro-*o*-phthalic anhydride is confirmed by oxidation of the compound to butane- $\alpha\beta\gamma\delta$ -tetracarboxylic acid, m. p. 188—189° [dianhydride, m. p. 246—248° (decomp.)]. H. WREN.

Asymmetric oxidation. Y. SHIBATA and R. TSUCHIDA (Bull. Chem. Soc. Japan, 1929, 4, 142—149).—A solution of *l*-amminochlorodiethylenediaminecobaltic bromide was added to a solution of *r*-3:4-dihydroxyphenylalanine containing a buffer solution of phosphate; the whole was then placed in a thermostat at 20°, and observations were made of the rotatory power of samples removed from time to time. The curve produced by plotting the angle of rotation against the time of reaction, although displaying marked irregularities for the first few hours, shows from its general type that the complex cobaltic bromide oxidises the *l*-component of racemic 3:4-dihydroxyphenylalanine more readily than the *d*-component, and that a levorotatory quinonic (?) compound is intermediately produced. The latter is then transformed into an inactive compound, the solution becoming less levorotatory and finally dextrorotatory owing to the remaining *d*-dihydroxyphenylalanine. The possible mechanism of the reaction is discussed. B. W. ANDERSON.

Chlorides of tetrachlorophthalic acid. A. KIRPAL and H. KUNZE (Ber., 1929, 62, [B], 2102—2106).—*as*-Tetrachlorophthalyl chloride, m. p. 137° (or $+C_6H_6$, m. p. about 118—120°, according to rate of heating), is prepared by the action of phosphorus pentachloride on tetrachlorophthalic acid under pressure at 220°. Distillation of the asymmetric chloride followed by immediate cooling of the distillate and extraction of it with cold light petroleum permits the isolation of *s*-tetrachlorophthalyl chloride, m. p. 48°, which passes slowly when solid, more rapidly when dissolved, and almost immediately in the presence of animal charcoal into the *as*-variety. The last-named substance is converted by protracted heating at its b. p. (more rapidly in presence of chlorine) into pentachlorobenzoyl chloride, m. p. 87°, slowly transformed by methyl alcohol into methyl pentachlorobenzoate, m. p. 97°. Treatment of *as*-tetrachlorophthalyl chloride with absolute ethyl alcohol at the ordinary temperature affords ethyl ψ -tetrachlorophthalate, m. p. 126°; protracted exposure of the ψ -ester to the reaction mixture results in its isomerisation to ethyl tetrachlorophthalate, m. p. 60.5°, under the influence of the liberated hydrogen chloride. *s*-Tetrachlorophthalyl chloride dissolves very readily in ethyl alcohol and the ψ -ester soon separates from the solution; possibly, the ψ -chloride of the hydrogen ester is intermediately formed. Thionyl chloride transforms ethyl hydrogen tetrachlorophthalate into the compound $C_6Cl_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} OEt \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} O$, m. p. 54°.

H. WREN.

Isomeric $\alpha\beta$ -diphenylglutaric acids. I. Optically inactive acids. II. Optically active acids. S. AVERY and W. D. MACLAY (J. Amer. Chem. Soc.,

1929, 51, 2833—2839).—I. When (*trans*)- α - β -diphenylglutaric acid (I), m. p. 226—228°, is heated with acetyl chloride at 140° the *anhydride* (II), m. p. 126.5°, of (*cis*)- α - β -diphenylglutaric acid (III), m. p. 208—210° (corr.) (cf. Meerwein and Dott, A., 1919, i, 21), is produced. Hydrolysis of the methyl ester, m. p. 143°, of I with alcoholic potassium hydroxide also affords III in addition to I. The amide prepared from II is identical with the monoamide obtained from γ -cyano- β - γ -diphenylbutyric acid (A., 1928, 1243) and is converted by boiling with alcoholic hydrochloric acid into the *imide*, m. p. 225—229°, of III. The same imide is obtained by treatment of methyl γ -cyano- β - γ -diphenylbutyrate with concentrated alcoholic potassium hydroxide, subsequent evaporation, acidification with acetic and hydrochloric acids, and re-evaporation. The *anilic acid* from II and aniline has m. p. 201—202°. The transformation III \rightarrow I occurs with hydrochloric acid at 200°. Hydrolysis of the esters of III with hydrochloric acid above 180° gives mainly I, whilst alkaline hydrolysis gives a mixture of I and III. Hydrolysis of the above cyano-compound with acid below 150° gives the amide and III; above 150° I and III are formed and the amount of I increases with increase of temperature.

II. Resolution of *trans*- α - β -diphenylglutaric acid is effected by brucine yielding d-, m. p. 224—226°, $[\alpha]_D^{25} +58.7^\circ$ in acetone, and l- α - β -diphenylglutaric acids, $[\alpha]_D^{25} -58^\circ$ in acetone, to which are assigned (+ α - β) and (- α + β) configurations, respectively. Similarly, III gives d-(+ α + β), $[\alpha]_D^{25} +140.6^\circ$ in acetone, and l-(- α - β)-diphenylglutaric acids, m. p. 202°, $[\alpha]_D^{25} -140^\circ$ in acetone. H. BURTON.

Syntheses in the hydroaromatic series. IV. Addition of maleic anhydride to arylated dienes, trienes, and fulvenes. O. DIELS and K. ALDER [with P. PRIES] (Ber., 1929, 62, [B], 2081—2087; cf. this vol., 819).—3 : 6-Diphenyl-*cis*- Δ^4 -tetrahydrophthalic anhydride, m. p. 207°, is prepared by melting *trans*-*trans*- α - β -diphenylbutadiene with maleic anhydride. The constitution of the compound follows from the transformation of the calcium salt of the corresponding acid into *p*-diphenylbenzene by distillation with a mixture of calcium oxide and zinc dust. α -Phenylbutadiene and maleic anhydride give 3-phenyl- Δ^4 -*cis*-tetrahydrophthalic anhydride, m. p. 120°, degraded to diphenyl. In these cases the addition takes place in the 1 : 4-position. On grounds of analogy, the product from α -phenyl- β -methylbutadiene is regarded as 3-phenyl-6-methyl- Δ^4 -*cis*-tetrahydrophthalic anhydride, m. p. 158—159°. Maleic anhydride yields the compounds $C_{22}H_{18}O_3$, m. p. 194°, with α - ζ -diphenylhexatriene, $C_{22}H_{16}O_3$, m. p. 168°, with 6 : 6-diphenylfulvene, $C_{12}H_{12}O_3$, m. p. 137°, with 6 : 6-dimethylfulvene, and $C_{18}H_{14}O_3$, m. p. 137—138°, with 6-styrylfulvene; the mode of addition has not been established definitely. H. WREN.

Studies in "strainless" rings. I. β -Substituted stereoisomeric decalins. K. A. N. RAO (J.C.S., 1929, 1954—1969).—A number of substituted decalins of the type $C_9H_{18}>C<\begin{smallmatrix} X \\ Y \end{smallmatrix}$, where X and Y are (a) identical, (b) different, (c) replaced by a symmetrical ring, (d) replaced by an unsymmetrical ring, have been

prepared and their stereoisomeric relationships studied. When X and Y are identical or replaced by a symmetrical ring only one isomeride corresponding with each decalin is formed. When X and Y are different, four isomerides are possible and replacement of X and Y by an unsymmetrical ring does not diminish the number of isomerides. These results are in harmony with Mohr's theory (A., 1919, ii, 229; 1922, i, 441). *cis*- and *trans*- β -Decalones (*cis*-, m. p. 105°, b. p. 119°/16 mm., $d_4^{18.5}$ 1.00298, n_D^{25} 1.49366; semicarbazone, m. p. 185—186°; *trans*-, b. p. 117°/16 mm., d_4^{22} 0.97624, n_D^{25} 1.48337; semicarbazone, m. p. 193°); condensed with ethyl cyanoacetate and alcoholic ammonia give the *cis*- and *trans*-decahydronaphthalene-2 : 2-dicyanoacetimides [*cis*-, m. p. 242—243° (decomp.); *trans*-, m. p. 280° (decomp.)], which are converted into the dicarbamyylimides (*cis*-, m. p. 260—261°; *trans*-, m. p. 234—235°). These on hydrolysis yield the *cis*- and *trans*-decalin-2 : 2-diacetic acids [*cis*-, m. p. 167°; ethyl ester, b. p. 213°/21 mm., $d_4^{18.5}$ 1.04874, n_D^{25} 1.47918 (*imide*, m. p. 205°; *anhydride*, m. p. 91°); *trans*-, m. p. 175° (*methyl ester*, b. p. 192°/12 mm.; *ethyl ester*, b. p. 209°/16 mm., $d_4^{19.5}$ 1.04115, n_D^{25} 1.47702; *imide*, m. p. 201°; *anhydride*, m. p. 37°, b. p. 240°/20 mm.)]. Each of the anhydrides gives a pair of *anilic acids* on keeping with aniline (*cis*-, stable form, m. p. 167°, unstable, m. p. 200°; *trans*-, stable form, m. p. 159—161°, unstable, m. p. 165—166°). Each pair yields the same *anil* (*cis*-, m. p. 210°; *trans*-, m. p. 205°).

$\Delta^2 : 3^{11} : 2^1$ -*trans*-Decahydronaphthalene-2-acetonitrile (octahydronaphthylacetonitrile), b. p. 164°/26 mm., was prepared by distillation of the acid obtained on hydrolysing ethyl *trans*-decahydro- β -naphthylidenecyanoacetate. The latter on treatment with alcoholic potassium cyanide gives the *dicyano-ester*, $C_{20}H_{16}>C(CN)\cdot CH(CN)\cdot CO_2Et$, b. p. 200°/18 mm., $d_4^{20.5}$ 1.04947, n_D^{25} 1.47594. Hydrolysis of this yields two 2-carboxy-*trans*-decahydronaphthalene-2-acetic acids [(A) m. p. 197°; *anilic acid*, m. p. 193°; *anil*, m. p. 166—167°; *di-p-toluidide*, m. p. 171°; *anhydride*, m. p. 94°; (B) m. p. 175°; *anilic acid*, m. p. 198°; *anhydride*, m. p. 98° (cf. Huckel and Wiebke, A., 1927, 150)]. α -*trans*-Decahydronaphthylidene-2-propionitrile, b. p. 170—172°/18 mm., $d_4^{19.5}$ 0.9802, n_D^{25} 1.51245, is prepared by hydrolysis of ethyl α -cyano- α - $\Delta^2 : 3^{11} : 2^1$ -*trans*-decahydronaphthalene-2-propionate, b. p. 192°/17 mm., $d_4^{18.4}$ 1.03663, n_D^{25} 1.49098, obtained by methylating ethyl *trans*-decahydro- β -naphthylidenecyanoacetate. Partial hydrolysis of ethyl α : 2-dicyano-*trans*-decahydronaphthalene-2-acetate gives two 2-carboxy-*trans*-decahydronaphthalene-2-acetimidides, m. p. 210° and 145°. The latter yields a *trans-amic acid*, $C_{10}H_{16}(CO_2H)\cdot CH_2\cdot CO\cdot NH_2$, m. p. 217°, when hydrolysed. D. W. HILL.

Condensation of pinonic acid with aldehydes. O. FERNANDEZ and G. DE MIRASIERRA (Rec. trav. chim., 1929, 48, 852—854).—Pinonic acid condenses with salicylaldehyde in presence of alcohol and sulphuric acid, yielding, probably, 2 : 2-dimethyl-3- β -carbethoxycyclobutyl o-hydroxystyryl ketone, m. p. 159—161° with softening; the analogous 4-hydroxy-3-methoxystyryl derivative, m. p. 240° with softening, is prepared in presence of aqueous sulphuric acid.

Aldehydes other than phenolic aldehydes do not condense with pinonic acid. H. BURTON.

Stereochemistry of diphenyl compounds. III. Resolution of 2:2'-dihydroxy-1:1'-dinaphthyl-3:3'-dicarboxylic acid. W. M. STANLEY and R. ADAMS (Rec. trav. chim., 1929, 48, 1035—1040).—Oxidation of 2:3-hydroxynaphthoic acid with ferric chloride in boiling aqueous solution, or more conveniently in alkaline solution, yields 2:2'-dihydroxy-1:1'-dinaphthyl-3:3'-dicarboxylic acid, m. p. 331—333° (decomp.; all m. p. are corr.) (ethyl ester, m. p. 230—232°). Resolution of this is effected with brucine; the l-acid (I) has m. p. 326—329° (decomp.), $[\alpha]_D^{25}$ —171.9° in pyridine (brucine salt, m. p. 244—246° after softening at 235—237°, $[\alpha]_D^{25}$ —84.9° in pyridine; ethyl ester, m. p. 218—220°, $[\alpha]_D^{25}$ —134° in pyridine), and the d-acid, m. p. 326—329° (decomp.), $[\alpha]_D^{25}$ +171° in pyridine. Racemisation of I is not effected by heating with acetic or hydrochloric acid; slight racemisation occurs with boiling potassium hydroxide solution. The isomerism of substituted *p*-phenyl-diphenyls is discussed briefly. H. BURTON.

Syntheses by means of radiant energy. III. Acenaphthene and benzaldehyde. R. DE FAZI (Atti R. Accad. Lincei, 1929, [vi], 9, 1004—1006).—The products formed when a benzene solution of benzaldehyde and acenaphthene was exposed in a sealed tube to sunlight for 2 years were: Ciamician and Silber's tetrameride (A., 1909, i, 306) and Mascarelli's trimeride (A., 1906, i, 962; 1910, i, 389) of benzaldehyde, stilbene, isostilbene, a resin, and 7-benzoylacenaphthene, m. p. 195—198°.

T. H. POPE.

Action of guanidine hydrogen carbonate on the sodium hydrogen sulphite additive products of benzylideneanilines. J. B. EKELEY and M. C. SWISHER (Rec. trav. chim., 1929, 48, 1052—1054).—When benzylideneaniline is dissolved in aqueous sodium hydrogen sulphite and the solution evaporated, sodium anilinophenylmethanesulphonate (I), $\text{NHPh}\cdot\text{CHPh}\cdot\text{SO}_3\text{Na}$, separates. This salt begins to decompose when removed from the mother-liquors. Treatment of I with guanidine hydrogen carbonate in aqueous solution gives the α -anilino benzyl ester, m. p. 143°, of guanidine hydrogen sulphite. This is decomposed by boiling with dilute acid to sulphur dioxide, benzylideneaniline, and guanidine, and with dilute alkali to benzaldehyde, aniline, and guanidine. The same ester is obtained by treating the benzaldehyde-sodium hydrogen sulphite additive compound with aniline and guanidine hydrogen carbonate in aqueous solution, or by treating a mixture of the aldehyde, amine, and guanidine carbonate with sulphur dioxide in aqueous medium. A similar reaction occurs when I is treated with aminoguanidine hydrogen carbonate or carbamide hydrochloride. The following esters of guanidine hydrogen sulphite are described: α -anilino-4-methylbenzyl, m. p. 172°; α -anilino-*o*-nitro-3:4-methylenedioxybenzyl, m. p. 205°; α -anilino-3:4-methylenedioxybenzyl, m. p. 163°; α -*p*-toluidinobenzyl, anhydrous and $+\text{H}_2\text{O}$, m. p. 148°; α -*p*-toluidino-3:4-methylenedioxybenzyl, m. p. 169°; α -*p*-toluidino-4-methylbenzyl, m. p. 176°; $\alpha\alpha'$ -*p*-phenylenediaminodi-

benzyl, m. p. 155°. *o*-Nitrobenzylideneaniline does not yield a compound analogous to I. H. BURTON.

Colour and constitution from the viewpoint of recent electronic theory. H. H. HODGSON (J. Soc. Dyers Col., 1929, 45, 259—263).—An electronic interpretation of the Reimer-Tiemann reaction as applied to phenol, *o*- and *m*-cresol, *o*- and *m*-chloro-, *m*-bromo-, and *m*-iodo-phenol is given. The results obtained in a study of the absorption maxima of the *p*-nitrophenylhydrazones of a series of substituted benzaldehydes are in accord with the electronic theory. The theory is applied to the influence of chlorine alone and in conjunction with the sulphonie acid group on the colours of substituted benzeneazo-phenols. A. I. VOGEL.

Polarimetric study of intramolecular rearrangement in inactive substances. VII. T. S. PATTERSON and G. THOMSON (J.C.S. 1929, 1895—1900).—In continuation of previous work (A., 1911, i, 648), the rate of change of a number of *o*-, *m*-, and *p*-substituted benzsynaldoximes into the *anti*-forms has been compared by observing the change of rotation induced in solutions of ethyl tartrate. The influence of the position and nature of substituent groups is shown by the following values of 1000*k*: benzsynaldoxime, 2.52; *o*-NO₂, 0.35; *m*-NO₂, 1.27; *p*-NO₂, 1.35; *m*-Cl, 1.32; *p*-Cl, 1.82; *o*-Br, 0.73; *m*-Br, 1.55; *p*-Br, 2.33; *m*-I, 1.27; *p*-I, 2.88; *p*-CH₃, 1.58. The following figures are recorded for methyl ethers: β -*O*-methyl-*m*-nitrobenzsynaldoxime, 0.23; β -*O*-methyl-*p*-nitrobenzsynaldoxime, 0.18. *N*-Methyl-*m*-nitrobenzaldoxime solution shows no change of rotation, and the change of rotation is too small for measurement of the rate of transformation of β -into α -acetylbenzaldoxime. R. K. CALLOW.

Catalytic hydrogenation under reduced pressure. III. Reduction of nitriles in a vacuum. R. ESCOURROU (Bull. Soc. chim., 1929, [iv], 45, 735—744; cf. A., 1928, 1353; this vol., 173).—When hydrogenated at 190°/240 mm. phenylacetone nitrile affords mainly phenylacetaldimine, b. p. 213—214°/750 mm., n_D^{20} 1.5402 (hydrochloride, m. p. 180° with sublimation), together with a little ethylbenzene and β -phenylethylamine; at 200°/220 mm. the aldimine is obtained alone. It is fairly stable in absence of air and moisture. In moist air it polymerises to the trimeric hydrate, $(\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{NH}\cdot\text{H}_2\text{O})_3$, m. p. 83—85° (sublimes); in dry air a compound of hydrobenzamide type is slowly formed. It is hydrolysed to ammonia and phenylacetaldehyde with boiling 5% potassium hydroxide, but not with water alone (cf. Mignouac, A., 1920, i, 442). Benzonitrile is converted in presence of nickel at 175°/10—11 mm. into benzaldimine, n_D^{20} 1.5725, d_4^{20} 1.009 (hydrochloride, m. p. 203—204°; cf. Busch, A., 1896, i, 677), which rapidly polymerises to hydrobenzamide on exposure to the air, and more slowly in a closed vessel; at 140°/50 mm., benzylamine and a fraction, b. p. 300—305°, with an ammoniacal odour are also formed.

R. BRIGHTMAN.

Isolation of the intermediate Grignard additive compound, $\text{CHPh}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{OMgBr}$. I. E. MUSKAT and H. LUDEMAN (Ber., 1929, 62, [B], 2284—2286).—The isolation of the compound

CHPh:CH·CHMe·OMgBr (also +1Et₂O) by the action of magnesium methyl bromide on cinnamaldehyde in ether is described. It is hydrolysed to styryl-methylcarbinol. The ether-free compound appears less active than the corresponding etherate, thus suggesting that the function of ether is to activate Grignard reagents, possibly by formation of oxonium salts.

H. WREN.

Isomerism of phthalaldehydic esters. A. K. KIRPAL and K. ZIEGER (Ber., 1929, 62, [B], 2106—2107).—The chloride of phthalaldehydic acid, m. p. 61°, is converted by methyl alcohol in the presence of potassium hydroxide exclusively into the ψ -ester. If the chloride is exposed to the action of methyl alcohol during 9 days, the normal ester results. Methyl ψ -phthalaldehydate is slowly transformed by alcoholic hydrogen chloride into the normal ester. ψ -Esters of phthalaldehydic acid therefore resemble α -ketonic esters in their behaviour towards alcoholic hydrogen chloride.

H. WREN.

Synthesis of syringin. H. PAULY and L. STRASSBERGER (Ber., 1929, 62, [B], 2277—2284).—Addition of potassium carbonate to a solution of pyrogallol dimethyl ether in anhydrous chloral leads to the production of 3:5-dimethylpyrogallyltrichloromethylcarbinol, m. p. 162°, converted into 4-hydroxy-3:5-dimethoxybenzaldehyde, m. p. 113°, in 75% yield; the potassium and sodium salts, semicarbazone, m. p. 188°, and benzidide, m. p. 260°, are described. The sodium derivative is converted by chloromethyl ether into 3:5-dimethoxy-4-methoxymethoxybenzaldehyde, b. p. 157—158°/2 mm., m. p. 54° (semicarbazone, m. p. 141.5°), which condenses with acetaldehyde in alkaline solution to 3:5-dimethoxy-4-methoxymethoxycinnamaldehyde, m. p. 102°, b. p. about 190°/2 mm. (partial resinification) [semicarbazone, m. p. 202°]. The last-named compound is hydrolysed by boiling 50% acetic acid containing a little sulphuric acid to 4-hydroxy-3:5-dimethoxycinnamaldehyde, m. p. 108° (potassium salt; semicarbazone, m. p. 211° to a red liquid; benzidide). Acetobromoglucose and the potassium compound afford 3:5-dimethoxy-4-tetra-acetylglucosyloxycinnamaldehyde, C₆H₇O₅Ac₄·O·C₆H₂(OMe)₂·CH:CH·CHO, m. p. 182°. Fermentative reduction of the aldehyde followed by treatment of the product with ammonia yields 3:5-dimethoxy-4-glucosyloxycinnamyl alcohol, m. p. 192°, [α]_D²⁰ -17.25° in water for the anhydrous material, identical with natural syringin. Hydrolysis of syringin with 5% hydrochloric acid affords non-crystalline, polymeric syringenin, m. p. about 160°. Fission with emulsin permits the isolation of the monomeric variety, m. p. 105—107°. H. WREN.

cis-trans-Isomerism and steric hindrance.

X. 1:3-Dipropylcyclopentan-2-one and 1:3-dipropylcyclopentan-2-ols. G. VAYON and J. FLURER (Bull. Soc. chim., 1929, [iv], 45, 763—767).—1:3-Dipropylidenecyclopentan-2-one, b. p. 122—125°/12 mm., obtained from the secondary product, b. p. 135—150°, in the condensation of propaldehyde and cyclopentanone (cf. this vol., 1290), by dehydration with oxalic acid, when hydrogenated in ether in presence of platinum-black is converted into

cis-1:3-dipropylcyclopentan-2-one, b. p. 96—97°/8 mm., d_4^{20} 0.892, n_D^{20} 1.4495 (semicarbazone, m. p. 158—159°, yielding on hydrogenation 1:3-dipropylcyclopentan-2-semicarbazide, m. p. 78—80°; oxime, b. p. 139—142°/10 mm.). The rate of reaction of cyclopentanone with hydroxylamine is about 10 times as great as that of 1-propylcyclopentan-2-one, and 440 times as great as that of cis-1:3-dipropylcyclopentan-2-one. When reduced with sodium and alcohol, cis-1:3-dipropylcyclopentan-2-one yields a mixture of 1:3-dipropyl-cis-cis-cyclopentan-2-ols, rich in the trans-isomeride, from which the trans-1:3-dipropyl-cis-cis-cyclopentan-2-ol, b. p. 108—109°/11 mm., 0.8930, n_D^{20} 1.4578 (hydrogen phthalate, m. p. 58.5—59.5°; 3:5-dinitrobenzoate, m. p. 45—46°; phenylurethane, m. p. 46—47°), is obtained through its dinitrobenzoate. Hydrogenation in acetic acid in presence of platinum-black affords a mixture rich in the cis-isomeride, from which cis-1:3-dipropyl-cis-cis-cyclopentan-2-ol, m. p. 33—33.5°, b. p. 106°/8 mm. (hydrogen phthalate, m. p. 117—119°; 3:5-dinitrobenzoate, m. p. 40.5—41.5°; phenylurethane, m. p. 118—119°), is isolated through its hydrogen phthalate. The sodium derivative of the cis-pentanol is converted into the trans-isomeride when heated at 180—190° in an atmosphere of nitrogen. In 75% alcohol the trans-hydrogen phthalate is hydrolysed 7.4 times as rapidly as the cis-isomeride at 68°, and 8 times as fast at 39°. Comparison of these results with those obtained on the hydrogen phthalates of the 1-propylcyclopentan-2-ols indicates that the steric effect of introducing the cis-propyl group into cis-1-propylcyclopentan-2-ol is to reduce the velocity coefficient 20 times, whilst the introduction of the trans-propyl group into the trans-isomeride decreases the velocity coefficient of hydrolysis only 5 times.

R. BRIGTMAN.

Halogen derivatives of acetophenone. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1929, 9, 532—537).—Quantitative yields of ω -chloro- ω -bromoacetophenone, m. p. 37—37.5°, are obtained by the bromination of ω -chloroacetophenone, but not by the chlorination of the corresponding bromo-derivative. The following substances are prepared: $\omega\omega$ -chlorobromo-3-nitro- and ω -4-dichloro- ω -bromoacetophenone, m. p. 43—44° and 83—83.5°, respectively, $\omega\omega$ -dichloro-3-nitroacetophenone, m. p. 57—58°, and ω -iodo-3-nitroacetophenone, m. p. 92—93°. R. TRUSZKOWSKI.

ω -Halogen derivatives of acetophenone. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1929, 9, 538—545).—The following substances have been prepared: ω -chloro- α - and - β -acetophenones, m. p. 34—36° and 62—63°, respectively, the corresponding iodo-derivatives, m. p. 46.5—48° and 91—91.5°; ω -bromo- β -acetophenone, m. p. 82.5—83.5°, and $\omega\omega$ -dichloro- β -acetophenone, m. p. 83—84°.

R. TRUSZKOWSKI.

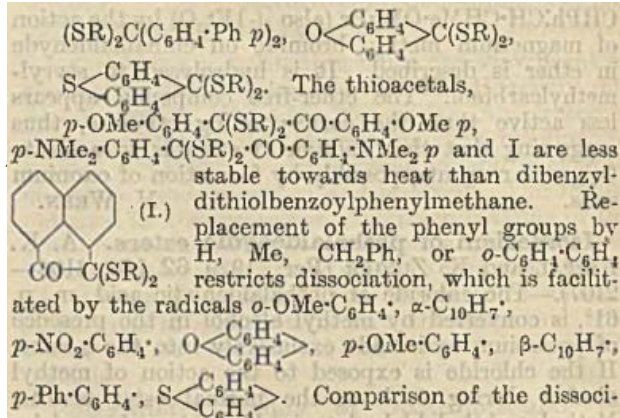
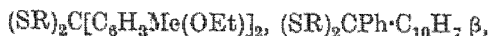
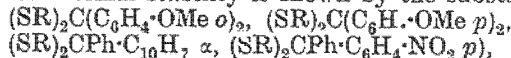
Halogen substitution products of 4-amino-benzophenone. W. A. WATERS (J.C.S., 1929, 2106—2111).—Halogenation of 4-amino- and 4-acetamido-benzophenone is in accordance with accepted views on substitution. The structure of 3:5-dichloro-4-aminobenzophenone (Chattaway, *ibid.*, 1904, 85, 340) is confirmed by conversion into 3:5-dichloro-

benzophenone, m. p. 65°. The α -oxime, m. p. 137°, of the latter yields 3:5-dichlorobenzanilide, m. p. 148°, whilst the β -oxime, m. p. 118°, gives a mixture of the dichlorobenzanilide and benz-3:5-dichloroanilide, m. p. 148-5°. 3-Bromo-4-acetamidobenzophenone, m. p. 106° (corr.), gives 3-bromo-4-aminobenzophenone, m. p. 158° (benzoyl derivative, m. p. 124°), on hydrolysis and 3:5-dibromo-4-acetamidobenzophenone, m. p. 214°. 3:5-Dibromo-4-aminobenzophenone, m. p. 148° (diacetyl derivative, m. p. 137°), gives 3:5-dibromobenzophenone, m. p. 75°, on deamination. 3-Iodo-4-aminobenzophenone, m. p. 177° (benzoyl derivative, m. p. 162°), from 4-aminobenzophenone and iodine monochloride in acetic acid, yields 3:5-di-iodo-4-aminobenzophenone, m. p. 153° (diacetyl derivative, m. p. 187°), at water-bath temperature with the same reagent. The structure of 3:5-di-iodobenzophenone, m. p. 91°, is established by synthesis from 3:5-dinitrobenzophenone, m. p. 131°, by way of 3-nitro-5-aminobenzophenone, needles, m. p. 130°, or plates, m. p. 146° (diacetyl derivative, m. p. 191° after sintering at 115—125°), 5-iodo-3-nitrobenzophenone, m. p. 118°, and 5-iodo-3-aminobenzophenone (not isolated). 3-Bromo-5-iodo-4-aminobenzophenone, m. p. 148° (diacetyl derivative, m. p. 161°), is obtained either by iodinating 3-bromo-4-aminobenzophenone or by brominating 3-iodo-4-aminobenzophenone. Nitration of 4-acetamidobenzophenone is not effected.

D. W. HILL.

Organic compounds of sulphur. XIV.
Relationship between the dissociation tendency of thioacetals and compounds of the ethane series; investigation of hexaphenylethane. A. SCHONBERG and O. SCHÜTZ [with M. ABEND, U. OSTWALD, and F. KAPLAN] (Ber., 1929, 62, [B], 2322—2337; cf. A., 1927, 667).—A comparison is effected between the thermal stabilities of dibenzylthioldiphenylmethane and a series of thioacetals by placing small amounts of the substances in precisely similar capillary tubes, which are evacuated, sealed, and placed for the same length of time in a bath of such temperature that both specimens are melted. Dissociation is evidenced by the formation of blue thiobenzophenone derivatives. Marked dependence of relative thermostability of thioacetals on temperature has not been observed. In addition to thiobenzophenone, the production of benzylmercaptan is always observed; other products (sulphur, hydrogen sulphide, stilbene, diphenyl disulphide) are formed according to the nature of the benzyl mercaptol and the temperature, but it is uncertain whether these are primary or secondary compounds. When dibenzylthioldiphenylmethane is adopted as standard, the following compounds exhibit greater heat stability (smaller tendency to dissociate): $\text{H}_3\text{C}(\text{SR})_2$, $\text{CHPh}(\text{SR})_2$, $\text{Me}_2\text{C}(\text{SR})_2$, $(\text{CH}_2\text{Ph})_2\text{C}(\text{SR})_2$.

$\text{C}_6\text{H}_5\text{C}(\text{SR})_2$ ($\text{SR})_2\text{CPh}\cdot\text{Bz}$ ($\text{R}=\text{CH}_2\text{Ph}$). Similar thermal stability is exhibited by the compounds $(\text{SR})_2\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}$ (*o*) and $(\text{SR})_2\text{C}(\text{C}_6\text{H}_4\text{Cl})_2$ (*p*), whereas smaller thermal stability is shown by the substances



H. WREN.

Heteropolar compounds of carbon. IX.
Action of the nitro-group on the halochromism of chalcones. W. DILTHEY, L. NEUKAUS, and W. SCHOMMER (J. pr. Chem., 1929, [ii], 123, 235—240).—By condensation of the appropriate substituted acetophenone with the substituted benzaldehyde the following chalcones are prepared; 4'-nitro-, m. p. 149—150°; 4'-nitro-4-methoxy-, m. p. 176—177°; 3'-nitro-, m. p. 131°; 3'-nitro-4-methoxy-, m. p. 171—172°; 2'-nitro-, m. p. 128—129°; 2'-nitro-4-methoxy-, m. p. 100°, and 2-nitro-, m. p. 125° (the last being best obtained with sodium methoxide as the condensing agent), and the effects of the substituent groups on the halochromism in concentrated sulphuric acid are compared. Contrary to its hypsochromic effect in the aldehyde component of the chalcone,

substitution of a nitro-group in the ketonic component has a bathochromic effect, the magnitude of which decreases in the order $p > m > o$. The 4 and 4' positions in the molecule are not optically equivalent. Thus a methoxy-group has a stronger bathochromic effect in the 4 (aldehyde) than in the 4' (ketone) position. Hence a bathochromic effect is produced by a positive substituent in the aldehyde and a negative substituent in the ketone component. It is suggested that this effect is due to the presence of a dipole in the chalcone molecule oriented with its positive end in the ketone component and that substituent groups which increase this dipole deepen the colour, and *vice versa*.

J. W. BAKER.

Tautomerisation of chalconesemicarbazones by light. H. STOBBE and K. BREMER (J. pr. Chem., 1929, [ii], 123, 241—256).—Both the α - and γ -chalconesemicarbazones (Heilbron and Wilson, J.C.S., 1912, 101, 1482) are stable in the dark, but exposed to ultra-violet light they become yellow, the change occurring readily even in diffuse daylight in the case of the γ -compound. Both yellow forms give colourless solutions in alcohol or chloroform, from which by concentration in the dark the colourless form crystallises out, whilst concentration in light yields the yellow forms. The colourless forms give yellow solutions in alcoholic sodium alkoxide solution, in sodium hydroxide, or in piperidine, from which the colourless form is obtained on acidification. These colour changes are explained by the existence of tautomeric forms of the types $R:N:NH:CO:NH_2$ (I), $R:N:NH:C(OH):NH$ (II), and $R:N:N:C(OH):NH_2$ (III) ($R=CHPh:CH:CPh:$). The yellow colour in sodium alkoxide solution is due not, as Heilbron and Wilson (*loc. cit.*) suggest, to stereoisomerism, but to salt formation with types II or III, whilst the yellow forms obtained by exposure to light are equilibrium mixtures of type I with type II or III. The absorption spectra of the α - and γ -semicarbazones in alcoholic and alcoholic sodium ethoxide solutions have been plotted. For a 10 mm. length in 0.01N-alcoholic solution the limit of absorption for the α - and γ -forms occurs at $1/\lambda$ 2650 and 2800, respectively (bands at 3000—4100 and 3300, respectively), whilst in alcoholic sodium ethoxide solution it is at $1/\lambda$ 2350 and 2525, respectively, salt formation causing a similar shift towards the red in each case. 4-Methylchalcone also gives two semicarbazones, α (stable to light), m. p. 193°, and γ (unstable to light), m. p. 185—187°, which are separated by fractional crystallisation from alcohol, the α being the less soluble; their absorption spectra in alcohol and alcoholic sodium ethoxide are similar to those of the chalconesemicarbazones. 4-Methoxychalcone also gives a γ -semicarbazone, m. p. 190° (Stobbe and Hensel, A., 1926, 1248), and an α -semicarbazone, m. p. 168° (stable to light), the latter being formed in hot alcoholic solution. The following substituted chalcones yield only one semicarbazone, 4-methyl-, γ , m. p. 172—174°; 4,4'-dimethyl-, γ , m. p. 186—187°; 4-methoxy-4'-methyl-, α , m. p. 184—186°; 4:4'-dimethoxy-, α , m. p. 177—178°; and 3:4-dioxymethylene-, α , m. p. 203—205°. The γ -forms are less stable to light and become coloured in diffuse daylight, whilst both α - and γ -forms become coloured on exposure to

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ultra-violet light for 15 min. Comparison of the above derivatives with the semicarbazone, m. p. 135—137°, of 4'-methylidihydrochalcone (*p*-tolyl β -phenylethyl ketone) and other saturated aromatic and aliphatic ketones and with various arylidenacetones shows that only the derivatives of unsaturated ketones become coloured on exposure to ultra-violet light, give coloured solutions in sodium ethoxide, or colours with ferric chloride, the change, therefore, being due to tautomerism consequent on the presence of conjugated double linkings, and the colour in the last two cases due to salt formation with the enol forms.

J. W. BAKER.

Oxidation of benzoin to diketones with iodine.

B. B. CORSON and R. W. McALLISTER (J. Amer. Chem. Soc., 1929, 51, 2822—2825).—Oxidation of benzoin, furoin, anisoin, and piperoin with iodine in presence of methyl-alcoholic sodium methoxide solution and in absence of oxygen affords good yields of benzil, furil, anisil, and piperil, respectively. A mechanism involving the intermediate formation of sodium stilbenedioxide is suggested. The method is not applicable to the preparation of aliphatic 1:2-diketones.

The reddish-purple coloration produced by treating benzoin with sodium methoxide solution is intensified by the addition of benzil; the diketone itself gives no coloration. The test is also given by furoin and benzofuroin, but not by anisoin or piperoin.

H. BURTON.

Auto-oxidation of benzoin in alkaline solution.

A. WEISSBERGER, H. MAINZ, and E. STRASSER (Ber., 1929, 42, [B], 1942—1952).—The purplish-red colour produced by addition of aqueous potassium hydroxide to alcoholic solutions of benzoin (cf. Hantzsch and Glover, A., 1907, i, 538) is not observed in the complete absence of air; the colour is discharged when the solutions are shaken with air. The sensitive, coloured compound is also produced when alkaline alcoholic solutions of benzoin are treated with nitrobenzene, *p*-benzoquinone, or benzil. Alkaline alcoholic solutions of benzil when warmed for a short time develop a violet colour which is discharged when the cold solution is shaken with air. If the solution is boiled for about 5 min., the coloration becomes purplish-red and decolorisation does not occur when the cold solution is shaken with air. Quantitative examination shows that 1 mol. of oxygen is required for the auto-oxidation of 1 mol. of benzoin and that the primary products are 1 mol. of benzil and 1 mol. of hydrogen peroxide or alkali peroxide. The last-named compound oxidises benzil to benzoic acid, whereas it scarcely attacks benzoin. The rate of absorption of oxygen by alkaline alcoholic solutions of benzoin is measured in an apparatus in which such thorough contact occurs between gas and liquid that the latter remains saturated with oxygen. Under these conditions the reaction proceeds at rates which depend on the alkalinity of the solutions, temperature, and solvent, but are independent of the concentration of the acyloin and of illumination. If the solutions become impoverished with respect to oxygen the stilbenediolate formed by isomerisation gradually accumulates and the violet compound in equilibrium with it and benzil is produced. The auto-oxidation

of benzoin appears to proceed in accordance with the schemes: $\text{OH}\cdot\text{CHPh}\cdot\text{COPh} + \text{KOH} \rightleftharpoons \text{OK}\cdot\text{CHPh}\cdot\text{COPh} + \text{H}_2\text{O}$ and $\text{OK}\cdot\text{CHPh}\cdot\text{COPh} + \text{O}_2 \longrightarrow \text{Ph}\cdot\text{CO}\cdot\text{COPh} + \text{KHO}_2$.
H. WREN.

Reducing effect of binary system, $\text{MgX}_2 + \text{Mg}$, on organic compounds in anhydrous solvents. M. GOMBERG (Rec. trav. chim., 1929, 48, 847—851).—The mechanism of the reaction with aromatic ketones, 1:2-diketones, acids, acyl peroxides, and aldehydes is discussed (cf. A., 1927, 245, 1190; 1928, 1373).

H. BURTON.

Action of hydrazine hydrochloride on aromatic ketones. N. SCHAPIRO [with BRACHMANN] (Ber., 1929, 62, [B], 2133—2136).—The action of hydrazine hydrate on ketones in absence of solvent or presence of alcohol leads to the production of hydrazones. The presence of strong mineral acids is excluded, since hydrolysis of the products is thereby induced. This is not the case with formic and acetic acids, in the presence of which ketazines are produced; these compounds are also produced smoothly and almost quantitatively when hydrazine hydrochloride in alcohol is used. Benzilketazine, m. p. 201—202°, and isatinketazine, $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_4$, decomp. about 300°, are described. Benzoin and hydrazine hydrochloride afford benzilketazine and amarone, m. p. 245°. Furoin and furil give brown, amorphous compounds which do not appear to be ketazines or hydrazones. Contrary to expectations, anisil gives *anisilhydrazone*, m. p. 163—164°.
H. WREN.

Some reactions of *mm'*-dinitrobenzil. A. A. BOON and H. B. NISBET (J.C.S., 1929, 1901—1902).—*mm'*-Dinitrobenzil condenses with *o*-phenylene- and *o*-tolylene-diamines to yield, respectively, 2:3-di-*mnitrophenylquinoxaline*, m. p. 208°, and the 5-methyl derivative, m. p. 208—210°. With benzidine in alcohol an additive compound, m. p. 163.5°, is formed, which may be utilised to separate *mm'*-dinitrobenzil from the product of nitration of benzil. An additive compound, m. p. 164°, is formed with *o*-toluidine. *mm'*-Dinitrobenzil condenses with 1 mol. only of acetophenone to yield *dehydroacetophenone-mm'*-dinitrobenzil (β -benzoyl- α -m-nitrobenzoyl-m-nitrostyrene), m. p. 158°. *mm'*-Dinitrobenzil yields no crystalline condensation product with acetone.

R. K. CALLOW.

Nuclear condensation of phenols and phenol ethers with nitriles yielding phenol and phenol ether ketimines and ketones. III. **Synthesis of cotogenin, protocotoin, isoprotocotoin, and methylprotocotoin (oxyleucotin).** J. HOUBEN and W. FISCHER (J. pr. Chem., 1929, [ii], 123, 89—109; cf. Späth and Bretschneider, A., 1928, 1136).—Condensation of phloroglucinol trimethyl ether (I) with acetonitrile in presence of ethereal hydrogen chloride and zinc chloride yields the *hydrochloride* of 2:4:6-trimethoxyacetophenoneimine, m. p. 95—96°, hydrolysed by boiling with water to 2:4:6-trimethoxyacetophenone, m. p. 100—103°. Similar condensation of resorcinol and 3:4-methylenedioxybenzonitrile (II) and subsequent hydrolysis affords a 21% yield of 2:4-dihydroxy-3':4'-methylenedioxybenzophenone, m. p. 215—216°; with ferric chloride as the condensing agent and prolonged treatment with

hydrogen chloride the yield of intermediate ketimine is improved. Phloroglucinol dimethyl ether and II give (ferric chloride method) a mixture of 46% of the ketimine hydrochloride (III) of 4-hydroxy-2:6-dimethoxy-3':4'-methylenedioxybenzophenone [*isoprotocotoin*], m. p. 165—166° (*hydrochloride*), and 11% of the ketimine hydrochloride (IV) of 2-hydroxy-4:6-dimethoxy-3':4'-methylenedioxybenzophenone [*protocotoin*], m. p. 141—142°. Isolation of IV is effected by prolonged treatment of the ethereal and aqueous mother-liquors from III with stannous chloride and hydrochloric acid. When the above condensation is carried out with zinc chloride the main product is III. Ferric or zinc chloride condensation of I and II gives the *hydrochloride* of the ketimine, m. p. 117—118°, of 2:4:6-trimethoxy-3':4'-methylenedioxybenzophenone [*methylprotocotoin*], m. p. 132—133°. 3:4-Diacetoxymethylbenzonitrile and I yield (zinc chloride method) after hydrolysis with aqueous methyl-alcoholic sodium hydroxide about 16% of 3:4-dihydroxy-2':4':6'-trimethoxybenzophenone (V) [*cotogenin*], m. p. 222.5° (corr.; decomp.). Hydrolysis of the initial reaction mixture with sodium hydroxide solution in presence of light petroleum and subsequent removal of zinc as sulphide affords the ketimine, m. p. 265° (decomp.; *hydrochloride*; *sulphate*), of V. Colour reactions of the above benzophenones with various reagents are given.

When a mixture of ferric chloride and ether is saturated with hydrogen chloride the compound $\text{FeCl}_3\cdot\text{HCl}\cdot 2\text{Et}_2\text{O}$ is formed.
H. BURTON.

Solubility of benzoquinhydrone in aqueous alcohol. A. E. BRODSKY and M. I. ALFEROV (Ber., 1929, 62, [B], 2132—2133).—The solubility of benzoquinhydrone in water and aqueous alcohol (25.55, 49.81, and 71.31 wt.-%) is 0.0158, 0.0330, 0.0684, and 0.1158 mol. per litre.
H. WREN.

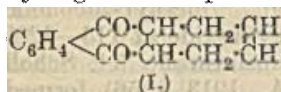
Derivatives of naphthaquinones. R. LANTZ and A. WAHL (Bull. Soc. chim., 1929, [iv], 45, 744—754).—Mainly a recapitulation of earlier work (A., 1925, i, 820, 910, 1159; 1926, 617; B., 1924, 902; 1925, 200; 1927, 39). When agitated with air and aniline in presence of copper hydroxide, 1-amino- β -naphthol yields the *cupric* derivative of 2-hydroxy- α -naphthaquinone-1-imine-4-anil, and phenyldinaphthoxazine, the latter probably resulting from condensation of the imine with the aminonaphthol. Nitroso- β -naphthol with aniline in presence of copper powder and in methyl alcohol gives the same products, but in the absence of copper the oxazine is not formed and 2-hydroxy- α -naphthaquinone-1-imine-4-anil, orange, m. p. 231—234° (decomp.), is obtained alone in both cases. With sodium hydrogen sulphite at 0° in alkaline solution the latter yields a colourless hydrogen sulphite, from which alkalis regenerate the imine, but acids afford anilino- β -naphthaquinone. Zinc and dilute acid reduce the sulphite to 1-amino-4-anilino- β -naphthol. 2-Hydroxy- α -naphthaquinone-1-imine-4-p-methylanil, m. p. 213—214° (decomp.), 2-hydroxy- α -naphthaquinone-1-imine-4-o-methylanil, m. p. 229—230° (decomp.), and 2-hydroxy- α -naphthaquinone-1-imine-4-p-aminoanil, decomp. 250°, are obtained by agitating 1-amino- β -naphthol-4-sulphonic acid in sodium hydrogen carbonate solution with air and

the amine. Reduction with hyposulphite or with hydrogen sulphide or stannous chloride in alcohol converts the imine-anils into 1-amino-4-arylamino-3-naphthols. 1-Amino-4-anilino-3-naphthol, oxidised to the imine in aqueous solution (cf. Goldstein and Radovanovitch, *A.*, 1926, 1134), in non-aqueous media yields an oxazine condensation product. The oxazine colours of Dahl (G.P. 82,097) are probably similarly formed by condensation of an intermediate imine with the aminonaphtholsulphonic acid followed by cyclisation accompanied by hydrolysis of an imino-group.

R. BRIGHTMAN.

Condensation of acenaphthenequinone with phenols. I. MATEI (Ber., 1929, 62, [B], 2095—2098).—Addition of concentrated sulphuric acid to a solution of acenaphthenequinone in phenol yields 7:7-di-*p*-hydroxyphenyl-8-ketoacenaphthene, m. p. 257—258° (diacetate, m. p. 141°). With quinol in presence of glacial acetic and concentrated sulphuric acids acenaphthenequinone affords anhydro-7:7-di-2':5'-dihydroxyphenyl-8-keto-acenaphthene, m. p. 281° (diacetate, m. p. 125° after softening at 110°). Resorcinol and pyrocatechol give corresponding di-2':4'-and 5':4'-dihydroxyphenylacenaphthones, m. p. 266—268° (decomp.) (cf. Zsuffa, *A.*, 1910, i, 861), and m. p. 250—270° after incipient decomp. above 200° (tetra-acetate, m. p. 97—98°). H. WREN.

Syntheses in the hydroaromatic series. VI. Partly hydrogenated naphtha- and anthraquinones with hydrogen in the γ - or δ -position. O. DIELS, K. ALDER, and G. STEIN [with P. PRIES and H. WINCKLER] (Ber., 1929, 62, [B], 2337—2372; cf. *A.*, 1928, 1018).—Addition of hydrocarbons with conjugated double linkings to quinones yields partly hydrogenated naphtha- and anthraquinones of the

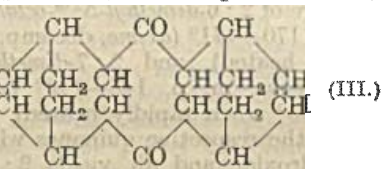
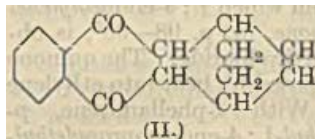


type I, which are actually diketones. It is proposed to consider them as quinone derivatives on account of their close relationships to these compounds. The unusual hydrogenation of the "twin" carbon atoms induces the authors to denote these positions by γ in the naphthalene and δ in the anthracene series.

α -Naphthaquinone is converted by butadiene at 100° into Δ^2 -tetrahydroanthraquinone (I), m. p. 105—106° (dioxime, decomp. 250° when rapidly heated). The very pronounced tendency of the δ -hydrogen atoms to migrate to the carbonyl group causes the compound to be converted by boiling acetic anhydride into 9:10-diacetoxy-1:4-dihydroanthracene, m. p. 263—262° [corresponding dibromide, m. p. 233—234° (decomp.)], hydrolysed by alcoholic potassium hydroxide to the potassium derivative of 9:10-dihydroxy-1:4-dihydroanthracene, also obtained by dissolving Δ^2 -tetrahydroanthraquinone in alcoholic potassium hydroxide. Exposure of the enolate solutions to air leads to the formation of anthraquinone. Treatment of an alcoholic solution of Δ^2 -tetrahydroanthraquinone with colloidal palladium in the absence of air causes migration of the δ -hydrogen atoms to the carbonyl group, with formation of 9:10-dihydroxy-1:4-dihydroanthracene, converted by crystallisation in presence of air into 1:4-dihydroanthraquinone, m. p. 208—210° (decomp.) when very rapidly heated. Re-

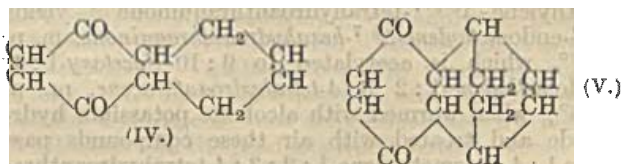
duction of Δ^2 -tetrahydroanthraquinone in presence of colloidal palladium yields 1:2:3:4-tetrahydroanthraquinone, m. p. 158°. Isoprene and α -naphthaquinone afford isoprene- α -naphthaquinone, $\text{C}_{15}\text{H}_{14}\text{O}_2$, m. p. 81°; the corresponding diacetate, $\text{C}_{19}\text{H}_{18}\text{O}_4$, m. p. 191°, is converted by successive treatment with alcoholic potassium hydroxide and air into 2-methylanthraquinone, m. p. 175°. $\Delta^{\alpha\gamma}$ -Dimethylbutadiene and α -naphthaquinone yield 1:3-dimethyl- Δ^2 -tetrahydroanthraquinone, m. p. 81°, from which the corresponding diacetate, m. p. 174°, and 1:3-dimethylantraquinone, m. p. 162°, are successively derived. 1:1:3-Trimethyl- Δ^2 -tetrahydroanthraquinone, m. p. 119° (from $\alpha\alpha\gamma$ -trimethylbutadiene), and its oxidation in alkaline solution by air to 1:1:3-trimethyl-1:4-dihydroanthraquinone, m. p. 162° (decomp.), are described.

$\Delta^{1:3}$ -cyclohexadiene and α -naphthaquinone afford 1:4-endoethylene- Δ^2 -tetrahydroanthraquinone (II), m. p. 135°, converted into the diacetate, $\text{C}_{20}\text{H}_{18}\text{O}_4$, m. p. 185, which is successively hydrolysed and oxidised by air to 1:4-endoethylene-1:4-dihydroanthraquinone, decomposed at 180—190° into ethylene and anthraquinone. *p*-Benzoquinone and cyclohexadiene at 100° yield 1:4:5:8-diendoethylene- $\Delta^{2:6}$ -octahydroanthraquinone (III), m. p. 196—197°, oxidised



by air in alcoholic alkaline solution to 1:4:5:8-diendoethylene-1:4:5:8-tetrahydroanthraquinone, which decomposes at about 180° into ethylene and anthraquinone. α -Phellandrene and α -naphthaquinone yield 1:4-endoisopropylethylene-2-methyl- Δ^2 -tetrahydroanthraquinone, m. p. 88°, transformed by oxidation into 1:4-endoisopropylethylene-2-methyl-1:4-dihydroanthraquinone, decomposed by heat into 2-methylantraquinone and isopropylethylene. α -Naphthaquinone is converted by α -phenylbutadiene into 1-phenylantraquinone, m. p. 177—178°.

γ -Hydrogenated naphthaquinones are very readily prepared by the addition of 1 mol. of diene hydrocarbon to 1 mol. of *p*-benzoquinone. Thus with butadiene in benzene at the atmospheric temperature *p*-benzoquinone yields $\Delta^{2:6}$ -tetrahydronaphthaquinone (IV), m. p. 58°, which on exposure to sunlight becomes transformed into a (?) polymeride, m. p. 252°. It is converted by acetic anhydride into 5:8-diacetoxy-



1:4-dihydronaphthalene, m. p. 134—135°, hydrolysed by alcoholic potassium hydroxide to 5:8-dihydroxy-1:4-dihydronaphthalene, m. p. 211—212°. The last-named compound is also obtained from tetrahydro-

naphthaquinone by the action of warm, glacial acetic acid containing a trace of hydrogen bromide. The acetate is catalytically hydrogenated in the presence of alcohol and colloidal palladium to 5:8-diacetoxy-1:2:3:4-tetrahydronaphthalene, m. p. 186—187°, hydrolysed to 5:8-dihydroxy-1:2:3:4-tetrahydronaphthalene, m. p. 185° (also obtained by catalytic reduction of 5:8-dihydroxy-1:4-dihydronaphthalene), which is identified by oxidation with ferric chloride to 1:2:3:4-tetrahydro- α -naphthaquinone, m. p. 5:8-Dihydroxy-1:4-dihydronaphthalene is similarly oxidised by ferric chloride to 1:4-dihydro- α -naphthaquinone, m. p. 109°. *p*-Benzoquinone and $\Delta^{1:3}$ -cyclohexadiene in benzene afford 1:4-endoethylenic- $\Delta^{2:6}$ -tetrahydro- α -naphthaquinone (V), m. p. 98° (corresponding diacetate, $C_{16}H_{14}$ m. p. 164°), isomerised by hydrogen bromide in glacial acetic acid to 5:8-dihydroxy-1:4-endoethylene-1:4-dihydronaphthalene, m. p. 178°, from which 1:4-endoethylene-1:4-dihydro- α -naphthaquinone, m. p. 98—99°, is obtained by oxidation with ferric chloride. The quinone is characteristically decomposed by heat into ethylene and α -naphthaquinone. With α -phellandrene, *p*-benzoquinone gives 2-methyl-1:4-endoisopropylethylenic- $\Delta^{2:6}$ -tetrahydro- α -naphthaquinone, m. p. 119°.

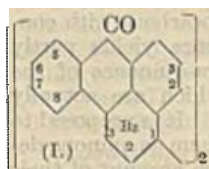
Bisdienequinones are obtained readily by the addition of 2 mols. of the diene to 1 mol. of *p*-benzoquinone. Thus isoprene and *p*-benzoquinone in alcohol at 100° afford a mixture of 2:6-dimethyl- $\Delta^{2:6}$ -octahydroanthraquinone, m. p. 170—171° (oxime, decomp. about 290° when rapidly heated), and 2:7-dimethyl- $\Delta^{2:6}$ -octahydroanthraquinone, m. p. 145—146° (dioxime, decomp. 290—295° when rapidly heated). Successive treatments of the respective quinones with alcoholic potassium hydroxide and air yields 2:6-dimethylanthraquinone, m. p. 237—238°, and 2:7-dimethylanthraquinone, m. p. 169°. The quinones are isomerised by boiling acetic anhydride, when heated at about 200°, or when treated with alkali hydroxide in alcohol to compounds, m. p. 243° and 242°, respectively, which can be similarly dehydrogenated to 2:6- or 2:7-dimethylanthraquinone. Von Euler and Josephson (A., 1920, i, 489) appear to have obtained a mixture of these two compounds by their more drastic treatment of isoprene with *p*-benzoquinone.

1:4-endoMethylene- $\Delta^{2:5:7}$ -tetrahydroanthraquinone does not yield a diacetate when treated with acetic anhydride, but, in consequence of its instability, is transformed into cyclopentadiene, α -naphthaquinol diacetate, and 1:4-endoethylene-1:4-dihydroanthraquinone, m. p. 156°. The last-named compound is reduced by hydrogen in presence of colloidal palladium to 1:4-endoethylene-1:2:3:4-tetrahydroanthraquinone, m. p. 138°. Hydrogenation of 1:4-endoethylene- $\Delta^{2:5:7}$ -tetrahydroanthraquinone yields 1:4-endoethylene- Δ^5 -hexahydroanthraquinone, m. p. 117°, which is acetylated to 9:10-diacetoxy-1:4-endoethylene-1:2:3:4-tetrahydroanthracene, m. p. 185°; when warmed with alcoholic potassium hydroxide and treated with air these compounds pass into 1:4-endoethylene-1:2:3:4-tetrahydroanthraquinone.

Acetylation of 1:4-endoethylene- Δ^2 -hexahydro-naphthaquinone (cf. Albrecht, A., 1906, i, 674) is similarly complicated by decomposition of the com-

pound with formation of cyclopentadiene; the main products are 9:10-diacetoxy-1:4:5:8-diendomethylene-1:4:7:8-tetrahydroanthracene, colourless crystals, m. p. 250°, quinol diacetate, m. p. 124—125°, and 1:4:5:8-diendomethylene-1:4:5:8-tetrahydroanthraquinone, red crystals, m. p. 252° (decomp.). The colourless acetyl compound is hydrolysed to 9:10-dihydroxy-1:4:5:8-diendomethylene-1:4:5:8-tetrahydroanthracene, m. p. 298° after darkening at 280°, which is oxidised by chromic acid in acetic acid to the red quinone, m. p. 252° (decomp.). 1:4:5:8-Diendomethylenedidecahydroanthraquinone is dehydrogenated by cautious treatment with bromine in chloroform to 9:10-dihydroxy-1:4:5:8-diendomethylene-1:2:3:4:5:6:7:8-octahydroanthracene, m. p. 289° (diacetate, m. p. 226°), which is oxidised by chromic acid in glacial acetic acid to 1:4:5:8-diendomethylene-1:2:3:4:5:6:7:8-octahydroanthraquinone, m. p. 252°. Catalytic reduction of 1:4:5:8-diendomethylene-1:4:5:8-tetrahydroanthraquinone yields 9:10-dihydroxy-1:4:5:8-diendomethylene-1:2:3:4:5:6:7:8-octahydroanthracene, m. p. 289° (diacetate, m. p. 226°). 1:4-endoMethylene-1:4-dihydro- α -naphthaquinone, m. p. 70°, is obtained by isomerisation of 1:4-endoethylene- Δ^2 -tetrahydro- α -naphthaquinone by hydrogen bromide in glacial acetic acid and subsequent oxidation of the product with ferric chloride. H. WREN.

Benzanthrone. A. LUTTRINGHAUS and H. NERESHEIMER [with H. WOLFF and H. EMMER] (Annalen, 1929, 473, 259—289).—Treatment of *Bz*-1-bromobenzanthrone with copper powder at 280—300° affords *Bz*-1:*Bz*-1'-dibenzanthronyl (I), m. p. 412—414°, which when treated with very concentrated methyl-alcoholic potassium hydroxide at 115—120° yields dibenzanthrone (cf. Scholl



and Seer, A., 1913, i, 56), formed by atmospheric oxidation of the intermediate dihydro-derivative. When benzanthrone (II) is treated with alcoholic potassium hydroxide at 100—105°, 2:2'-dibenzanthronyl (III), m. p. 320—321°, is obtained together with small amounts of 2-hydroxybenzanthrone (IV) (Perkin and Spencer, J.C.S., 1922, 121, 474), and a phenolic substance (removed by treatment of the crude product with anhydrous sodium carbonate and methyl *p*-toluenesulphonate in presence of trichlorobenzene at 195°). Treatment of II in presence of finely-divided potassium hydroxide and benzene with isopropyl alcohol at 30—35° in a current of nitrogen also affords III; it is produced similarly with methyl and ethyl alcohols at 85° and 70—75°, respectively. Sodium anilide in aniline solution (prepared by treating aniline containing small amounts of nickel oxide and copper-bronze with sodium at 170—180° in a current of nitrogen) at 40—45° converts II into III; at the same time a small amount of 2-anilinobenzanthrone, m. p. 215°, is formed. This last-named substance is converted by 50% potassium hydroxide solution at 250° into IV. The formation of 2:2'-dibenzanthronyl from benzanthrone is presumed to occur through a primary enolisation of the keto-group with the pro-

duction of a quinonoid system resulting in free valency at position 2, whereby doubling of the molecule occurs, the resulting dihydro-derivative being oxidised by air. 6:6'-*Dimethyl*-, m. p. 357—358°, and 6:6'-*dichloro-2:2'-dibenzanthronyls* (V), m. p. 407—408°, are obtained by similar treatment of the corresponding benzanthrone with alcoholic potassium hydroxide. Fusion of III with potassium hydroxide and sodium acetate at 240—250° also yields dibenzanthrone (6:6'-*dimethyl* derivative obtained similarly); ring closure is also effected by heating with 80% sulphuric acid containing a small amount of mercuric sulphate at about 200°, but the product is contaminated with, probably, sulphonic acids. 6:6'-*Dichlorodibenzanthrone* is obtained by the acid treatment of V. 2-Aminobenzanthrone is converted by the Sandmeyer reaction into 2-chlorobenzanthrone (VI), m. p. 204—205°. Treatment of an equimolecular mixture of II and VI with sodium anilide at 5° in a current of nitrogen yields about 50% of the theoretical amount of III together with 2-anilinobenzanthrone. 6-Methyl- (VII), m. p. 329—330°, and 6-chloro-2:2'-*dibenzanthronyl* (VIII), m. p. 313—314°, are obtained similarly from VI and 6-methyl- and 6-chloro-benzanthrone, respectively. Treatment of a solution of 2:6-dichloroanthraquinone in slightly diluted sulphuric acid with a mixture of glycerol and copper-bronze at 130—135° affords 2:6-dichlorobenzanthrone, m. p. 234°, which when treated with II and potassium anilide yields VIII. Potassium hydroxide fusion of VII gives 6-methyldibenzanthrone.

When benzanthrone is treated with an alcoholic potassium hydroxide melt at temperatures between 120° and 220° a mixture of dibenzanthrone and *iso*-dibenzanthrone (cf. Scholl and Seer, *loc. cit.*) results. The maximum amount of the *iso*-derivative (about 33%) is formed at 170—175°; at 220° only dibenzanthrone is obtained. With *isopropyl* alcohol and potassium hydroxide the corresponding figures for the *iso*-derivative are 37% and 140°. The isomerides are readily separated owing to the insolubility of the sodium salt of the dihydroisodibenzanthrone in 4% sodium hydroxide solution. The production of the *iso*-derivative occurs presumably through the intermediate 2:Bz-1'-dibenzanthronyl (formed by addition of a benzanthrone molecule at the Bz-1-position to position 2 of an enlised benzanthrone molecule), which was not detected. 2:Bz-1'-*Dibenzanthronyl* (IX), m. p. 331—332°, is obtained in about 50% yield when an equimolecular mixture of II and Bz-1-chlorobenzanthrone (X) is treated with sodium anilide at -5° in a current of nitrogen. Conversion of IX into isodibenzanthrone is effected by treatment with alcoholic potassium hydroxide at 130° and subsequent heating of the aqueous solution in presence of air, or with sodium anilide at 125° in a current of nitrogen. Nitration of benzanthrone in nitrobenzene suspension with 87% nitric acid first at the ordinary temperature and then at 40—50° affords Bz-1-nitrobenzanthrone, m. p. 244—245° (isolated by washing the nitration product with much alcohol), reduced by 15% sodium sulphide solution to Bz-1-aminobenzanthrone, m. p. 239—240°. Diazotisation of this with nitrosylsulphuric acid, subsequent treatment of the diazonium sulphate with hydrofluoboric acid, and

decomposition of the diazonium fluoborate at 150° yields Bz-1-fluorobenzanthrone (XI), m. p. 194—195°. An equimolecular mixture of II and XI is converted by treatment with sodium anilide into IX. 6-Methyl- (XII), m. p. 371—372°, and 6-chloro-2:Bz-1-dibenzanthronyl (XIII), m. p. 375—376, are prepared similarly from X and the corresponding benzanthrone. Alcoholic potassium hydroxide treatment of XII and XIII affords 6-methyl- and 6-chloro-isodibenzanthrone.

When XI is treated with sodium anilide at -5° to 2° in a current of nitrogen and then acidified, 36% of the theoretical amount of Bz-1-fluoro-2:Bz-1'-*dibenzanthronyl*, m. p. 350—352°, is produced, presumably by addition of the halogen in one molecule to the activated 2-position of the second molecule, and subsequent elimination of sodium fluoride. This fluoro-derivative is converted by alcoholic potassium hydroxide at 110—125° into isodibenzanthrone.

H. BURTON.

Saponins, sapogenins, and related substances.

I. Trimethylnaphthalene from gypsogenin. L. RUZICKA and A. G. VAN VEEN (Rec. trav. chim., 1929, 48, 1018—1024).—Crude *Gypsophila* saponin is hydrolysed by dilute aqueous-alcoholic sulphuric acid to gypsogenin (I) (the sapogenin of van der Haar, A., 1927, 341). Thermal decomposition of I at 290° in an atmosphere of carbon dioxide gives no recognisable product, whilst the methyl ester of I (cf. Karrer and others, A., 1924, i, 1091) is decomposed at 400—500°, yielding an ether-like product, b. p. 125—135°/12 mm., d_4^{25} 0.969, n_D^{25} 1.513. Dehydrogenation of this with selenium at 300—320° affords a product, b. p. 125—140°/12 mm., which yields a picrate, m. p. 127—128°, identical with the trimethylnaphthalene picrate obtained from amyris (this vol., 932). The same trimethylnaphthalene fraction is formed by similar dehydrogenation of I at 330—360°; a further small fraction, b. p. 140°/0.3 mm., gives an unidentified picrate, m. p. 138°. Oxidation of the crude trimethylnaphthalene with potassium ferricyanide affords the acid (methyl ester, m. p. 152—153°) previously described (this vol., 932).

Cholatrienecarboxylic acid (Wieland and Weil, A., 1912, i, 830) is dehydrogenated by selenium at 330°, yielding mainly a product, b. p. 210—230°/high vac.; only traces of picrates were isolated from the material of lower b. p.

H. BURTON.

Saponins, sapogenins, and related substances.

II. Relation between sapogenins, higher terpene compounds, and sterols. L. RUZICKA and A. G. VAN VEEN (Z. physiol. Chem., 1929, 184, 69—82; cf. preceding abstract).—The sapogenins, æscigenin, caryocarsapogenin, cyclamiretin, guaiac-sapogenin, glycyrrhetic acid, hederagenin, mimusops-sapogenin, quillaiasapogenin, sarsasapogenin, ursolic acid, sugar-beet sapogenin, and the triterpenes betulin and lupeol were dehydrogenated by means of selenium and the products fractionated. From the middle fractions of all except sarsasapogenin and lupeol a picrate, m. p. 127°, was obtained. The hydrocarbon was regenerated and the styphnate formed; this was identical with the styphnate of trimethylnaphthalene, for which the name sapotalin is proposed. The lower fraction of sarsasapogenin

yielded methylheptenone. Amyrin, lupeol, and betulin, unlike cholesterol, give no precipitate with digitonin.

J. H. BIRKINSHAW.

Interpretation of the colorimetric hydrogenation curve of carotinoids. L. ZECHMEISTER and V. VRABELY (Ber., 1929, 62, [B], 2232—2235; cf. A., 1928, 524, 1252).—The graph connecting the intensity of colour (as percentage of original intensity) with the mols. of hydrogen absorbed during the catalytic treatment in glacial acetic acid of methylbixin (which undoubtedly contains nine double linkings in uninterrupted conjugation) is a straight line which becomes inflected shortly before the point representing the absorption of 8 mols. The curve exactly corresponds with the analogous carotin curve to the point $9H_2$. The result does not contradict the hypothesis that the double linkings of carotin and xanthophyll fall into two groups, but the division is more probably into $9+2$ than into $8+3$, as previously assumed.

Bixin may be determined colorimetrically by comparison with 0.2% potassium dichromate.

H. WREN.

Cyclamin. E. BURES and J. BERGAUER (Časopis Českoslov. Lek., 1928, 8, 208—211; Chem. Zentr., 1929, i, 2655).—Extraction of the tubers of wild *Cyclamen Europæum* with 89% alcohol yields *cyclamin*, m. p. 254° (decomp.) after purification, which reacts with alkali to form a substance of lactonic nature. Cyclamin is strongly hæmolytic. A. A. ELDRIDGE.

Principal constituent of olive gum (resin). Olivil and derivatives. B. L. VANZETTI (Gazzetta, 1929, 59, 373—378).—A republication of work already abstracted (cf. Koerner and Vanzetti, A., 1903, i, 430; 1912, i, 352).

R. K. CALLOW.

Constitution of active principle of *Embellia Ribes*. I. R. KAUL, A. C. RAY, and S. DUTT (J. Indian Chem. Soc., 1929, 6, 577—586).—Extraction of the dry berries of *Embellia Ribes* (*Vidanga* or *Baberang*) with benzene affords an aliphatic oil and *embelin* (I), $C_{18}H_{28}O_4$, m. p. 142° [previously named embelic acid (Warden, A., 1889, 408; Heffter and Feuerstein, A., 1900, i, 498)]. Embelin contains two reactive hydroxyl groups and two keto-groups, since it furnishes the following derivatives: *lead* and *silver* salts; *diacetate*, m. p. 54° ; *dibenzoate* (II), m. p. $97-98^\circ$ [cf. Heffter and Feuerstein, *loc. cit.*; *dioxime*, m. p. 139° ; *disemicarbazone*, m. p. 221° (decomp.)]; *dicarbethoxy-derivative*, m. p. 266° (decomp.); *dimethyl ether*; *dioxime* (III), m. p. 278° ; *tetra-oxime*, m. p. 175° (indicating ketonisation of the hydroxyl groups present); *bisphenylhydrazine*, m. p. $189-190^\circ$ (decomp.); *disemicarbazone*, m. p. 236° (decomp.); *dihydrazine*, m. p. $204-205^\circ$. When I is boiled with aniline *dianilinoembelin* (IV), m. p. $167-168^\circ$ (cf. *loc. cit.*) [*dioxime*, m. p. 162° (decomp.)], obtained also from III and aniline; *disemicarbazone*, m. p. 145° (decomp.)], results. *Di-o-toluidino-*, m. p. $144-145^\circ$; *di(methylamino)-*, m. p. 216° , and *di(ethylamino)-embelin*, m. p. 212° , are also described. These amino-derivatives are hydrolysed by hydrochloric acid to I. Secondary amines and I do not react. *Dianilinodibenzoyl-embelin*, m. p. 176° , is prepared by benzoylation of IV or from aniline and II. Treatment of I with moist zinc dust in boiling acetic anhydride

affords the *tetra-acetyl* derivative, m. p. 124° , of *di-hydroembelin* [previously named dihydroembelic acid (*loc. cit.*)]. Bromination of I in carbon tetrachloride solution gives a *tetrabromo-derivative*, m. p. 132° , whilst oxidation with nitric acid (*d* 1.51) yields *iso-dodecoic acid*. Oxidation with potassium permanganate affords oxalic and *isododecoic acids* and not formic and dodecoic acids as stated by Heffter and Feuerstein (*loc. cit.*).

H. BURTON.

Paleuphorbons from resin of *Euphorbia palustris*. L. J. A. MÜLLER (J. pr. Chem., 1929, [ii], 123, 148—159).—Extraction of the dry, acid-free resin with 96% alcohol and subsequent purification of the solid extracted by crystallisation from acetone affords 10 fractions (designated *paleuphorbon* 1 to 10). These have varying m. p. and analytical compositions. *Paleuphorbon* 1 (composition $C_{38}H_{62}O_4$) sinters at 75° , becomes opaque at 83° , and melts at 96° (all m. p. are corr.) with frothing, $[\alpha]_D^{25} +37.23^\circ$ in benzene, when heated at 140° eliminates water, yielding a brittle lac, m. p. $72-73^\circ$, $[\alpha]_D^{25} +40.83^\circ$ in benzene. Addition of bromine occurs to *paleuphorbon* 1 in chloroform solution, but similar treatment of the lac causes substitution. Acetylation of *paleuphorbon* 10 (composition $C_{35}H_{62}O_2$), which sinters at 105° and melts with frothing at 115° , with acetic anhydride gives a very small amount of a *diacetate*, m. p. 129° . The various fractions are partly precipitated by digitonin in alcohol solution. The non-precipitable parts of the ten fractions fall into two classes, (a) sinter above 70° and m. p. above 80° , (b) m. p. about 70° . The recovered euphorbons from the digitonin complexes (by heating with benzene) afford three groups, (A) sinter at 70° , m. p. 75° , (B) sinter and melt between 76° and 98° , and (C) sinter and melt above 100° .

H. BURTON.

"Cadechol" and "camphochol." H. RHEIN-BOLDT, O. KÖNIG, and E. FLUME (Z. physiol. Chem., 1929, 184, 219—224).—M.-p. curves show that deoxycholic and apocholic acids form 1:1 molecular compounds with camphor. By crystallising or fusing the components together 2:1 compounds are obtained.

J. H. BIRKINSHAW.

Xanthophyll. II. L. ZECHMEISTER and P. TUZSON (Ber., 1929, 62, [B], 2226—2232; cf. this vol., 1252).—Xanthophyll is rapidly and economically obtained from stinging nettles by extraction with aqueous alcohol, followed by a modification of the method of Willstätter and Mieg (A., 1907, i, 865); chlorophyll and carotin are neglected. Catalytic hydrogenation of the product leads to disappearance of the colour after absorption of 8 mols. of the gas, and the intermediate product has the composition of a hexadecahydroxanthophyll. The perhydro-compound is, however, dextrorotatory, whereas the earlier compound (*loc. cit.*) was levorotatory. From the present material the acetone method yields xanthophylls, the perhydro-derivatives of which are less markedly but decidedly dextrorotatory. Perhydro-xanthophyll appears optically stable when heated at 80° for several hrs. and then preserved for a year. Analytically pure specimens of xanthophyll obtained from the same plant material by the acetone and alcohol methods had respectively $[\alpha]_D^{25} +137^\circ$ and

+192° in chloroform, whereas a second set of specimens from material gathered by the authors had $[\alpha]_D$ 162.5° and +139°. The "alcohol" preparations are not altered by exposure to acetone, and the "acetone" products are unchanged by alcohol. Xanthophyll from the green leaf appears to be composed of similar but oppositely active components.

Carotin and xanthophyll appear to absorb 8 mols. of bromine in chloroform solution, the former substance reacting slightly the more slowly. The substances are distinguished qualitatively from one another by the transitory formation in the case of xanthophyll of a temporary, olive-green colour which becomes brown and could not be obtained with carotin.

H. WREN.

Isoprene and caoutchouc. XVI. Constitution of caoutchouc. H. STAUDINGER and H. F. BONDY (Ber., 1929, 62, [B], 2411—2416).—The *cyclo*-products derived from caoutchouc and gutta-percha are unsaturated compounds which absorb bromine and iodine chloride without thereby allowing an exact determination of the number of double linkings in the molecule. On exposure to air they undergo auto-oxidation, absorbing 1 atom of oxygen for 3—8 isoprene residues in about 2 years. The mean mol. wt., viscosity of the solutions, and the temperatures at which the products soften and liquefy do not thereby undergo marked alteration. The products with greater mean mol. wt. liquefy at higher temperatures than those with smaller mol. wt., since the intermolecular forces are greater. The slight changes in the structure of the chains due to auto-oxidation do not appreciably affect the physical properties. It is therefore considered that the determinations of mol. wt. of the *cyclo*caoutchoucs afford true values not obscured by association and that the differences in the viscosities of the solutions depend on differences in mol. wt., and not on degree of association. Since the *cyclo*-products are hemicolloidal in character, the eucolloidal caoutchouc and gutta-percha must have a much higher mol. wt., considerably above 10,000, as previously deduced.

The conclusions of Meyer and Mark (A., 1928, 1252) are adversely criticised.

H. WREN.

Constitution of stannic acid. P. PFEIFFER and O. ANGERN (Z. anorg. Chem., 1929, 183, 189—192).—*Cineole trichlorotrihydroxystannate*, $[\text{SnCl}_3(\text{OH})_3][\text{H}\cdot\text{C}_{10}\text{H}_{18}\text{O}]_2$, has been prepared by treatment with cineole of a solution of the crystalline compound, $\text{SnCl}_3\text{OH}\cdot\text{H}_2\text{O}\cdot\text{Et}_2\text{O}$, obtained from an aqueous solution of stannic chloride by addition of ether. The substance is also produced by warming cineole with stannic chloride pentahydrate until a clear liquid is obtained, and cooling the mixture. The corresponding *tribromo*-compound, $[\text{SnBr}_3(\text{OH})_3][\text{H}\cdot\text{C}_{10}\text{H}_{18}\text{O}]_2$, has been prepared by an analogous method.

H. F. GILLBE.

Piperitone. IX. Oxidation reactions of piperitone. J. READ, A. J. WATTERS, G. J. ROBERTSON, and R. S. HUGHESDON (J.C.S., 1929, 2068—2076).—Hydrogenation of piperitone in the presence of colloidal palladium at 25° gave thymol in yields of 3—25%, accompanied by isomenthone. Vaporised piperitone mixed with hydrogen and passed over

palladised asbestos at 350° gave small quantities of thymol; similar treatment, using a platinised asbestos catalyst, yielded 22% of thymol, whilst with a nickel-pumice catalyst at 355° the product contained 10% of thymol. The hydrogenation of piperitone is a reversible process and the conditions favouring the dehydrogenative phase have been partly elucidated. The mechanism of the dehydrogenation is discussed; the hydrogenation of piperitone is considered to be an essential preliminary to its dehydrogenation and Δ^2 -enol-menthone to be the probable precursor of thymol in the processes investigated.

Piperitone is stable towards alkaline potassium ferricyanide and other mild oxidants, and was practically unaffected when vaporised and passed over nickel oxide at 360° in admixture with air. Similar procedures using 5% platinised asbestos at 340° gave 10% yields of thymol.

Piperitone does not yield stable dihalogenides, but the halogenated ketone undergoes spontaneous evolution (accelerated by heat) of hydrogen bromide with the formation of thymol, bromomenthone, and tarry material. The decomposition of the halogenated product was also accomplished by heating with quinoline, calcium carbonate, etc. The yields of thymol were greatest when bromine was used and least with iodine.

Emulsification of piperitone with bromine water led to a mixture of piperitone dibromide and bromohydrin. *dl*-Piperitone chlorohydrin, m. p. 101—102°, was isolated by long shaking of a solution of piperitone in acetone containing acetic acid with an aqueous solution of chlorocarbamide; it was unaffected by chromic anhydride in acetic acid solution, and sodium amalgam or zinc dust reconverted it into piperitone. Treatment with sodium methoxide led to an impure *methoxyl* derivative, 1.4748, whilst heating with excess of moist silver oxide gave a substance, n_D^{20} 1.4640, possibly 2-hydroxy- Δ^6 -menthen-3-one.

R. J. W. LE FEVRE.

Piperitone. X. Synthesis of certain menthadienes, menthenes, and menthanols. J. READ and A. J. WATTERS (J.C.S., 1929, 2165—2172).—Piperitone reacts readily with the appropriate Grignard reagents to form directly 3-substituted homologues of α -terpinene; intermediate Δ^1 -menthenols cannot be isolated. The following Δ^1 :3-menthadienes are described: 3-*methyl*-, b. p. 184—186°/737 mm., d_4^{25} 0.8585, n_D^{25} 1.4845; 3-*ethyl*-, b. p. 83—85°/15 mm., 199—202°/737 mm., d_4^{25} 0.8631, n_D^{25} 1.4854; 3-*n-propyl*-, b. p. 104—106°/14 mm., d_4^{25} 0.8872, n_D^{25} 1.4865; 3-*phenyl*-, b. p. 145—148°/15 mm., d_4^{25} 0.9552, n_D^{25} 1.5525. The first three hydrocarbons were slightly dextro-rotatory when prepared from *dl*-piperitone owing to interaction between the Grignard reagents and the levorotatory impurity present in the *Eucalyptus* piperitone used.

In contrast to the above results, both *l*-menthone and *d*-isomenthone react with Grignard reagents to give 3-substituted menthan-3-ols; the following are recorded: 3-*methyl*-, b. p. 101—102°/17 mm., $[\alpha]_D^{16}$ —6.47°, d_4^{25} 0.8964, n_D^{25} 1.4605; 3-*ethyl*-, b. p. 112—113°/16 mm., 217—219°/759 mm., $[\alpha]_D^{16}$ +1.54°, d_4^{25} 0.8992, n_D^{25} 1.4650; 3-*n-propyl*-, b. p. 123—125°/16 mm., $[\alpha]_D^{16}$ —0.68°, d_4^{25} 0.8957, n_D^{25} 1.4664; 3-*phenyl*-,

b. p. 170—172°/18 mm., $[\alpha]_D^{25} -22.87^\circ$, $d_4^{25} 0.9872$, 1.5265; 3-methyl-isomenthan-3-ol, b. p. 105—106°/20 mm.; 3-ethyl-, b. p. 105—106°/10 mm., and 3-phenyl-, b. p. 150—152°/9 mm. Each of the foregoing menthanols undergoes dehydration by heating with anhydrous oxalic acid or sodium hydrogen sulphate to the corresponding known substituted menthone. The products from piperitone are individuals, but those from the menthones are probably mixtures of stereoisomerides. None of the ketones reacts with magnesium isopropyl iodide (steric hindrance?).

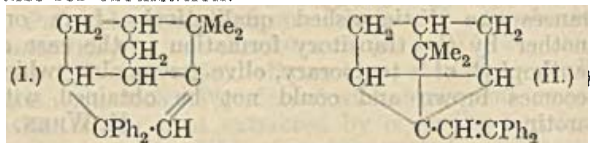
l-Piperitone and *d*-isomenthone gave gummy compounds when treated with specially prepared magnesium bromide under ether; *l*-menthone gave a crystalline compound, $2C_{10}H_{18}O \cdot MgBr_2$. Recovery of the ketones from these by addition of water gave a partly "inverted" *d*-isomenthone and a completely racemised piperitone, suggesting that the complexes should have some such enol formula as $CR^1 \cdot O \cdots (MgBr_2) \cdots O \cdot CR^2$

$\begin{array}{c} H \\ | \\ CR^1 \cdot O \cdots (MgBr_2) \cdots O \cdot CR^2 \\ | \\ H \end{array}$

Piperitone reacts with alcoholic potassium cyanide to yield a stable dicyclic anhydramide, $C_{11}H_{17}ON$, b. p. 151—153°/13 mm., $d_4^{25} 0.9720$, $n_D^{25} 1.4680$. R. J. W. LE FEVRE.

Camphenes acylated in the ω -position. P. LIPP and M. QUAEDEVILIE (Ber., 1929, 62, [B], 2311—2322; cf. A., 1927, 883).— ω -Acetylcamphene, b. p. 112.6—114° (corr.)/14 mm., $d_4^{25} 0.98178$, $[\alpha]_D^{25} -43.66^\circ$, is prepared: (i) yield 10.7% by the action of acetonitrile on the product of the action of magnesium and bromocamphene in ether (intermediate *ketimine hydrochloride*, decomp. 171—173°), (ii) yield 2.3% from camphene, acetyl chloride (preferably bromide), and magnesium bromide in ether, and (iii) yield 5.2% from camphene, acetyl chloride, and tin tetrachloride in ether. The *semicarbazone*, m. p. 199.5—200.5° (corr.; decomp.), and *oxime*, m. p. (indef.) 95—105°, are described. As an $\alpha\beta$ -unsaturated ketone it exhibits halochromism when treated with concentrated mineral acids. It is reduced by hydrogen in presence of spongy platinum to *acetylisocamphane*, b. p. 117°/11 mm. [*semicarbazone*, m. p. 203° (decomp.)]. It is oxidised by permanganate to acetic acid and camphenilone. With magnesium methyl iodide it yields ill-defined products, whereas it is converted by magnesium phenyl bromide through the non-isolable carbinol into the *hydrocarbon*, $C_9H_{14}C:CH \cdot CPh:CH_2$, b. p. 126—127°/0.19 mm., readily auto-oxidised with elimination of the methylene group as formaldehyde. "Grignarded" ω -bromocamphene and *isovaleronitrile* afford ω -*isovalerylcamphene*, b. p. 131—132°/9 mm., $d_4^{25} 0.9437$ [*semicarbazone*, m. p. 186—187° (decomp.)]. The action of benzonitrile on "Grignarded" ω -bromocamphene is remarkable for the stability of the intermediate *ketimine*, b. p. 132—133°/0.4 mm. (*hydrochloride*, decomp. 213.5—214.5°; *chloroplatinate*). ω -Benzoylcamphene has b. p. 137—138.5°/0.7 mm., $d_4^{25} 1.0568$. It is oxidised by permanganate to benzoic acid and camphenilone. Hydrogen bromide in glacial acetic acid is added with quantitative production of ω -benzoylbornyl bromide, m. p. 73°, smoothly transformed into ω -benzoylborneol. The carbonyl group of ω -benzoylcamphene does not react

with the customary ketonic reagents. The action of magnesium methyl iodide gives the hydrocarbon described above from ω -acetylcamphene and magnesium phenyl bromide. With the last-named reagent ω -benzoylcamphene appears to yield mainly the compound (I), b. p. 176—177°/0.5 mm., m. p. 83—84°, which is shown to contain one ethylenic linking. Oxidation of the hydrocarbon with permanganate is complex and yields only benzoic acid; this is true also for ozonisation.



The action of magnesium phenyl bromide on phenylcamphylidenedihydrofuran (*loc. cit.*) gives α -*diphenyl- β -tricyclenylethylene* (II), b. p. 183—186°/0.5 mm., m. p. 70—71°, which absorbs markedly more than 1 mol. of hydrogen and is converted by ozone into benzophenone and tricyclenic acid. The oxygen bridge of furan appears less stable than usually considered towards Grignard reagents. The formulation of the furan derivative is thus confirmed, but it is not completely homogeneous; when oxidised it yields small amounts of camphenilone, due to the presence of ω -benzoylcamphene. H. WREN.

Constitution of Manasse's β -hydroxycamphor and a new method of preparing epicamphor. III. J. BREDT and M. BREDT-SAVELSBERG [with E. BUND] (Ber., 1929, 62, [B], 2214—2216).— β -Hydroxycamphor in aqueous solution is reduced by sodium amalgam to epicamphor, m. p. 182° (*semicarbazone*, m. p. 230°), which yields bromoepicamphor, m. p. 133°, $[\alpha]_D^{25} -68^\circ$ in ethyl alcohol. Manasse's β -hydroxycamphor is therefore 2-hydroxy-3-ketocamphane. H. WREN.

New crystalline compounds from essential oils. H. WIENHAUS and H. SCHOLZ (Ber. Schimmel, 1929, 267—282).—I. **Bulnesol, a compound occurring with guaiol in guaiacum wood oil.** When guaiacum wood oil is triturated with acetone and the filtered solution is cooled in a freezing mixture, an unsaturated, dicyclic, tertiary sesquiterpene alcohol *bulnesol*, $C_{15}H_{26}O$ (I), m. p. 69—70°, b. p. 136—138°/4 mm., $d_4^{25} 0.9389$, $n_D^{25} 1.48915$, isomeric but not identical with guaiol, separates. The potassium derivative is converted by phthalic anhydride in xylene and subsequent acidification into a liquid *hydrogen phthalate* (amorphous silver, m. p. indefinite, 103—109°, and potassium salts, amorphous *phenylurethane*, and α -*naphthylurethane*, oily *chromate*). Bulnesol is not reduced by hydrogen and platinum in methyl alcohol, but in acetic acid solution it is converted into the saturated *dihydrobulnesol*, m. p. 75—76° (liquid *chromate*). Oxidation with aqueous potassium permanganate in benzene solution at 0° converts I into a *ketoglycol*, $C_{15}H_{24}O(OH)_2$, m. p. 173°, but no crystalline acid could be obtained. Oxidation with 45% hydrogen peroxide in acetic acid at 25° yields a liquid *substance*, $C_{15}H_{22}O_3$, the trihydric alcohol similar to that obtained by the oxidation of guaiol not being obtained. When I is heated with 85% formic acid the corresponding unsaturated

hydrocarbon, *bulnesene* (II). $C_{15}H_{24}$, b. p. 113.5—115°/6 mm., d^{20}_D 0.9149, n^{20}_D 1.50467, α_D -14.4° (? in 1 dm. tube), which is probably a mixture of isomerides, is obtained. A similar mixture is obtained by heating I with zinc at 250°. Catalytic reduction of II with platinum-black in acetic acid yields a saturated hydrocarbon, $C_{15}H_{28}$, b. p. 107—109°/5 mm., d^{20}_D 0.8910, n^{20}_D 1.47994, α_D -12.7°.

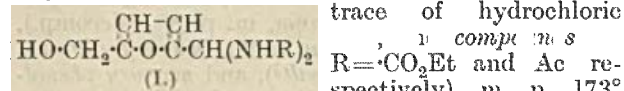
II. *Cryptomeradol*, a sesquiterpene alcohol from Japanese cedarwood oil. By removal of primary and secondary alcohols from this oil (from *Cryptomeria japonica*, Don.) by heating with phthalic anhydride in benzene first at 80° and again at 130° and fractionation of the unesterified portion is obtained an unsaturated, tertiary sesquiterpene alcohol, *cryptomeradol*, $C_{15}H_{26}O$ (III), m. p. 79—80°, b. p. 141—142°/4 mm., d^{20}_D 0.9515, n^{20}_D 1.49317, α_D +24.2° (methyl ether, b. p. 133.5—134.5°/5 mm., d^{20}_D 0.9503, n^{20}_D 1.49601, α_D +34.1°; amorphous hydrogen phthalate, phenylurethane, and α -naphthylurethane; liquid chromate). This is reduced by hydrogen and platinum-black in acetic acid at 20°/751 mm. to the saturated dihydro-derivative, m. p. 81—82° (liquid chromate), the methyl ether being similarly reduced to dihydrocryptomeradyl methyl ether, b. p. 124.5—125.5°/5 mm., d^{20}_D 0.9365, n^{20}_D 1.48626, α_D +11.3°. Oxidation of III with potassium permanganate at 0° yields a substance, m. p. 107—108°, probably the trihydric alcohol $C_{15}H_{25}(OH)_3$, but no crystalline acid could be isolated.

III. *Germacrol*, a crystalline compound from Bulgarian geranium oil. The solid fraction of Bulgarian geranium oil (described erroneously as tricosane, $C_{23}H_{48}$, by Rovesti; Notiz. chim.-ind., 1927, 2, 438) has the composition $C_{16}H_{24}O$ and is given the name *germacrol* (IV), m. p. 54—55°, d^{20}_D 0.9549, n^{20}_D 1.51610, optically inactive. By reduction with platinum-black and hydrogen in acetic acid, 6 atoms of hydrogen are absorbed and fractionation of the product yields two fractions, b. p. 120—123°/3.5 mm., d^{20}_D 0.9156, n^{20}_D 1.47662, and b. p. 123—126°/3.5 mm., d^{20}_D 0.9188, n^{20}_D 1.47838, both having the composition $C_{16}H_{20}O$. Germacrol probably contains only two double linkings and an oxide ring which is converted into a tertiary alcohol group in the hexahydro-compound. In agreement with this, IV yields no colour with chromic oxide in carbon tetrachloride, whilst the hexahydro-derivative becomes reddish-yellow, and with sodium in anhydrous ether gives a substance resembling an alkoxide. J. W. BAKER.

l-Difenchyl ether and *l*-difenchene. O. ZEITSCHIEL (Ber. Schimmel, 1929, 317—324).—*l*-Fenchyl alcohol is converted by 10% of sulphuric acid at 100° into *l*-difenchyl ether, b. p. 151—152°/4 mm., d^{20}_D 0.946, n^{20}_D 1.48439, $[\alpha]_D$ -74.00°, which is unattacked by heating with sodium, but is oxidised by hot nitric acid (d 1.355) to fenchone. The ether is not obtained by heating fenchyl alcohol in benzene solution with fused zinc chloride, the product of this reaction being *l*-difenchene, b. p. 158°/4 mm., 321—325°/751 mm., d^{20}_D 0.9488, n^{20}_D 1.50762, $[\alpha]_D$ -5.15°. J. W. BAKER.

Furan compounds derived from sugars. IV. Compounds from hydroxymethylfurfuraldehyde and acid amides and glycine anhydride. J.

KARASHIMA (Z. physiol. Chem., 1929, 184, 268—271).— ω -Hydroxymethylfurfuraldehyde and carbamide react in aqueous solution at 100° in an atmosphere of carbon dioxide, forming a small amount of a compound, $C_8H_{12}O_4N_4$, m. p. 164°. With ethyl carbamate and acetamide in presence of



trace of hydrochloric acid, $R = \text{CO}_2\text{Et}$ and Ac respectively, m. p. 173° and 206°, respectively, result in yields of 31.8% and 18.7%; benzamide yields the substance $C_{20}H_{18}O_4N_2$, m. p. 180°.

ω -Acetoxymethylfurfuraldehyde condenses with glycine anhydride in presence of acetic anhydride and sodium acetate at 120—130°, affording 2:5-diketo-3:6-di- ω -acetoxymethylfurfurylidene-piperazine, m. p. 220° (decomp.). H. BURTON.

Preparation and properties of new furan compounds. H. WIENHAUS and H. LEONHARDI (Ber. Schimmel, 1929, 223—232).— β -2-Furylacraldehyde (König and Hey, A., 1926, 175) is reduced with hydrogen at 80°/20 atm. in alcoholic solution with a nickel catalyst to 2-furfurylacetaldehyde, b. p. 59—61°/4 mm., d^{20}_D 1.074, n^{20}_D 1.47818 (semicarbazone, m. p. 82—83°; dimethylacetal, b. p. 77°/4 mm., d^{20}_D 1.026, n^{20}_D 1.45502), together with a fraction, b. p. 61—76°/4 mm., which is probably the corresponding alcohol. Similar reduction of α -2-furyl- $\Delta^{\alpha\gamma}$ -hexadien- ϵ -one (Rohmer, A., 1898, i, 300) at 100° gives γ -furfuryl-butyl methyl ketone, b. p. 93—95°/2 mm., d^{20}_D 0.995, n^{20}_D 1.47023 (semicarbazone, m. p. 121—122°). Furfuraldehyde condenses with methyl isobutyl ketone in the presence of 2% alcoholic potassium hydroxide to give β -2-furyl- α -isopropylvinyl methyl ketone (or ? β -2-furylvinyl isobutyl ketone), b. p. 115—116°/3 mm., d^{20}_D 1.011, n^{20}_D 1.55282 (semicarbazone, m. p. 175—176°). Reduction of furfurylidene mesityl oxide at 140—150°/24 atm. yields β -2-tetrahydrofuryl ethyl isobutyl ketone, b. p. 103—106°/3 mm., d^{20}_D 0.939, n^{20}_D 1.44982. Furfuraldehyde condenses with butyl acetate in the presence of sodium to give, in poor yield, butyl β -2-furylacrylate, b. p. 117—118°/3 mm., d^{20}_D 1.045, n^{20}_D 1.53361. The corresponding isomyl ester, b. p. 136—139°/5 mm., d^{20}_D 1.025, n^{20}_D 1.52438, is similarly prepared. J. W. BAKER.

Hoesch syntheses of phenolic ketones. III. Condensation of phenylcyanopyruvic esters with polyhydric phenols. W. BORSCHÉ and J. NIEMANN (Ber., 1929, 62, [B], 2043—2045).—Ethyl phenylcyanopyruvate reacts with resorcinol in glacial acetic acid in presence of zinc chloride and hydrogen chloride, yielding ethyl 7-hydroxy-3-phenylcoumarin-4-carboxylate (+H₂O), m. p. 190—191°, hydrolysed to 7-hydroxy-3-phenylcoumarin-4-carboxylic acid (+H₂O), m. p. 300—301°. Ethyl 7-methoxy-3-phenylcoumarin-4-carboxylate, m. p. 123—124° (from the hydroxy-ester and diazomethane) yields successively 7-methoxy-3-phenylcoumarin-4-carboxylic acid, m. p. 288°, and 7-methoxy-3-phenylcoumarin, m. p. 124°. Under similar conditions, orcinol and ethyl phenylcyanopyruvate afford ethyl 7(?)-hydroxy-3-phenyl-5(?)-methylcoumarin-4-carboxylate, m. p. 231°, whereas phloroglucinol yields ethyl 5:7-dihydroxy-3-phenyl-

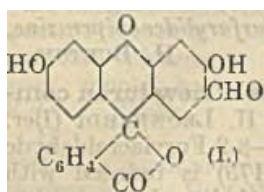
coumarin-4-carboxylate, decomp. 298°. Ethyl acetoacetate and resorcinol give 7-hydroxy-4-methylcoumarin.

H. WREN.

Phthalein-metal compounds. E. BURES, J. BERGAUER, and A. KRACIK (Casopis Českoslov. Lek., 1928, 8, 180—183; Chem. Zentr., 1929, i, 2532).—*Mercury fluorescein* [potassium, m. p. 85° (decomp.), sodium, lithium, and barium salts], *mercury dibromofluorescein* (corresponding salts), and *mercury phenolphthalein* (corresponding salts) are described.

A. A. ELDRIDGE.

Aldehydofluorescein and dyes derived from it. R. N. SEN and K. N. BANERJEE (J. Indian Chem. Soc., 1929, 6, 505—516).—The Reimer-Tiemann reaction with fluorescein (oxime, not melted at 260°)



affords *aldehydofluorescein* (I), not melted at 260° (45% yield; *phenylhydrazone*, *semicarbazone*, and *dioxime*, all m. p. above 260°), which dyes wool and silk with a deep orange shade. Alkaline solutions of I are red with a

subdued green fluorescence. Condensation of I with aminoazobenzene, *p*-toluidine, *p*-nitroaniline, benzidine, *o*-, *m*-, and *p*-phenylenediamines, and rosaniline affords the corresponding *azomethines*, all of which have m. p. above 260°. These dye wool and silk with shades varying from yellow to brown. Condensation of I with dimethylaniline gives *pp'*-*tetramethyldiaminodiphenylfluoresceinylmethane*, m. p. 70—72°, oxidised by lead peroxide to a blue dye. The corresponding *diphenylfluoresceinylmethane* derivative, not melted at 260°, from *o*-cresotic acid and I is oxidised by nitrosyl sulphate at 50—60° to a red dye. This gives a deep brown shade to wool and silk. The pyronine *dyes* from *m*-dimethylaminophenol and resorcinol and I give wool and silk bluish-violet and orange-red shades, respectively. Fluorescein and *m*-dimethylaminophenol afford a *dye*, softens at 245° (dyes bluish-pink), whilst the *pentabromo*-derivative of the pyronine from resorcinol and I dyes with a deep red shade.

H. BURTON.

Condensation of esters with resorcinol, dimethylaniline, and *m*-diethylaminophenol. R. N. SEN and A. MUKHERJI (J. Indian Chem. Soc., 1929, 6, 557—563).—When ethyl benzoate (1 mol.) is heated with resorcinol (2 mols.) and zinc chloride at 180° in a current of hydrogen chloride (cf. A., 1925, i, 554) an improved yield of resorcinolbenzein (Sen and Sinha, A., 1924, i, 288) (*potassium salt*; *bromo*-derivative, decomp. 200°) is obtained. The following are prepared similarly, using the appropriate ester: *resorcinol-o-nitrobenzein*, not melted at 290°; *-o-amino*-benzein; *-p-aminobenzein*, decomp. 290° (*dibromo*-derivative); *-naphthalein*, not melted at 290° (*tetra*-*bromo*-derivative, decomp. 260°); *-stearcin* (I), and *-ole-ein* (II), softens at 140° (*hexabromo*-derivative, C₃₀H₃₆O₃Br₆). These compounds dye wool and silk with shades varying from yellow to red (*bromo*-derivatives), and alkaline solutions are deep red, showing usually a green fluorescence when diluted. The difference in solubility of I and II in benzene is utilised in their separation from the reaction mixture

obtained from olive oil and resorcinol. Dyes similar to the above are formed analogously from resorcinol and castor and coconut oils. When ethyl benzoate (1 mol.) and resorcinol (1 mol.) are heated at 140° in presence of zinc chloride, 2:4-dihydroxybenzophenone results; pyrogallol yields similarly 2:4:6-trihydroxybenzophenone. The former ketone reacts with 1 mol. of resorcinol at 180°, giving resorcinolbenzein.

Dimethylaniline condenses with ethyl benzoate and salicylate in presence of phosphoryl and zinc chlorides, yielding malachite-green and *o-hydroxymalachite-green* (bluish-green; the colours given in parentheses are the shades on wool, silk, and tanned cotton), respectively. *m*-Diethylaminophenol and ethyl benzoate, anthranilate, and stearate in presence of zinc chloride condense to *benzorhodamine*, softens at 210° (bluish-red), *anthranilorhodamine*, and *stearorhodamine* (pink), respectively.

H. BURTON.

Behaviour of anthocyanins at varying hydrogen-ion concentrations. B. H. BUXTON and F. V. DARBISHIRE (J. Genetics, 1929, 21, 71—80).—Anthocyanins are differentiated as of the blue or red group according to the reaction of coloured flowers in media of varying hydrogen-ion concentrations. The effect of yellow flavones on the colours is considered.

CHEMICAL ABSTRACTS.

Cyclic sulphides. IV. J. VON BRAUN and K. WEISSBACH (Ber., 1929, 62, [B], 2416—2425; cf. A., 1925, i, 1445).—Addition of a solution of benzylthiolacetyl chloride in chloroform to aluminium chloride covered with carbon disulphide affords benzyl chloride and 4-ketoisothiochroman, C₆H₄<CH₂:S<CO-CH₂

m. p. 64° (cf. Lesser and Mehrländer, A., 1923, i, 827); the *semicarbazone*, m. p. 236°, and condensation product with isatin, C₁₇H₁₁O₂NS, m. p. 255—260° (decomp.) after darkening at 220°, are described. Reduction of the ketone by Clemmensen's method

leads to 1-methylthiophthalan, C₆H₄<CH₂:S<CHMe> p. 115—116°/16 mm. (*methiodide*, m. p. 137°; *mercurichloride* compound, m. p. 121°), which is prepared synthetically from α -methyl-*o*-xylylene bromide and potassium monosulphide. With potassium disulphide, the bromide yields the substance

b. p. 145—150°/13 mm., m. p. 40°.

Phenyl α -methylbenzyl sulphide, b. p. 167—170°/15 mm., is prepared by the action of amalgamated zinc and hydrochloric acid on phenacyl phenyl sulphide or on a mixture of acetophenone and thiophenol; the corresponding sulphone has m. p. 114°. The isomeric *phenyl β -phenylethyl sulphide*, b. p. 188°/16 mm. (sulphone, m. p. 58°), is derived from β -phenylethyl bromide and the sodium compound of thiophenol.

4-Ketoisothiochroman is reduced by sodium amalgam to 4-hydroxyisothiochroman, b. p. 138—140°/0.1 mm., converted by phosphorus trichloride into 4-chloroisothiochroman, b. p. 117°/0.4 mm. Either chloro- or hydroxy-compound is transformed by zinc and hydrochloric acid into isothiochroman in poor yield. If the hydroxy-compound is heated above 200° or, preferably, distilled with potassium hydrogen sulphate

in a vacuum, isothiochromen, $C_6H_4 \begin{smallmatrix} CH_2 \cdot S \\ \diagdown \quad \diagup \\ CH=CH \end{smallmatrix}$, b. p. 124°/13 mm., is obtained; it is distinguished from isothiochroman by the readiness with which it becomes polymerised.

Reduction of ketoisothiochromanoxime with sodium and alcohol causes rupture of the heterocyclic ring with formation of α -o-tolylethylamine, b. p. 89–91°/14 mm. (hydrochloride, m. p. 173°; picrate, m. p. 206°; quaternary methiodide, m. p. 176°, degraded to o-methylstyrene), and a base $SH \cdot CH_2 \cdot C_6H_4 \cdot CHMe \cdot NH_2$, or $C_6H_4Me \cdot CH(NH_2) \cdot CH_2 \cdot SH$, b. p. 144–146° (picrate, m. p. 168°; unstable hydrochloride). If, however, the oxime is reduced by sodium amalgam, the product is 4-aminoisothiochroman, b. p. 153–155°/14 mm. (hydrochloride, m. p. 229°; picrate, m. p. 219°). When cautiously treated with methyl iodide, the amine gives the quaternary iodide, $C_{12}H_{18}NSI$, m. p. 162°, converted by treatment with silver oxide and distillation into isothiochromen and 4-dimethylaminoisothiochroman, b. p. 154–155°/13 mm. (very hygroscopic hydrochloride; picrate, m. p. 113°).

β -Phenylethylthiolacetic acid, m. p. 61°, b. p. 185°/4 mm., prepared from chloroacetic acid, sodium hydroxide, and β -phenylethyl mercaptan, is converted into the corresponding chloride, b. p. 175–176°/15 mm., which is transformed by aluminium chloride into β -phenylethyl chloride and 1-keto-6:7-benzohexamethylene sulphide, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH_2 \\ \diagdown \quad \diagup \\ CO-CH_2-S \end{smallmatrix}$, b. p. 181–183°/15 mm. (oxime, m. p. 151–152°; semicarbazone, m. p. 244°). Similarly, γ -phenylpropylthiolacetic acid, b. p. 187–188°/0.6 mm., yields the corresponding chloride, b. p. 193–195°/13 mm., converted by aluminium chloride into γ -phenylpropyl chloride and ketobenzheptamethylene sulphide, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH_2 \cdot CH_2 \\ \diagdown \quad \diagup \\ CO-CH_2-S \end{smallmatrix}$, b. p. 160°/0.4 mm.

Phenacyl bromide is transformed by dimethylamine in benzene into phenacyldimethylamine, b. p. 126–128°/18 mm. (picrate, m. p. 150°). The base is converted by zinc in hydrochloric acid solution into dimethylamine, ethylbenzene, and (?) α -chloroethylbenzene. H. WREN.

Sulphur-containing hydroxyquinones [thionaphthens]. I. G. FARRENIND. A.-G.—See B., 1929, 807.

Condensation products and vat dyes of the benzanthrone series. I. G. FARRENIND. A.-G.—See B., 1929, 808.

Preparation of 2-phenylpyrroline. P. LIPP and H. SEELES (Ber., 1929, 62, [B], 2456–2458).— γ -Chlorobutyronitrile is converted by magnesium phenyl bromide in ether into 2-phenylpyrroline, m. p. 45°, b. p. 118°/11 mm. (hydrochloride, m. p. 206–207°), converted by phthalic anhydride into γ -phthalimidopropiophenone. H. WREN.

Existence of the *p*-indole ring. H. SOBOTKA (Ber., 1929, 62, [B], 2191–2194; cf. von Braun, A., 1912, i, 497; Ferber, this vol., 308).—Unsuccessful attempts to obtain the hypothetical *p*-dihydroindole are described. Treatment of β -phenylethyl bromide with nitric acid (*d* 1.52) at –70° affords β -*p*-nitro-

phenylethyl bromide, m. p. 68°; the by-products contain β -*m*-nitrophenylethyl bromide in considerable amount. β -*p*-Nitrophenylethyl chloride, m. p. 48°, is similarly prepared in satisfactory yield. Reduction of the nitro-compounds in alcoholic solution in presence of platinum oxide leads smoothly to *p*- β -bromoethylaniline hydrobromide, m. p. 219° (decomp.) [corresponding hydrochloride, m. p. 214–216° (decomp.)], and *p*- β -chloroethylaniline hydrochloride, m. p. 210–211° (decomp.). *p*- β -Bromoethylbenzanilide has m. p. 137°. *p*- β -Bromoethylaniline, when heated in ether at a temperature not exceeding 65°, appears to yield the base, $CH_2Br \cdot CH_2 \cdot C_6H_4 \cdot NH \cdot [CH_2]_2 \cdot C_6H_4 \cdot NH_2$, and products of high mol. wt. H. WREN.

4-Phenyldihydro-2-picolone. W. GORDEN (J. pr. Chem., 1929, [ii], 123, 169–188).—The main product of the hydrolysis of ethyl 4-phenyldihydro-2-picolone-3:5-dicarboxylate (ethyl 6-keto-4-phenyl-2-methyltetrahydropyridine-3:5-dicarboxylate) (I) (Knoevenagel and Brunswig, A., 1902, i, 640) with boiling 8% sodium hydroxide is ethyl 6-keto-4-phenyl-2-methyltetrahydropyridine-3-carboxylate (II), m. p. 156° (also obtained by heating I with sodium acetate and acetic anhydride). Contrary to Knoevenagel and Brunswig (*loc. cit.*), only a very small yield (29%) of the corresponding free acid (III), $+H_2O$ and anhydrous, m. p. 199–202° (decomp.), could be obtained. In agreement with the resistance of II to hydrolysis, the free acid could not be esterified. Attempted hydrolysis of II converts it into γ -aceto- β -phenylbutyric acid. Great difficulty was found in decarboxylating III by heating at 190°. From the product, having an indefinite m. p. 130–270°, only a small quantity of a substance, m. p. indefinite 265° (decomp.), could be isolated. This is erroneously described by Knoevenagel and Brunswig as 4-phenyldihydro-2-picolone, but a mol. wt. determination shows that it consists of a double molecule formed by union of two dihydropyridine nuclei during decarboxylation. By dry distillation of III, however, 4-phenyldihydro-2-picolone, m. p. 141°, is actually obtained and is identical with the specimen obtained by the method of Vorlander and Knoetzsch (A., 1897, i, 285) and described by them as the amide anhydride of γ -acetyl- β -phenylbutyric acid (lit. m. p. 137°). This product has the correct (mono) mol. wt., and the specimens obtained by either method are converted by distillation with zinc in a current of hydrogen into 4-phenyl-2-methylpyridine [Bülow and Issler, A., 1903, i, 718; picrate, m. p. 210–213° (decomp.) (lit. 203°); perchlorate, m. p. 142–143°; chloroplatinate, m. p. 211–213° (decomp.); chloroaurate, m. p. 161–163°]. J. W. BAKER.

Stereoisomerism in substituted 1:2:3:4-tetrahydroquinolines. I. S. G. P. PLANT and R. J. ROSSER (J.C.S., 1929, 1861–1870).—2:3-Dimethylquinoline, prepared by a modification of Pfizinger's method (A., 1898, i, 207), yields on reduction the *cis*- and *trans*-forms of 2:3-dimethyl-1:2:3:4-tetrahydroquinoline, (A), m. p. 38–39° (benzoyl derivative, m. p. 92°; hydrochloride, m. p. 240–243°; picrate, m. p. 178°), and (B), liquid (benzoyl derivative, m. p. 96–97°; hydrochloride, m. p. 169–170°). The 2:3-dimethyl-1:2:3:4-tetrahydro-

quinoline described by Ferratini (cf. A., 1893, i, 602) is a mixture of the two forms, whilst the compound described by von Braun, Gmelin, and Schultheiss (A., 1923, i, 836) is the *B* modification, although somewhat impure. A method of separating the products is described and the relative amounts of the two forms present in the reduction product have been determined in four cases, using different reducing agents.

Reduction of 2 : 3-dimethyl-4-keto-1 : 4-dihydroquinoline, m. p. 319—320° (hydrochloride, m. p. 248—249°), with sodium amalgam yields first 2 : 3-dimethylquinoline, and with excess of the reducing agent the two tetrahydro-compounds. The reduction of tetrahydro-acridone (cf. A., 1925, i, 63) probably proceeds by similar stages.

2 : 3-Diphenylquinoline (cf. Pfitzinger, *loc. cit.*) with certain reducing agents also yields a mixture of stereoisomerides, 2 : 3-diphenyl-1 : 2 : 3 : 4-tetrahydroquinoline (*A*), m. p. 130—131°, insoluble in aqueous hydrochloric acid, but yielding with dry hydrogen chloride in ether a hydrochloride, m. p. 198—199°; (nitrosoamine, m. p. 150°; acetyl derivative, m. p. 145°), and (*B*), m. p. 92° (hydrochloride, m. p. 239—242°; nitrosoamine, m. p. 138°). The effect of various reducing agents on the relative proportions of the two stereoisomerides formed has also been studied in this case.

It is not known in either case which of the stereoisomerides has the *cis*- and which the *trans*-configuration (cf. A., 1928, 527). The bearing of the results on previous work on stereoisomerism in polycyclic structures is discussed.

R. CHILD.

Derivatives of tetrahydrocarbazole. VIII. Formation and reactions of nitric acid addition products. S. G. P. PLANT and K. H. RUTHERFORD (J.C.S., 1929, 1970—1975; cf. A., 1926, 1151; 1928, 1259).—The 9-*o*-, -*m*-, and -*p*-toluoyl- and -chlorobenzoyl-tetrahydrocarbazoles all give with nitric acid in glacial acetic acid solution 5-nitro-substitution products; the 9-*p*-toluoyl and 9-*p*-chlorobenzoyl compounds give also, like 9-benzoyltetrahydrocarbazole (J.C.S., 1923, 123, 676), products formed by addition of OH and NO₂ at the double linking.

9-*o*-Toluoyltetrahydrocarbazole, b. p. 260—270°/22 mm. (from tetrahydrocarbazole by successive treatment with magnesium ethyl bromide and *o*-toluoyl chloride), on nitration yields the 5-nitro-compound, m. p. 154°; 9-*m*-toluoyltetrahydrocarbazole, b. p. 260—290°/12 mm., gives the 5-nitro-derivative, m. p. 148°, and the 9-*p*-toluoyl compound, b. p. 250—280°/12 mm., m. p. 126°, gives a 5-nitro-derivative, m. p. 136°, and the additive product, 11-nitro-9-*p*-toluoyl-10-hydroxyhexahydrocarbazole, m. p. 149° (decomp.). 9-*o*-Chlorobenzoyl-, b. p. 260—270°/20 mm., m. p. 117° (5-nitro-derivative, m. p. 195°), 9-*m*-chlorobenzoyl-, b. p. 250—280°/15 mm., m. p. 93° (5-nitro-derivative, m. p. 155°), and 9-*p*-chlorobenzoyl-, b. p. about 285°/18 mm., m. p. 106° (5-nitro-compound, m. p. 148°, and 11-nitro-9-*p*-chlorobenzoyl-10-hydroxyhexahydrocarbazole, m. p. 153°), derivatives of tetrahydrocarbazole are described. All of the 5-nitro-substitution products mentioned give on hydrolysis the corresponding acid and 5-nitrotetrahydrocarb-

azole. Benzoylation of 6-nitrotetrahydrocarbazole (J.C.S., 1921, 119, 1825) leads to the 9-benzoyl derivative, m. p. 180°, and of 7-nitrotetrahydrocarbazole (from cyclohexanone-*m*-nitrophenylhydrazones) to the 9-benzoyl compound, m. p. 138°. Nitric acid has no effect on 5-, 6-, or 7-nitro-9-benzoyltetrahydrocarbazoles, nor on 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole. The last-named compound is converted by boiling alcohol into 9-benzoyl-10 : 11-dihydroxyhexahydrocarbazole, m. p. 142°, which with boiling aqueous-alcoholic potassium hydroxide gives 11-hydroxytetrahydrocarbazolenine, m. p. 79° (cf. *loc. cit.*). The mechanism of the conversion of 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole into 8-*o*-benzamidobenzoylvaleric acid by means of alkalis is discussed.

9-Cinnamoyltetrahydrocarbazole, m. p. 117°, gives on nitration a mixture of the 5-nitro-compound, m. p. 177°, and 9-cinnamoyl-10 : 11-dihydroxyhexahydrocarbazole, m. p. 204°.

R. CHILD.

Stereoisomerism in polycyclic systems. VI. B. K. BLOUNT, W. H. PERKIN, jun., and S. G. P. PLANT (J.C.S., 1929, 1975—1987).—A mixture of ethyl cyclopentanone-2-carboxylate and aniline, when kept for a fortnight in a vacuum over calcium chloride, gave ethyl 1-anilino-Δ^{1:2}-cyclopentene-2-carboxylate, which at 260° readily passed into 12-keto-2 : 3 : 5 : 12-tetrahydro-β-quinindene, m. p. 327° (after previous blackening); this compound by reduction with sodium amalgam followed by benzoylation of the crude bases gave a mixture of two stereoisomeric 5-benzoyl-2 : 3 : 4 : 5 : 12 : 13-hexahydro-β-quinindenes, *A*, m. p. 173°, and *B*, m. p. 158—159°.

When boiled together ethyl cyclopentanone-2-carboxylate and aniline yielded cyclopentanone-2-carboxyanilide, m. p. 104°, which with hot sulphuric acid formed 5-keto-2 : 3 : 5 : 6-tetrahydro-α-quinindene, m. p. 256°. Reduction as above led to the 5-keto-2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindenes, *A*, m. p. 210—211°, and *B*, m. p. 135-5°, whilst similar treatment but with sodium and boiling alcohol in addition gave, after benzoylation, only one of the two possible modifications of 6-benzoyl-2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene, m. p. 94-5—95°, from which, by hydrolysis with alcoholic potassium hydroxide, 2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene, m. p. 42-5° (6-phenylcarbamyl derivative, m. p. 99°), was obtained.

Ethyl cyclohexanone-2-carboxylate and aniline, under the conditions employed for the cyclopentanone analogue, formed ethyl 1-anilino-Δ^{1:2}-cyclohexene-2-carboxylate, m. p. 58-5°, converted by heating into tetrahydroacridone; when boiled together, however, cyclohexanone-2-carboxyanilide, m. p. 105—105-5°, was produced. By the action of hot sulphuric acid on the last compound 9-keto-5 : 6 : 7 : 8 : 9 : 10-hexahydrophenanthridine, m. p. 267—268°, was obtained.

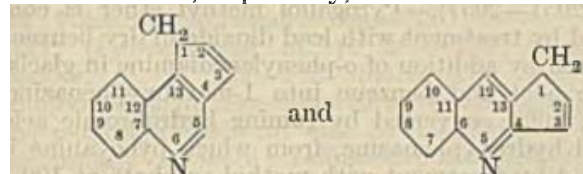
An alcoholic solution of aniline and 2-hydroxymethylenecyclopentanone precipitated slowly 2-phenyliminomethylcyclopentanone, from which hot sulphuric acid etc. produced ammonium 2-phenyliminomethylcyclopentanone-4'-sulphonate and thus the free acid.

A mixture of anthranilic acid and α-hydrindone heated to 210° afforded 14-keto-7 : 14-dihydrobenzo-

β -quinindene, m. p. above 360° ; cyclopentanone and aniline condensed to form small yields of a substance, $C_{17}H_{19}O_2N$, m. p. 272° .

The colour reactions of most of the above and other compounds in 65% sulphuric acid at 0° with one drop of concentrated aqueous potassium dichromate have been determined; those giving a crimson colour contain the *N*-acyltetrahydroquinoline structure, whilst those giving a blue colour contain the *N*-acyldihydroindole structure. Strychnine falls in the latter group and should therefore contain an *N*-acyldihydroindole skeleton, e.g., as in the latest formula of Fawcett, Perkin, and Robinson.

The nomenclature of the parent substances has been modified slightly in this paper: α - and β -quinindenes are now, respectively,



R. J. W. LE FEVRE.

2-Ethylpyrrole. (FRL.) M. E. A. DE JONG (Rec. trav. chim., 1929, 48, 1029—1030).—The various methods of preparation quoted in the literature are examined. Thermal decomposition of *N*-ethylpyrrole at 650° and careful fractionation of the product formed appears to be a suitable method of preparation.

H. BURTON.

Formation of aminopyridine by the action of ammonia on pyridine in presence of catalysts. J. P. WIBAUT and L. M. F. VAN DE LANDE (Rec. trav. chim., 1929, 48, 1005—1009).—Small amounts of 2-aminopyridine are formed when a mixture of pyridine vapour and ammonia is passed over iron- and nickel-asbestos catalysts at 300 – 500° . In absence of catalyst at 550° or with baked clay at 600° traces of 2:2'-dipyridyl result. The reaction is endothermic: $C_5H_5N + NH_3 \rightarrow NH_2 \cdot C_5H_4N + H_2$ —4.4 kg.-cal. The heat of reaction between benzene and ammonia is calculated to be —8.0 kg.-cal. (cf. Briner, Ferrero, and Luserna, A., 1924, i, 503).

H. BURTON.

Action of benzoyl peroxide on pyridine. J. OVERHOFF and G. TILMAN (Rec. trav. chim., 1929, 48, 993—996).—Interaction between pyridine and benzoyl peroxide at 100° occurs mainly, $(CO_2Ph)_2 + C_5H_5N \rightarrow Ph \cdot CO_2H + CO_2 + Ph \cdot C_5H_4N$ (cf. Gelissen and Hermans, A., 1925, i, 379); 46% of a mixture of 2- and 4-phenylpyridines is isolated. Small amounts of benzene, 4-pyridyldiphenyl, m. p. 175° , and *p*-phenylbenzoic acid are also isolated.

H. BURTON.

Derivatives of quinoline [atophan]. R. WOLF-FENSTEIN.—See B., 1929, 835.

Pyrimidines. CVIII. Synthesis of nitrogen-substituted uracils of known constitution. T. B. JOHNSON (Rec. trav. chim., 1929, 48, 872—874).—Preliminary details of a method of synthesising 3(*N*)-alkyluracils are given. Treatment of benzylidenemethylamine with malonic acid in warm alcohol affords about equal amounts of cinnamic acid and

α -methylamino- β -phenylpropionic acid, m. p. 168 – 169° . The last-named acid is converted by potassium cyanate into the corresponding carbamide, which when treated with hydrochloric acid yields 4-phenyl-3-methyl-4:5-dihydrouracil, m. p. 158 – 159.5° . Bromination of this affords the 5-bromo-derivative, which when treated with pyridine or dilute alkali loses hydrogen bromide, forming 4-phenyl-3-methyluracil.

H. BURTON.

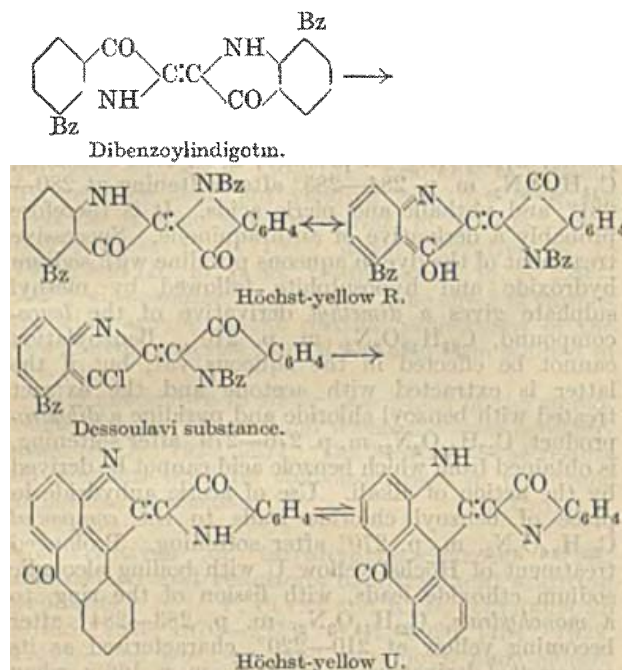
Indigotin group. VIII. Complex reaction products from indigotin and benzoyl chloride.

T. POSNER, W. ZIMMERMANN, and S. KAUTZ (Ber., 1929, 62, [B], 2150—2166; cf. A., 1926, 1155, 1156).—Hochst-yellow U, $C_{30}H_{18}O_3N_2$, m. p. 284° , is prepared from Hochst-yellow R or Dessoulay's compound (cf. Diss., Neufchatel, 1909) by prolonged action of warm, concentrated sulphuric acid. It is oxidised by boiling nitric acid (*d* 1.4) through a compound, $C_{18}H_9O_4N_3$, m. p. above 360° , to a substance, $C_{14}H_6O_6N_2$, m. p. 284 – 285° after softening at 280 – 281° , and phthalic and picric acids. It is therefore probably a derivative of anthraquinone. Successive treatment of the dye in aqueous pyridine with sodium hydroxide and hyposulphite followed by methyl sulphate gives a dimethyl derivative of the leuco-compound, $C_{25}H_{18}O_3N_2$, m. p. 210° . Benzoylation cannot be effected in the aqueous vat, but if the latter is extracted with acetone and the extract treated with benzoyl chloride and pyridine a dihydro-product, $C_{23}H_{14}O_3N_2$, m. p. 276 – 279° after softening, is obtained from which benzoic acid cannot be derived by the action of alkali. Use of acetic anhydride in place of benzoyl chloride leads to the compound $C_{25}H_{16}O_3N_2$, m. p. 270° after softening. Prolonged treatment of Hochst-yellow U with boiling alcoholic sodium ethoxide leads, with fission of the ring, to a monohydrate, $C_{23}H_{14}O_3N_2$, m. p. 283 – 284° after becoming yellow at 210 – 220° , characterised as its monomethyl derivative, $C_{24}H_{16}O_3N_2$, m. p. 166° ; when heated, the hydrate regenerates the dye.

Hochst-yellow R, $C_{30}H_{18}O_3N_2$, m. p. 350° , is oxidised by boiling concentrated nitric acid to picric and benzoic acids; the formation of phthalic acid was not observed. Treatment of the leuco-product with benzoyl chloride gives a monobenzoyl compound, $C_{37}H_{24}O_5N_2$, m. p. 223° . Treatment with alcoholic sodium ethoxide affords a yellow acid, $C_{14}H_{11}O_3N$, m. p. 178° , of unknown constitution and benzoic acid; in another experiment, azobenzene, the above acid, benzoic acid, and a colourless, unrecognised acid, m. p. 225 – 227° (ammonium salt), were obtained. Treatment of indigotin with boiling benzoyl chloride in presence of zinc chloride affords Hochst-yellow R, whereas a mixture of R and U is obtained if benzoyl chloride is replaced by benzoic anhydride at 150 – 160° .

Treatment of indigotin with benzoyl chloride and copper powder in xylene yields a small amount of Hochst-yellow R and a "xylene substance," $C_{37}H_{22}O_5N_2$, m. p. 243 – 244° , hydrolysed by sulphuric acid to benzoic acid and Hochst-yellow R, oxidised by nitric acid to picric and benzoic acids, and yielding with sodium ethoxide the same compounds as yellow R, including azobenzene. The "xylene substance"

is obtained from Höchst-yellow R by the action of benzoyl chloride and copper powder in boiling xylene and similarly from diacetylindigotin. The Dessoulavi compound is derived from Höchst-yellow R by prolonged treatment with boiling acetic anhydride and acetyl chloride and from dibenzoylindigotin and benzoyl chloride. With methyl-alcoholic ammonia it gives a derivative, $C_{30}H_{20}O_2N_4$, m. p. 247°. Höchst-yellow U with acetic anhydride and zinc dust affords the dihydroleuco-monoacetate, $C_{25}H_{18}O_3N_2$, softening at 230°. Ciba-yellow and sodium methoxide yield a product, $C_{23}H_{16}O_4N_2$, m. p. 273°. The relationships of the substances are indicated as follows:



The following compounds are incidentally described: benzoyl-2-indole-2'-thionaphthenindigotin, m. p. 281°; dibenzoyl-2-indole-2'-thionaphthenleuco-indigotin, $C_{30}H_{18}O_4NS$, m. p. 234°; tribenzoyl-2-indole-2'-thionaphthenleucoindigotin, m. p. 222°, and the corresponding triacetyl compound, m. p. 210—215°.

H. WREN.

Phthalazines. I. J. S. AGGARWAL, N. L. DARBARI, and J. N. RAY (J.C.S., 1929, 1941—1945).—Arylbenzoylhydrazones, $CHAr:N-NHBz$, are converted into phthalazines by dehydration with phosphoric oxide, phosphorus oxychloride, or (best) amyl-alcoholic hydrogen chloride. The reduction products ($C:N \rightarrow CH:NH$) of the arylbenzoylhydrazones do not undergo intramolecular dehydration. The phthalazines are hydrolysable to *o*-aldehydoketones. The following substances are described: veratraldehydebenzoylhydrazone, m. p. 176°; 6:7-dimethoxy-1-phenylphthalazine, m. p. 193—194°; *s*-benzoyl-3:4-dimethoxybenzylhydrazine, m. p. 79°, by reduction of the above hydrazone by sodium amalgam in alcohol; anisaldehydebenzoylhydrazone, m. p. 147°; 7-methoxy-1-phenylphthalazine, m. p. 167° (picrate, m. p. 208°); *s*-benzoyl-4-methoxybenzylhydrazine, m. p. 96°; piperonaldehydebenzoylhydrazone, m. p. 170°;

6:7-methylenedioxy-1-phenylphthalazine, m. p. 200°; *s*-benzoyl-3:4-methylenedioxybenzylhydrazine, m. p. 130°; 1-phenylphthalazine, m. p. 174—175°, from benzaldehydebenzoylhydrazine (Curtius, A., 1891, 56); *s*-benzoylbenzylhydrazine, m. p. 115°; *m*-nitrobenzaldehydebenzoylhydrazone, m. p. 190°; 6(or 8)-nitro-1-phenylphthalazine, m. p. 165°; *o*-methoxybenzaldehydebenzoylhydrazone, m. p. 179°; 5-methoxy-1-phenylphthalazine, m. p. 135°; *s*-benzoyl-*o*-methoxybenzylhydrazine, m. p. 80°.

Aqueous copper sulphate and alcoholic benzoylhydrazine give an almost quantitative precipitate of a copper salt. R. CHILD.

Synthesis of pyocyanine and certain homologues. F. WREDE and E. STRACK (Ber., 1929, 62, [B], 2051—2057).—Pyrogallol methyl ether is converted by treatment with lead dioxide in dry benzene followed by addition of *o*-phenylenediamine in glacial acetic acid and benzene into 1-methoxyphenazine, m. p. 169°, converted by fuming hydrobromic acid into 1-hydroxyphenazine, from which pyocyanine is derived by treatment with methyl sulphate at 100°; the constitution of the dye has not been completely established. Treatment of 1-hydroxyphenazine with ethyl sulphate at 140° affords 10:10'-diethylnorpyocyanine, m. p. 173°, which closely resembles pyocyanine, but is more stable to air in presence of alkali; the chloroplatinate, m. p. 225—228°, chloraurate, m. p. 177°, perchlorate, m. p. 277° after softening at 265°, and picrate are described. 10:10'-Din-propylnorpyocyanine, $C_{30}H_{28}O_2N_4$, m. p. 168°, its chloroplatinate, m. p. 228°, chloraurate, m. p. 177°, perchlorate, m. p. 272°, and picrate, incipient decomp. 180°, have been prepared.

2:3-Dinitroanisole, m. p. 118°, prepared from *m*-nitroanisole and nitric acid (*d* 1.48) at 0°, is reduced by stannous chloride and hydrochloric acid to 2:3-diaminoanisole hydrochloride, m. p. 250°. 3-Amino-2-methylaminoanisole hydrochloride, m. p. 250° (decomp.), could not be condensed to a phenazine derivative. 2:3-Diaminoanisole hydrochloride and 3:5-diamino-*o*-benzoquinone afford 1:3-diamino-8(5)-methoxyphenazine, isolated as the perchlorate, m. p. 171—173°. De-amination of the compound yields 1-methoxyphenazine. H. WREN.

Bases containing two isoquinoline rings. R. CHILD and F. L. PYMAN (J.C.S., 1929, 2010—2021).—A number of compounds containing two isoquinoline nuclei united through the 1:1'-positions by chains of methylene groups have been synthesised for comparison with emetine. The following amides were obtained by heating mixtures of the appropriate ethyl ester and amine: oxalo-, malono-, succino-, glutaro-, adipo-, pimelo-, subero-, azelao-, sebaco-, nonane-1:9-dicarboxy-, and decane-1:10-dicarboxy-di- β -phenylethylamides with m. p. 186° (lit. 180°, 186°), 129—130°, 200°, 159—160°, 184°, 147—148°, 166, 151°, 159°, 151—152°, and 157°, respectively; oxalo-, succino-, glutaro-, adipo-, pimelo-, subero-, azelao-, sebaco-, nonane-1:9-dicarboxy-, and decane-1:10-dicarboxy-di- β -veratrylethylamides with m. p. 173—174°, 174—175°, 131°, 169°, 143—144°, 161°, 148—149°, 156°, 152—153°, and 155—156°, respectively; adipodi-

β -piperonylethylamide had m. p. 208°. From ethyl succinate N- β -phenylethylsuccinimide, m. p. 133—134°, and N- β -veratrylethylsuccinimide, m. p. 129°, were also formed.

Ring closure was effected with adipo-, pimelo-, and sebaco-di- β -veratrylethylamides (failures attended attempts with the corresponding β -phenylethylamides) by boiling with phosphorus oxychloride in toluene solution. Thus were prepared, in order, $\alpha\delta$ -bis-(6 : 7-dimethoxy-3 : 4-dihydroisoquinolyl-1)-butane, m. p. 172—173° [hydrochloride, m. p. 263—264° (decomp.)]; hydriodide, m. p. 260—261° (decomp.); hydrogen sulphate, m. p. 255—260° (decomp.); succinate, m. p. 202—203° (decomp.); dimethiodide, m. p. of monohydrate, 240—241° (decomp.), reduction of which by tin and hydrochloric acid gave $\alpha\delta$ -bis-(6 : 7-dimethoxytetrahydroisoquinolyl-1)-butane, m. p. 127° [hydrochloride, m. p. 268—270° (decomp.)]; lactate, m. p. 212—213° (decomp.). The above dimethiodide by digestion with silver chloride followed by reduction with tin and hydrochloric acid gave eventually $\alpha\delta$ -bis-(6 : 7-dimethoxy-2-methyltetrahydroisoquinolyl-1)-butane, m. p. 108—109° (hydrochloride, m. p. 244—245°).

$\alpha\epsilon$ -Bis-(6 : 7-dimethoxy-3 : 4-dihydroisoquinolyl-1)-pentane, m. p. 57—58° [hydrochloride, m. p. 235—236° (eff.)]; hydriodide, m. p. 220—222° (decomp.); hydrogen tartrate, m. p. 189—190° (eff.); dimethiodide, m. p. 236—237° (decomp.); $\alpha\epsilon$ -bis-(6 : 7-dimethoxytetrahydroisoquinolyl-1)-pentane hydrochloride, m. p. 225—227°; $\alpha\theta$ -bis-(6 : 7-dimethoxy-3 : 4-dihydroisoquinolyl-1)-octane, m. p. 116° [hydrochloride monohydrate, m. p. 172° (eff.)], anhydrous, m. p. 208—210° (decomp.); hydriodide, m. p. 208—209° (eff.); succinate, m. p. 187°; and $\alpha\delta$ -bis-(6 : 7-methylenedioxy-3 : 4-dihydroisoquinolyl-1)-butane, m. p. 210—211° [hydrochloride dihydrate, m. p. 270° (decomp.)]; hydriodide, m. p. 277—280° (decomp.); dimethiodide, m. p. 285—287° (decomp.), were prepared analogously to the above butane derivatives. Qualitative tests showed that azelao-, subero-, nonane-1 : 9-dicarboxy-, and decane-1 : 10-dicarboxy-di- β -veratrylethylamides also underwent isoquinoline condensation under the action of phosphorus oxychloride.

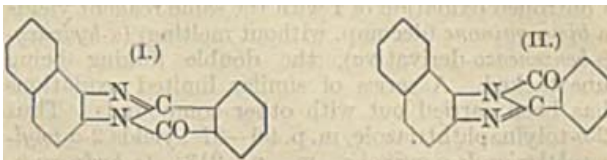
Similar treatment of succinodi- β -veratrylethylamide resulted in extensive decomposition, whilst glutarodi- β -veratrylethylamide gave small yields of a base, $C_{25}H_{30}O_4N_2$, isolated as hydriodide, m. p. 239—240° (corresponding hydrochloride, m. p. 199—200°), along with traces of a second hydriodide, $C_{25}H_{32}O_5N_2 \cdot HI$, m. p. 203—204°. (All m. p. given above are corr.)

Of the seven compounds examined for amebicidal properties none prevented the growth of *Entamoeba histolytica* in cultures at a dilution of 1 in 5000, whilst emetine was effective in a dilution of 1 in 500,000. Similarly, they had neither antimalarial nor trypanocidal activities. Methyl and ethyl β -3 : 4-dimethoxyphenylpropionates, m. p. 38—39°, b. p. 194°/30 mm., 174—175°/12 mm., and m. p. 13°, b. p. 193°/20 mm., d_{4}^{25} 1.123, respectively, are described incidentally in an improved preparation of β -veratrylethylamine.

R. J. W. LE FEVRE.

Diphthalimidonaphthalenes and benzoylene-naphthiminazoles. G. B. CRIPPA and P. GALIMBERTI (Gazzetta, 1929, 59, 510—519).—The reaction

which takes place when 1 : 2-naphthylenediamine is heated with phthalic anhydride has been reinvestigated. From the product obtained at 170°, 1 : 2-diphthalimidonaphthalene, m. p. 280°, is extracted by chloroform. The residue contains 1 : 2(1' : 2')-benzoylene- β -naphthiminazole (I), m. p. 299—300°, accompanied by 1' : 2'-naphthiminazole-2-benzoic acid. At 270—280° the chief product is 1 : 2(1' : 2')-benzoylene- α -naphthiminazole (II), m. p. 208° (cf. Bistrzycki and



Risi, A., 1926, 67). 1 : 2-Diphthalimidonaphthalene is converted by boiling potassium hydroxide solution into 1 : 2-naphthylenediphthalamic acid, $C_{10}H_6[NH \cdot CO \cdot C_6H_4 \cdot CO_2H]_2$, which is dehydrated to the phthalimido-compound when heated. The constitutions of the isomerides I and II have been confirmed by synthesis. 1-Nitro- β -naphthylamine yields 1-nitro-2-phthalimidonaphthalene, m. p. 203°, which is reduced by iron and acetic acid to a mixture of 1-amino-2-phthalimidonaphthalene (not isolated, but yielding I when boiled in acetic acid) and I. Similarly, 2-nitro-1-phthalimidonaphthalene, m. p. 211°, is converted into II. The following compounds are also described: 1 : 4-diphthalimidonaphthalene, m. p. above 320° (from 1 : 4-naphthylenediamine and phthalic anhydride); 1 : 4-naphthylenediphthalamic acid; 1-nitro-4-phthalimidonaphthalene, m. p. 223°; 1-nitronaphthalene-4-phthalamic acid; 1-amino-4-phthalimidonaphthalene (yielding 1 : 4-diphthalimidonaphthalene with phthalic anhydride); 1 : 5-diphthalimidonaphthalene, m. p. 253°; 1 : 5-naphthylenediphthalamic acid.

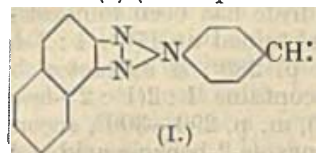
R. K. CALLOW.

α - and β -Isatol. G. HELLER and A. SILLER (J. pr. Chem., 1929, [ii], 123, 257—261).—Acetylation of α -isatol with acetic anhydride and sulphuric acid gives an acetyl derivative (I), $C_{26}H_{17}O_7N_3$, m. p. 245—246° (decomp.) after sintering and darkening above 235°, thus demonstrating the termolecular nature of the parent substance (cf. Hantzsch, A., 1925, i, 700). Oxidation of α -isatol with chromic oxide and acetic acid affords a 85.4% yield of anhydroisatin-*o*-aminobenzanilide (II), formed also in small amount by similar oxidation of I. When β -isatol is heated with acetic acid (cf. A., 1925, i, 1166) there is obtained isatoid (III), m. p. 210—211° (cf. Hantzsch, loc. cit.), whilst chromic acid oxidation gives a 50% yield of II. When an alkaline solution of III is kept, II is formed (cf. A., 1920, i, 765).

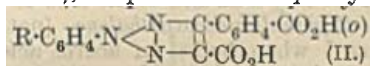
H. BURTON.

Di-($\alpha\beta$ -naphth-1 : 2 : 3-triazolyl)stilbene. G. CHARRIER (Gazzetta, 1929, 59, 479—489).—Bromination of 2-*p*-tolyl- $\alpha\beta$ -naphth-1 : 2 : 3-triazole in hot nitrobenzene yields the ω -dibromo-compound, m. p. 230—231°. Treatment of the latter under various conditions gives none of the expected anthracene derivative. When heated with copper powder in nitrobenzene it yields 4' : 4''-di-(2-naphthtriazolyl)-

stilbene (I) (decomp. without melting). The latter is oxidised by chromic acid in acetic acid and acetic anhydride to 2-phenylnaphthtriazole-o-quinone-*p*'-carboxylic acid (decomp. without



melting), which yields with phenylhydrazine the α -hydroxy- β -benzeneazo-derivative, m. p. 283—284°. Controlled oxidation of I with the same reagent yields a bis-o-quinone (decomp. without melting) (α -hydroxy- β -benzeneazo-derivative), the double linking being unattacked. A series of similar limited oxidations has been carried out with other compounds. Thus 2-o-tolynaphthtriazole, m. p. 96—97°, yields 2-o-tolynaphthtriazole-o-quinone, m. p. 213° (α -hydroxy- β -benzeneazo-derivative, m. p. 137—148°; phenazine derivative, m. p. 209—210°), or, with excess of chromic acid, the *p*'-carboxylic acid. Similarly, the *m*-tolyl compound, m. p. 123—124°, gives the o-quinone, m. p. 210° (α -hydroxy- β -benzeneazo-derivative, m. p. 190°; phenazine derivative, m. p. 251—252°), or, by oxidation with hydrogen peroxide, 2-*m*-tolyl-4-o-carboxyphenyl-1:2:3-triazole-5-carboxylic acid (II; R=*m*-Me), m. p. 240°. The *p*-tolyl compound,



m. p. 148—149°, yields the o-quinone, m. p. 216—217° (α -hydroxy- β -benzeneazo-derivative, m. p. 184—185°; phenazine derivative, m. p. 258°), which with alkaline permanganate or hydrogen peroxide in acetic acid yields 2-*p*-carboxyphenyl-4-o-carboxyphenyl-1:2:3-triazole-5-carboxylic acid (II; R=*p*-CO₂H), m. p. 288°. The last acid is also obtained directly from 2-*p*-tolynaphthtriazole and from the ω -dibromo-compound. 2-*p*-Bromophenylnaphthtriazole, m. p. 202°, yields the o-quinone, m. p. 195—196° (α -hydroxy- β -benzeneazo-derivative, m. p. 235°; phenazine derivative, m. p. 306°). ω -Dibromo-2-*p*-tolynaphthtriazole yields the o-quinone (decomp. without melting) (α -hydroxy- β -benzeneazo-derivative, m. p. 196°; phenazine derivative, m. p. 282°). R. K. CALLOW.

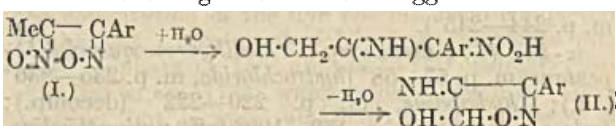
Dimethyldipropylalloxantin and its reduction potential. E. BILMANN and T. TER BRAAK (Rec. trav. chim., 1929, 48, 919—921).—Treatment of theobromine with aqueous potassium hydroxide and propyl iodide or of the silver theobromine with this iodide gives propyltheobromine, m. p. 137°. Oxidation of the latter with potassium chlorate and hydrochloric acid at 50° and subsequent reduction of the alloxan produced with hydrogen sulphide affords dimethyldipropylalloxantin. Determination of the reduction potential of this by the method previously described (A., 1923, ii, 605) gives values of 0.3643 and 0.3616 volt at 18° and 25°, respectively. The value for tetramethylalloxantin is modified to 0.3660 volt at 18° (cf. *loc. cit.*). H. BURTON.

Synthesis of mesoporphyrins. H. FISCHER and A. KIRRMANN (Compt. rend., 1929, 189, 467—469).—Three more of the isomeric mesoporphyrins, I, IV, and XIV (cf. Ber., 1927, 60, 2645) have been synthesised by fusion of the appropriate pair of bromodipyrrylmethenes with succinic acid, and the following derivatives prepared: mesoporphyrin I [methyl, m. p. 170°

(191° on remelting), and ethyl, m. p. 167°, esters; copper, m. p. 217°, iron, m. p. about 265°, salts]; mesoporphyrin IV (methyl ester, m. p. 238°; copper, m. p. 267°, and iron, m. p. 270°, salts); mesoporphyrin XIV (methyl ester, m. p. 210°; copper, m. p. 215°, and iron, m. p. 261°, salts). They are also differentiated from natural mesoporphyrin (IX) by the solubilities of their sodium salts, that of natural mesoporphyrin being precipitated when the concentration of sodium hydroxide exceeds 0.1*N*, whilst the new isomerides remain soluble in 2% sodium hydroxide, the sodium salts crystallising slowly from a 3% solution.

J. W. BAKER.

Dioximes. LIV. G. PONZIO and M. TORRES (Gazzetta, 1929, 59, 461—478).—The "isooxazole transformation" (cf. Angeli, A., 1893, i, 261; Wieland and Semper, A., 1908, i, 108), which takes place when certain "arylmethylglyoxime peroxides" [actually arylmethylfuroxans (I); cf. Ponzio, A., 1928, 888] are heated with alcoholic potassium hydroxide, is now shown to yield 4-imino-5-hydroxy-3-aryl-4:5-dihydroisooxazoles (II), not the 4-oximino-compounds, and the following mechanism is suggested:



4-Imino-5-hydroxy-3-*p*-anisyl-4:5-dihydroisooxazole (III), m. p. 182° (decomp.) (cf. Wieland and Semper, *loc. cit.*), is conveniently prepared by the addition of *p*-anisylmethylfuroxan to a hot alcoholic solution of sodium ethoxide, and separates on acidification. The action of phenylhydrazine in acetic acid yields a substance, C₂₃H₁₈ON₄, m. p. 129°. The hydroxyl group in III reacts with the formation of a benzoyl derivative, m. p. 147°, a methyl ether, m. p. 108°, and a phenylurethane, m. p. 166° (decomp.). Ethyl nitrite yields the 4-nitrosimino-derivative, m. p. 83—84° (decomp.) [silver and sodium (+2H₂O) salts]. By boiling with an aqueous solution of hydrazine, III is isomerised to 4-amino-*o*-hydroxy-3-*p*-anisylisooxazole, m. p. 122—123° (decomp.) (IV), which is reconverted into the imino-compound by sodium hydroxide solution. It yields *p*-methoxybenzonitrile with hot dilute sulphuric acid, and is converted by phenylcarbimide into the phenylurethane of the imino-compound. The anisylidene derivative has m. p. 159—160° (decomp.). 4-Amino-5-chloro-3-*p*-anisylisooxazole, m. p. 81—82° [hydrochloride, m. p. 159—160° (decomp.)], is obtained from III or IV and concentrated hydrochloric acid, or, best, by treatment of IV with hydrogen chloride in ether. The following derivatives are described: benzylidene, m. p. 128—129°; anisylidene, m. p. 68°; acetyl, m. p. 155—156°; benzoyl, m. p. 165—166°. Reduction of III with zinc dust in sodium hydroxide solution yields 4-amino-3-*p*-anisyl-4:5-dihydroisooxazole, m. p. 80° [hydrochloride, m. p. 198° (decomp.)]; derivatives: acetyl, m. p. 133—134°; benzoyl, m. p. 148°; anisylidene, m. p. 109—110°].

The following analogous compounds are also described: 4-imino-*o*-hydroxy-3-phenyl-4:5-dihydroisooxazole, m. p. 179—180° (decomp.) [methyl ether, m. p. 90° (decomp.)]; acetyl derivative, m. p. 104°

(decomp.); *benzoyl* derivative, m. p. 152° (decomp.); *phenylurethane*, m. p. 153—154° (decomp.); *substance*, m. p. 119°, formed by the action of phenylhydrazine; 4-amino-5-hydroxy-3-phenylisooxazole, m. p. 105° (decomp.); 5-chloro-4-amino-3-phenylisooxazole, m. p. 73° [hydrochloride, m. p. 142° (decomp)]; derivatives: *benzylidene*, m. p. 62—63°; *acetyl*, m. p. 127—128°; *benzoyl*, m. p. 172°; 4-imino-5-hydroxy-3-p-bromophenyl-4:5-dihydroisooxazole, m. p. 184—185° (decomp.); 4-amino-5-hydroxy-3-p-bromophenylisooxazole, m. p. 112—113° (decomp.); 5-chloro-4-amino-3-p-bromophenylisooxazole, m. p. 98—99°; 4-imino-5-hydroxy-3-p-methoxybromophenyl-4:5-dihydroisooxazole, m. p. 198° (decomp.); 4-amino-5-hydroxy-3-p-methoxybromophenylisooxazole, m. p. 143° (decomp.); 5-chloro-4-amino-3-p-methoxybromophenylisooxazole, m. p. 128° (decomp.).

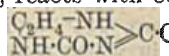
Phenylethylglyoxime, m. p. 215—216° (decomp.), is converted by the action of sodium hypochlorite into an oily peroxide which does not react with sodium ethoxide, and is, therefore, probably a true peroxide (cf. A., 1928, 888), although the furoxan structure in which the reactive methyl group is not in the nucleus is not excluded.

R. K. CALLOW.

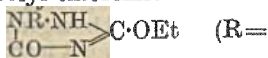
Ketophenmorpholine synthesis from 5-amino-eugenol. E. PUXEDDU and G. SANNA (*Gazzetta*, 1929, 59, 519—524).—5-Amino-eugenol reacts with chloroacetyl chloride to give 5-chloroacetamidoeugenol, m. p. 89° (dibromide, m. p. 125°); this is converted by heating with alcoholic potassium hydroxide into 8-methoxy-3-keto-6-allyl-2:3-dihydro-1:4-benzoxazine, m. p. 194°, which yields two substances, m. p. 125° and 175°, when treated with bromine.

R. K. CALLOW.

Formation of heterocyclic compounds from ethyl carbethoxythiocarbamate. P. C. GUHA and S. R. A. SALETORÉ (*J. Indian Chem. Soc.*, 1929, 6, 565—575).—Ethyl carbethoxythiocarbamate (I), m. p. 46° (cf. Delitsch, A., 1875, 358) (methyl derivative, m. p. 32—33°, obtained from methyl iodide and the potassium derivative of I; benzyl derivative, m. p. 45—46°), reacts with ethylenediamine, forming the compound



small amounts of the substances $[\text{CO}_2\text{Et}\cdot\text{N}\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{CH}_2]_2$ and $\text{CO}_2\text{Et}\cdot\text{N}\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}(\text{SH})\cdot\text{N}\cdot\text{CO}_2\text{Et}$, m. p. 101—102° and 123°, respectively. With *o*-phenylenediamine the compound (II, C_6H_4 replaced by C_6H_4), m. p. about 330°, results. Hydrazine hydrate and I afford 5-ethoxy-3-keto-2:3-dihydro-1:2:4-triazole, m. p. 170—172° (2-phenyl derivative, m. p. 150—151°, obtained similarly from phenylhydrazine), hydrolysed by hydrochloric acid to urazole. 4-Phenyl- and 4-p-tolyl-thiosemicarbazides furnish the compounds



$\text{NHPh}\cdot\text{CS}\cdot$ and $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{CS}\cdot$, respectively), m. p. 246—248° and 186—187°, respectively. 2-Di-p-tolyl-guanidino-5-ethoxy-3-keto-2:3-dihydro-1:2:4-triazole, m. p. 229—230°, is formed from I and amino-di-p-tolylguanidine and is hydrolysed by hydrochloric acid to a substance, m. p. 256—257° (decomp.). Carbamide and thiocarbamide yield 4:6-diketo-

m. p. 171—173°, and 2-ethoxy-6-keto-4-thioketo-3:4:5:6-tetrahydro-1:3:5-triazine, m. p. 150° after shrinking at 110°, respectively. Aniline, *o*- and *p*-toluidines, α - and β -naphthylamines, and benzidine react with I, giving *s*-diphenyl-, *s*-di-*o*- and di-*p*-tolyl-, *s*-di- α - and di- β -naphthyl-carbamides, and carbonylbenzidine, respectively.

H. BURTON.

Benzidine rearrangement in heterocyclic series. III. B. C. DAS-GUPTA and P. K. BOSE (*J. Indian Chem. Soc.*, 1929, 6, 495—504).—Phenacyl bromide and 1-m-nitrophenylthiosemicarbazide, m. p. 187° (from *m*-nitroaniline, potassium thiocyanate, and alcoholic hydrogen chloride), react in alcohol, forming 2-m-nitrophenylhydrazino-4-phenylthiazole, m. p. 192—193° (acetyl derivative, m. p. 186°), which when boiled with dilute hydrochloric acid undergoes a benzidine rearrangement (cf. A., 1928, 188; this vol., 79) into 2-amino-4-phenyl-5-*o*-nitro-p-aminophenylthiazole, m. p. 253° (picrate, m. p. 213°; dihydrochloride, decomp. 230°; diacetyl derivative, decomp. above 295°). Similarly, 2-m-nitrophenylhydrazino-4-p-tolylthiazole, m. p. 189° (acetyl derivative, m. p. 178°), yields 2-amino-4-p-tolyl-5-*o*-nitro-p-aminophenylthiazole, m. p. 163° (decomp.) [diacetyl derivative, m. p. 253° (decomp.)], and 2-m-nitrophenylhydrazino-4-methylthiazole, m. p. 138° (decomp.) (acetyl derivative, m. p. 155°), affords 2-amino-5-*o*-nitro-p-aminophenyl-4-methylthiazole, decomp. 110° (diacetyl derivative, decomp. 180°). Similar rearrangements are undergone by 2- α -naphthylhydrazino-4-phenyl-, m. p. 174° (acetyl derivative, m. p. 160—161°), 2- α -naphthylhydrazino-4-p-tolyl-, m. p. 180° (acetyl derivative, m. p. 161°), and 2- α -naphthylhydrazino-4-methylthiazoles, m. p. 188° (decomp.; acetyl derivative, m. p. 149—150°), giving 2-amino-4-phenyl-5-4'-amino- α -naphthyl-, m. p. 236° (decomp.) [picrate, m. p. 193°; dihydrochloride, m. p. 245° (decomp.)]; diacetyl derivative, m. p. 248°, 2-amino-4-p-tolyl-5-4'-amino- α -naphthyl-, m. p. 280° (diacetyl derivative, m. p. 208°), and 2-amino-5-4'-amino- α -naphthyl-4-methyl-thiazoles, decomp. 110° (diacetyl derivative, decomp. 260°), respectively.

Phenacyl bromide and 1-*o*-nitrophenylthiosemicarbazide, m. p. 201°, react in alcohol, forming the compound (I) $\begin{array}{c} \text{CR}\cdot\text{N} \\ \text{CH}\cdot\text{S} \end{array} > \text{C}\cdot\text{NH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{OH}$ (*o*) (R=Ph), decomp. 190° (acetyl derivative, m. p. 175°), soluble in alkali hydroxide solution, giving a deep violet coloration. Formation of I occurs presumably by rearrangement of the intermediate 2-*o*-nitrophenylhydrazino-4-phenylthiazole. The substance (I, R=*p*-Me·C₆H₄·), m. p. 185° (decomp.) (acetyl derivative, m. p. 206°), and the compound (I, R=Me), decomp. 165° (acetyl derivative, m. p. 167°), are prepared similarly from ω -bromo-*p*-methylacetophenone and chloroacetone, respectively. The analogous compounds [I, $\cdot\text{NO}\cdot\text{OH}$ (*o*)= $\cdot\text{NO}\cdot\text{OH}$ (*p*); R=Ph, *p*-Me·C₆H₄·, and Me, respectively] from 1-*p*-nitrophenylthiosemicarbazide, m. p. 203°, and ω -bromoacetophenone, ω -bromo-*p*-methylacetophenone, and chloroacetone have m. p. 189° (decomp.) (acetyl derivative, m. p. 185°), 178° (acetyl derivative, m. p. 182°), and decomp. 145° (acetyl derivative, m. p. 178°), respectively.

H. BURTON.

The lupin alkaloids. II. G. R. CLEMO and R. RAPER (J.C.S., 1929, 1927—1940; cf. A., 1928, 1030; Schopf and others, *ibid.*, 1144; Karrer and others, this vol., 200).—*Lupinus luteus* is a better source than *L. pilosus* of *l*-lupinine, $C_{10}H_{19}ON$, m. p. 70—71°. Lupinine methiodide, m. p. 305—306°, on fusion in a vacuum with potassium hydroxide and treatment of the resulting base (b. p. 108—110°/10 mm.) with methyl iodide yields α -methyl-lupinine methiodide, m. p. 224—225°. The usual Hofmann method leads to a mixture of bases yielding a mixture of methiodides, m. p. 190—205°; treatment of the mixture of methyl-lupinines so obtained with phosphorus pentachloride gives a mixture of chloromethyl-lupinines (b. p. 90—92°/1 mm.), the mixed methiodides of which are separated into α -chloromethyl-lupinine methiodide, $C_{11}H_{20}NCl, MeI$, m. p. 215—216°, and β -chloromethyl-lupinine methiodide, m. p. 182°; these both yield bases, $C_{12}H_{22}NCl$, b. p. 100°/1 mm., when subjected to Hofmann degradation. These do not yield crystalline picrates or methiodides; it is therefore uncertain whether one or more chloromethyl-lupinines are present in these products.

Chlorolupinine methiodide, $C_{10}H_{18}N, MeI$, m. p. 204°, by treatment with silver oxide followed by vacuum distillation yields ψ -anhydrolupinine, $C_{10}H_{17}N$, b. p. 63°/0.5 mm., $[\alpha]_D^{25} -35.3^\circ$ in acetone [picrate, m. p. 154°; chloroplatinate, m. p. 210° (decomp.)]. This base gives two stereoisomeric methiodides, α , m. p. 172°, and β , m. p. 263°; treatment of the former with silver chloride and distillation of the resulting methochloride regenerates ψ -anhydrolupinine, whilst treatment with silver oxide by the Hofmann method leads to a base, b. p. 60°/1 mm., yielding with methyl iodide ψ -anhydromethyl-lupinine methiodide, $C_{11}H_{19}N, MeI$, m. p. 186—187°. The same product is similarly obtainable from the mixture of α - and β - ψ -anhydrolupinine methiodides.

ψ -Anhydrodihydrolupinine, $C_{10}H_{19}N$, b. p. 58—59°, $[\alpha]_D^{25} +21.7^\circ$ in acetone (picrate, m. p. 176—177°; α -methiodide, m. p. 310—312°; a second methiodide could not be isolated pure), is obtained by reduction of ψ -anhydrolupinine with hydrogen and palladium.

Treatment of chlorolupinine methiodide with silver oxide at 100° and subsequent degradation furnishes anhydromethyl-lupinine, $C_{11}H_{19}N$, b. p. 63°/1 mm., which is not quite homogeneous, although one anhydromethyl-lupinine (α) preponderates (picrate, m. p. 162—163°; chloroplatinate, decomp. 210°; methiodide, m. p. 191—192°); the base undergoes a complex change when heated with 15% hydrochloric acid, among the products being an isomeric base (methiodide, $C_{11}H_{19}N, MeI$, m. p. 219°). Anhydromethyl-lupinine methiodide on Hofmann degradation gives a high-boiling (? polymeric) base. Anhydromethyl-lupinine is reduced with hydrogen and palladium to a mixture of anhydrodihydromethyl-lupinines, $C_{11}H_{21}N$, b. p. 60°/1 mm.; this mixture gives mainly α -, m. p. 195—196°, and β -, m. p. 145—146°, -methiodides, and also traces of γ -methiodide, m. p. 199—200°, presumably derived from β -anhydromethyl-lupinine in the starting material; α -anhydrodihydromethyl-lupinine picrate has m. p. 145—146°, β -picrate, m. p. 132°. Anhydrolupinine, under reduction conditions similar to the above, yields a mixture of

lupinanes, $C_{10}H_{21}N$, i.e., absorbs four atoms of hydrogen. The foregoing results on the degradation of chlorolupinine methiodide are discussed in the light of Karrer's formula for lupinine (this vol., 201), ψ -anhydrolupinine on this basis appearing to contain

an eight-membered ring fused to piperidine,



N-Piperidyl-lupinine, $C_{15}H_{28}N_2$, strongly alkaline, b. p. 128—130°/1 mm. (from chlorolupinine and piperidine in the presence of sodium acetate and copper powder), differs from sparteine and deoxylupanine in forming a dimethiodide, m. p. 324° (decomp.), and in not containing an easily oxidisable $\cdot CH_2\cdot$ group.

When distilled with potassium hydroxide in a vacuum, sparteine methiodide (α - or α' -) yields a methylsparteine, $C_{16}H_{28}N$, b. p. 135—136°/1 mm., not identical with the known isomerides (Moureu and Valeur, A., 1908, i, 44; Schöpf, *loc. cit.*) [methiodide, m. p. 247° (decomp.)].

Oxysparteine (cf. Schöpf, *loc. cit.*) has b. p. 204°/9 mm., m. p. 86—87°, $[\alpha]_D^{25} -10.4^\circ$ in alcohol [picrate, m. p. 185° (Schöpf, 183°); methiodide, m. p. 231° (Ahrens, A., 1893, i, 232, 191—193°), methosulphate, m. p. 179°]. Hofmann degradation of oxysparteine methiodide leads to α -methyloxysparteine, $C_{16}H_{26}ON_2$, m. p. 85—87° (picrate, m. p. 248°; methosulphate, m. p. 268°); treatment of oxysparteine methosulphate with sodium amalgam gives the same base. Fusion of oxysparteine methiodide with potassium hydroxide produces β -methyloxysparteine, b. p. 210—215°/1 mm., m. p. 86°, $[\alpha]_D^{25} +55.8^\circ$ (picrate, m. p. 237°; methiodide, $C_{16}H_{26}ON_2, MeI, 2H_2O$, m. p. 247°); fusion of the α -base with potassium hydroxide gives the β -isomeride.

Hofmann degradation of β -methyloxysparteine methiodide leads partly to the original material and partly to a dimethyloxysparteine, $C_{17}H_{28}ON_2$ (methiodide, m. p. 194°); the latter methiodide is almost entirely converted by the Hofmann method into the original base, and does not lose trimethylamine.

The action of cyanogen bromide on α -methyloxysparteine gives an additive product, $C_{16}H_{26}ON_2, 2CNBr$, decomp. 244°, and a compound, $C_{16}H_{23}ON_3$, m. p. 202°, in which a methyl group is replaced by cyanogen.

The new results on sparteine are discussed in the light of Karrer's suggested formulæ. R. CHILD.

Identification of atropine with Wagner's reagent. C. C. FULTON (J. Assoc. Off. Agric. Chem., 1929, 12, 312—317).—In the identification of atropine by means of iodine and potassium iodide, four types of crystal can be distinguished at very high magnification, viz., I, reddish-brown rods, II, yellow plates, III, bicoloured yellow and red crystals, and IV, orange-red hexagonal elongated plates. All types are very small, but increase in size in the order given and also change from one to the other in this order as the proportion of atropine or of potassium iodide is increased, but all require an excess of iodine to atropine. If iodine is not in excess, red and yellow prisms are formed as described by Putt (A., 1913, ii, 259). For the formation of the various types of crystal a reagent containing 1 g. of potassium iodide

in 100 c.c. of water and the following amounts of potassium iodide is recommended: I, 2.75 g.; II, 8 g.; III, 35 g.; and IV, 50 g. The reagent containing the lowest concentration of potassium iodide is the most sensitive and it will definitely identify atropine at a concentration of 1 : 200,000.

H. J. DOWDEN.

Microchemical reactions of sparteine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 809—812).—The most sensitive reactions are those with cadmium and zinc iodides, and gold chloride, which will detect 0.5—1 mg. at a dilution of 1 in 1000.

S. I. LEVY.

Identity of pectinin with carnegin. E. SPATH and F. KUFFNER (Ber., 1929, 62, [B], 2242—2243).—Comparison of the hydrochlorides, picrates, and trinitro-*m*-tolyl oxides of carnegin and pectinin from *Cereus pecten aboriginum*, Engelm., establishes the identity of the alkaloids. Pectinin is therefore 6 : 7-dimethoxy-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydro-isoquinoline. It is optically inactive. The replacement of the name pectinin by carnegin is advocated.

H. WREN.

Angostura alkaloids. IV. 4-Methoxy-2-*n*-amylquinoline, a basic component of angostura bark. E. SPATH and J. PIKL (Ber., 1929, 62, [B], 2244—2251).—The total bases of the angostura bark are separated into phenolic and non-phenolic compounds and the latter into stronger and weaker bases. The bulk of the casparin and galipin is separated (as hydrochlorides) from the more strongly basic fraction and the residual bases are distilled with steam. The distillate yields 4-methoxy-2-*n*-amylquinoline, b. p. 110—115°/0.001 mm. [chloroplatinate, m. p. 220° (decomp.); picrate, m. p. 132° after softening]. Treatment of the base with methyl iodide followed by distillation in a vacuum yields the methoxyl-free substance, $C_{15}H_{19}ON$, m. p. 101°. Hydrolysis of the base with fuming hydrochloric acid at 185—190° affords 4-hydroxy-2-*n*-amylquinoline, m. p. 144°, converted by diazomethane into the natural alkaloid. Oxidation of the compound, m. p. 101°, gives hexoic acid. The phenolic base is transformed by phosphorus pentachloride and phosphoryl chloride into 4-chloro-2-*n*-amylquinoline, converted by hydrogen in presence of palladised charcoal into 2-*n*-amylquinoline, b. p. 150—155°/11 mm. (chloroplatinate; picrate, m. p. 124—126°). 2-*n*-Amylquinoline is prepared synthetically by condensation of 2-methylquinoline with *n*-butaldehyde to the unsaturated base, $C_{14}H_{15}N$, b. p. 167—168°/13 mm. (picrate, m. p. 140.5—141.5°), and hydrogenation of the latter compound in presence of palladised charcoal. 4-Hydroxy-2-*n*-amylquinoline is synthesised by condensation of ethyl hexoylacetate, b. p. 118—121°/13 mm., with aniline and heating of the product, $NPh \cdot C(C_5H_{11}) \cdot CH_2 \cdot CO_2Et$, at 250—255°, and is methylated to the alkaloid. Oxidation of the synthetic phenolic base with potassium permanganate affords *N*-hexoylantranilic acid, m. p. 93.5°, identical with the product derived from *n*-hexoyl chloride and anthranilic acid in ether.

H. WREN.

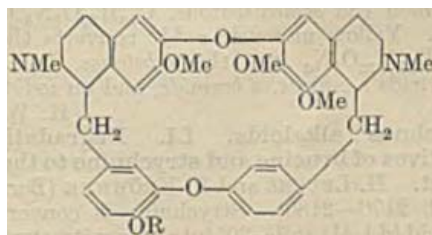
Chloroiodoquinine. F. X. ERBEN (Ber., 1929, 62, [B], 2393—2394).—The action of iodine chloride on quinine salts in dilute aqueous solution affords

chloroiodoquinine, $C_{20}H_{24}O_2N_2ClI$, m. p. about 155° after darkening at about 100°, in which addition appears to have occurred by saturation of the double linking in the vinyl group. Hydroquinine hydrochloride, when treated with chlorine in aqueous solution in the presence of iodine, gives iodohydroquinine, $C_{20}H_{25}O_2N_2I$.

H. WREN.

Constitution of oxyacanthine. E. SPATH and J. PIKL (Ber., 1929, 62, [B], 2251—2260; cf. Spath and Kolbe, A., 1926, 82; Gadamer and von Bruchhausen, *ibid.*, 627).—The formation of a simple dicarboxylic acid during the cautious oxidation of oxyacanthine could not be established. Fusion of the alkaloid with alkali hydroxide gives *p*-hydroxybenzoic acid, which cannot be present originally as the *p*-hydroxy- or *p*-methoxybenzyl residue, since anisic acid is not obtained by the oxidation of oxyacanthine or its methyl ether. Oxyacanthine is conveniently converted by diazomethane into its methyl ether, from which the dimethiodide (*loc. cit.*) is prepared. The salt is transformed into the corresponding ammonium base, which, when boiled with potassium hydroxide, gives an optically inactive base, $C_{40}H_{46}O_2N_2$, m. p. 152—153° after slight softening. Oxidation of the base with potassium permanganate affords 2-methoxydiphenyl ether 3 : 4'-dicarboxylic acid, m. p. 313—314° (vac.) (methyl ester, m. p. 97—98°, also synthesised from methyl *p*-bromobenzoate and the potassium derivative of methyl isovanillate).

The ready degradation by the methods of Hofmann and Emde establishes the presence of two tetrahydro-isoquinoline nuclei in oxyacanthine. These processes and determination of methylimino-groups prove both nitrogen atoms to be monocyclically combined and to be united with a methyl group. Further, oxyacanthine must be so constituted that the first stage of the Hofmann degradation causes the production of a base without an asymmetric carbon atom. The benzene nuclei of the two isoquinoline residues carry the four residual oxygen atoms of the alkaloid. In oxyacanthine methyl ether, three of the four oxygen atoms of the isoquinoline complexes are present as methoxyl, whilst for the fourth an ether-like union between the two benzene nuclei remains. The following constitutions are therefore deduced for oxyacanthine ($R=H$) and its methyl ether ($R=Me$).



The position of the hydroxyl group in oxyacanthine is elucidated as follows. The alkaloid is transformed into its ethyl ether and thence into the corresponding dimethiodide, $C_{41}H_{50}O_6N_2I_2$. The salt, after successive treatment with silver oxide and potassium hydroxide, gives the base, $C_{41}H_{48}O_6N_2$, m. p. 131—132°, oxidised to 2-ethoxydiphenyl ether 3 : 4'-dicarboxylic acid, m. p. 288.5—289.5° (methyl ester).

The following compounds have been prepared for

purposes of comparison: *methyl isovanillate*, m. p. 66—67°; *2-methoxydiphenyl methyl ether 4:4'-dicarboxylate*, m. p. 71—72° (corresponding acid, m. p. 256—257°); *2:2'-dimethoxydiphenyl methyl ether 3:3'-dicarboxylate*, m. p. 135—136° [corresponding acid, m. p. 294—296° (vac.)]; *3-bromoanisic acid*, m. p. 214°.

H. WREN.

Potentiometric determination of morphine with an iodo-mercuric reagent. L. MARICQ (Bull. Soc. chim. Belg., 1929, 38, 265—275).—Morphine may be determined satisfactorily as follows. To 10 c.c. of a 0.1% solution of the alkaloid are added 10 c.c. of a reagent prepared by adding a slight excess of mercuric iodide to 4.150 g. of potassium iodide in 100 c.c. of water, and about 0.5 g. of mercuric iodide. The mixture is shaken, heated on a water-bath for 30 min., cooled, diluted to 50 c.c., and filtered. The filtrate is titrated electrometrically after adding nitric acid and diluting.

C. W. GIBBY.

Strychnos alkaloids. L. Transformations of the base, $C_{17}H_{20}O_3N_2Br_2$, from cacothelin. H. LEUCHS (Ber., 1929, 62, [B], 1929—1935).—The compound $C_{17}H_{20}O_3N_2Br_2$ is strongly alkaline and cannot be alkylated with diazomethane or methyl alcohol and hydrogen chloride. The *methiodide*, m. p. 245° (decomp.) after becoming discoloured, *nitrate*, *hydriodide*, m. p. 235—240° (decomp.), and *hydrochloride* are described. The *sulphate*, *acetate*, and *sulphite* appear freely soluble. It does not react with hydroxylamine or semicarbazide. With bromine in hydrobromic acid it affords the compound $C_{17}H_{16}O_3N_2Br_4.HBr$. It is converted by methylalcoholic ammonia at 100° into the compound $C_{17}H_{21}O_3N_2Br$, isolated as the *hydrobromide*. With aqueous ammonia the substances $C_{17}H_{22}O_4N_3.HBr$ and $C_{17}H_{20}O_4N_2.HBr$ are obtained. The compound $C_{16}H_{24}O_4N_2.HBr$ is prepared from it by means of barium hydroxide. Treatment of the hydrobromide with silver carbonate or sodium hydroxide gives the free base, $C_{17}H_{23}O_5N_2$ (*methiodide*, decomp. about 220° after softening at 210°; *acetyl derivative*, m. p. 118° after softening at 95°), which does not appear to contain the carboxyl or carbonyl group. The bromide of the compound $C_{17}H_{22}O_5N_2$ is oxidised by bromine in hydrobromic acid to the substance $C_{17}H_{20}O_7N_2.HBr$, from which the *semicarbazone*, $C_{18}H_{25}O_7N_5.HBr$, is derived. Yellow mercuric oxide converts the compound $C_{17}H_{22}O_5N_2$ into the substance $C_{17}H_{22}O_8N_2$, which yields a *nitrate*, a *bromide*, and an *iodide*.

H. WREN.

Strychnos alkaloids. LI. Degradation of derivatives of brucine and strychnine to the same product. H. LEUCHS and F. KROHNKE (Ber., 1929, 62, [B], 2176—2180).—Strychnine is converted by nitric acid (*d* 1.41) at 0—20° into mononitrostrychnine, m. p. 240° after softening (nitrate; *perchlorate*; *picrate*), converted by boiling 5% nitric acid into dinitrostrychnine nitrate. Dinitrostrychnine hydrate is transformed by methylalcoholic hydrogen chloride into the methyl ether [*hydrochloride*, $C_{22}H_{24}O_7N_4.HCl$, softening at 215—230° (decomp.)]. Nitrostrychnine nitrate and dinitrostrychnine hydrate nitrate are reduced by stannous chloride and hydrochloric acid to aminostrychnine, m. p. 275—278° (vac.), and

diaminostrychnine, m. p. not below 300°, respectively. Oxidation of either amine by chromic acid in aqueous sulphuric acid affords the acid, $C_{17}H_{22}O_6N_2$, [α]_D²⁵ + 45.5° in water, identical in all respects with the acid obtained from brucine. Brucine is therefore the *o*-dimethoxy-derivative of strychnine.

Nitrostrychnine in acetone is oxidised by permanganate to nitrostrychninonic acid, m. p. 256—266° (decomp.) after softening according to the rate of heating.

H. WREN.

Strychnos alkaloids. LII. Reduction and oxidation of the C_{17} alkaloids from brucine. H. LEUCHS and A. HOFFMANN (Ber., 1929, 62, [B], 2303—2311).—The mother-liquors from the oxidation of cacothelin are rendered ammoniacal and extracted with chloroform and the base, $C_{17}H_{20}O_3N_2Br$, is separated as the hydrobromide or sulphurous acid compound. It contains an alcoholic hydroxyl group, since it readily yields a monoacetyl derivative analysed as the *acetate*, $C_{19}H_{22}O_4N_2Br_2.C_2H_4O_2$, which softens and becomes discoloured at about 210°, and the *hydrobromide*. The sulphurous acid compound is transformed by methylalcoholic ammonia into the base $C_{17}H_{21}O_3N_2Br$, m. p. 232—234° (decomp.) (*hydrobromide*). Reduction of the base, $C_{17}H_{20}O_3N_2Br_2$, with sodium amalgam yields two isomeric bases, $C_{17}H_{22}O_3N_2$, m. p. 220° after softening at 120°, and m. p. 290° (decomp.) after becoming discoloured at 270° or m. p. 300° (vac., decomp.), respectively. Under non-reproducible conditions a *hydriodide*, $C_{17}H_{20}O_3N_2.2HI$, has been isolated. Oxidation of the base $C_{17}H_{22}O_3N_2$, m. p. 220°, with chromic acid affords the compound, $C_{17}H_{22}O_4N_2$, isolated as the *hydrobromide*, m. p. 220° (decomp.) after softening at 93°. The preparation of the alkaloid, $C_{17}H_{22}O_5N_2$, by hydrolysis of the base $C_{17}H_{20}O_3N_2Br_2$ with barium hydroxide and its *mono*- and *di*-acetyl derivatives is described. Oxidation of the alkaloids $C_{17}H_{20}O_3N_2Br_2$ in water or acetone and $C_{17}H_{22}O_5N_2$ in water with permanganate gives no recognisable products. With chromic acid the last-named base gives a substance, $C_{17}H_{22}O_6N_2$, which is further oxidised to an acid, $C_{17}H_{20}O_6N_2$, identical with that described by Wieland and Münster (this vol., 707), who assign the composition $C_{17}H_{22}O_6N_2$ to it.

H. WREN

Bromination of several phenylarsinic acids. A. LEULIER and Y. DREYFUSS (J. Pharm. Chim., 1929, [viii], 10, 258—263).—In part an account of work already published (this vol., 945). Bromination of 3-nitro-4-hydroxyphenylarsinic acid with 48% hydrobromic acid and hydrogen peroxide gives an 84% yield of the *monobromo*-derivative, decomp. 280°. A 70% yield of a *monohalogeno*-derivative is similarly obtained from 3-nitro-4-aminophenylarsinic acid; no definite product could be obtained with stovarsol, whilst oxanilarsinic acid is unattacked. The toxicity of phenylarsinic acid (lethal dose for a guinea-pig 0.05 g. per kg.) is increased by increasing bromine substitution (lethal dose 0.01 g. per kg. for the *monobromo*-, <0.01 g. per kg. for the *dibromo*-derivative).

J. W. BAKER.

Synthesis of 4:4'-dithiolarsenobenzene. S. KRISHNA and R. KRISHNA (J. Indian Chem. Soc.,

1929, 6, 665—672).—Treatment of an alkaline solution of potassium ethyl xanthate with diazotised *p*-aminophenylarsinic acid at 55—60° and hydrolysis of the intermediate *p*-xanthyl-diazobenzene-arsinic acid (potassium salt) with hydrochloric acid affords 4:4'-dithiolarsenobenzene (I), decomp. above 280° (disodium and potassium salts; dihydrochloride; disulphate). Acetylation of I with acetyl chloride gives the diacetyl derivative (+AcCl), whilst I and thionyl chloride yield a product hydrolysed by water to the substance,

$\text{SO}_2\text{H}\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{As}(\cdots\text{SO}_2\text{H})\cdot\text{As}(\cdots\text{Cl})\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{SO}_2\text{H}$ (tri-sodium salt). Additive compounds of I and the following substances are described (the numbers in parentheses are the number of mols. of the substance per 1 mol. of I); ethyl chloroformate (1), picric acid (2), perchloric acid (2), methyl iodide (2); with methyl sulphate 4:4'-dimethyldithiolarsenobenzene, +2Me₂SO₄, results. Oxidation of I with chlorine in alcoholic suspension gives probably *p*-sulphophenylarsinic acid (II), whilst with 30% nitric acid II and diphenyl disulphide-4:4'-diarsinic acid are formed. Oxidation with alkaline hydrogen peroxide affords *p*-thiophenylarsinic acid, decomp. above 250°.

The Béchamp reaction with potassium benzenesulphonate gives an impure sulphophenylarsinic acid (unstable chloride decomposing into benzenesulphonyl chloride and arsenic acid).

H. BURTON.

Derivatives of phenarsazine. O. SEIDE and J. GORSKI (Ber., 1929, 62, [B], 2186—2191).—10-Chloro-5:10-dihydrophenarsazine is converted by magnesium methyl iodide into 10-methyl-5:10-dihydrophenarsazine, m. p. 107—108°; 10-ethyl-5:10-dihydrophenarsazine, m. p. 71—72°, 10-phenyl-5:10-dihydrophenarsazine, m. p. 148—149°, and 10- α -naphthyl-5:10-dihydrophenarsazine, m. p. 154—155°, are prepared similarly by use of magnesium and the requisite alkyl or aryl bromide. Chlorine in carbon tetrachloride converts 10-methyl-5:10-dihydrophenarsazine into a perchloride, decomposed when heated with formation of 10-chloro-5:10-dihydrophenarsazine, also obtained similarly from 10-phenyl-5:10-dihydrophenarsazine. When heated in a current of hydrogen chloride at 100—150°, 10-methyl-5:10-dihydrophenarsazine is decomposed into methyl-dichloroarsine and diphenylamine; reaction apparently proceeds without production of intermediate compounds, since the same products result when the compound is heated with an equimolecular amount of hydrogen chloride in chloroform at 100°. 10-Phenyl-5:10-dihydrophenarsazine similarly yields diphenylamine and phenyldichloroarsine. 10-Chloro-5:10-dihydrophenarsazine is converted by hydrogen chloride into arsenic trichloride and diphenylamine.

H. WREN.

Thiazoles. XV. Benzthiazole arsenicals of arspenamine (salvarsan) type. M. T. BOGERT and F. G. HESS (Rec. trav. chim., 1929, 48, 904—911).—2-*o*-Hydroxyphenylbenzthiazole, m. p. 131.7—132.2° (cf. A., 1926, 531), reacts with arsenic acid at 150—160°, forming 2-*o*-hydroxyphenylbenzthiazole-*s*'-arsinic acid (I), m. p. about 315.5° (decomp.; all m. p. except this are corr.), obtained also by the Bart reaction on 2-5'-amino-2'-hydroxyphenylbenzthiazole

(II), m. p. 190—190.5° (diacetyl derivative, m. p. 268—268.5°). Treatment of zinc *o*-aminophenylmercaptide with 5-nitrosalicylaldehyde in boiling acetic acid and decomposition of the product formed with hydrogen sulphide affords 2-5'-nitro-2'-hydroxyphenylbenzthiazole, m. p. 219.1—219.6°, reduced by sodium hyposulphite in sodium hydroxide solution to II. Coupling of benzenediazonium chloride with 2-*o*-hydroxyphenylbenzthiazole and reduction of the resulting dye with sodium hyposulphite also gives II. Nitration of I with nitric (*d* 1.42) and sulphuric acids affords the corresponding 3'(?)-nitro-derivative, m. p. 297.7—298.7°, reduced by stannous chloride and hydrochloric acid in acetic acid solution to 5(?)5'(?)-diamino-4:4'-dihydroxy-3:3'-di-(2-benzthiazolyl)-arsenobenzene dihydrochloride. Alkaline sodium hyposulphite reduction of I gives 4:4'-dihydroxy-3:3'-di-(2-benzthiazolyl)arsenobenzene, m. p. 240.8—241.3°. 2-*op*-Dihydroxyphenylbenzthiazole, m. p. 201—201.5° (diacetate, m. p. 196.1—196.6°), reacts with arsenic acid at 160—170°, yielding the corresponding 5'(?)-arsinic acid, m. p. about 279.9° (decomp.), reduced by stannous chloride and hydrochloric and acetic acids to impure 4:6:4':6'-tetrahydroxy-3:3'-di-(2-benzthiazolyl)arsenobenzene. 2-3':4'-Dihydroxyphenylbenzthiazole (diacetate, m. p. 155.9—156.4°) has m. p. 222.3—222.8°, and is obtained from zinc *o*-aminophenylmercaptide and protocatechualdehyde.

H. BURTON.

Halogenomercuriphenols. J. F. CAIUS and J. H. WADIA (J. Indian Chem. Soc., 1929, 6, 613—616).—Treatment of an alkaline solution of 2:4-diacetoxymmercuriphenol with a saturated solution of the appropriate sodium halide and subsequent acidification with acetic acid affords 2:4-difluoro-, m. p. 197.5—198°; 2:4-dichloro-, decomp. 278°; 2:4-dibromo-, colours at 230°, and 2:4-di-iodo-dimercuriphenol, decomp. 142°. The mixture of *o*- and *p*-acetoxymmercuriphenols obtained during the mercuriation of phenol is treated with the sodium halide and the mixture of halogenomercuriphenols extracted with boiling water to give the *o*-compound and with alcohol to yield the *p*-derivative. The following are described: *o*-fluoro-, m. p. 192.5°; *o*-chloro-, m. p. 146—146.5°; *o*-bromo-, m. p. 121.5—122°; *o*-iodo-, m. p. 106.5°; *p*-fluoro-, m. p. 204°; *p*-chloro-, m. p. 216°; *p*-bromo-, colours at 185° without melting, and *p*-iodomercuriphenol, becomes yellow at 180° without melting.

H. BURTON.

Mercurated terephthalic acid. F. C. WHITMORE and L. L. ISENHOUR (J. Amer. Chem. Soc., 1929, 51, 2785—2787).—When ethyl terephthalate is heated with mercuric acetate and a small amount of acetic acid at 117°, or when terephthalic acid is boiled with a mixture of mercuric and sodium acetates and aqueous acetic acid, anhydro-2-hydroxymercuriterephthalic acid (I) is obtained. Treatment of I with phosphorus pentachloride in chloroform suspension affords the corresponding chloride, converted by the usual methods into *n*-butyl 2-chloromercuriterephthalate (II), m. p. 82—85°, 2-chloromercuriterephthalamide, and 2-chloromercuriterephthalanilide, not melted at 300°. *n*-Butyl 2-chloromercuribenzoate is obtained similarly to II and is hydrolysed more readily than II by boiling 90% alcohol. 2-Bromoterephthalic

acid is obtained when I is treated with a solution of bromine in sodium bromide. H. BURTON.

Mercuration of aurin and attempts to mercurate other triphenylmethane dyes. F. C. WHITMORE and G. J. LEUCK (J. Amer. Chem. Soc., 1929, 51, 2782—2784).—Treatment of aurin with mercuric acetate in a boiling mixture of ethyl acetate and acetic acid affords *acetoxymercuriaurin* (I). With alcohol and a small amount of acetic acid as solvent *di(acetoxymercuri)aurin* results, whilst in alcohol *tri(acetoxymercuri)aurin* (II) is formed. When I is boiled with alcohol, II and aurin are obtained, and prolonged treatment of I or II with sodium chloride and boiling alcohol gives *tri(chloromercuri)aurin*. Pararosaniline is mercurated readily to a *tri(acetoxymercuri)*-derivative. A small amount of a dimercurated product is obtained from the base of malachite-green, but crystal-violet, *N*-phenyl-methyl-violet, and malachite-green are not mercurated.

H. BURTON.

Aromatic tin compounds of higher mol. wt. E. KRAUSE and K. WEINBERG (Ber., 1929, 62, [B], 2235—2241).—4-Bromodiphenyl ether, b. p. 165.5/16 mm., m. p. 18°, d_{4}^{25} (vac.) 1.4225, n_D^{25} 1.60877, prepared from *p*-dibromobenzene, phenol, potassium hydroxide, and copper-bronze, is converted by the successive action of magnesium and tin tetrachloride into *tin tetra-p-phenoxyphenyl*, m. p. 171°. *p*-Chlorobromobenzene is converted analogously into *tin tetra-p-chlorophenyl*, m. p. 199° (also +2C₆H₆), which, when brominated in presence of pyridine at -15°, affords *tin tri-p-chlorophenyl bromide*, m. p. 96—97° after softening at 94°. Treatment of an ethereal solution of the bromide with aqueous potassium hydroxide yields *tin tri-p-chlorophenyl hydroxide*, from which *tin tri-p-chlorophenyl chloride*, m. p. 110—111° after softening at 107°, and *tin tri-p-chlorophenyl iodide*, m. p. 93—95° after softening at 91°, are derived. *Tin tri-p-chlorophenyl fluoride* is best obtained from the bromide in ether-alcohol and aqueous-alcoholic potassium fluoride. The tetra-*p*-chlorophenyl compound and bromine in carbon tetrachloride yield *tin di-p-chlorophenyl dibromide*, m. p. 73° after slight softening, decomp. about 300°. *Hexa-p-chlorophenyldistannane*, m. p. 139°, is obtained from tin tri-*p*-chlorophenyl bromide and sodium in boiling xylene. *Tin tri- α -naphthyl chloride*, m. p. 204—205°, and *tin tri-p-anisyl fluoride*, decomp. 239°, are obtained in attempts to prepare the corresponding tetra-compounds. The following mixed tin aryls are derived from tin triphenyl halides and the requisite magnesium aryl halide; *tin triphenyl p-phenoxyphenyl*, m. p. 161—162° after slight softening; *tin triphenyl p-chlorophenyl*, m. p. 139°; *tin triphenyl p-bromophenyl*, m. p. 224°.

H. WREN.

Crystalline tripeptide from living cells. (Sir) F. G. HOPKINS (Nature, 1929, 124, 445).—A crystalline tripeptide containing glycine, glutamic acid, and cysteine has been isolated from extracts of yeast and red blood corpuscles, the separation being based on the insolubility of the cuprous salt in *N*-sulphuric acid. Hence glutathione, as previously described by the author, is not an individual substance.

A. A. ELDRIDGE.

Detection of pyrrole- and pyridine-ring systems in proteins. N. TROENSEGAARD and H. G. MYGIND (Z. physiol. Chem., 1929, 184, 147—156).—By acetylation of gliadin, hydrogenation of the product with sodium and amyl alcohol, and cold hydrolysis followed by fractionation of the bases, piperidine hydrochloride was isolated. None could be obtained from globin, serum-albumin, and serum-globulin. Casein gave isoamylamine.

J. H. BIRKINSHAW.

Clupein. I. K. FELIX and K. DIRR (Z. physiol. Chem., 1929, 184, 111—131).—Clupein was esterified by methyl alcohol and hydrochloric acid and the product was divided into four fractions by their differing solubility in methyl-alcoholic hydrogen chloride. These four protamine esters differ in composition, optical activity, methoxyl content, and in mol. wt. The clupeins possess esterifiable carboxyl groups, but no free amino-groups. A crystalline substance with characteristic properties was isolated, browning at 220° and decomposing sharply at 242°.

J. H. BIRKINSHAW.

Thymonucleic acid. P. A. LEVENE and E. S. LONDON (J. Biol. Chem., 1929, 83, 793—802).—Hydrolysis of thymonucleic acid with intestinal juice yields *guanine nucleoside*, $[\alpha]_D^{25}$ -36.0° in *N*-sodium hydroxide; *hypoxanthine nucleoside*, no m. p., shrinking at 200°, $[\alpha]_D^{25}$ -21.0° in dilute sodium hydroxide; *thymine nucleoside*, m. p. 185°, $[\alpha]_D^{25}$ +32.5° in *N*-sodium hydroxide; *cytidine nucleoside*, no m. p., shrinking at 190°, $[\alpha]_D^{25}$ +40° in water. The hypoxanthine nucleoside is presumably derived from adenine nucleoside; all the above nucleosides yield, when hydrolysed, the appropriate base and a deoxy-pentose (cf. this vol., 590). The formula of thymonucleic acid thus becomes C₃₉H₅₁O₂₅N₁₅P₄.

C. R. HARRINGTON.

Substituted proteins. Nitration and iodination of globin. H. BAUER and E. STRAUSS (Biochem. Z., 1929, 211, 163—190).—The amount of iodine attached to carbon in iodinated derivatives of ovalbumin, serum-albumin, and serum-globin is stoichiometrically related to their tyrosine contents. The tyrosine takes up two atoms of iodine, not by adsorption. Globin takes up, in addition, two more atoms of iodine which are situated in the histidine portion of the molecule. Nitroglobin, which contains one nitro-group in the tyrosine portion and one in the tryptophan portion of the molecule, can be reduced to aminoglobin. When nitroglobin is iodinated one atom of iodine enters the tyrosine portion and two atoms enter the histidine portion. Part of the iodine of iodoglobin and of idonitroglobin is eliminated by cold sulphurous acid. This part is probably attached to an imino-group. It is deduced from their iodine contents that globin and nitroglobin after iodination in hydrogen carbonate solution contain two imino-groups capable of taking up iodine, whilst nitroglobin after iodination in ammoniacal solution contains three such groups. These groups are the points attacked by pepsin-hydrochloric acid. The changes in solubility in dilute acid that the substituted proteins undergo and the extent to which they are attacked (if at all) by pepsin-hydrochloric acid are

described and compared with the changes the proteins themselves undergo on heating. W. MCCARTNEY.

Micro-determination of carbon in solid substances by oxidation with chromic and sulphuric acids. A. BOIVIN (Compt. rend. Soc. Biol., 1929, 100, 502—504; Chem. Zentr., 1929, i, 2560).—Oxidation of the carbon monoxide formed in Nicloux's method is completed by means of a glowing platinum wire, oxygen originating from the heated mixture.

A. A. ELDRIDGE.

Micro-determination of carbon in precipitates. A. BOIVIN (Compt. rend. Soc. Biol., 1929, 100, 505—507; Chem. Zentr., 1929, i, 2560—2561).—The material is collected on an asbestos plug in a constricted glass tube; the relevant portion is cut off and the determination is completed by Nicloux's method.

A. A. ELDRIDGE.

Elementary organic analysis by Pregl's microchemical method. F. HERNLER (Mikrochem., 1929, Pregl Fest., 140—153).—An account of the author's experience with Pregl's methods; a new form of apparatus for maintaining the lead peroxide employed at a constant temperature during the analysis is described.

H. F. HARWOOD.

Adaptation of Pregl's micro-combustion to a semi-micro-combustion method for determination of carbon and hydrogen. W. M. LAUER and F. J. DOBROVOLNY (Mikrochem., 1929, Pregl Fest., 243—252).—A method based on those of Pregl and Wise for the determination of carbon and hydrogen in organic substances; 20 mg. of material suffice for the analysis, and the weighings may be carried out on an ordinary balance sensitive to 0.05 mg. It is claimed that the technique is more easily acquired than that of the usual macro-combustion method.

H. F. HARWOOD.

Adaptation of Pregl's micro-combustion to a semi-micro-combustion method for determination of nitrogen. W. M. LAUER and C. J. SUNDE (Mikrochem., 1929, Pregl Fest., 235—242).—A method for the determination of nitrogen in organic compounds which is based on Pregl's microchemical method but does not necessitate the use of a microbalance has been devised; 20 mg. of material suffice for the analysis, and the weighings can be carried out on an ordinary balance sensitive to 0.05 mg.

H. F. HARWOOD.

Simultaneous determination of nitrogen and mercury in the microchemical analysis of organic mercury compounds. F. HERNLER (Mikrochem., 1929, Pregl Fest., 154—164).—The front portion of the combustion tube used projects 80—120 mm. beyond the furnace, and during the determination of the nitrogen this part is kept well cooled by being wrapped with wet cloths. When the nitrogen determination is complete, the nitrometer is disconnected, and the combustion tube connected with a weighed glass tube packed with gold wire, into which the mercury is driven by gentle heating. The results are quite satisfactory, but the method requires very careful work.

H. F. HARWOOD

Microanalytical determination of sulphur in organic compounds by a volumetric method. A. FRIEDRICH (Mikrochem., 1929, Pregl Fest., 91—

102).—A combustion of the substance is made by Dennstedt's method, using 4—7 mg. of the compound, the evolved gases being passed through dilute hydrogen peroxide. The resulting solution is evaporated on a water-bath and titrated with *N*/45-sodium hydroxide. A quantity of *N*/45-sulphuric acid equivalent to the alkali used is then added, the solution is evaporated to dryness, and the hydrogen sulphate present is determined by a second titration, this corresponding with the sulphuric acid formed by the combustion. The method yields satisfactory results for substances which contain either nitrogen or halogen in the molecule in addition to sulphur, but has so far not been tested for compounds containing all three of these elements.

H. F. HARWOOD.

Micro-determination of selenium and tellurium in organic compounds. H. D. K. DREW and C. R. PORTER (J.C.S., 1929, 2091—2095).—Accurate methods for the quantitative precipitation and filtration of 3—5 mg. of selenium or tellurium are described. The processes are modifications of the larger-scale gravimetric methods. Halogens can be determined accurately in the presence of tellurium.

J. G. A. GRIFFITHS.

Micro-analytical determination of iodine in organic substances. T. LEPERT (Mikrochem., 1929, Pregl Fest., 266—271).—The following procedure is recommended; 5 mg. of the material are burnt in oxygen according to Pregl's method, and the iodine is absorbed in concentrated sodium hydroxide. The solution is exactly neutralised with 2*N*-sulphuric acid, 3 drops excess of acid are added, and the whole is diluted to 60 c.c.; 2 c.c. of bromine are added, and the excess is expelled by maintaining the solution at the b. p. for 7 min. by a vigorous current of steam. After cooling, 1 g. of potassium iodide is added, and the liberated iodine titrated with 0.01*N*-thiosulphate.

H. F. HARWOOD.

Microchemical determination of iodine [in organic substances]. G. LUNDE, K. CLOSS, and J. BÖE (Mikrochem., 1929, Pregl Fest., 272—292).—The iodine in the material is converted into alkali iodide by treatment with potassium hydroxide and carbonate, ignition being repeated until all organic matter has been destroyed; the addition of a little nitrate is advisable in certain cases. The cold mass is extracted with 96% alcohol, the extract evaporated, and the iodine in the residue determined either colorimetrically or volumetrically. Special precautions must be taken if the original material contains much lime, otherwise the whole of the iodine cannot be extracted by alcohol. In order to determine the iodine present in various forms of combination in an organic substance, the material is extracted with water, and the "lipoid iodine" removed from the acidified solution by extraction with ether. "Albuminoid iodine" can be precipitated by the addition of alcohol or acetone, and the "inorganic iodine" determined by liberation with nitrous acid and extraction with ether, or by precipitation with palladous chloride.

H. F. HARWOOD.

Rapid volumetric determination of formic and acetic acids in presence of each other. P. FUCHS (Z. anal. Chem., 1929, 78, 125—127).—The solution containing the acids is exactly neutralised

with *N*-sodium hydroxide, and boiled to expel any acetaldehyde. Solid sodium acetate and an excess of a saturated solution of mercuric chloride are added, and the liquid is kept just below the b. p. for 15 min., when the following reaction occurs: $\text{HCO}_2\text{Na} + 2\text{HgCl}_2 = \text{NaCl} + \text{Hg}_2\text{Cl}_2 + \text{HCl} + \text{CO}_2$. The cooled solution is filtered and the free acid in the filtrate titrated with *N*-sodium hydroxide. H. F. HARWOOD.

Colorimetric determination of methylglyoxal, dihydroxyacetone, and glyceraldehyde. E. BAER (*Arbeitsphysiol.*, 1928, 1, 130—135; *Chem. Zentr.*, 1929, i, 2087).—Mendel and Goldscheider's method for the determination of lactic acid has been extended to that of the above substances. Proteins and carbohydrates are removed with phosphotungstic acid and calcium hydroxide and copper sulphate, the residual solution then being treated with concentrated sulphuric acid and alcoholic veratraldehyde. The determination of methylglyoxal, dihydroxyacetone, or glyceraldehyde is made colorimetrically, standard and test solutions being compared with a dilute alcoholic solution of carbol-fuchsin containing a drop of orange G solution. The accuracy is 4 mg.-%, 0.02 mg. being determinable. A. A. ELDRIDGE.

Determination of arylamides of aromatic sulphonic acids. K. HELLER and Z. FLEISCHMANN (*J. pr. Chem.*, 1929, [ii], 123, 146—147).—The sulphonylarylamide is dissolved in an excess of 0.1*N*-sodium hydroxide [whereby salt formation occurs, $\text{R}\cdot\text{SO}_2\text{NHR}' + \text{NaOH} \rightarrow \text{R}\cdot\text{SO}(\text{NR})(\text{ONa}) + \text{H}_2\text{O}$] and titrated with 0.1*N*-hydrochloric acid until a faint turbidity appears. The method is accurate to the extent of about 1%. Pyrazolones can also be titrated with sodium hydroxide as above. H. BURTON.

Determination of basic amino-acids in small amounts of protein. H. O. CALVERY (*J. Biol. Chem.*, 1929, 83, 631—648).—The method of Vickery and Leavenworth (*A.*, 1928, 511) has been modified for application to 5 g. of protein, and the modified method applied to caseinogen and edestin. In the latter case the results agree well with those already obtained by the above-mentioned authors. The determinations by actual isolation were satisfactorily checked in the case of histidine by nitrogen determinations and by the methods of Hanke and Koessler (*A.*, 1920, ii, 784) and of Plimmer and Phillips (*A.*, 1924, ii, 576), the technique of the latter method being discussed in detail; in the case of arginine, determinations of the total nitrogen of the arginine fraction were useless, but the method of Van Slyke (*A.*, 1912, ii, 1008) gave results in good agreement with those of isolation. For quantitative precipitation of histidine by mercuric sulphate, the sulphuric acid concentration must be 3—5%.

C. R. HARRINGTON.

Determination of tyrosine and of tryptophan by the method of Tillmans, Hirsch, and Stoppel. H. BAUER and E. STRAUSS (*Biochem. Z.*, 1929, 211, 191—198).—The method (*cf. A.*, 1928, 1278) cannot be used in the case of food-proteins which are insoluble in hot dilute nitric acid or undergo alteration if heated with the acid. If proteins are kept in contact with nitric acid (*d* 1.42) for 18 hrs. at the ordinary temperature and allowance is made for the fact that the tyrosine present may be either mono- or di-nitrated, satisfactory results are obtained. In the case of certain proteins the results must be checked by those obtained by other methods. The modified method cannot be used for iodinated or nitrated globins.

W. MCCARTNEY.

Biochemistry.

Micro-respiration apparatus for simultaneous determination of oxygen and carbon dioxide. J. FRHR. VON LEDEBUR (*Mikrochem.*, 1929, *Pregl Fest.*, 253—265).—An apparatus permitting the simultaneous determination of oxygen and carbon dioxide is described, the former gas being determined by volume and the latter by absorption in 0.012*N*-barium hydroxide and measurement of the change in electrical conductivity of this solution. The accuracy attainable in the case of both gases is 0.5 c.mm. if the temperature be kept constant to 0.05°. The complete absorption of the carbon dioxide requires up to 40 min. even if the apparatus be shaken, hence readings should not be taken more frequently than every half-hour. H. F. HARWOOD.

Role of hæmoglobin in the blood. A. B. HASTINGS (*Coll. Symp. Mon.*, 1928, 6, 139—154).—A discussion. CHEMICAL ABSTRACTS.

Relation between hæmoglobin content and oxygen supply of the organism. F. MAINZER (*Pflüger's Archiv*, 1928, 220, 234—242; *Chem. Zentr.*, 1929, i, 1958).

Blood-cell metabolism. IV. Effect of methylene-blue on metabolism of leucocytes. E. S. G. BARRON. **V. Metabolism of leucocytes.** E. S. G. BARRON and G. A. HARROP, jun. (*J. Biol. Chem.*, 1929, 84, 83—87, 89—100).—IV. Methylene-blue causes increase in the oxygen consumption of leucocytes and increased oxidation of dextrose during glycolysis (decreased formation of lactic acid); the effects are less marked than those previously observed with mammalian erythrocytes (this vol., 460).

V. For the successful observation of the metabolism of the white cells it is necessary to centrifuge for a short time only, to work in low concentration and for short periods, and to avoid cooling and the use of anticoagulants which interfere with respiration. Glycolysis produced by polynuclear lymphocytes is about five times as great as that produced by leucocytes; in their fermentative reactions the leucocytes resemble normal cells and the polynuclear lymphocytes cancer cells. C. R. HARRINGTON.

Development of foetal blood in the cow. I. Volume, dry matter, and corpuscular hæmoglobin content of cow's blood. II. Foetal blood.

D. VON DESEO (Pflüger's Archiv, 1928, 221, 321—326, 327—335; Chem. Zentr., 1929, i, 1956).—Cow's blood contains 197 g. of water per 100 g. of dry substance (86 wt.-% hæmoglobin); during the development of the fœtus the dry matter in the blood rose from 26 to 29 wt.-%. A. A. ELDRIDGE.

Rate of settling of red blood-corpuscles and surface tension. A. PINES and M. JOFFE (Biochem. Z., 1929, 211, 420—425).—There is no relation between the settling rate and the surface tension at the plasma/air boundary. J. H. BIRKINSHAW.

Tryptoporphyrin. G. MONASTERIO (Biochem. Z., 1929, 212, 71—79; cf. A., 1928, 82).—The small amount of iron which remains in tryptoporphyrin prepared by the method of Frankel and Prinz cannot be removed by any of the processes known to succeed in the case of hæmatin. By some of these processes the chief constituent of tryptoporphyrin is attacked and small amounts of a compound having an iron content similar to that of hæmin but without its spectroscopic properties can be isolated. It is concluded that the iron in hæmoglobin and in hæmatin is present in two forms, in one of which the iron is loosely bound, whilst in the other it resists the effects of the processes mentioned.

W. MCCARTNEY.

Determination of fibrinogen by centrifuging. K. SAMSON (Med. Klin., 1928, 4 pp.; Chem. Zentr., 1929, i, 2339).—The fibrinogen is precipitated at 55° in a graduated tube, cooled, and the height of the column of precipitate is read after centrifuging for a definite time. The tubes are graduated by parallel nitrogen determinations.

A. A. ELDRIDGE.

Sulphur content of fibrins from various mammals. Z. ASZÓDI (Biochem. Z., 1929, 212, 158—161).—The sulphur content of fibrin from men, pigs, cattle, horses, and dogs has been determined and compared with that of the globulin from the same animals. Values which varied considerably from species to species and from individual to individual were obtained. In the dog there was usually less, in the horse usually more, sulphur in the fibrin than in the globulin.

W. MCCARTNEY.

Sulphur content of various serum-globulins. Z. ASZÓDI (Biochem. Z., 1929, 212, 102—114; cf. this vol., 206).—The sulphur contents of serum-globulin from men, pigs, cattle, horses, and dogs have been determined. Great individual variations in these contents are found within the same species. Serum-globulin from dogs usually contains more than 1.30% S, but values as high as this are only occasionally found in the other animals. There is no connexion between either the sex or the purity of the breed of a dog and the sulphur content of its serum-globulin.

W. MCCARTNEY.

Behaviour of Congo-red to serum-colloids. Determination of blood by the Congo-red method of Griesbach. L. HEILMEYER (Biochem. Z., 1929, 212, 430—442).—The absorption spectrum of Congo-red in serum solutions is essentially different from that in aqueous solutions due to union with serum-colloids. This forms a source of error in Griesbach's method (Deut. med. Woch., 1921) for determination of blood.

The error is quantitatively ascertained and is dependent on the absolute concentration of the serum-Congo-red solution.

P. W. CLUTTERBUCK.

Determination of proteins in blood-serum. F. SCHNEIDER (Biochem. Z., 1929, 211, 207—212).—The refractometric method of Robertson, the Kjeldahl method, and the gravimetric method for the determination of proteins in blood-serum have been compared. Serum from 51 subjects, some in a mild, others in a chronic, pathological condition, was used. The results of the Kjeldahl and gravimetric methods agreed satisfactorily. Those of the refractometric method were less accurate. Where great accuracy is not required, the refractometric method, which is rapid, may be used. If the limits of error must not exceed ± 0.3 g.-%, one of the other methods should be employed.

W. MCCARTNEY.

Amylase of horse-serum and the variation of its activity as a function of successive bleedings. B. ROUSSEV, Z. GRUZEWSKA, and G. ROUSSEL (Compt. rend., 1929, 189, 501—503).—Sterile serum from the animal was incubated with a sterilised 1.4% starch solution for 24 hrs. at p_H 7.4—7.6. After deproteinisation the sugar was determined by Bertrand's method. Since dextrose was the only sugar obtained at the end of 48 hrs., maltase must be present in the sera. The experimental results indicate a periodicity in the activity of the amylase as a function of the bleedings as well as an individual variation in the amylase activity of different sera.

C. C. N. VASS.

Changes in activity of blood-catalase. A. KULTJUGIN and G. SAVOSTJANOV (Biochem. Z., 1929, 211, 131—143).—The activity of catalase from erythrocytes of the cat in blood solutions decreases when the solutions are kept, at a rate which is much greater during the first 2½ hrs. than in the second and varies according to the animal from which the blood is taken. Rise of temperature also causes reduction of the activity, which is completely lost at 60°. The presence of chlorides or nitrates greatly reduces the activity, but sulphates have little effect. Blood-serum from various animals, blood- and egg-albumin increase the activity as their concentrations increase (up to 1%); soluble starch, gelatin, and dextrin are without influence, although all these colloids retard the loss of activity which occurs in their absence on preserving the solutions. This protecting effect of the colloids (except starch and gelatin) persists when the temperature is raised except in the case of the higher concentrations of the colloids. The influence of chlorides and nitrates is greatly reduced and sometimes suppressed altogether if blood-serum from various animals, blood-albumin, or egg-albumin is present. Starch and gelatin do not affect the influence of these electrolytes.

W. MCCARTNEY.

Action of the bile and bile acids on serum-lipases in the organism. A. BACULO and E. LANTRIA (Riv. Pat. Sper., 1928, 3, 52—59; Chem. Zentr., 1929, i, 2064).—The lipolytic activity of dog-serum is uninfluenced by addition of dog's or ox bile, but the inhibitive action of quinine is no longer observed. Sodium taurocholate appears to be more active than the glycocholate.

A. A. ELDRIDGE.

Fate of acetylcholine in the blood. G. VIALE and J. M. SONCINI (Pflüger's Archiv, 1929, **221**, 594—598; Chem. Zentr., 1929, i, 2199).—The esterase, supposed by Galehr and Plattner to hydrolyse acetylcholine, is not present in the blood. It is not proved that the vagus substance is identical with acetylcholine. A. A. ELDRIDGE.

Chemical modifications of blood following intravenous injection of urea. B. V. FUENTES, J. DUOMARCO, and A. MUNILLA (Rev. asoc. med. Argentina, 1928, **41**, 885—909).—Intravenous injection of urea (1.5—5.0 g. per kg.) into dogs causes an increase in the ratio urea : total-nitrogen (normally 0.5) to 0.9, the total blood-nitrogen exceeding 100 mg. No modification of the blood-uric acid, creatine, or creatinine, or of the calcium, sodium chloride, and inorganic phosphorus metabolism was observed.

CHEMICAL ABSTRACTS.

Micro-determination of creatinine and creatine in blood. E. KOPLOWITZ (Biochem. Z., 1929, **211**, 475—486).—The methods, depending on the colour reaction of creatinine with alkaline sodium picrate solution, permit of the determination of creatinine and creatine in blood-plasma and total blood in 20 c.c. of blood. No difference in creatinine and creatine content was found between arterial and venous blood.

J. H. BIRKINSHAW.

Determination of uric acid in blood. II. J. D. B. H. VAN ASSENRAAD (Pharm. Tijdschr. Ned.-Indie, 1929, **6**, 65—69; Chem. Zentr., 1929, i, 1974).—The uric acid is oxidised to allantoin with potassium ferricyanide in the cold; dextrose is not attacked under these conditions. A mixture of serum (3 c.c.), water (3 c.c.), and 1.65% uranyl acetate solution (3 c.c.) is centrifuged, and 3 c.c. of the clear liquid is treated with 2.5 c.c. of a solution containing 0.329 g. of potassium ferricyanide and 6 g. of sodium carbonate per litre; after at least 5 min. 2 drops of concentrated sulphuric acid are added, the solution is diluted to 20 c.c., and the colour is compared with that of standard solutions of uric acid which have been similarly treated.

A. A. ELDRIDGE.

Determination of cholesterol [in blood]. E. HERZFELD (Schweiz. med. Woch., 1928, **58**, 103—110; Chem. Zentr., 1929, i, 2089—2090).—Serum is treated dropwise with absolute alcohol, boiled, and filtered, the residue being washed first with alcoholic chloroform, and then with chloroform alone. The residue on evaporation of the filtrate is dissolved in warm chloroform. Aliquot portions diluted to varying degrees are tested by Liebermann's reaction. In disease of the liver and in diabetes the blood-cholesterol is high (300—800 mg.-%).

A. A. ELDRIDGE.

Determination of blood-cholesterol. G. FETICH (Klin. Woch., 1929, **8**, 362—363; Chem. Zentr., 1929, i, 2089).—The serum-cholesterol is hydrolysed by Aczel's method, extracted with chloroform, and the extract is subjected to Liebermann and Burchard's reaction, the green colour being compared in an Autenrieth colorimeter.

A. A. ELDRIDGE.

Physico-chemical state of lecithin and cholesteryl esters in blood-serum and -plasma. M. A. MACHEBEUF (Bull. Soc. chim., 1929, [iv], 45,

662—666).—The phosphoaminolipin-protein previously described (this vol., 206, 838) is very resistant to fractionation and is regarded as a compound of lecithin and cholesteryl esters with plasma-proteins. The lipins isolated by treating its solutions with boiling alcohol to coagulate the proteins and then extracting with ether are insoluble in water even in presence of ammonia or serum-albumin, and yield unstable milky aqueous suspensions from which ether extracts the lipins.

R. BRIGHTMAN.

Inorganic constituents of the blood of pupæ of butterflies (*Sphinx pinastri*, *Pieris brassicae*) and changes in the content of these constituents during the pupal stage. L. BRECHER (Biochem. Z., 1929, **211**, 40—64).—In addition to a minute quantity of sodium, the blood of the pupæ of *S. pinastri* contains the following average amounts of inorganic material per 100 c.c.: potassium, 137.8 mg., calcium, 33 mg., magnesium, 56 mg., chlorine, 59.5 mg., phosphorus, 66 mg. (total phosphorus 207 mg.). As regards the potassium, calcium, magnesium, and inorganic phosphorus contents of the blood there is no difference between male and female pupæ. The blood contains an excess of 0.050 g.-equiv. per litre of bases which are presumably combined with organic acids. During the period in which *P. brassicae* is passing through the caterpillar and pupal stages there is an increase in the potassium content, a decrease in the calcium and chlorine contents, and a large decrease in the magnesium content of its blood. The total phosphorus content of the blood first falls, then rises greatly during the same period. W. MCCARTNEY.

Serum-calcium in the negro. C. L. HARRELL (Amer. Rev. Tuberculosis, 1929, **19**, 350—352).—The average normal value was 10.93 mg. per 100 c.c. (0.43 mg. higher than for white individuals); in suspected tuberculosis the value was 9.8 mg.

CHEMICAL ABSTRACTS.

Micro-determination of calcium in serum and plasma. B. GROAK (Biochem. Z., 1929, **212**, 47—52).—The calcium in 0.1 c.c. of serum or plasma is precipitated by ammonium oxalate and the excess of permanganate left after the oxalic acid liberated by sulphuric acid has been oxidised is determined by addition of potassium iodide and titration with thio-sulphate. The accuracy of the method (error $\pm 2.5\%$) is greater than that of the Kramer-Tisdall process.

W. MCCARTNEY.

Composition of bone. VII. Equilibration of serum solutions with calcium hydrogen phosphate. M. J. SHEAR, M. WASHBURN, and B. KRAMER. **VIII. Conductivity titrations of calcium ions.** M. J. SHEAR, B. KRAMER, and L. RESNIKOFF (J. Biol. Chem., 1929, **83**, 697—720, 721—735).—VII. On shaking either distilled water or artificial serum with calcium hydrogen phosphate, equilibrium is attained after 1 hr. The ionic solubility product $[Ca]^{++} \times [HPO_4]^{---}$ is $(3.2 \pm 0.1) \times 10^{-6}$ at the ordinary temperature and $(3.4 \pm 0.1) \times 10^{-6}$ at 38° for artificial serum. Sera in which the product $Ca \times P$ (expressed in mg. per 100 c.c.) is less than 50 (i.e., all rachitic sera) are under-saturated with respect to calcium hydrogen phosphate. The results are discussed in their possible relation to the process of calcification.

VIII. Normal conductivity titration curves were obtained on adding solutions of sodium chloride, sodium acetate, and sodium lactate to one of calcium chloride; abnormal curves were obtained with sodium citrate and calcium chloride, which affords additional evidence for the supposed formation of a slightly ionised soluble calcium citrate complex.

C. R. HARRINGTON.

Simple apparatus for the determination of the alkali reserve of the blood. M. SCHLESINGER (Biochem. Z., 1929, 212, 115—126).—The apparatus consists of a U-shaped tube one arm of which forms the reaction vessel whilst the other (longer) arm, which is a capillary tube, is graduated. By its use the volume of carbon dioxide in 100 c.c. of blood is directly obtained and with the help of the tables given the alkali reserve can be calculated. One c.c. of plasma is used.

W. MCCARTNEY.

Determination of p_H and carbon dioxide in single small sample of blood-serum. A. T. SHOHL (J. Biol. Chem., 1929, 83, 759—763).—A special apparatus is described which permits the determination of the p_H of 0.1—0.2 c.c. of blood-serum or plasma by the method of Hastings and Sendroy (A., 1924, ii, 869) and the subsequent use of the same sample for determination of carbon dioxide by the manometric method of Van Slyke and Neill (A., 1924, ii, 872).

C. R. HARRINGTON.

Measurement of p_H in flowing liquids. K. GOLLWITZER-MEIER and W. STEINHAUSEN (Pflüger's Archiv, 1928, 220, 551—557; Chem. Zentr., 1929, i, 2337).—Measurements on circulating blood are described.

A. A. ELDRIDGE.

Micro-determination of p_H of blood and other biological fluids. A. J. SALLE (J. Biol. Chem., 1929, 83, 765—772).—By means of a special apparatus which enables minimal contact to be obtained between the solution and a platinum electrode previously saturated with hydrogen, equilibrium is reached so rapidly as to obviate the difficulties due to the evolution of carbon dioxide and the liberation of oxygen from oxyhaemoglobin. It thus becomes possible to make rapid electrometric determinations of the p_H of small amounts of blood, the results obtained agreeing well with those of colorimetric determinations.

C. R. HARRINGTON.

Acid-base equilibrium of the blood. I. Normal variation in p_H and carbon dioxide content of blood-serum. I. P. EARLE and G. E. CULLEN. II. Changes in acid-base equilibrium during the day. G. E. CULLEN and I. P. EARLE (J. Biol. Chem., 1929, 83, 539—544, 545—559).—I. In normal individuals the p_H of the blood-serum lies usually between 7.4 and 7.5, not between 7.3 and 7.4 as previously stated (A., 1922, ii, 672).

II. There is a general tendency for an increase of 0.01—0.07 in the p_H of normal human blood-serum from early morning to late evening. Fluctuations due to digestion are irregular, and moderate exercise has little effect.

C. R. HARRINGTON.

Determination of carbon in filtrates of precipitated blood. J. ROCHE (Compt. rend. Soc. Biol., 1929, 100, 278—280; Chem. Zentr., 1929, i, 1844).—

The filtrate after treatment of the blood with phosphotungstic acid is evaporated with sodium sulphate at the ordinary temperature over sulphuric acid, the residue being transferred to Nicloux's apparatus for the determination. The results are accurate to 1—2%.

A. A. ELDRIDGE.

Content of reducing substances in the blood of some invertebrates. B. KISCH (Biochem. Z., 1929, 211, 292—294).—Only traces of reducing substances were found in the blood of *Aplysia*, but 0.01—0.02 mg. per 100 c.c. was present in the blood of *Sipunculus*, *Carcinus*, and *Eriphia*.

J. H. BIRKINSHAW.

Blood-sugar of *Selachii*. B. KISCH (Biochem. Z., 1929, 211, 276—291).—Reducing substances in the blood of *Scyllium* and *Torpedo* amount to 20—40 mg. per 100 c.c. The amount is independent of the fulness of the stomach and intestines. Extirpation of the liver leads to a lowering of the blood-sugar to 5—10 mg. per 100 c.c. after several days. Asphyxia causes hyperglycaemia, noticeable at 15° only after 1 hr., but earlier at higher temperatures. Water rich in oxygen causes a still further increase in the blood-sugar, which returns to normal only after several days. The increase in sugar is derived from the liver, since it does not arise when the sugar is removed. Adrenaline causes marked asphyxia in *Scyllium*.

J. H. BIRKINSHAW.

Mitogenetic radiation of blood. A. POTOZKY and I. ZOGLINE (Biochem. Z., 1929, 211, 352—361; cf. Gurwitsch and Gurwitsch, A., 1928, 914).—The mitogenetic sources of radiation of mammalian blood (in contrast to frog's blood) are of two kinds, namely, glycolysis and oxidation of polypeptides. The failure of the mitogenetic radiation of blood taken during fasting is due to an inhibition of these two enzymic processes.

J. H. BIRKINSHAW.

Blood coagulation. XX. Inhibition of blood coagulation by heparin. XXI. Blood coagulation and the fluorine content of the blood. B. STUBER and K. LANG (Biochem. Z., 1929, 212, 16—21, 96—101).—XX. By checking glycolysis heparin retards the coagulation of blood, very greatly *in vitro*, less so *in vivo*. Intravenously injected it has no effect on the sodium, calcium, chlorine, or albumin content of the blood.

XXI. In Kiel the blood of residents contains fluorine and it coagulates more slowly than the blood of residents of Freiburg-im-Breisgau, which contains none. Kiel drinking water contains six times as much fluorine as does Freiburg drinking water, and fluorine is found in Kiel milk but not in Freiburg milk. Since, also, the blood of haemophiles and of animals such as geese (of which the blood coagulates very slowly) has a high fluorine content, it is concluded that increase in the time of coagulation is due to the presence of fluorine.

W. MCCARTNEY.

Effect of alkali on oleate and taurocholate haemolysis. K. C. SEN, A. C. ROY, and N. N. MITRA (J. Indian Chem. Soc., 1929, 6, 489—494).—The haemolysis of sheep's erythrocytes by mixtures of potassium oleate and sodium hydroxide varies considerably with experimental conditions. When the oleate concentration is comparatively small the

haemolytic action of the oleate-alkali mixture may exceed that of the pure oleate. With medium concentrations of oleate the action of the mixture is invariably lower than that of the pure oleate, whilst with high concentrations of oleate the reverse action takes place. The time-dilution curves often show abnormalities. The time interval after which the alkali is added to the oleate-corpuscle mixture is important; the results obtained are similar to those using normal serum (this vol., 951). It is suggested that the acceleration of haemolysis by normal serum is due to its alkali content. A retardation or acceleration of taurocholate haemolysis is observed, using small amounts of sodium hydroxide, depending on whether the alkali is added to the corpuscles before or after the haemolyser.

H. BURTON.

Cold-haemagglutinin. N. YU (Acta Med. Keijo, 1928, 11, 23—34).—Cold-agglutinin is the haemagglutinin which reacts strongly at 0° but is not active at 37°. Rabbit serum contains the auto-cold-haemagglutinin, but horse serum contains little. The substance is not injured by heating for 30 min. at 60°, is slightly affected at 65°, and is destroyed at 70°.

CHEMICAL ABSTRACTS.

Content of complement compounds in dialysed guinea-pig serum. Content of complement compounds in the fractions obtained by precipitation with ammonium sulphate. Content of complement compounds in guinea-pig serum fractionated by passing carbon dioxide through it. Action of alcohol on the complement of guinea-pig serum. H. TOKUNAGA (Acta Schol. Med. Univ. Imp. Kyoto, 1928, 11, 273—286, 287—296, 297—312, 313—317).

CHEMICAL ABSTRACTS.

Separation of cystine from histidine. Basic amino-acids of human hair. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1929, 83, 523—534).—Cystine is more or less completely precipitated by the metallic precipitants (particularly silver) customarily employed for the isolation of histidine and must therefore be expected to occur as an impurity in preparations of the latter. Cystine, however, whether partly racemised or not, forms an insoluble copper compound, and can be conveniently separated from histidine by boiling the solution with cupric hydroxide. Human hair was hydrolysed with hydrochloric acid, the greater part of the cystine was removed by direct crystallisation, and the basic amino-acids were then determined by the author's method, utilising the above-mentioned copper compound to remove the rest of the cystine; there was then found histidine 0.5%, arginine 8.0%, and lysine 2.5%; the cystine amounted to 16.5%.

C. R. HAREINGTON.

Composition of flesh of the Italian buffalo. C. COLELLA and M. NAPOLI (Arch. Sci. biol., 1928, 13, 235—240; Chem. Zentr., 1929, i, 2197).—The following values are recorded: water 75.96, dry residue 24.04, ash 1.15, total nitrogen 3.49, fatty acids 1.11, total phosphorus 0.186%.

A. A. ELDRIDGE.

Occurrence of anserine and carnosine in reptiles and birds. F. A. HOPPE-SEYLER, W. LINNEWER, and F. LINNEWER (Z. physiol. Chem., 1929, 184, 276—280).—Varying amounts of anserine

(this vol., 944) have been isolated by the method previously described (*loc. cit.*) from the muscle-tissue of the hen, turkey, pigeon, crow, and crocodile. Carnosine is probably not present in the muscle of the goose and the above birds, but it has been isolated from the boa constrictor (anserine not present) and the crocodile. Anserine nitrate has m. p. 220—222° (*cf. loc. cit.*).

H. BURTON.

Generative glands. I. The substance $C_6H_{13}O_5N_6Me_3$ in testes. S. FRANKEL and G. MONASTERIO (Biochem. Z., 1929, 212, 61—65).—Fresh tissue from testes is boiled with water containing acetic acid, and the extract is concentrated in a vacuum and mixed with warm alcohol. After precipitation of gelatinous material the solution is again evaporated in a vacuum until crystallisation begins. The substance thus obtained has the formula $C_6H_{13}O_5N_6Me_3$, the methyl groups being attached to nitrogen. Recrystallised from water, in which it is easily soluble, it has m. p. 279°, and $[\alpha]_D^{25} +173.91^\circ$. It is a neutral substance sparingly soluble in alcohol. It does not reduce ammoniacal silver solutions and it fails to react with bromine or with many other commonly used reagents. Fermentations by yeast are not accelerated by the substance. W. MCCARTNEY.

Composition of bone skeletal substance. R. KLEMENT (Z. physiol. Chem., 1929, 184, 132—142).—The inorganic portion of bone consists principally of basic calcium phosphate, $3Ca(PO_4)_2 \cdot Ca(OH)_2$, with smaller amounts of calcium carbonate and alkali hydrogen carbonate.

J. H. BIRKINSHAW.

Cholesterol content of mucous membrane of human large intestine. M. BÜRGER and H. D. OETER (Z. physiol. Chem., 1929, 184, 257—260; *cf. this vol.*, 839).—The cholesterol content of the mucous membrane is approximately 1.8% and is about three times as great as the amount in the total intestinal wall (*cf. loc. cit.*). Sterol esters are not detectable.

H. BURTON.

Determination of cholesterol in gall-stones. M. ALIAZZI-MANCINI (Biochem. Terap. sperim., 1929, 16, 9—13; Chem. Zentr., 1929, i, 1974).—The cholesterol is extracted with ether and purified, or is acetylated, and the acid liberated by hydrolysis is titrated.

A. A. ELDRIDGE.

Unsaponifiable substance. II. Unsaponifiable substance, cholesterol, and fatty acid in incubated eggs. E. IGARASHI (Sei-i-kwai Med. J., 1929, 48, No. 1, 19—32).—Fertilised eggs of a particular hen contain large quantities of unsaponifiable matter and more cholesterol than unfertilised eggs, in which the two quantities are nearly equal. The amino-acid contents are similar.

CHEMICAL ABSTRACTS.

Arachidonic acid in lipins of thyroid, adrenal, and spleen. J. B. BROWN (J. Biol. Chem., 1929, 83, 777—782).—The fatty acids obtained by hydrolysis of the lipins from thyroid, adrenal, and spleen were converted into their methyl esters and the latter were brominated. The amount of arachidonic acid, calculated from the weight of ether-insoluble bromide, was 0.4, 5.5, and 4.0% of the total fatty acids, respectively. Arachidonic acid is the only highly

unsaturated acid to occur in the lipins of the above-mentioned organs. C. R. HARINGTON.

A new highly unsaturated fatty acid in the lipins of the brain. J. B. BROWN (J. Biol. Chem., 1929, 83, 783—791).—Lipin from ox brain was hydrolysed and the fatty acid fraction esterified with methyl alcohol; 10% of the original material was recovered as cholesterol, and 24% as methyl esters which could be distilled from 185° to 280°. Determination of the ether-insoluble bromides indicated 11.5—18.4% of highly unsaturated acids. Reduction of the ether-insoluble bromides yielded a mixture of methyl arachidonate and (possibly) methyl tetracosapentenoate. C. R. HARINGTON.

Cerebroside [content of brain]. P. KIMMELSTIEL (Biochem. Z., 1929, 212, 359—362).—During the first 2 hrs. after removal of brain from an animal, decomposition of cerebroside occurs with liberation of reducing substances, and this must be taken into account in determining the cerebroside content in terms of the galactose liberated on hydrolysis.

P. W. CLUTTERBUCK.

Influence of formalin fixation on lipins of central nervous system. A. WEIL (J. Biol. Chem., 1929, 83, 601—609).—Preservation of central nervous tissue in a 4% aqueous solution of formaldehyde results in a progressive hydrolysis of the phosphatides, the phosphoric acid passing into the fixing fluid; the cerebrosidés are scarcely affected, so that formalin-fixed central nervous tissue contains an abnormally high proportion of the latter compounds; this fact accounts for certain histological phenomena hitherto unexplained. C. R. HARINGTON.

Effect of formalin fixation of organs on the extractability of the lipins. P. KIMMELSTIEL (Z. physiol. Chem., 1929, 184, 143—146; cf. Mladenović and Lieb, this vol., 591).—In alcohol-ether extracts of organs fixed with formalin, low values for phosphatides but normal values for cholesterol and cerebrosidés are obtained. J. H. BIRKINSHAW.

Protein-sulphuric acid ester in the liver. S. FRANKEL and G. MONASTERIO (Biochem. Z., 1929, 211, 264—269).—In an investigation of the substances in ox liver of value in pernicious anaemia a peptide-sulphuric acid ester was isolated. It contains the tyrosine group and a carbohydrate group, but no tryptophan, phenylalanine, or cystine.

J. H. BIRKINSHAW.

Protein-sulphuric acid ester from the anterior lobe of the pituitary. S. FRANKEL and G. MONASTERIO (Biochem. Z., 1929, 211, 259—263).—A substance resembling a globulin isolated from the anterior lobe of the pituitary was found to be the sulphuric acid ester of a protein. It contains tyrosine and phenylalanine groups, but no tryptophan or cystine. It promotes the clotting of blood.

J. H. BIRKINSHAW.

Mol. wt. of myoprotein, determined by Du Noüy's surface-tension method. L. DE CARO (Atti R. Accad. Lincei, 1929, [vi], 9, 1025—1029).—Before reaching the corresponding dynamic value, the surface tension of very faintly alkaline aqueous solutions of the myoprotein of the dog exhibits three

characteristic minima at the dilutions 1:37,000, 1:55,000, and 1:80,000. If these correspond with the formation of unimolecular layers of different orientations, the dimensions of the molecular parallel-epiped are 225.6, 151.7, and 104.3 Å., respectively, the volume of the molecule is $3,569,513 \times 10^{-24}$ c.c., its mass $2,644,084 \times 10^{-24}$ g., and the mol. wt. 16×10^5 ; for the anhydrous myoprotein this value for the mol. wt. is probably much too high. The proportion of myoprotein in muscle is sufficient to cover approximately the whole surface of the myofibrils with a unimolecular layer. T. H. POPE.

Occurrence of preformed methylguanidine in muscle tissue. S. A. KOMAROV (Biochem. Z., 1929, 211, 326—351).—Since in the isolation of methylguanidine by the silver-baryta and the mercuric acetate methods the possibility of oxidation of creatine to methylguanidine is not excluded, the presence of the base in muscle was shown by isolation as the pure picrate by way of the picrolonate from the phosphotungstate fraction of ox-muscle extract. The best yield of the base was 0.06 g. per kg. of fresh muscle. This represents only a portion of that actually present. J. H. BIRKINSHAW.

Occurrence of muscle-adenylic acid and hexosemonophosphoric acid (lactacidogen) in the heart. K. POHLE (Z. physiol. Chem., 1929, 184, 261—264).—Muscle-adenylic acid (Embdén and Schmidt, this vol., 591) has been isolated in 0.02% yield from the muscle-tissue of ox heart by the method of Embden and Zimmermann (A., 1927, 749). The hexosemonophosphoric acid present has a smaller rotatory power ($[\alpha]_D^{25} +19.77^\circ$) than that isolated from rabbit muscle (Embdén and Zimmermann, *loc. cit.*). H. BURTON.

Distribution of argininephosphoric acid in the musculature of invertebrates. O. MEYERHOF (Arch. Sci. biol., 1928, 12, 536—548; Chem. Zentr., 1929, i, 2203).—The argininephosphoric acid, which is present in the musculature of various invertebrates, is decomposed by muscular activity; its distribution in the invertebrates examined is recorded.

A. A. ELDRIDGE.

Sodium, potassium, calcium, and magnesium in muscle fluid and its ultra-filtrate. G. QUAGLIARIELLO (Atti R. Accad. Lincei, 1929, [vi], 9, 1029—1030).—None of the sodium, about one third of the potassium, and about two fifths of the calcium and magnesium of the muscle fluid of the dog are present in a form incapable of ultra-filtration. T. H. POPE.

Lipolytic action of saliva. B. KOLDAJEV and PRKUL (Biochem. Z., 1929, 212, 53—60).—Saliva from fistulæ in the parotid and submaxillary glands of dogs has a distinct lipolytic effect on tri- and mono-butylin and on olive oil, that from the parotid gland having a more powerful effect than that from the submaxillary. The lipolytic action is independent of the kind of food consumed and of the amount of amylolytic enzyme in the saliva, is most vigorous at p_H 7.6—7.8, and is destroyed when the saliva is boiled. Saliva from fistulæ of the parotid glands of dogs to which dilute hydrochloric acid has been administered does not hydrolyse fats. W. MCCARTNEY.

Theories of hydrochloric acid formation in the stomach. F. HOLLANDER (J. Amer. Inst. Homœopathy, 1929, 22, 311—321).—The gastric juice of an accessory stomach (Pavlov pouch) in dogs had p_H 0.90 ± 0.01 (0.55% HCl); identical values for free hydrochloric acid and total acidity were obtained. Neutral chlorides were absent. Hydrolysis of sodium chloride occurred when similar isotonic solutions were separated by the skin of a recently killed frog. The results are discussed from the physiological point of view.

CHEMICAL ABSTRACTS.

Composition of "histamine-gastric juice." L. GRIMBERT and P. FLEURY (Compt. rend. Soc. Biol., 1929, 100, 312—314; Chem. Zentr., 1929, i, 2203).—After administration of histamine the gastric juice contains an abnormal amount of protein, the average nitrogen content being 14.4%.

A. A. ELDRIDGE.

Determination of fat-splitting [activity] in duodenal juice. A. SCHMIDT-OTT and K. H. STAUDER (Deut. Arch. klin. Med., 1929, 163, 156—160; Chem. Zentr., 1929, i, 2453—2454).—The lipase value of fasting duodenal juice is practically constant (by Willstätter's method, 0.64 unit); in non-pathological cases the value is greater during the digestive process than during fasting. Bile has an activating effect. In pathological conditions the results are variable.

A. A. ELDRIDGE.

Determination of urinary sugar with fermentation tubes. H. MELCHER (Apoth.-Ztg., 1929, 44, 305; Chem. Zentr., 1929, i, 1974).—The mercury (5 g.) and yeast (0.3 g.) used with Lohnstein's tube are accurately weighed, urine containing more than 1% of sugar is diluted with normal urine, and fermentation is allowed to proceed for 9—10 hrs. at 37° (cf. Will, Apoth.-Ztg., 1929, 44, 56).

A. A. ELDRIDGE.

Urine adialysate. H. PRIBRAM (Biochem. Z., 1929, 211, 412—419).—Intravenous injection of the non-dialysable portion of human urine into rabbits produced miosis and a state of sleep.

J. H. BIRKINSHAW.

Nitrification of urine treated with clay and the loss of free nitrogen which it undergoes. W. GRODZINSKA (Bull. Acad. Polonaise, 1928, B, 251—299).—Urine which has been treated with clay, either by being filtered several times through it or by keeping in contact with it, allows the growth of nitrifying bacteria, with consequent nitrification of part of the nitrogen it contains, at higher concentrations than does untreated urine, which at 10% concentration exhibits an antiseptic action. The degree of nitrification depends on the concentration of the urine. Cow's urine whether treated with clay or not readily gives up part of its nitrogen, this process being independent of nitrification.

W. O. KERMACK.

Influence of feeding on certain acids in the faeces of infants. I. Comparison of effects of human and modified cow's milk on the excretion of volatile acids. J. R. GERSTLEY, C. C. WANG, R. E. BOYDEN, and A. A. WOOD (Amer. J. Dis. Children, 1928, 35, 580—589).—The total titratable acidity and volatile acid content of the faeces remain

constant during feeding with human milk, but wide variations follow the ingestion of cow's milk mixtures.

CHEMICAL ABSTRACTS.

Amino-acid content of the blood in health and disease. E. G. SCHMIDT (Arch. Int. Med., 1929, 44, 351—361).—The amino-acid content of the blood determined by Folin's colorimetric method employing sodium 3-naphthaquinone-4-sulphonate does not alter significantly from the normal in patients suffering from a considerable variety of diseases, including renal diseases, with the exception of leucæmia and acute yellow atrophy, in which cases it is considerably increased. It is also concluded from the literature that a rise in amino-acid content also takes place in polycythæmia vera, and in poisoning from hydrazine sulphate, "synthalin," chloroform, and phosphorus.

W. O. KERMACK.

Cancer and blood-lactic acid. E. HAINZ (Klin. Woch., 1929, 8, 546; Chem. Zentr., 1929, i, 2555).—In a case of cancer of the lower lip (male) the blood-lactic acid value was 17.5 mg. per 100 c.c., the normal value being 19 mg. per 100 c.c.

A. A. ELDRIDGE.

Lactic acid formation in tissue culture. F. DEMUTH and R. MEIER (Biochem. Z., 1929, 212, 399—418).—Hen fibroblasts (of cartilage and heart) and rat fibroblasts form considerably less lactic acid in proportion to their increase in growth than rat sarcoma and mouse carcinoma. In hen fibroblasts the quotient lactic acid (mg.)/size of culture (mm.²) is dependent on the velocity of growth and on the duration of the experiment. The more quickly a culture attains a given size, the smaller is the quotient. With equal velocity of growth the quotient increases with the duration of the experiment. With slowly growing fibroblasts and with rat sarcoma and mouse carcinoma the quantity of lactic acid is dependent on the size of the culture.

P. W. CLUTTERBUCK.

Mitogenetic behaviour of blood from carcinomatous animals. L. GURWITSCH and S. SALKIND (Biochem. Z., 1929, 211, 362—372).—The blood of carcinomatous mice and men is found to lack mitogenetic power. In the case of mice this phenomenon belongs to the early symptoms of carcinoma. The enzymic processes on which the mitogenetic radiation depends are inhibited in carcinomatous blood.

J. H. BIRKINSHAW.

Colloidal lead in cancer treatment. R. K. NEWMAN (J. Cancer Res. Comm. Univ. Sydney, 1929, 1, 106—113).—A review. Blair Bell's method of preparing solutions of colloidal lead in the presence of gelatin and calcium chloride is considered the most satisfactory, and Wyard's failure to obtain results is attributed to the fact that his preparation was not truly colloidal. The effectiveness of a colloidal lead preparation appears to lie in its ability to initiate tumour regression. The only other preparation which has been successfully used is the colloidal lead orthophosphate of Ullman.

P. G. MARSHALL.

Halibut tumour oil. E. D. KAMM (Rept. Lanes. Sea-Fish. Lab., 1928, 125—127).—The oil separated from a lipoma found in the body-cavity of a halibut (*Hippoglossus vulgaris*) was mobile and of a pale yellow colour. It had n_D^{20} 1.4750, iodine value

171.5, saponification equivalent 312.3, unsaponifiable material 0.4%, in which was a slight trace of sterol(s) precipitable by digitonin, but no squalene. An approximate analysis of the fatty acids (methyl ester fractionation) gave: saturated acids, C_{14} 0.13%, C_{16} 9.81%, C_{18} 5.2%; unsaturated acids, C_{16} , C_{18} , C_{20} , C_{22} (with respective average unsaturations of $-2H$, $-2.5H$, $-3.2H$, $-10H$), 5.09, 42.09, 25.93, and 10.71%, respectively. No trace of vitamin-A was found, and negative results were obtained with antimony and arsenic chloride colour tests. Small absorption bands were shown at 2705 and 2775 Å. and an inflexion at λ 2896 Å., indicating probably the presence of a small amount of ergosterol.

E. LEWKOWITSCH.

Gymnema sylvestre in diabetes mellitus. R. N. CHOPRA, J. P. BOSE, and N. R. CHATTERJEE (Indian J. Med. Res., 1928, 16, 115—124).—Gymnemic acid, or an extract of the leaves of *G. sylvestre* (which contain a substance which hydrolyses sucrose, and an oxidase-like substance which acts on dextrose), when administered subcutaneously to rabbits, does not affect the blood-sugar. CHEMICAL ABSTRACTS.

Effect of uncooked starches on the blood-sugar of normal and of diabetic subjects. II. S. M. ROSENTHAL and E. E. ZIEGLER (Arch. Int. Med., 1929, 44, 344—350).—Uncooked starch may be administered in considerable quantities (50—75 g.) to normal or diabetic persons without appreciably increasing the blood-sugar. In the majority of cases, normal and diabetics, a slight fall in blood-sugar occurs within 1 hr. after administration of the starch.

W. O. KERMACK.

Failure of a diabetic patient to utilise dried artichoke powder. L. E. WESTCOTT and E. C. WISE (Arch. Int. Med., 1929, 44, 362—367).—The carbohydrate tolerance of the patient was not increased by the administration of dried powdered artichoke; it appears therefore that this powder has no advantage over starch as a diabetic food.

W. O. KERMACK.

Effect of liver on the blood-sugar. H. BLOTNER and W. P. MURPHY (J. Amer. Med. Assoc., 1929, 92, 1332—1336).—Liver fractions effective in the treatment of pernicious anaemia do not affect the blood-sugar, whilst ineffective fractions behave similarly. Liver treatment in diabetes lowers the blood-sugar.

CHEMICAL ABSTRACTS.

Pathological fat metabolism. II. Conditions in which colloidal silver restrains phosphorus fatty degeneration. C. CIACCO and G. TRIMARCHI (Boll. Soc. Ital. Biol. sper., 1928, 3, 106—108; Chem. Zentr., 1929, i, 2202).

Respiratory metabolism in infancy and childhood. VIII. Respiratory exchange in marasmus: basal metabolism. S. Z. LEVINE, J. R. WILSON, and G. GOTTSCHALL (Amer. J. Dis. Children, 1928, 35, 615—629).

CHEMICAL ABSTRACTS.

Millon reaction of urine in mental diseases. H. LIEB and E. SCHADENDORFF (Z. physiol. Chem., 1929, 184, 108—110; cf. Scheimer, this vol., 465).—The crystalline substance from the urine of patients suffering from mental diseases isolated according to

Scheimer's method is sodium acetate. The Millon reaction is due to impurity. J. H. BIRKINSHAW.

Cerebrospinal fluid in myxoedema. W. O. THOMPSON, P. K. THOMPSON, E. SILVEUS, and M. E. DAILEY (Arch. Int. Med., 1929, 44, 368—373).—In myxoedema the protein content of cerebrospinal fluid is high and is reduced after administration of thyroid. The ratio of chloride in the fluid to that in plasma is decreased by administration of thyroid to myxoedematous patients.

W. O. KERMACK.

Effect of prolonged ultra-violet irradiation in experimental rickets. P. SCHULTZER (Biochem. Z., 1929, 211, 445—453).—Young rats fed on a rachitic diet for 23 weeks did not develop rickets when irradiated with ultra-violet light, although there was some osteoporosis. The treated rats grew better than the control animals.

J. H. BIRKINSHAW.

Calcium and magnesium metabolism in rickets. W. SCHULER (Monatsschr. Kinderheilk., 1928, 36, 25—41; Chem. Zentr., 1929, i, 2074).—In a 14 months old child recovering from rickets the average calcium retention was 0.523 g. CaO and the magnesium retention 0.229 g. MgO.

A. A. ELDRIDGE.

Effect of parenterally administered organic and inorganic phosphates in rickets. W. HEYMANN (Z. Kinderheilk., 1928, 45, 232—241; Chem. Zentr., 1929, i, 2074).—Of the phosphorus administered parenterally as sodium glycerophosphate, 50% is excreted as inorganic phosphate in the urine of normal infants, whereas up to 100% may be so excreted by rachitic infants. In neither case is disodium hydrogen phosphate retained.

A. A. ELDRIDGE.

Disturbance of phosphate metabolism in rickets. II. Excretion of endogenous phosphate. III. Blood-phosphate curves of rachitic and non-rachitic infants after parenteral administration of organic and inorganic phosphate. W. HEYMANN (Z. Kinderheilk., 1928, 46, 575—583, 584—587; Chem. Zentr., 1929, i, 2074).—The inorganic phosphate content of body fluids is diminished in rickets, whilst the excretion of endogenous phosphorus in the urine is twice as great as normally. Increased hydrolysis of organic phosphates occurs in rickets. The blood-phosphate curve is abnormally flat in rickets; organic phosphate and disodium hydrogen phosphate gave similar results.

A. A. ELDRIDGE.

Proteins in blood-serum and in pathological serous fluids. C. ACHARD and A. ARCAND (Compt. rend., 1929, 189, 510—512).—Blood-serum contains more albumin, globulin, and myxoprotein than does the plasma of pathological serous fluids. It is concluded that the proteins of serous fluids are derived chiefly, although not exclusively, from the blood-serum.

A. A. GOLDBERG.

Analysis of a preputial stone. G. SOIKA (Arch. Pharm., 1929, 267, 465—467).—The stone, which weighed 10.47 g., consisted of a hard core and a softer shell. The chief constituents were calcium and magnesium urates and calcium, magnesium, and magnesium ammonium phosphates. S. COFFEY.

Calcium content of muscular tissue during parathyroid tetany. H. H. DIXON, H. A. DAVENPORT, and S. W. RAWSON (J. Biol. Chem., 1929, **83**, 737—739).—No difference was observed between the calcium content of the striated muscle of normal and of parathyroidectomised dogs. C. R. HARRINGTON.

Muscle-phosphorus. III. Distribution of acid-soluble phosphorus compounds during parathyroid tetany. H. A. DAVENPORT, H. H. DIXON, and S. W. RAWSON (J. Biol. Chem., 1929, **83**, 741—746).—No change was observed in the content or distribution of acid-soluble phosphorus in the striated muscle of dogs as the result of parathyroid-ectomy. C. R. HARRINGTON.

Correlation of calcium metabolism, parathyroid function, and chronic pulmonary tuberculosis. II. P. ELLMAN (Tubercle, 1929, **10**, 257—266).—In pulmonary tuberculosis the serum-calcium varies within normal limits. Calcium retention is promoted by the administration of calcium or parathyroid extract over long periods.

CHEMICAL ABSTRACTS.

Course and duration of experimental uræmia and salt content of the brain cortex. E. KERPEL-FRONIUS and F. LEOVEY (Arch. exp. Path. Pharm., 1929, **144**, 372—380; cf. this vol., 345).—In experimental uræmia of rabbits brought about by ligation of the ureters, the sodium chloride in the grey substance of the brain is increased by 16.8% and in the white substance by 12.7%. The corresponding figures for residual nitrogen are 142% and 93%, respectively. Ingestion of sodium chloride or of carbamide accelerates death, but does not otherwise essentially alter the findings. W. O. KERMACK.

Colloidal gold for use in Lange's reaction. Use of electro-dialysed water in preparation of gold sols. R. WERNICKE and F. MODERN (Anal. Assoc. Quím. Argentina, 1928, **16**, 247—256).—In order to prepare gold sols for use in Lange's reaction (with cerebrospinal fluid), distilled water electro-dialysed through parchment paper is employed with good results. Collodion membranes cannot be used. If dextrose is used as the reducing agent and the boiling of the alkaline solution is prolonged before addition of the gold salt, the sol obtained is less sensitive in Lange's reaction, but more sensitive to the addition of salts. R. K. CALLOW.

Ratio of urea-nitrogen to non-protein-nitrogen in the blood in normal pregnancy. W. DENIS, E. L. KING, and F. BRIGGS (Amer. J. Obstet. Gyn., 1929, **17**, 386—391).—In normal pregnancy there is usually a slight decrease in the non-protein-nitrogen (*a*) and a large decrease in the urea-nitrogen (*b*) of the blood. During pregnancy the ratio *b*:*a* diminishes, whilst after parturition it increases.

CHEMICAL ABSTRACTS.

Effect of age on the rate of dying of skeletal muscles. C. F. FAILEY and G. VAN WAGENEN (Z. physiol. Chem., 1929, **184**, 209—218).—The rate at which the power of synthesising hexosediphosphoric acid is lost by the muscle of the rat and calf on keeping depends on the animal's age, being greater the younger is the animal. The rate falls more quickly at 18° than at 0°. J. H. BIRKINSHAW.

Combination of carbon dioxide with muscle; its heat of neutralisation and its dissociation curve. G. STELLA (J. Physiol., 1929, **58**, 49—66).—The neutralisation of 1 mol. of carbonic acid in resting or fatigued muscle gives rise to 9400 g.-cal., 75% of which must be due to neutralisation of muscle-protein and 25% to inorganic buffers. The carbon dioxide dissociation curves of frog's muscle indicate that the interior of muscle is more acid than blood at the same pressure of carbon dioxide. Between *p_H* 7 and 8, the hydrogen-ion concentration of muscle is proportional to pressure of carbon dioxide.

E. BOYLAND.

Is there a definite relationship between lactic acid- and ammonia-formation in muscle contraction? M. LEHNARTZ (Z. physiol. Chem., 1929, **184**, 183—195).—The ammonia formed by isotonic, auxotonic, or isometric stimulation of frog's gastrocnemius depends on the interval between successive stimuli. For 100 stimuli at 4 sec. intervals no ammonia is formed; the amount is considerable with 1 sec. intervals. The lactic acid/ammonia ratio varies from 9—22 with 1 sec. intervals to infinity at the longer intervals. J. H. BIRKINSHAW.

Elimination of lactic acid in athletics. I. SNAPPER and A. GRÜNBAUM (Deut. med. Woch., 1929, **55**, 181; Chem. Zentr., 1929, i, 1710).—In athletics lactic acid (1—2 g.) is almost always eliminated. In short exercise it is excreted in the urine, whilst in long-continued exercise it is eliminated chiefly through the skin. During rest the sweat has a high lactic acid (0.25—0.3%) and a low chlorine (up to 0.16%) concentration; during work the corresponding values are 0.1% and 0.27—3.5%.

A. A. ELDRIDGE.

Excretion of acids in the urine during work. III. Excretion of phosphorus during work of varying intensity. M. S. RESNITSCHENKO and N. P. KOSMIN (Biochem. Z., 1929, **212**, 87—95).—Short periods of vigorous muscular activity cause the inorganic phosphorus content and the acidity of human urine to increase. Exceptions to this rule may occur, and the volume of the urine, the nature of the activity, the experimental conditions, and the state of combination of the phosphorus must be taken into account when the metabolic changes are being considered. W. MCCARTNEY.

Physico-chemical phenomena during regeneration. III. Buffering [effects] in the tissues of regenerating limbs of axolotl. N. OKUNEFF (Biochem. Z., 1929, **212**, 1—15).—In the regenerating limbs of axolotl the buffering power of the tissues as compared with that of normal tissues increases during the first three weeks, and during this period, in addition to the normal maximum of buffering power (*p_H* between 6 and 7), a second maximum (*p_H* between 5 and 6) is encountered. The acidosis of the first two days of the regeneration period is accompanied by increase of buffering power; there follows, in the period between the two waves of acidosis (third and fourth days), a slow increase of buffering power, and this reaches its maximum at the time of the second wave of acidosis (fifth to eighth day). Normal values are attained at the

end of the third week after amputation, *i.e.*, one week before the return of normal reaction. The increase in buffering power in the initial stages of regeneration may be due either to local accumulation of decomposition products of proteins or of cartilage or to increase in the adsorptive powers of the tissues.

W. MCCARTNEY.

Source of lactic acid in the central nervous system. H. JUNGMAHN and P. KIMMELSTIEL (Biochem. Z., 1929, 212, 347—358).—The changes of lactic acid, inorganic phosphorus, cerebroside, and glycogen contents of freshly-removed brain are investigated after keeping for 1 min. and 1 hr., respectively. A few seconds after removal the lactic acid content of brain increases very rapidly and the glycogen content decreases and then remains constant. When the lactic acid and glycogen values have attained their maximal and minimal values the cerebroside content decreases slowly. The inorganic phosphorus increases considerably. The lactic acid of brain arises most probably from glycogen and not from cerebroside-galactose, since the breakdown of the latter is too slow to account for the rapid formation of lactic acid.

P. W. CLUTTERBUCK.

Carbohydrate exchange and degradation of the dextrose molecule. E. SCHNEIDER and E. WIDMANN (Klin. Woch., 1929, 8, 536—541; Chem. Zentr., 1929, i, 2204).—After intravenous injection of dextrose into dogs the blood-sugar rises to a smaller extent than is anticipated; the lactic acid remains constant. Injection of dihydroxyacetone affects neither the blood-sugar nor the lactic acid, presumably being converted immediately into carbon dioxide and water. Lactic acid is first converted into the alkali salt and then transformed into glycogen, which is stored by the liver; repeated injection of small quantities of lactic acid gradually raises the blood-sugar, the storing capacity of the liver for glycogen being overstepped. Intravenous injection of a small quantity of methylglyoxal does not affect the blood-sugar or lactic acid; repeated doses gradually raise the blood-sugar and lactic acid and diminish the alkali reserve.

A. A. ELDRIDGE.

Physiological efficiency of lactose, lactic acid, and sucrose, and the influence of these substances on resorption of nutrients by ruminants. W. VOLTZ and H. JANTZON (Z. Tierzücht., 1929, 11, 13 pp.; Chem. Zentr., 1929, i, 2440).—The physiological efficiency for ruminants was 77.7, 62.0, and 62.5%, respectively, of the energy content.

A. A. ELDRIDGE.

Resorption of pentoses in nutrition, and the assimilation of pentoses. A. ROCHE (Compt. rend. Soc. Biol., 1929, 99, 1973—1976; Chem. Zentr., 1929, i, 1709).—In experiments with animals, xylose and arabinose passed into the blood, but pentose was not detected in the blood after administration of xylan or araban.

A. A. ELDRIDGE.

Furan compounds derived from sugars. III. Fate of acetoxymethylfurfurylideneacetic acid in animal organism. J. KARASHIMA (Z. physiol. Chem., 1929, 184, 265—267; cf. A., 1927, 1107).—Administration of sodium ω -acetoxymethylfurfurylideneacetate (this vol., 450) to the dog leads to the

excretion in the urine of 16.9—29.6% of ω -carboxy-2-furfurylideneacetic acid + H₂O, decomp. 235°, m. p. (anhydrous) 277°; with the rabbit or hen 11.2—32.1% of hydroxymethylfurfurylideneacetic acid (*loc. cit.*) is excreted.

H. BURTON.

Metamorphosis of insects. J. HALLER (Acta Biol. Exp., Warsaw, 1928, 2, 225—315).—The percentage compositions of *Deilephila euphorbiae* larvæ, pupæ, and imagos are respectively as follows: water 79, 75, 68.25; fats 3.5, 3.83, 6.10; nitrogen 1.54, 2.21, 3.34; protein 9.375, 13.30, 19.7; chitin 0.676, 1.30, 3.13; ash 0.90, 1.175, 1.90, and non-nitrogenous extractives 6.55, 5.435, 0.92. The total energy used up during metamorphosis is a fairly constant quantity per unit body-weight of different insects and amounts in this case to 1833 g.-cal., of which 32.5% is supplied by fat and 67.5% by other substances. During the stage of pupation, 44.8% of the energy requirements are supplied by fat, 13% by protein, and 42.2% by carbohydrates, whilst in the pupa stage only 21.6% is given by fat, 41.3% by proteins, and 37.1% by carbohydrates. The average percentage composition of the mature butterflies on death from inanition is: water 55.7, fat 4.5, nitrogen 4.96, protein 28.1, chitin 7.5, ash 3.08, and non-nitrogenous extractives 1.04. During the period of inanition, 964 g.-cal. are used, of which 499 are supplied by fat, 435 by protein, and 26 by carbohydrates.

R. TRUSZKOWSKI.

Chemical composition of the hæmolymph of *Deilephila euphorbiae* larvæ. A. MOKŁOWSKA (Acta Biol. Exp., Warsaw, 1929, 3, 241—253).—The following values in mg. per 100 c.c. are found for the hæmolymph (*d* 1.031) of the larva of *D. euphorbiae*: total nitrogen 1180, protein-nitrogen 825, non-protein-nitrogen 355, amino-acid-nitrogen 170, uric acid 14, dextrose (?) 127, calcium 41.25, magnesium 43.5, iron 5.8, ionic chlorine 48.6, phosphate-phosphorus 12.05. The amino-acid content is practically independent of conditions of nutrition. In the pupal stage, the protein-nitrogen content remains constant, whilst the uric acid content falls almost to zero, pointing to a sharp decrease in protein metabolism. The protein content of the hæmolymph of fully grown larvæ falls to one half after 4—5 days of inanition, whilst amino-acid, uric acid, and non-protein-nitrogen contents remain constant. These differences between artificial and physiological inanition are confirmed by refractometric measurements, very similar readings being obtained in artificial inanition and during moults (46 and 37) and in fed larvæ and pupæ (61.5 and 65).

R. TRUSZKOWSKI.

Normal standard of the gastric functions in Egyptians. A. BEY, M. GAFAF, and H. ERFAN (J. Egyptian Med. Assoc., 1929, 12, 80—88).—In experiments on 100 normal individuals (19—26 years), using the fractional test-meal devised by Rehfuß, the volume of resting gastric juice varied between 3 and 200 c.c. (average 59 c.c.). The average free acidity was equivalent to about 12 c.c. of 0.1N-sodium hydroxide, whilst the average for total acidity was 30 c.c. No case of achlorhydria was observed. Hypertonic stomachs have a normal acidity, whilst hypotonic stomachs have an acidity which is either normal or increased.

P. G. MARSHALL.

Production of ammonia from amino-acids in surviving organs. A. BORNSTEIN and H. F. ROESE (Biochem. Z., 1929, 212, 127—136).—When surviving livers, lungs, or limbs from fasting dogs are perfused with blood from fasting dogs the ammonia content of the blood either does not change or falls slightly. If glycine is added to the blood the ammonia content increases, very greatly in the liver (up to 100 times normal), slightly in the lungs, and not at all in the limbs. Alanine, asparagine, and aspartic acid act like glycine, but leucine has no effect, at any rate in the liver. W. MCCARTNEY.

Decomposition of proteins and amino-acids of food as measured by the ammonia [content] of the blood. A. BORNSTEIN (Biochem. Z., 1929, 212, 137—148; cf. preceding abstract).—Intravenous administration of glycine, alanine, or asparagine to fasting dogs is followed, in a few minutes, by considerable increase in the ammonia content of their blood. The urea content of the blood also increases, but after a longer period. Oral administration of the amino-acids leads to the same results, but after much longer periods (about 1 hr.). Similarly, feeding with raw fat-free meat causes increase in the ammonia and urea contents of the blood after 4—5 hrs. W. MCCARTNEY.

Exclusive meat diet. Effect on carbohydrate tolerance. Effect on blood constituents. E. TOLSTOI (J. Biol. Chem., 1929, 83, 747—752, 753—758).—After 1 year on an exclusive meat diet the carbohydrate tolerance was diminished, but returned to normal after 2—4 weeks' resumption of a normal diet. No significant changes in the composition of the blood were observed except for an increase in the fats and cholesterol; these abnormalities also rapidly disappeared on return to normal food. C. R. HARINGTON.

Variation of glutathione in isolated organs. I. S. VISCO and S. CASTAGNA (Boll. Soc. Ital. Biol. sperim., 1928, 3, 282—283; Chem. Zentr., 1929, i, 2203).—In the isolated liver the glutathione content is diminished during the first 12 hrs.; this is followed by an increase over the original value and a final diminution. A. A. ELDRIDGE.

Crystalline tripeptide from living cells. M. DIXON and N. U. MELDRUM (Nature, 1929, 124, 512).—Unlike impure glutathione, pure glutathione does not catalyse the oxidation of the proteins of thermostable muscle preparations. The crystalline reduced form is auto-oxidisable owing to the presence of traces of catalytic metals, but is rendered stable towards oxygen by treatment with kaolin owing to removal of the metals by adsorption. A. A. ELDRIDGE.

Role of the liver in the metabolism of purine substances. PAROULEK (Acta Med. Scand., 1928, 68, 79—95; Chem. Zentr., 1929, i, 1836).—When minced liver is kept at a constant temperature for several hours the uric acid content increases. If uric acid is added, a considerable part of it disappears. Autolysis of minced liver leads to an increase in ammonia, non-protein-nitrogen, and hydrogen-ion concentration. A. A. ELDRIDGE.

Changes in the amount of carotinoids in hen's eggs during incubation. H. VON EULER and H. HELLSTRÖM (Biochem. Z., 1929, 211, 252—258).—The colours (measured in a tintometer) produced when antimony trichloride acts on chloroform solutions of xanthophyll and of lutein are very similar. Spectroscopic examination shows that the amount of lutein in the yolks of incubating eggs changes only slightly between the sixth and the twelfth days, and up to the twelfth day there is little or no consumption of lutein. Lutein exhibits specific growth-promoting properties. W. MCCARTNEY.

Metabolism of the hexone bases and the origin of the purine nucleus in the development of hen's eggs. G. RUSSO (Arch. Sci. biol., 1927, 10, 128—137; Chem. Zentr., 1929, i, 2200).—During the embryonic development of the hen there is a marked diminution of arginine and histidine. Since only a fraction of this serves for the production of guanidine and creatine, the remainder is regarded as the precursor of pyrimidine and purine, both of which increase during the process. A. A. ELDRIDGE.

Embryonic metabolism. IV. Basic amino-acids of the hen's egg during development. H. O. CALVERY (J. Biol. Chem., 1929, 83, 649—656).—The arginine content of the hen's egg remains constant throughout the whole period of development. Determinations of histidine and lysine gave inconsistent results, but there is a general tendency for both these bases to diminish in amount during development. Arginine therefore is not a precursor of purines, whilst histidine may be. C. R. HARINGTON.

Embryochemical investigations with the injection method. I. Uric acid formation in the hen's embryo. M. TOMITA and M. TAKAHASHI (Z. physiol. Chem., 1929, 184, 272—275).—Injection of solutions of carbamide, lactic or tartronic acid into eggs and incubation for 14—19 days causes an increase in the amount of uric acid in the allantoic liquid and embryo. A mixture of carbamide and tartronic acid gives under parallel conditions a greatly increased amount of uric acid. The changes involved are probably: lactic acid ——— tartronic acid
carbamide $\xrightarrow{\text{dialuric acid}}$ carbamide $\xrightarrow{\text{uric acid}}$ uric acid (cf. Wiener, Hofmeister's Beiträge, 1902, 2, 42). H. BURTON.

"Internal cycle" of iodide in man. F. BERGER (Klin. Woch., 1929, 8, 118—119; Chem. Zentr., 1929, i, 2075).—In 1.5 hrs. after the injection of alkali iodide 90.6 mg. of iodine were excreted by the kidneys, and 32.6 mg. through the gastric glands. The quotient $100\text{I}^{\text{I}}/\text{Cl}^{\text{I}}$ is for the blood 1.36, stomach 7.83, and urine 9.65—48.6. A. A. ELDRIDGE.

Behaviour of iodine in body fluids after ingestion of alkali iodides and iodoproteins. G. BARKAN and W. LEISTNER (Klin. Woch., 1929, 8, 117—118; Chem. Zentr., 1929, i, 2075).—After administration of alkali iodide intravenously or perorally, "organic" iodine was not found in the blood or urine. Feeding of rabbits and dogs with iodised protein is followed by the appearance of some "organic" iodine in the blood and particularly in the urine. A. A. ELDRIDGE.

Radium content of some foodstuffs. E. BURKSER, M. SCHAPIRO, and K. BRONSTEIN (Biochem. Z., 1929, 211, 323—325).—The radium content of various animal and vegetable foodstuffs, determined by the emanometer, was in all cases of the order 10–15%.

J. H. BIRKINSHAW.

Boundary surface energy and activity in a protoplasm model. V. EFIMOV and P. REHBINDER (Biochem. Z., 1929, 211, 154—162).—Using Nirenstein's mixture (Pflüger's Archiv, 1920, 179, 233) and the apparatus of Rehbinder (J. Biol. Med. exp., Moscow, 1927, 4, 939) the boundary surface tensions of aqueous solutions of dyes (neutral-red, toluidine-blue, crystal-violet, formyl-violet, trypan-blue, fuchsin-S) have been measured. The boundary surface activities of these dyes at the interface Nirenstein's mixture–aqueous solution run parallel to their coefficients of distribution in the two phases, i.e., to their staining powers. The limit of adsorption is reached at low concentrations and corresponds with complete saturation of the interface with oriented molecules of the dye. The results of parallel experiments showed that many dyes which exhibit great boundary surface activity at the interface aqueous solution–oil are almost or quite inactive at the surface aqueous solution–air. The biological consequences of this are emphasised.

W. MCCARTNEY.

Swelling of [cod] fish skins in solutions of inorganic and organic acids. J. C. KERNOT and J. KNAGGS (with Appendix by M. KAYE) (Proc. Roy. Soc., 1929, B, 105, 280—297).—Measurements have been made of the degree of swelling undergone by cod skins (in the fresh or dried condition or after treatment with sodium hydroxide solution and sulphur dioxide solution), when immersed in dilute solutions of hydrochloric acid, sodium hydroxide, or organic acids. In solutions of hydrochloric acid or sodium hydroxide dry or treated skins swell more than wet, whatever the concentration of the acid or alkali, but dry skins swell more than treated skins between p_H 3.5 and 8.0. With dry skins the percentage swelling is practically constant in the range p_H 1—11.0. With all skins, below p_H 4.0 and above p_H 11.0, considerable quantities of nitrogen go into solution. With fatty acids (acetic, propionic, and butyric) the swelling of wet and treated fish skins increases with the mol. wt. of the acids, the swelling of the treated being three to four times as great as that of the wet skins at the same p_H . In the case of dry skins, the swelling is greater with acetic acid and least with butyric acid. The following acids have also been employed: mono-, di-, and tri-chloro-acetic, lactic, pyruvic, oxalic, tartaric, citric, and salicylic. It has not been possible to explain completely the complicated results observed. Cod skin differs histologically from mammalian skin in that the fibres are not interwoven, but are arranged in layers, the fibres of one layer being at right angles to those of the next and being held together by an occasional fibre. The structure is irreversibly altered by drying and by treatment with alkali followed by sulphur dioxide. Cod skin contains very small amounts of elastic fibre tissue and no fatty material.

W. O. KERMACK.

Biometry of calcium, inorganic phosphorus, cholesterol, and lipid phosphorus in the blood of rabbits. III. Influence of various types of light environment. A. R. HARNES (J. Exp. Med., 1929, 49, 859—882).—After an accommodation period following exposure to light, the effects may be grouped in the order: ultra-violet light, Cooper-Hewitt lamp light or daylight, total darkness.

CHEMICAL ABSTRACTS.

Changes in the ion content of organs [of animals] exposed to irradiation and to the climate of high altitudes. A. LOEWY and L. PRINCUSSEN (Biochem. Z., 1929, 212, 22—34).—Rats, some of which were kept under normal conditions, some exposed to ultra-violet irradiation, and some living in air kept at a pressure of 0.5 atm. were allowed to grow under otherwise identical conditions in Berlin and in Davos. Determinations of the potassium, calcium, and magnesium contents of their livers, lungs, hearts, kidneys, and hind-leg bones showed that irradiation, and still more reduced atmospheric pressure, cause absolute increase in the calcium contents and absolute decrease in the potassium contents of these parts of the body. The favourable effects, in disease, of irradiation and of the climate of high altitudes may be related to these changes.

W. MCCARTNEY.

Stimulation of metabolism by alcohol. L. D. SEAGER, D. J. VERDA, and W. E. BURGE (Science, 1929, 69, 383—384).—Direct determinations with goldfish show that ethyl alcohol stimulates sugar metabolism to nearly the same extent as do fat and protein.

L. S. THEOBALD.

Adrenaline content of blood during narcosis. H. SCHLOSSMANN and H. MÜGGE (Arch. exp. Path. Pharm., 1929, 144, 133—141).—The increase of adrenaline in the peripheral arterial blood which occurs during anaesthesia (chloroform, ether, or acetylene) is due to liberation of adrenaline by the adrenals, not by direct action of the anaesthetic, but as the result of the lowering of the blood-pressure.

W. O. KERMACK.

Detection of veronal in urine. A. KÜHN (Deut. Z. ges. gerichtl. Med., 1929, 13, 115—123; Chem. Zentr., 1929, i, 2562—2563).—The urine (100 c.c.) is acidified with sulphuric acid and treated with potassium permanganate solution until the precipitate no longer redissolves. After 5—10 min. the precipitate is removed with hydrogen peroxide, and the liquid is then evaporated in a vacuum to 20—30 c.c. After repeated (mechanical) extraction with ether the united ethereal extracts are evaporated and the veronal is purified with animal charcoal followed by sublimation. The yield is 85—95%.

A. A. ELDRIDGE.

Oxidation of dextrose in phloridzin glycosuria. W. M. BOOTHBY, C. M. WILHELMJ, and H. E. C. WILSON (J. Biol. Chem., 1929, 83, 657—679).—Complete phloridzinisation raises the basal metabolic rate of dogs as much as 90% above the normal level; administration of dextrose to dogs in this condition causes a decrease in the heat production and an increase in the respiratory quotient corresponding with oxidation of 18—25% of the ingested sugar.

Since the dextrose accounted for by oxidation and excretion was not in excess of that administered, no evidence was obtained of the conversion of fat into sugar.

C. R. HARRINGTON.

Effect of small doses of phloridzin on the excretion of nitrogen. P. THOMAS, M. MALEVA-NAIA, and R. IMAS (*Compt. rend. Soc. Biol.*, 1929, **100**, 375—377; *Chem. Zentr.*, 1929, i, 2202).—In addition to excretion of sugar, phloridzin causes an increase in the total nitrogen, particularly urea-nitrogen, dependent on the dose. There is also increased elimination of creatinine. Protein degradation is of greater importance than glycosuria in phloridzin poisoning.

A. A. ELDRIDGE.

Ammonium chloride acidosis. H. DENNIG, D. B. DILL, and I. H. TALBOTT (*Arch. exp. Path. Pharm.*, 1929, **144**, 297—310).—When ammonium chloride is administered to a normal person marked acidosis is present during the first 5—7 days, and an excess of sodium and potassium is excreted in the urine, most of the acid being neutralised by these bases. By the second week the production of ammonia by the body has increased so that the hydrogen-ion concentration of the blood is again normal and the excessive secretion of sodium and potassium ceases. It therefore appears that during acidosis the production of ammonia increases only slowly and reaches its maximum in 5—7 days. In the same way when the administration of ammonium chloride is stopped after 2 weeks, the excess production of ammonia by the body does not cease at once, but drops only gradually, so that alkalosis is produced, which gradually disappears.

W. O. KERMACK.

Action of caffeine on membranes and proteins. H. BRUHL (*Biochem. Z.*, 1929, **212**, 291—317).—Filtration experiments using collodion membranes on which protein had been deposited showed a reversible increase of permeability in presence of caffeine and also on displacement of the p_H to the isoelectric point of the protein, the former being due to changes of the degree of dispersion of the protein covering the pore walls and the latter to changes of the degree of swelling. Caffeine increases the degree of dispersion of such colloids and increases the solubility of amino-acids, probably on account of the formation of complex compounds having a greater solubility, the complex formation being demonstrable by compensation dialysis in the case of proteins and by f.-p. determinations in the case of amino-acids. The diuretic effect of caffeine is explained in terms of the results of these filtration experiments.

P. W. CLUTTERBUCK.

Alteration of the basal metabolism on imbibing chicory and chicory-coffee beverages. S. SCHIMMEL, M. DYE, and C. S. ROBINSON (*Z. Unters. Lebensm.*, 1929, **57**, 576—584).—Addition of chicory to coffee does not hinder extraction of caffeine and caffetannic acid from the latter. Ingestion of 200 c.c. of water at 50—60° has no effect on the basal metabolism; 200 c.c. of coffee infusion prepared from 20 g. of coffee containing 0.25 g. of caffeine raised the basal metabolism about 6%. Addition of 10% of chicory did not alter this effect, and an infusion of

10 g. of chicory in 200 c.c. of water had no effect by itself.

W. J. BOYD.

Action of pilocarpine on the blood-sugar. J. SZEP (*Arch. exp. Path. Pharm.*, 1929, **144**, 277—282).—The blood-sugar of a rabbit (2—3 kg.) falls after the subcutaneous administration of 1 mg. of pilocarpine, whilst if larger doses are administered a rise in blood-sugar precedes a fall. When 1.5 mg. of pilocarpine is administered through a stomach tube a rise in blood-sugar takes place, but when fed without a tube the blood-sugar falls. The rise is the result of irritation by the tube.

W. O. KERMACK.

Metabolism of heart-muscle. I. Heart-glycogen. M. HAENDEL and A. MUNILLA (*Biochem. Z.*, 1929, **212**, 35—46).—The glycogen contents of the heart-muscle, skeletal muscle, and liver and the sugar content of the blood of dogs receiving intraperitoneal injections of dextrose to which digitalis, ouabain, caffeine, camphor, calcium chloride, potassium chloride, adrenaline, insulin, or thyroxine had been added have been determined. Digitalis caused considerable reduction in heart-glycogen, but not in muscle- or liver-glycogen. Ouabain, in large doses, caused mobilisation of glycogen generally, in small ones, reduction in heart- and liver-glycogen. Large doses of camphor reduced all the glycogen values, but small doses had no effect on the heart-glycogen. The action of caffeine was similar to that of camphor, but the former acted more powerfully on muscle-glycogen. Potassium chloride had no effect on heart-glycogen but reduced muscle- and liver-glycogen. Calcium chloride greatly reduced heart-glycogen and, in large doses, muscle- and liver-glycogen also. Adrenaline had a general mobilising effect on the glycogen. The heart-glycogen was not affected by insulin. Thyroxine had little effect on the glycogen content of the heart, but it reduced the muscle- and liver-glycogen. Ouabain, camphor, and calcium chloride caused hyperglycaemia. Potassium chloride caused hypoglycaemia.

W. MCCARTNEY.

Action of antimony compounds on the adrenals. R. N. CHOPRA, J. C. GUPTA, and S. G. CHOUDHURY (*Indian J. Med. Res.*, 1928, **16**, 441—446).—With rabbits intravenous injection of organic antimony compounds causes an increase in the adrenaline content of the adrenals.

CHEMICAL ABSTRACTS.

Cobalt and blood. KLARA WALTNER and KARL WALTNER (*Klin. Woch.*, 1929, **8**, 313; *Chem. Zentr.*, 1929, i, 2069).—A toxicological study of the effect on the blood of rats of ingestion or injection of cobalt salts.

A. A. ELDRIDGE.

Preparation of colloidal lead. D. GANASSINI (*Arch. Ist. Biochim. Ital.*, 1929, **1**, 3—12).—Colloidal lead stabilised by means of sodium thiosulphate exhibits perfect colloidal properties and very gradual maturation. It undergoes partial sulphuration, which becomes very slow in presence of gelatin, affects less than one fourth of the metal in a month, and is not complete after 6 months. The preparation is more stable than any other yet described. The traces of lead sulphide formed on ageing are not toxic and do not diminish the biological activity.

T. H. POPE.

Colloidal lead in toxicological tests. G. LORENZINI (Arch. Ist. Biochim. Ital., 1929, 1, 13—26).—Ganassini's colloidal lead (preceding abstract) is harmless in therapeutic doses, rabbits tolerating doses sixtyfold those given to human beings. Even in the colloidal state, lead hydroxide is toxic in very small doses, and exerts an intense hæmolytic effect and an irritant action on the kidneys. Without addition of sodium thiosulphate, colloidal lead is appreciably toxic, especially towards the elements of the blood. T. H. POPE.

Pharmacological action of stabilised colloidal lead. I. SIMON (Arch. Ist. Biochim. Ital., 1929, 1, 47—68).—In contact with the tissues of the organism, colloidal lead passes into the granular metallic state. This occurs in subcutaneous, peritoneal, and pulmonary tissues, in the anterior chamber of the eye, and, when the preparation is injected intravenously, in all the internal organs with the exception of the central nervous system. With intravenous injection, the fixation of the colloidal lead may be facilitated by retarding local circulation. Sabbatani's results (A., 1914, i, 356, 357) are confirmed. T. H. POPE.

Therapy of mercury poisoning. E. HESSE (Arch. exp. Path. Pharm., 1929, 144, 327—330; cf. A., 1927, 73; also Haskell and Forbes, this vol., 470).—In confirmation of previous results, the power of strontium thioacetate to counteract the effects of the administration of mercuric chloride to mice, rabbits, rats, guinea-pigs, and cats has been demonstrated. W. O. KERMACK.

Pathological fat formation. II. The problem of lecithin. G. ROSENFELD (Biochem. Z., 1929, 211, 270—275).—Hens suffering from phosphorus poisoning, when fasting, receiving dextrose alone, or dextrose and caseinogen, all showed about the same percentage of lecithin in the total extract of the liver as did unpoisoned fasting controls. J. H. BIRKINSHAW.

Malt-amylase. VII. Adsorption of amylase from malt extracts by kaolin and elution [of the amylase therefrom]. T. SABALITSCHKA and R. WEIDLICH (Biochem. Z., 1929, 211, 229—238; cf. this vol., 721).—The amylase in aqueous malt extracts, the dry substance of which contains 96% of maltose, is completely adsorbed by kaolin at p_H 4.2 (19.5 g. of malt require 2.5 g. of kaolin). The adsorbed amylase is removed by elution with sodium phosphate solution at p_H 7.6 and remains active. Aqueous solution of carbon dioxide at p_H 5.9 does not remove the adsorbed amylase. As a result of this adsorption and elution process the activity of the dry substance from the malt extracts is increased fifteen to seventeen times and the loss of amylase is 38—40%. W. MCCARTNEY.

Invertase from honey. P. E. PAPADAKIS (J. Biol. Chem., 1929, 83, 561—568).—The acceleration of the hydrolysis of sucrose by invertase from honey in presence of β -glucose (cf. Nelson and Sottery, A., 1925, i, 104) was not observed in presence of *d*- and *l*-arabinose and of xylose. Mercuric chloride inhibits the hydrolysis when the p_H is between 5.7 and 4.23; this inhibition, as well as the much slighter one

caused by α -methylglucoside, may be neutralised by addition of β -glucose. C. R. HARRINGTON.

Fission of lecithins. H. PAAL (Biochem. Z., 1929, 211, 244—251).—Lecithin from egg-yolk is completely hydrolysed in 6 hrs. by boiling alcoholic solution of potassium hydroxide. In alcoholic solution it is hydrolysed slightly by lipase from pig pancreas at 30° and still less at lower temperatures, but when in water or glycerol emulsions it is not attacked by the enzyme even when activators are present and the hydrogen-ion concentration is most favourable for attack. On exposure to air it is gradually oxidised. W. MCCARTNEY.

Glyceric acid monophosphoric acid. M. VOGT (Biochem. Z., 1929, 211, 1—16; cf. Neuberg and others, A., 1928, 1215).—The properties of salts of glyceric acid monophosphoric acid have been investigated and a crystalline barium salt, $C_3H_5O_7 \cdot PBa_2 \cdot H_2O$, has been prepared. The salts of the acid are more easily soluble than but otherwise very similar to those of glyceric acid diphosphoric acid, the difference in solubility of the zinc salts being probably sufficient to allow it to be used in quantitative separation of the acids. The mono-acid can be hydrolysed by phosphatases from various sources and the glyceric acid liberated can be isolated. The glyceric acid so obtained is optically inactive. W. MCCARTNEY.

Thermolability of glycerophosphodehydrogenase. N. ALWALL (Skand. Arch. Physiol., 1929, 55, 100—103; Chem. Zentr., 1929, i, 2543—2544).—Muscle-glycerophosphodehydrogenase does not differ from succinodehydrogenase in thermolability. If muscle-fumarase is first destroyed by heat, the succinodehydrogenase contains less nitrogen and is less active than Anderssen's product. A. A. ELDRIDGE.

Correlation of synthesis and breakdown of active substances of muscle. E. LEHNARTZ (Z. physiol. Chem., 1929, 184, 1—55).—The enzymic synthesis of phosphocreatine is considerable in muscle press-juice at suitable p_H (about 7). At the same time at alkaline reaction there is a breakdown of lactacidogen and pyrophosphoric acid. The adenylic acid ion is found to be specific for the synthesis of pyrophosphoric acid. Under its influence the synthesis takes place more quickly than any other ionically-stimulated chemical process in muscle. This ionic action is a property of muscle-adenylic acid only. Inosic acid and adenosine are quite inactive. J. H. BIRKINSHAW.

Lactic acid fermentation of warm-blooded tissue. II. Effect of potassium and calcium ions on the existence of the extra-fermentation of salivary gland and liver tissue of rats. O. ROSENTHAL (Biochem. Z., 1929, 211, 295—322; cf. this vol., 722).—An extension of previous experiments on the extra-fermentation of the liver to that of the salivary glands. The action of potassium and calcium ions is substantially the same for both types of tissue. The extra-fermentation is greatly restricted by the absence of calcium and potassium during the aerobic period. The cation effect is reversible. Both cations have a favourable effect on the extra-ferment-

ation, and differences of degree only between liver and submaxillary are found in the effect of the cations, indicating that the mechanism is the same in both cases.

J. H. BIRKINSHAW.

Formation and isolation of methylglyoxal in glycolysis by animal enzyme. M. VOGT (Biochem. Z., 1929, 211, 17—39).—Methylglyoxal is formed during the glycolysis of animal organs and (assuming that 1 mol. of hexose gives 2 mols. of keto-aldehyde) yields of 17.9—27.4% are obtained. In the case of alcohol-ether preparations of liver and kidney of pigs and of extracts of liver, kidney, and muscle of pigs and rabbits, the best conditions for producing good yields of methylglyoxal have been determined. Methylglyoxal accumulates only if co-enzyme is absent or not present in large amounts. Hexosediphosphate is a suitable substrate for the production of methylglyoxal, but none was obtained from dihydroxyacetone or from glyceraldehyde.

W. MCCARTNEY.

Glycolytic power of various organs and its dependence on co-enzyme content. H. KRAUT and E. BUMM (Z. physiol. Chem., 1929, 184, 196—204).—The addition of co-enzyme from rat sarcoma to mouse carcinoma and to brain, spleen, kidney, and muscle of rats and human blood causes an increase in glycolysis. In carcinoma tissue the glycolysis is not increased beyond the ordinary maximum, but the value in the case of the brain reaches double the normal. The co-enzyme can be almost completely washed out of the kidney and spleen.

J. H. BIRKINSHAW.

Rennin coagulation. Influence of hydrogen ions on the separation of casein by the action of electrolytes. C. LA ROTONDA (Annali Chim. Appl., 1929, 19, 310—328).—The effect of addition of various inorganic and organic acids on the coagulation of de-fatted milk by three different salt solutions of similar reaction has been investigated. The milk was de-fatted either immediately after milking or after being heated. The results show either that the coagulation of the casein does not occur at the isoelectric point or that the isoelectric point for casein is not p_H 4.7—4.6. The process thus depends, not merely on the degree of acidity, but also on the nature of the acid present.

T. H. POPE.

Non-specificity of proteolytic organ-enzymes. X. UTKINA-LJUBOVZOVA and O. STEPFUHN (Biochem. Z., 1929, 211, 426—444).—The liver, thyroid, kidneys, lungs, heart, brain, muscle, spleen, erythrocytes, and leucocytes of the ox and rabbit's liver contain three proteolytic enzymes with optima at p_H 3.4, 5.4, and 7.4. These enzymes are identical whatever their source and non-specific in their action.

J. H. BIRKINSHAW.

Action of pepsin-hydrochloric acid after trypsin-kinase. K. FELIX and A. LANG (Z. physiol. Chem., 1929, 184, 205—208).—By subjecting a trypsin-kinase digestion of oxyhæmoglobin at various stages of hydrolysis to the action of pepsin-hydrochloric acid no increase in the linkings hydrolysable by pepsin is observed. From the beginning the trypsin acts on the "pepsin linkings."

J. H. BIRKINSHAW.

The p_H optimum in the action of trypsin on fibrin. H. J. VONK and A. HEYN (Z. physiol. Chem., 1929, 184, 169—182).—The optimum p_H for the action of trypsin on fibrin is 11.3, in accordance with Ringer's results. This optimum is not displaced when the time of action is increased. There is a second small optimum at p_H 8.

J. H. BIRKINSHAW.

Plant proteases. XIV. Proteases of higher plants. O. AMBROS and A. HARTENECK (Z. physiol. Chem., 1929, 184, 93—107; cf. this vol., 606).—The action of hydrocyanic acid on various plant proteinases was examined after removal of the peptidases by adsorption. All the proteinases belong to the papain type, activated by hydrocyanic acid. According to the distribution of the proteinase and the dipeptidase in the plant a complex activated or inhibited by hydrocyanic acid predominates.

J. H. BIRKINSHAW.

Specificity of animal proteases. XVII. Proteinase and carboxypolypeptidase from pancreas. E. WALDSCHMIDT-LEITZ and A. PURR (Ber., 1929, 62, [B], 2217—2226).—Pancreas trypsin is not homogeneous, but consists of a proteinase and a polypeptidase termed carboxypolypeptidase. The separation of the two enzymes in their natural mixtures depends on the choice of adsorbent and the hydrogen-ion concentration of the solution. In an acid medium, both enzymes are absorbed only to a slight extent by aluminium hydroxide C_7 , whereas in neutral solution the carboxypolypeptidase is mainly adsorbed. Complete separation of the tryptic enzyme mixture is thus readily effected. Proteinase and carboxypolypeptidase are specifically activated by enterokinase, which does not change in activity towards the two enzymes after protracted purification. The action towards the enzymes differs. Proteinase, free from activator, is inactive towards all substrates investigated, whereas carboxypolypeptidase under similar conditions is able to hydrolyse a series of substances. The actions of activator-free carboxypolypeptidase are identical with those of "non-activated pancreas trypsin." As far as the degradation of complex substrates such as protamines is concerned, the activator causes an extension of the range of specificity and not simply an increase in the rate of action. The action of proteinase is confined to the fission of actual proteins, for example, caseinogen, histone, and the protamines, whereas that of carboxypolypeptidase includes the hydrolysis of polypeptides of definite composition, acylated amino-acid, and peptides and protamines. The action of carboxypolypeptidase is greatly influenced by the degree of ionisation of the free carboxyl group in the substrates, which is increased by the introduction of acid residues in amino-acids and peptides or of definite amino-acid residues, for example, tyrosine. A configurative influence of the amino-acid containing the free carboxyl group is also observed. The hydrolysis of certain substrates, such as protamines, by proteinase and carboxypolypeptidase does not denote an identity in enzyme action. In the case of clupeine it is found that the individual enzyme actions are independent from one another and consequent.

H. WREN.

Specificity of peptidases. III. Affinity measurements on animal dipeptidase. E. WALDSCHMIDT-LEITZ and G. VON SCHUCKMANN (Z. physiol. Chem., 1929, 184, 56—68; cf. A., 1928, 672).—The dissociation of enzyme-substrate complex for dipeptidase from pig's intestine on glycyl-tyrosine is smallest at p_H 7.8 (the maximum of activity- p_H curve). The form of this curve is determined by the position of the equilibrium between enzyme and substrate. The dissociation constants of dipeptidase from intestine, pancreas, and spleen all have the value 0.0026, indicating a close relationship of the chemically active groups.

J. H. BIRKINSHAW.

Hydrolysis of glycylglycine, alanylglycine, and leucylglycine by intestinal and malt peptidases. K. LINDERSTRØM-LANG and M. SATO (Z. physiol. Chem., 1929, 184, 83—92).—Of the two peptidases from intestinal erepsin, one (optimum p_H 7.3) hydrolyses alanylglycine about forty times as fast as the other (optimum p_H 8.1). Malt also contains two distinct enzymes. One (optimum p_H 7.8) contained in proteinase-free peptidase is inactive to glycylglycine and the other (optimum p_H 8.6) from the glycerol extract is active towards glycylglycine, alanylglycine, and leucylglycine, also to leucylglycylglycine.

J. H. BIRKINSHAW.

Influence of hydrogen-ion concentration on enzymes. IV. Cause of the erepsin-decomposing action of acids. K. HISHIKAWA (Exp. J. Digestive Dis., 1928, 3, 167—177).—In 0.25N-*N*-acid erepsin is completely decomposed in 1 hr., independently of the degree of dissociation of the acid; with more dilute acid, the velocity of decomposition is parallel to the degree of dissociation. The resistance of erepsin to acids is greatest at p_H 5.5—6.8.

CHEMICAL ABSTRACTS.

Specificity of enzymic fission of dipeptides. H. VON EULER, S. MYRBACK, and K. MYRBACK (Ber., 1929, 62, [B], 2194—2199).—Extract from germinated barley hydrolyses leucylglycine about 15—20 times as rapidly and alanylglycine about 8 times as rapidly as glycylglycine. The relationship differs markedly from that observed with other extracts of germinated seeds and other animal organs. Hydrolysis of leucylglycine is restricted 3 times as strongly by leucine as by glycine and very markedly by glycylglycine.

H. WREN.

Physiological selection of enzymes by alcohol. L. SEMICHON (Ann. Inst. Pasteur., 1929, 43, 1210—1218).—Only one of the four groups of micro-organisms of the ripe grape, namely, *Saccharomyces ellipsoideus*, can increase the concentration of alcohol in sterile grape juice above 5% and thrive in concentrations up to 14% of alcohol. To effect continuous fermentation alcohol to a concentration of 4% should be added to the must which has been previously treated with sulphur dioxide in order to kill the bacteria, when a selection of the ferments takes place exclusively in favour of *S. ellipsoideus*. Similar results have been obtained when solid media containing alcohol are inoculated.

C. C. N. VASS.

Manometric determination of gas in fermentations. A. L. RAYMOND (J. Biol. Chem., 1929,

83; 611—618).—A manometric apparatus for the determination of gas formed in fermentations is described.

C. R. HARRINGTON.

Fermentation products. IV. Relation of the acetyl group to fermentation. T. HIGAST (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 627—639).—Attention is directed to the fact that many products of fermentation contain the acetyl group. A colorimetric (nitroprusside) method for the qualitative detection of the acetyl group is given.

A. A. GOLDBERG.

Effect of various preparations on growth of baker's and brewer's yeasts. R. J. WILLIAMS, M. E. WARNER, and R. R. ROEHM (J. Amer. Chem. Soc., 1929, 51, 2764—2773).—Six strains of yeast (three baker's and three brewer's) are compared in their behaviour towards " α - and β -bios" (Eddy and Kerr, Proc. Soc. Exp. Biol. Med., 1928, 25, 340), " β -bios I" (inositol) (Eastcott, A., 1928, 1056), and the preparation (A) previously described (Williams, Wilson, and von der Ahe, A., 1927, 592). The various yeasts grow at different rates and it is found that addition of yeast extract to the authors' synthetic medium stimulates growth, maximum crops being obtained when the largest amounts of extract are added. A short growth period (18 hrs.) is better than a long one (48 hrs.) for quantitative measurements. Adsorption of A on fuller's earth gives two fractions, (B) adsorbed, (C) unadsorbed. When B is used in conjunction with C growth in two cases is stimulated very markedly by very small doses of B. In absence of C little effect is shown by B. With C and " α - and β -bios" no appreciable increase in growth is observed, and the action of B is not supplemented by either " α - or " β -bios." Inositol, in the doses used, has little effect on the growth of any of the yeasts in absence or presence of B, and Eastcott's conclusion (*loc. cit.*) that " β -bios I" and inositol are identical does not appear justified.

H. BURTON.

Separation of nitrogen during yeast fermentations. N. N. IVANOV and F. A. KRUPKINA (Biochem. Z., 1929, 212, 255—266).—In short fermentations of sugar solutions with pure cultures of *Saccharomyces cerevisiae*, *apiculatus*, *Pastorianus*, and *Ludwigii*, nitrogen passes into solution as a result of decomposition of yeast protein. The process of nitrogen separation is bound up with that of fermentation, since in presence of unfermentable sugar (*S. Ludwigii* and maltose) no such separation of nitrogen occurs, and it must be distinguished from the smaller nitrogen liberation obtained during autolysis of yeast in water.

P. W. CLUTTERBUCK.

Sulphite fermentation. F. POLAK (Biochem. Z., 1929, 212, 363—398).—The effect on the yield of glycerol and aldehyde and on the rate of fermentation, of variations in the medium, saturation with carbon dioxide, and variations in the rate of increase of sulphite concentration is investigated. The most suitable medium for sulphite fermentation (18% of sulphite) contains 1% of potassium phosphate, 1% of magnesium sulphate, 0.5% of ammonium sulphate, and 0.5% of calcium carbonate, the yeast sowing being 8% (all figures calculated on the sugar content). Using this medium, the same yeast can be

employed for nine successive fermentations. With large amounts of ammonium sulphate, the yeast suffers injury and fermentation takes much longer. On the other hand, with a high sulphite concentration (54%) and saturation with carbon dioxide, a somewhat better yield of glycerol is obtained with higher concentrations of ammonium sulphate, e.g., with 0.2% and 1.2% of ammonium sulphate the yields are 30.80 and 37.84%, respectively, but the time of fermentation is longer, and with still greater amounts of sulphate the yield falls away. Even when the most suitable conditions are chosen (*i.e.*, using calcium carbonate, small amounts of ammonium salts and gradual increase of sulphite concentration) it was not found possible to increase the yield of aldehyde above 17%. In the initial stages the aldehyde content is always equal to and the alcohol greater than the free carbon dioxide. The results favour the view that the sulphite fermentation is based on a coupled reaction. P. W. CLUTTERBUCK.

Behaviour of sodium glucosesulphite with yeast. C. NEUBERG (Biochem. Z., 1929, 212, 477—489).—The mechanism of sulphite fermentation by coupled reaction (see preceding abstract) is adversely criticised. Sodium glucosesulphite is unfermentable in all concentrations by either top or bottom yeast and it retards the fermentation of added hexose. If a quantity of base be added to sodium glucosesulphite, typical fermentation is obtained, the result being as if free sugar was formed and the liberated toxic hydrogen sulphite converted into the non-toxic neutral sulphite. If sodium glucosesulphite (2 mols.) is fermented along with sugar (1 mol.) and sodium hydrogen carbonate (2 mols.) the sulphur dioxide distributes itself between fixed and free sugar and the aldehyde formed is the same as from 3 mols. of sugar and 2 mols. of sodium sulphite. The fixation of aldehyde is a true fixation of a product of fermentation and is not due to the breakdown of an initially formed stable sugar sulphite. P. W. CLUTTERBUCK.

Production of coproporphyrin by yeast. H. FINK (Biochem. Z., 1929, 211, 65—130).—Experiments with two strains of yeast (*Saccharomyces anamensis*) which were propagated for more than a year in a medium and under conditions which led to the accumulation of coproporphyrin gave the following results. More than 30 generations were grown, but the great accumulation of porphyrin did not cause the death of the yeasts. During satisfactory growth and good fermentation the p_H falls from the neutral point to 4. The number of cells which give red fluorescence, measured in alternate generations, is proportional to the number of dead cells present. The glycogen content of the cells is high and is always accompanied by low protein content. The respiratory properties and fermenting powers of the yeasts, compared with those of ordinary yeast, show that an alteration in the type of metabolism has taken place. Accompanying great accumulation of porphyrin there is a formation and disappearance of intensely red dyes in the production of which light seems to play a part. The dyes may be originally present as uncoloured substances which are subse-

quently transformed by the action of light. In all the yeasts, even in the oldest cultures, the spectrum of cytochrome is recognisable. In the neighbourhood of p_H 4 there is an isoelectric region for coproporphyrin and in this region its properties assume critical values. Most of the coproporphyrin (70—80%) of the yeast-cells exists adsorbed on their surfaces and is easily removed without damage to the cells. The remainder exists within the cells. Conversely, yeast will remove coproporphyrin quantitatively by adsorption from very greatly diluted solutions. The porphyrin does not penetrate the living cells. W. McCARTNEY.

Physical and biological study of the dextro-rotatory sterol isolated from beer yeast. R. FABRE and H. SIMONNET (J. Pharm. Chim., 1929, [viii], 10, 289—291).—See this vol., 809.

Co-enzyme and vitamin-B. H. VON EULER and K. MYRBACK (Svensk Kem. Tidskr., 1929, 41, 209—211; cf. A., 1928, 1158).—From a co-enzyme preparation (activity about 75,000) a barium salt (activity 58,000) of composition Ba 20.7, P 4.82, N 11.95, pentose 17.2%, corresponding approximately with the atomic ratios N : P : Ba = 5 : 1 : 1, has been prepared. Both the activity and the composition of the salt are unchanged by reprecipitation from aqueous solution with alcohol and co-enzyme of unchanged activity can be regenerated from it. Co-enzyme is probably a nucleoside, and lowering of its activity runs parallel with fission of organic phosphorus from the preparations. It is very similar to but not identical with vitamin-B.

J. W. BAKER.

Co-enzyme. XVI. Further isolation experiments. H. VON EULER and K. MYRBACK (Z. physiol. Chem., 1929, 184, 163—168).—See preceding abstract.

Metabolic effects of mitogenetic rays. H. GESENIUS (Biochem. Z., 1929, 212, 240).—When cultures of *Saccharomyces ellipsoideus* are exposed to the action of mitogenetic irradiation the metabolism of the cells undergoes alterations.

W. McCARTNEY.

Cytochrome. I. Reduction time of normal tissue and yeast. II. Reduction time of benignant and malignant tumour tissue. R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1929, 184, 246—256).—I. The tissue is suspended in isotonic sodium chloride solution and the cytochrome and haemoglobin present are oxidised by shaking with air. The time necessary for the oxidised pigment to return to the reduced state is termed the reduction time. This varies with different normal tissues (rats) and depends also on various physical and chemical factors. The effects of temperature, hydrogen-ion concentration, and added reagents have been studied. With decrease in temperature the reduction time is prolonged (cf. Keilin, A., 1925, 1, 1112). The p_H of the medium has little effect on the time so long as the buffer action of the tissue protein suffices; when this does not suffice a retardation is observed. With added urethanes (to testicle) and alcohols (to yeast), increase in the homologous series causes an increase in the reduction time. Heavy metals, arsenic, and potassium cyanide prolong the

reduction time; yeast extract counteracts the effect of arsenic, whilst glycine (causes acceleration alone) neutralises the poisoning effect of copper sulphate.

II. The reduction time of benignant and malignant tumour tissue is invariably longer than that of the normal tissue. The glutathione content of the normal or diseased tissue has no direct relationship to the reduction time. Addition of glycine causes a diminution in certain cases (ovarial and gastric) of carcinoma.

H. BURTON.

Intracellular oxidising substances. W. LOELE (Arch. path. Anat. Physiol., 1926, 262, 39—60; 1927, 264, 809—827; Chem. Zentr., 1929, i, 2430).—A study of the α -naphthol, benzidine, and indophenol reactions with vegetable and animal cells.

A. A. ELDRIDGE.

Relation between oxidases, vital staining, post-mortal staining, and morphology of cells. W. LOELE (Arch. path. Anat. Physiol., 1927, 265, 827—843; Chem. Zentr., 1929, i, 2430).

A. A. ELDRIDGE.

Relation of oxidising substances in bacteria and yeasts to cellular oxidases. W. LOELE (Arch. path. Anat. Physiol., 1928, 267, 733—745; Chem. Zentr., 1929, i, 2430).—Naphthol- and benzidine-oxidases are found in yeasts; the appearance of the reaction is dependent on the nutrient medium and the age of the culture. Certain groups of bacteria give the oxidase reaction.

A. A. ELDRIDGE.

Role of carbohydrates in biological oxidations and reductions. Experiments with pneumococcus. R. DUBOS (J. Exp. Med., 1929, 50, 143—160).—Washed cells of pneumococcus can reduce dyes and oxidised thiol compounds only in the presence of metabolites, such as dextrose. The reduction of 1 mol. of methylene-blue appears to require almost 1 mol. of dextrose. The reduction is accelerated by meat infusion. Those systems which can reduce methylene-blue are able to form peroxides.

E. BOYLAND.

Bacterial oxidation of compounds of the p-phenylenediamine series. S. ELLINGWORTH, J. M. McLEOD, and J. GORDON (J. Path. Bact., 1929, 32, 173—183).—The ease of bacterial oxidation of p-phenylenediamine derivatives increases with the number of methyl groups in the molecule. When oxygen is allowed access to bacterial colonies previously exposed to a solution of the diamine, the monomethyl compound is the least, and the tetraethyl compound the most, toxic. CHEMICAL ABSTRACTS.

Bacterial oxidation of phenanthrene. V. O. TAUSON (Planta, Arch. wiss. Bot., 1928, 5, 239—273; Chem. Zentr., 1929, i, 2066).—Bacteria which can utilise phenanthrene as a source of carbon occur in the soil of oil-bearing districts. *Bacillus phenanthrenicus bakiensis*, *B. gurikus*, and *Bacterium phenanthrenicum* oxidise phenanthrene between p_H 4.0 and 8.7 without marked production of acid. Since all three varieties can utilise pyrocatechol, salicylic acid, saligenin, and quinic acid, two can utilise quinol, and one phenol, the reaction probably proceeds in the following stages: phenanthrene, saligenin, o-hydroxybenzaldehyde, salicylic acid, pyrocatechol.

A. A. ELDRIDGE.

Biochemical reactions of streptococci. G. J. HUCKER (Zentr. Bakt. Par., 1929, I, 111, 31—64; Chem. Zentr., 1929, i, 2545).—Two groups of streptococci are differentiated. The first (aromatic) group, represented by *S. Kefir*, forms l-lactic acid and fairly large quantities of volatile acids; lactose is first hydrolysed. Lævulose is preferred to dextrose as a source of carbon. The second group, typified by *S. lactis* and *S. pyogenes*, forms d-lactic acid and comparatively small quantities of volatile acids. Streptococci from milk and milk products form acetic acid and traces of propionic and higher acids, whilst human pathogenic streptococci form acetic and probably formic acids.

A. A. ELDRIDGE.

Production of carbon dioxide by streptococci. G. J. HUCKER (Zentr. Bakt. Par., 1929, II, 77, 145—150; Chem. Zentr., 1929, i, 2435).—With most of the streptococci examined the production of carbon dioxide was increased correspondingly with the peptone content of the nutrient medium, whilst addition of sugar did not affect it. Exceptions are recorded.

A. A. ELDRIDGE.

Respiration of luminous bacteria and the effect of oxygen tension on oxygen consumption. C. S. SHOUP (J. Gen. Physiol., 1929, 13, 27—45).—Luminous bacteria suspended in *Limulus* serum consume oxygen and produce carbon dioxide at a rate independent of the oxygen pressure provided that this is between 152 and (approx.) 22.8 mm. At a lower oxygen pressure the respiratory activity gradually decreases until at 2 mm. it is reduced to 50% and at this point luminescence becomes dim. Pure nitrogen stops respiratory activity and pure oxygen irreversibly inhibits oxygen consumption. The curve for rate of oxygen consumption with oxygen concentration agrees with the Langmuir equation expressing the amount of gas adsorbed in unimolecular layer at catalytic surfaces at various gas pressures.

W. O. KERMACK.

Reducing intensity of luminous bacteria. E. N. HARVEY (J. Gen. Physiol., 1929, 13, 13—20).—The oxidation-reduction potential of a suspension of *B. Fischeri*, a fluorescent bacterium, in 0.25M-phosphate buffer at p_H 7.6 has been investigated by observing its effects on a series of "Redox" indicators. All indicators used, with the exception of indigomonosulphonate, were ultimately reduced by the bacteria, the more positive quickly even in presence of air, the more negative ones slowly and after the luminescence had disappeared and the available oxygen was practically exhausted. Under anaerobic conditions the reduction potential may be placed at r_H 8—10, whilst under aerobic conditions it appears to be about r_H 18—20. Potassium ferricyanide does not cause the luminescence to disappear and this is taken to indicate that this strong oxidising agent does not penetrate into the bacteria. The disappearance of the fluorescence after the addition of small quantities of quinone indicators may be due either to the oxidation of a luciferin-like compound in the bacteria or to a toxic effect of the indicator.

W. O. KERMACK.

Fermentation of dextrose and xylose by nodule bacteria from lucerne, clover, pea, and soybean.

M. FOOTE, W. H. PETERSEN, and E. B. FRED (Soil Sci., 1929, 28, 249—256).—Cultures of *Rhizobium meliloti*, *R. trifolii*, *R. leguminosarum*, and *R. japonicum* grown in sugar media with chalk or basic slag produced greater sugar destruction than when grown in the absence of these substances. The rate of fermentation declined with increasing age of the cultures. The maximum number of organisms per culture usually developed about 10 days after inoculation.

A. G. POLLARD.

Fixation of atmospheric nitrogen by *Phoma radicis callunae*, and a new method for investigating nitrogen fixation by micro-organisms. W. N. JONES and M. L. SMITH (Brit. J. Exp. Biol., 1928, 6, 167—189).—*Calluna vulgaris* can utilise sufficient atmospheric nitrogen to prevent nitrogen starvation. An apparatus for studying the fixation of nitrogen by micro-organisms is described. The mycorrhizal fungus of *C. vulgaris*, when grown in a nitrogen-free medium, utilises more dextrose when molecular nitrogen is available.

CHEMICAL ABSTRACTS.

Biological production of nitrite in organic media. E. RUNOW (Zentr. Bakt. Par., 1929, II, 77, 193—205; Chem. Zentr., 1929, i, 2435).—A strain of bacteria which, when grown on an organic medium with ammonium sulphate, forms nitrite has been isolated; the amount of nitrite produced depends on the presence of a nutrient medium containing carbon, on the quantity of ammonium sulphate, on the temperature, and on the aeration. Tyrosinase is present.

A. A. ELDRIDGE.

Conditions of amine production by *B. coli*. G. ROSKE (Jahrb. Kinderheilk., 1928, 120, 186—195; Chem. Zentr., 1929, i, 2435).—In dextrose-bouillon, but not in peptone-bouillon unless acid, *B. coli* produced tyramine and histamine. Buffering with lactate diminishes the production of amine.

A. A. ELDRIDGE.

Lipins of tubercle bacilli. IV. Purified wax of tubercle bacilli. R. J. ANDERSON (J. Biol. Chem., 1929, 83, 505—522).—The crude wax obtained from tubercle bacilli (A., 1927, 1114) was purified by precipitation with methyl alcohol from its solution first in ether and then in toluene, yielding a substance with m. p. 200—205°. This material was subjected to exhaustive hydrolysis with alcoholic potassium hydroxide; at an early stage a substance separated which was soluble in water and, after hydrolysis by acid, reduced Fehling's solution. The other hydrolytic products were separated in the usual manner, yielding an unsaponifiable saturated substance, having C 81.7%, H 13.64%, m. p. 57—58°, and possessing both acidic and alcoholic properties, which is regarded as possibly a mixture of higher alcohols and fatty acids, and a mixture of fatty acids containing palmitic, stearic, oleic, and cerotic acids together with a liquid unsaturated acid having $[\alpha]_D^{20}$ —1.65°, which is analogous to phthioic acid (this vol., 1108). When hydrolysed with alcoholic hydrochloric acid, the original wax yielded a water-soluble fraction containing glycerophosphoric acid and a mixture of reducing sugars giving pentose reactions. The original material is therefore regarded

as a complex phosphatide containing a large proportion of carbohydrate.

C. R. HARRINGTON.

Bacteria. XXIX. De-fatted residue of avian tubercle bacilli. A. G. RENTFREW (J. Biol. Chem., 1929, 83, 569—577).—Avian tubercle bacilli were dried, pulverised, and de-fatted; the material was extracted with water and the filtrate yielded 0.35% of coagulable protein and 1.4% of carbohydrate together with an alcohol-insoluble fraction of undetermined nature. Extraction of the residue with dilute alkali and treatment of the extract with acetic acid yielded 2.9% of protein. The avian strain therefore differs from the human strain (cf. Coghill, A., 1926, 1277) chiefly in its lower content of carbohydrate and of alkali-soluble protein. Acid hydrolysis of the residue yielded further amounts of waxy material.

C. R. HARRINGTON.

Tuberculin fractions prepared from non-protein culture media. F. EBERSON and E. WOLFF (Amer. Rev. Tuberculosis, 1929, 19, 327—349).—The preparation of clinical test material is described. Of the original tuberculin, 3.44% was insoluble in alcohol, 1.6% was insoluble and 0.86% soluble in ether.

CHEMICAL ABSTRACTS.

Separation of invertase from cells. N. N. IVANOV and M. A. KUDRJAVEVA (Biochem. Z., 1929, 212, 241—254).—Separation of invertase from *Aspergillus niger* is very small in acid medium and increases as the p_H approaches neutrality, decreasing on adding oxalic acid and increasing with calcium carbonate. It occurs both as a result of growth of the mould and to a greater extent as a result of autolytic processes which bring about decrease of the weight of the mycelium. Separation of the enzyme occurs when the mould is grown on peptone, starch, or glycogen, but occurs to the greatest extent on sucrose and inulin, and to the least on a mixture of dextrose and laevulose or on invert-sugar. The results favour the view that the hydrolysis of sucrose occurs on the surface of the mycelial protoplasm.

P. W. CLUTTERBUCK.

Heart hormone. XI. L. HABERLANDT (Pflüger's Archiv, 1929, 221, 576—590; Chem. Zentr., 1929, i, 2197—2198).—A study of sensitivity.

A. A. ELDRIDGE.

Heart hormone. Active constituent of Haberlandt's frog's heart hormone. R. RIGLER (Pflüger's Archiv, 1929, 221, 509—525; Chem. Zentr., 1929, i, 2197).—The Haberlandt effect is caused by two distinct substances; one is potassium, and the other is an ether-soluble substance.

A. A. ELDRIDGE.

Assay of insulin. K. SARGIN (Arch. exp. Path. Pharm., 1929, 144, 173—189).—Methods for the biological assay of insulin are discussed and criticised.

W. O. KERMACK.

Action of insulin on the free muscle-sugar of the normal and diabetic heart. E. W. H. CRUICKSHANK and S. PROSAD (Indian J. Med. Res., 1928, 16, 473—477).—The addition of insulin to the normal heart reduces the free sugar. When the diabetic heart is treated with normal blood which contains insulin the effect in reducing the sugar is greater than the change due to merely perfusing the diabetic heart with normal blood.

CHEMICAL ABSTRACTS.

Regulation of carbohydrate metabolism.
Renal excretion of insulin. A. PARTOS (Pflüger's Archiv, 1929, 221, 562—570; Chem. Zentr., 1929, i, 2437).—Experiments on rabbits and man show that insulin is a constituent of the urine, but is lacking in hunger, alimentary hyperglycemia, and pancreas diabetes. Adrenaline glycosuria in fasting animals does not cause an increase in the production of insulin. A. A. ELDRIDGE.

Glycogen of the internal ear of the guinea-pig.
VI. Changes due to the injection of insulin.
VII. Post-mortem changes. H. TANAKA (Sci-i-Kwai Med. J., 1929, 47, No. 12, 1—11, 12—26).—The effect of insulin is identical with that on the glycogen of other organs. After death, the glycogen of the internal ear disappears almost completely within 30 min. CHEMICAL ABSTRACTS.

Tissue respiration. V. Effect of thyroxine, adrenaline, and insulin on the oxygen uptake of the surviving rat's diaphragm. G. PAASCH and H. REINWEIN (Biochem. Z., 1929, 211, 468—474; cf. A., 1928, 1287).—No increase in the oxygen uptake of the surviving rat's diaphragm was caused by addition of thyroxine, adrenaline, or insulin.

J. H. BIRKINSHAW.

Presence, distribution, and mode of excretion of the thyroid secretion in experimental hyperthyroidism, and corresponding observations on adrenaline and other hormones. E. GIACOMINI (Boll. Soc. Ital. Biol. sperim., 1927, 2, 955—1001; Chem. Zentr., 1929, i, 2198).—With animals overfed with thyroid gland, thyroxine or a substance having a similar action can be detected in almost all organs, particularly the liver and bile; the substance is present in the urine. After adrenal feeding, adrenaline can be detected in the urine and bile.

A. A. ELDRIDGE.

Method of action of the thyroid hormone. II. **Serum-proteases.** R. WEIL and M. LANDSBERG (Biochem. Z., 1929, 211, 144—153; cf. this vol., 725).—The method of Utkin-Ljubovzov (A., 1926, 648) for the determination of trypsin in serum is not quantitative and it was not found possible in this or other ways to detect an increase in the proteolytic enzymes in serum following administration of thyroxine. The results of investigations on the behaviour of enzymes in hyperthyroidism support the physico-chemical theory of the action of the thyroid hormone.

W. MCCARTNEY.

Relation of the pituitary to carbohydrate metabolism. A. K. PICKAT (J. Méd.-biol., 1927, 4, 40—62; Chem. Zentr., 1929, i, 917).—The pituitary secretion is considered to stimulate sugar metabolism. Pituitary deficiency is associated with a disturbance of the hormonal equilibrium. A. A. ELDRIDGE.

Purification of extracts containing the growth-promoting principle of the anterior pituitary. H. M. TEEL (Science, 1929, 69, 405—406).—The growth-promoting principle may be salted out by addition of anhydrous sodium sulphate to a neutralised alkaline extract of the glands at 35°. Attempts to fractionate further the globulin group of proteins in which the growth-promoter is precipitated re-

sulted in a division of the substance between the fractions. L. S. THEOBALD.

Effect of extracts containing the growth principle of the anterior pituitary on the blood chemistry of dogs. H. M. TEEL and O. WATKINS (Amer. J. Physiol., 1929, 89, 662—685).—The injection of these extracts reduced the non-protein-nitrogen of the blood. E. BOYLAND.

Melanophore hormone in the human pituitary. K. EHRHARDT (Münch. med. Woch., 1928, 76, 321; Chem. Zentr., 1929, i, 2548).—Except in certain pathological conditions, the human pituitary contains the melanophore hormone. A. A. ELDRIDGE.

Relationship between vitamin-A and carotinoids. H. VON EULER, P. KARRER, and M. RYDBOM (Ber., 1929, 62, [B], 2445—2451).—Examination of the action of lycopin, bixin, capsanthin, α -crocetin, dihydro- α -crocetin, xanthophyll, di-iodocrocin, dihydroisonorbixin, dihydro- α -crocetin methyl ester, fucoxanthin, zeaxanthin, lutein, and tri-iodocrocin towards antimony chloride shows that the Carr-Price test (A., 1926, 870) is given by many carotinoids which do not promote growth and hence that the reaction is not generally applicable to the investigation of vitamin-A. The depth of colour is very greatly influenced by oxidation of the carotinoid and a sensitive method for the examination of carotinoid preparations may be founded on this observation.

Lycopin, bixin, capsanthin, norbixin, dehydronorbixin, fucoxanthin, and dihydro- α -crocetin methyl ester do not promote growth in rats. Carotin, m. p. 182—183°, in daily doses of 0.03 mg. causes continuous growth. The nature of the preparation does not exclude the possibility of the presence in the carotin of a very active substance, but the purest carotin preparations are the most active vitamin-A preparations yet obtained. Carotin from stinging nettles is found to be slightly less active than that from carrots; it is thus evident that, if accompanying impurities are responsible for biological activity, they do not occur solely in the carrot. Experiments with dihydro- α -crocetin have not given well-defined results, possibly owing to the unusually ready oxidisability of the compound even in oil solution. Di-iodocrocin is found to be active and the probability is indicated that it is not the carotin derivative itself, but a product derived from it after resorption which is the growth-promoting factor. Results with lutein are variable. H. WREN.

Relation of carotin to vitamin-A. T. MOORE (Lancet, 1929, ii, 380—381).—Carotin fed to rats does not accumulate as such in the liver, but there is a marked increase in the vitamin-A content of the liver, as measured by the antimony trichloride colour reaction. E. BOYLAND.

So-called vitamin-A reactions. G. MONASTERIO (Biochem. Z., 1929, 212, 66—70).—Although the various reactions believed to be characteristic of vitamin-A are always given by cod-liver oil, experiments with butter, olive oil, and eggs show that these reactions are, in their present form, unsatisfactory for the purpose for which they are intended. Biological tests must always be applied. W. MCCARTNEY.

Relation of soil fertility to vitamin-A content of leaf lettuce. M. DYE and J. W. CRIST (J. Nutrition, 1929, 1, 335—338).—The vitamin-A content increased with the chlorophyll content, but was not otherwise necessarily associated with plant vigour.

CHEMICAL ABSTRACTS.

Action of gallosterin. M. MATSUOKA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 723—734).—Biological experiments show that, contrary to the statement of Shimidzu, gallosterin (vitamin-A-cholic acid) does not possess the activity of vitamin-A.

A. A. GOLDBERG.

Vitamin-A and -D content of cod-liver meal. E. M. CRUICKSHANK (Rep. World's Poultry Cong., 1928 (1927), 246—247).—Experiments on chickens are described.

CHEMICAL ABSTRACTS.

Vitamin-A and -D content of cod-liver meal. E. M. CRUICKSHANK, E. B. HART, and J. G. HALPIN (Poultry Sci., 1927, 7, 9—16).

Influence of vitamins-A, -B, -D, iron, copper, ox muscle, and liver on the course of and regeneration from the anaemia of rice disease. R. W. WHITEHEAD and O. W. BARLOW (Amer. J. Physiol., 1929, 89, 542—547).—Rats fed on polished rice and salts develop a secondary anaemia which is prevented by the addition of 2% of compressed yeast to the diet, but not by the addition of vitamins-A and -D, or of iron and copper. Ox liver or muscle prevents this anaemia, but yeast is not active as a curative agent.

E. BOYLAND.

Activity and nitrogen content of fractions obtained in the concentration of antineuritic vitamin of brewer's yeast. A. SEIDELL (Rec. trav. chim., 1929, 48, 855—859).—Extraction of brewer's yeast (nitrogen content of dry product 9.4%) with water and subsequent adsorption of the extracted vitamin on fuller's earth affords a preparation containing about 55% of the original vitamin; subsequent adsorption of the mother-liquor affords only slightly active products. About 28% of the vitamin originally present is retained by the insoluble yeast protein (nitrogen content of dry product 8.83%).

H. BURTON.

Isolation of anti-beriberi vitamin. B. C. P. JANSSEN (Rec. trav. chim., 1929, 48, 984—985; cf. A., 1927, 382).—Silicotungstic acid is a more specific precipitant for the vitamin than phosphotungstic acid, and alcoholic platinum chloride solution can be replaced by alcoholic cadmium chloride (provided the solution is not too dilute).

H. BURTON.

Vitamin-B content of various yeasts and of the wheaten bread prepared with them. A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1929, 212, 80—86; cf. this vol., 221).—Observation of pigeons and rats fed with various kinds of yeast and with bread made with the yeasts showed that the influences of the two factors present in vitamin-B must be considered separately. Brewer's yeast contained two or three times as much antineuritic factor as did baker's yeasts, but there was the same amount of growth-promoting factor in both kinds. In order to keep alive pigeons which received all the bread they could eat, the amount of yeast in the bread had to be

increased to three times that usual in bakeries. Similarly, normal amounts of yeast in bread had to be increased if growth was to be promoted in rats.

W. MCCARTNEY.

Differentiation of vitamins-B₁ and -B₂ in yeast by heat and ultra-violet irradiation. C. KENNEDY and L. S. PALMER (J. Biol. Chem., 1929, 83, 493—496).—The claim of Hogan and Hunter (A., 1928, 1059) that ultra-violet irradiation causes differential destruction of vitamin-B₂ in yeast could not be confirmed.

C. R. HARRINGTON.

Differences in vitamin-B and -C content of cereal grains during germination. C. KUCERA (Compt. rend. Soc. Biol., 1928, 99, 967—970; Chem. Zentr., 1929, i, 2065).—During germination wheat, rye, and barley contain similar quantities of vitamin-C, whilst with oats a smaller quantity was produced.

A. A. ELDRIDGE.

Vitamin content of cereals and legumes. J. BUCEK (Compt. rend. Soc. Biol., 1929, 100, 427—428; Chem. Zentr., 1929, i, 2791).—Antipolyneuritic doses for pigeons of wheat, rye, barley, oats, maize, beans, and vetch are recorded.

A. A. ELDRIDGE.

Vitamin-C content of legumes during germination. F. SIMONIK (Compt. rend. Soc. Biol., 1929, 100, 431—432; Chem. Zentr., 1929, i, 2788).—Legumes form vitamin-C during germination more rapidly than do cereals.

A. A. ELDRIDGE.

Diminution of the vitamin-B content of cereals and legumes during germination. C. KUCERA (Z. Tierzücht., 1929, 13, 387—390; Chem. Zentr., 1929, i, 2788).—In rye and wheat the vitamin-B cannot be detected after germination for 6 and 18 days, respectively. Legumes, after germination for 28 days, still contain 15% of their original vitamin.

A. A. ELDRIDGE.

Vitamin-B content of the polished rice "koji." R. TAKATA (J. Soc. Chem. Ind. Japan, 1929, 32, 626—627).—"Koji" is a product of cereals on which *Aspergillus oryzae* is grown. The contents of growth-promoting and antineuritic vitamins in the koji prepared from polished rice are determined by using young albino rats and pigeons, respectively. The rats (32—46 g.) fed with 76% of the koji as the sole source of these vitamins grew somewhat below the normal rate, reaching 105—142 g. in 3 months. Then the growth stopped and their weights began to decrease, whilst those fed with 76% of polished rice died within 2 months. The pigeons fed with 78% of the koji died in 30—41 days, showing the symptoms of polyneuritis, whilst those fed with polished rice died in 23—35 days. As the polished rice, which is the raw material of the koji, is devoid of vitamin-B, *A. oryzae* can synthesise this vitamin.

K. KASHIMA.

Calcium in urine and blood during administration of lemon juice. A. LEVI (Boll. Soc. Biol. sper., 1928, 3, 67—70; Chem. Zentr., 1929, i, 2199).—After administration of lemon juice the calcium content of the urine is markedly increased, whilst the blood-calcium falls somewhat.

A. A. ELDRIDGE.

Vitamins and light. I. Relation between rickets, ultra-violet light, and the Russell effect

(photoactivity) with various substances, particularly lipins. J. KRIZENECKY (Sbornik Českoslov. Akad. Zemed., 1928, 3, 587—682; Chem. Zentr., 1929, i, 2202).—Photoactivity is not a characteristic of animal and vegetable fats. Photo-activation is an oxidation process, the active particles being oxidation products. A. A. ELDRIDGE.

Calcification of organs under the influence of vitamin-D. C. R. H. RABL (Deut. med. Woch., 1929, 55, 63—64; Chem. Zentr., 1929, i, 2325).—Excess of calcium in the organism does not lead to pathological calcification so long as vitamin-D is lacking; calcification by feeding vitamin-D and injecting calcium carbonate is described. A. A. ELDRIDGE.

Quantitative response to varying intake of vitamin-D. H. C. SHERMAN and H. K. STIEBELING (J. Biol. Chem., 1929, 83, 497—504).—Rats at the age of 3—4 weeks were transferred to a diet adequate in all respects except for its content of vitamin-D; normal calcification, as determined by the calcium content of the fresh femurs, occurred in those cases where the diet was supplemented with dried whole (summer) milk to the extent of 5% of the total calories. When smaller amounts of dried milk were given the degree of calcification bore an approximately quantitative relationship to the amount of supplement. In such tests it is unnecessary to subject the animals to preliminary vitamin-D starvation.

C. R. HARINGTON.

Mode of action of irradiated ergosterol on the myelin forms of lecithin. C. J. BOND (Lancet, 1929, ii, 328—329).—Irradiated ergosterol increases the production of myelin forms of lecithin in water.

E. BOYLAND.

Biological inactivity of ergosterol peroxide. W. HEUBNER and F. HOLTZ (Klin. Woch., 1929, 8, 456—457; Chem. Zentr., 1929, i, 2439).—Ergosterol peroxide, $C_{27}H_{42}O_3$, produced by irradiation of ergosterol in an atmosphere containing oxygen, does not possess biological activity. A. A. ELDRIDGE.

Effect of X-rays on ergosterol. M. SUMI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 640—644).—Vitamin-D, formed by irradiation of ergosterol with ultra-violet light, is destroyed by 4 hrs. exposure to X-rays. The spectrum of ergosterol and activated ergosterol extends further into the ultra-violet region after irradiation with X-rays.

A. A. GOLDBERG.

Influence of cold periods on the respiration of plants. A. HÉE (Compt. rend., 1929, 189, 370—372).—Measurements of respiratory activity of both old and young leaves were made in the dark, and the results expressed in mg. of carbon dioxide expired per hour per g. dry weight. With old leaves the value rises from about 0.558 to 1.411 mg. after subjecting the material to cold lasting 12 days, with a minimum of -13° . The amount of the rise in respiratory activity varies according to the intensity of the cold. With young leaves a temperature of 0° to -2° produces a lowering of respiratory activity, and even after intense cold the rise is of less significance than with old leaves. In all cases the respiratory activity soon becomes normal again at temperatures above 0° .

P. G. MARSHALL.

Transformation of sugars in the ripening of the fruits of the water melon. N. N. IVANOV, R. S. ALEXANDROVA, and M. A. KUDRJAVZEVA (Biochem. Z., 1929, 212, 267—279).—During the ripening of water melon fruits, dextrose is formed in the early stages and is gradually transformed into laevulose. When the latter begins to preponderate, the two sugars begin to combine, giving sucrose. Cultivation of the wild form of water melon also leads to the appearance of sucrose.

P. W. CLUTTERBUCK.

Transformation of carbohydrates during the ripening of bananas. M. BRIDEL and C. BOURDOUIL (Compt. rend. 1929, 189, 543—545).—Starch is converted into sucrose in ripening bananas.

A. A. GOLDBERG.

Methods for the determination of the nitrogenous constituents of a cyanophoric plant, *Prunus laurocerasus*. M. E. ROBINSON (Biochem. J., 1929, 23, 1099—1113).—Methods for the determination of total, insoluble, non-coagulable, protease-, cyanide-, ammonia-, amide-, and nitrate-nitrogen are described. These were studied on the leaves of *Prunus laurocerasus* and seedlings of *Sorghum vulgare*. The methods are applicable to small quantities (10—20 g.) of material.

S. S. ZILVA.

Origin of ethereal oils in plants. L. FRANCESCONTI (Annali Chim. Appl., 1929, 19, 333—343).—A scheme is suggested for the course of the reactions giving rise to the various terpene derivatives found in pelargonium oil (cf. A., 1925, i, 759). T. H. POPE.

Effect of some salts on the germination of the seeds of *Amarantus retroflexus*. L. B. N. AXENTSEV (Biochem. Z., 1929, 211, 454—467).—Solutions of potassium and calcium nitrate stimulate the germination of the seeds of *A. retroflexus*. These salts do not affect the seed hulls, but the inner portions; they also lessen the swelling and protect against the poisoning effect of ether and phenol. The cations and anions are arranged in a lyotropic series by their protective action. Aluminium nitrate shows strong protective power. The stimulating action of the salts is not connected with the increase in hydration of the colloids.

J. H. BIRKINSHAW.

Enzyme content of seeds of different sources. M. J. LISCHKEVITSCH and S. P. PRIZEMINA (Biochem. Z., 1929, 212, 280—290).—The enzyme content of wheat and barley seeds varies with the climatic conditions of growth, the catalase, amylase, and protease contents being considerably greater when the seeds are grown in northern or mountainous southern districts. Relationships are obtained between the catalase, amylase, and protease contents and also between the lipolytic power and high acid value of the oil of the castor-oil plant.

P. W. CLUTTERBUCK.

The seeds of the earth, their coming and going. W. KINZEL (Arch. Pharm., 1929, 267, 455—465).—Chiefly botanical, dealing with the effects of light, temperature, and nature of environment on germination.

S. COFFEY.

Influence of the iodine ion on the growth and cell increase of halophytes. J. STOKLASA (Biochem.

Z., 1929, 211, 213—228).—The effect of the addition of potassium iodide to the nutrient medium supplied to sugar-beet plants growing in pure sand has been studied at all stages of growth. For the formation of new living plant material in halophytes the presence of iodine is indispensable, and plants which receive iodine (in addition to that which is present naturally) grow better, produce more sugar, and their leaves contain more chlorophyll than do controls. The absorption of iodine is greatest in the early stages of growth. At the stage where chlorophyll begins to decompose there is a great decrease in the iodine content of the leaves and when the chlorophyll disappears the iodine also disappears and collects in the upper part of the roots. At other times there is always more iodine in the leaves than in the roots. The acidity of the sap of the leaves and roots of plants receiving added iodine is very much reduced. This reduction is due to the presence of an oxidase which, in the presence of iodine (and of iron), decomposes organic acids. Oxalic acid, which plays a specially important part in the growth of sugar beet, is much more plentiful in plants poor in iodine than in those rich in iodine. The leaves and roots of sugar-beet plants contain a substance which yields furfuraldehyde and is much more plentiful in plants rich in iodine than in controls. Plants which receive toxic amounts of iodine contain great amounts (up to 10%) of compounds yielding furfuraldehyde.

W. MCCARTNEY.

Iodine liberator from *Laminaria*. G. LUNDE and K. CLOSS (Nature, 1929, 124, 578).—The "iodine liberator" in *L. digitata* (cf. Dillon, this vol., 360; Kay, this vol., 612) is not an iodide oxidase nor potassium iodate; it liberates only in acid solution most of the iodine present in the fresh aqueous extract.

A. A. ELDRIDGE.

X-Ray photography of mineral accumulations in plants. C. L. CRUTCHFIELD (Plant Physiol., 1929, 4, 145—154).—X-Ray photography is more sensitive than microchemical methods for the detection of accumulations of aluminium and iron in the nodes of maize stalks. The method is available for the study of the translocation of salts in plants.

CHEMICAL ABSTRACTS.

Mineral constituents of fungi. W. FRIESE (Z. Unters. Lebensm., 1929, 57, 604—613).—The ash contents of fungi calculated on the dry substance was found to increase during growth from 6—9% in the young organism to 9—11.6% at the beginning of decay. The composition of the ash varied in individuals of the same species according to the nature of the soil and woodlands. *Boletus edulis* from a Dolomite region contained much more lime and magnesia and much less silica than the same species grown in a sandstone country. The ash of the species examined contained 46—55% K_2O and 20—33.4% P_2O_5 . The stalks contained less ash than the pileus, the epidermis of the latter being richest in ash. All the species contained iron and manganese and in all but one (*Amanita phalloides*) the pileus was richer in manganese than the stalk. The saps of the species examined in this respect (*Lactaria deliciosa* and *L. volema*) were low in ash content, but contained both iron and manganese.

W. J. BOYD.

Mineral constituents of lucerne. B. W. DOAK (New Zealand J. Sci. Tech., 1929, 11, 108—111).—Analyses of lucerne grown on variously fertilised soils are recorded. The proportion of mineral constituents varied considerably with the nature of the fertiliser used and with weather conditions. The calcium content of lucerne was greater than that of grass pasture. In feeding values, grass pasture and lucerne in its younger stages have similar protein and carbohydrate contents, but the crude fibre of lucerne is the smaller.

A. G. POLLARD.

Effects of storage on alcoholic extracts of plant tissues. Amino-acid changes. J. E. WEBSTER (Plant Physiol., 1929, 4, 141—144).—Under all the conditions examined, storage of alcoholic extracts of spinach resulted in a decrease of amino-nitrogen.

CHEMICAL ABSTRACTS.

Assimilation of carbamide by higher plants. K. PIRSCHLE (Biochem. Z., 1929, 212, 466—474).—Fourteen different kinds of plants were grown in water culture using on the one hand carbamide and on the other ammonium nitrate as source of nitrogen. After 4—5 weeks, the roots were cut in small pieces and incubated with carbamide and the ammonia formed was titrated. The roots of the carbamide cultures showed a greater power to liberate ammonia than those of the nitrate cultures. Similar behaviour in respect of the leaves of the plants was not obtained.

P. W. CLUTTERBUCK.

Mineral content of grain. J. E. GREAVES and C. T. HIRST (J. Nutrition, 1929, 1, 293—298).—The following maximum, minimum (and average) values % are recorded: Ash: wheat 2.94, 1.35, (1.85); oats 4.87, 1.68, (4.05); barley 3.71, 2.08, (3.00); maize 1.79, 1.65, (1.73). Calcium: oats (0.117), wheat (0.09), barley (0.086), maize (0.15). Magnesium: wheat (0.184), oats (0.181), barley (0.181), maize (0.203). Sulphur: wheat (0.204), oats (0.19), barley (0.155). Potassium: wheat (0.476), oats (0.57), barley (0.561), maize (0.39). Phosphorus: wheat (0.331), oats (0.364), barley (0.351), maize (0.334). Iron: wheat (0.005), oats (0.007), barley (0.006).

CHEMICAL ABSTRACTS.

Distribution of nitrogen in some fruits. P. R. v. D. R. COPEMAN (Proc. Dept. Conf. S. Africa, Div. Chem., 1929, 394—399).—Grapes of the Hanepoot variety contained in 1925 0.017—0.034% of nitrogen in the juice, 0.060—0.072% in the berry, 0.211—0.446 g. in 100 berries, whilst in 1926 the berries contained 0.046—0.070% of nitrogen. The proportion of nitrogen in the berry is greatest at maturity. Nitrogen in apricot pulp varied from 0.108 to 0.218%, and the weight of nitrogen per 100 fruits from 3.71 to 4.68 g. In this case the proportion of nitrogen in the pulp decreased during ripening, but the absolute amount in the whole fruit showed little change. Washington Navel oranges from the Eastern Province (S.A.) averaged 0.188, 0.201, and 0.120% of nitrogen in the skin, rag, and juice, and one sample of pips contained 0.807%. Pears of the Louise Bonne variety contained 0.125, 0.063, 0.053, and 2.81% of nitrogen in the skin, pulp, juice, and pips, respectively. Spraying apricots and oranges with lead arsenate and

nicotine sprays had no significant effect on the nitrogen content of the fruits. E. HOLMES.

Agar. M. LUDTKE (Biochem. Z., 1929, 212, 419—429).—Examination of the hydrolysate of agar showed that besides galactose, a second reducing substance was present in considerable amount. After quantitative removal of galactose by phenylmethylhydrazine and of the excess of hydrazine with benzaldehyde a reducing syrup was obtained which gave the same reducing value by Fehling's and by the hypiodite methods and did not therefore contain ketose. If the hydrolysis is effected by dilute sulphuric acid and the acid removed with barium, the neutral filtrate contains barium. The barium content after removing galactose and decolorising rose to 16% of the dry substance. The acid content of the hydrolysate increased with duration of heating and the reducing value simultaneously decreased, but the hydrazine value remained practically constant. The acid was therefore formed from the second reducing substance. The substance is not of the uronic acid type. It contains a small amount of lævulic acid. A substance containing sulphur can also be obtained in solution by treatment of the agar with ammoniacal hydrogen peroxide or on hydrolysis by hypochlorite, the preparation therefrom containing 3% of sulphur.

P. W. CLUTTERBUCK.

Chemical composition of Alaskan lichens, G. C. SPENCE and O. F. KRUMBOLTZ (J. Assoc. Off. Agric. Chem., 1929, 12, 317—319).—An indication of the value of Alaskan lichens as fodder is afforded by the analyses of 21 varieties, chemical composition being recorded under the headings moisture, fat, fibre, protein, ash, and nitrogen-free extract.

H. J. DOWDEN.

Pectins of fruits. F. EHRLICH and A. KOSMAHL (Biochem. Z., 1929, 212, 162—239).—Oranges, red currants, and strawberries were investigated. The pectins from these fruits (the peel of the oranges was used) are built up from the same units—galacturonic acid (4 mols.), arabinose (1 mol.), galactose (1 mol.), acetic acid (2 mols.), and methyl alcohol (2 mols.)—as are those from sugar beet. As regards the products of hydrolysis of the various pectins, those of orange peel and sugar beet are equal in amount, whilst the differences found between the sugar beet and the other two fruits are due to the influence of enzymes and of the method of preparation. The constitution of the pectic acids of the fruits is probably the same as that of the pectic acid of sugar beet (cf. this vol., 1273).

W. MCCARTNEY.

Pectic acid and methyl alcohol contents of Russian tobacco. G. GABEL and G. KIPRIANOV (Biochem. Z., 1929, 212, 337—346).—The amount of pectic acid in a number of kinds of tobacco varied from 13 to 20% of the dry weight. The acid is present in unfermented cigarette tobacco as the dimethyl and in fermented as the monomethyl ester. The mean methyl alcohol content of unfermented tobacco is 0.945%, of fermented Russian cigarette tobacco 0.411—0.717%, of cigarette tobacco 0.228—0.401, and of pipe tobacco 0.074—0.158, whilst the ratio of methyl alcohol to pectic acid (as percentage) is of unfermented tobacco 5.5—6.4, of fermented

Russian cigarette tobacco 2.9—3.2, of cigarette tobacco 1.2—2.6, and of pipe tobacco 0.4—0.7 (cf. A., 1927, 385; 1928, 95). P. W. CLUTTERBUCK.

Tobacco fermentation. T. ANDREADIS (Biochem. Z., 1929, 211, 378—394).—The tobacco was ripened in a closed system so that the volatile products (methyl alcohol and carbon dioxide) could be collected and measured. The pectin methyl alcohol in the tobacco diminished by about 30% during fermentation, the lignin methyl alcohol increased by about 100%. In unfermented tobacco pectase, hexose-diphosphatase, lipase, and amylase were found, but no glyoxalase.

J. H. BIRKINSHAW.

Carbohydrates of the phosphatides [of soya bean]. B. REWALD (Biochem. Z., 1929, 211, 199—201).—If phosphatide from soya bean after purification by precipitation with acetone and ethyl acetate is brought into colloidal solution in water, the solution shaken with ether until no more material goes into solution, and the emulsion which is formed destroyed with alcohol and salt, a clear aqueous solution, free from fat and phosphatide, is obtained. This solution does not reduce Fehling's solution, but after boiling with acid reduction takes place and dextrose can be identified in the solution. The phosphatide in the ether can be completely freed from carbohydrate by repetition of the process. No directly-reducing sugar is found during the process and the phosphorus content of the phosphatide rises. Experiment shows that lecithin from yolk of egg may contain very small amounts of a di- or poly-saccharide. It follows that no pentoses or hexoses are naturally associated with phosphatides and that there is no chemical combination between them and the carbohydrates with which they are found.

W. MCCARTNEY.

Constituents of *Arctium Lappa*. I. J. SHINODA and M. KAWAGOE (J. Pharm. Soc. Japan, 1929, 49, 94—97).—From the ethereal extract of the crushed seeds of *Arctium Lappa*, an oil is obtained from which, on keeping, crystals of palmitic acid separate. The alcoholic extract of the seeds which have previously been extracted four times with ether contains a compound, $C_{23}H_{38}O_6 \cdot H_2O$ (from hot water), m. p. 112°, to which the name *arctiin* has been given. When *arctiin* is heated with 29% sulphuric acid for 2 hrs., dextrose is split off and *arctigenin*, $C_{22}H_{26}O_6$, m. p. 102°, is obtained, which reduces ammoniacal silver solution, gives a bluish-green colour with ferric chloride, and is soluble in sodium hydroxide but insoluble in sodium carbonate solution. This compound is also obtained from the ethereal extract of the seeds of *A. Lappa* after these have been kept for 8—9 months. When *arctigenin* is oxidised by potassium permanganate in acetone solution it yields veratric acid and, probably, formic acid, and when fused with alkali, protocatechuic acid and formic acid. *Arctigenin* gives a tribromo-derivative, $C_{22}H_{23}O_6Br_3$, m. p. 194—195°, which when oxidised with potassium permanganate yields 6-bromoveratric acid and on reduction with copper and zinc is reconverted into *arctigenin*. By treatment of *arctigenin* with methyl sulphate or diazomethane, a compound, $C_{23}H_{28}O_6$, m. p. 125—127°, is obtained which on nitration yields *nitromethylarctigenin*, ${}_{23}CH_{24}O_6(NO_2)_4$, m. p. 204—

206°. Treatment of aretigenin with alcoholic alkali followed by acidification yields a compound, m. p. 117—118°, soluble in sodium carbonate, from which aretigenin is recovered on recrystallisation. This reaction indicates the presence of a lactone ring.

W. O. KERMACK.

Examination of roots and leaves of *Saussurea Lappa*, Clarke. I. S. GHOSH, N. R. CHATTERJEE, and A. DUTTA (J. Indian Chem. Soc., 1929, 6, 517—522).—The dry root contains 1.51% of essential oil (cf. Semmler and Feldstein, A., 1915, i, 429), about 6% of resin, 18% of inulin, small amounts of a bitter substance, tannins, fixed oil, potassium nitrate, and sugars, and 0.05% of an alkaloid (termed *saussurine*), isolated by extraction with alcoholic ammonia. The dry leaves contain 0.02% of *saussurine* but no essential oil.

H. BURTON.

Ligno-cellulose group. I. Constituents of water hyacinth (*Eichornia crassipes*). H. K. SEN, P. P. PAL, and S. B. GHOSH (J. Indian Chem. Soc., 1929, 6, 673—690).—The green plant (ash content 1.1%; organic matter 3.7%) contains starch in all its parts, but the air-dried plant (moisture 13.46%; ash 19.75%; fats 7.7%; α -, β -, and γ -cellulose 42.23%; lignin 11.1%; nitrogenous matter 5.55%) is starch-free. The ash contains appreciable amounts of potassium chloride, calcium phosphate, aluminium oxide, and alkali carbonate. Acetylation of the fat-free, dried plant with boiling acetic anhydride and subsequent separation of the lignin by treatment with 2% chlorine dioxide solution gives a cellulose acetate (30.27% Ac) containing hemicellulose. When the product is first delignified and then acetylated the acetyl content of the cellulose acetate is 20.82%. Treatment of these partly acetylated derivatives with 17.5% sodium hydroxide solution removes the hemicellulose and acetyl groups, affording α -cellulose. Acetylation of the crude or chlorine peroxide-treated cellulose with a mixture of acetic acid, acetic anhydride, and sulphuric acid gives a cellulose triacetate. Extraction of the dry plant with boiling water and subsequent hydrolysis with sulphuric acid of varying concentration under pressure affords varying amounts of reducing sugars, mainly pentoses. Preliminary extraction with boiling 5% sulphuric acid and subsequent hydrolysis yields only small amounts of fermentable sugars. Other experiments on the hydrolysis of the plant are described. Destructive distillation of the dry plant at 500° and 1000° yields mainly oxides of carbon, hydrogen, methane, nitrogen, and a residue of charcoal. Preliminary experiments on the bacterial decomposition (by septic tank fluids) of the green plant are described.

H. BURTON.

Alkaloid content of chlorophyll from *Datura stramonium* leaves. M. JANICSEK (Ber. ungar. Pharm. Ges., 1929, 5, 86—95; Chem. Zentr., 1929, i, 1840—1841).—Extracts of the leaves with alcohol followed by benzene contained 0.58—2.76% of alkaloid; extraction in a Soxhlet apparatus removes almost the whole of the alkaloid.

A. A. ELDRIDGE.

Colouring matters of *Carthamus*. V. ASTRADA (Rev. farm. Buenos Aires, 1929, 2, 159—160).—*Carthamus* flowers contain H_2O 9.10, nitrogenous

substances 17.50, resin 42.50, cellulose 13.0, fat 3.90, starch 2.90, ash 11.10%. The yellow colouring matter, probably a quinoline derivative, is soluble in water but not in the usual organic solvents. Another yellow substance, contained in the cell membrane of the petals, is soluble in alkali.

CHEMICAL ABSTRACTS.

Modification of Mayer's "hæmalum." J. E. SASS (Stain Tech., 1929, 4, 127—129).—A satisfactory strain for botanical work is made as follows. To a hot solution of 50 g. of ammonium alum in 1 litre of water are added 1 g. of hæmatoxylin and 1 g. of sodium iodate. The mixture is then cooled and filtered. The stain is best when freshly prepared, but keeps for at least 6 months.

H. W. DUDLEY.

Inversion method for determination of hydrogen-ion concentration of wine. G. AGABALIANZ (Biochem. Z., 1929, 211, 373—377).—An improved thermostat for high temperatures, specially adapted to the determination of p_H by inversion of sucrose, is described.

J. H. BIRKINSHAW.

Determination of p_H , particularly of blood, using the antimony electrode and by colorimetric methods. H. G. K. WESTENBRINK, J. A. A. PIETERS, and J. J. L. PIETERS (Arch. Neerland. Physiol., 1929, 14, 386—393).—Satisfactory results in the micro-determination of the p_H of blood cannot be obtained with antimony electrodes, whether in the compact metallic form or electrolytically deposited on platinum as described by Brinkman and Buytendijk (A., 1928, 1391). The colorimetric method of Hawkins (J. Biol. Chem., 1923, 57, 493) is shown to give results closely agreeing with that of Cullen (A., 1922, ii, 672), and is regarded as the most satisfactory method for micro-determination.

K. V. THIMANN.

Determination of hydrogen exponent by means of the step-photometer. I. A. JANKE and S. KROPACSY (Biochem. Z., 1929, 213, 154—169).—The use of the photometer for determination of p_H depends on the equilibrium between the pseudo- and the ionised form of the indicator. The indicators recommended for use around neutrality are the nitrophenols. The step-photometer of Pulfrich gives p_H values correct to 0.05 and can be used for cloudy or coloured solutions, since no standard is necessary. The method is described.

J. H. BIRKINSHAW.

Micro- and histo-chemical identification of alkaloids. A. NIETHAMMER (Biochem. Z., 1929, 213, 138—141).—Reinecke salt gives characteristic crystalline precipitates with many alkaloids and is recommended as a specific group reagent. In the tissue the reaction is seldom obtained, more frequently in the tissue juice. Saponins give a red colour.

J. H. BIRKINSHAW.

Twin tubes with membrane filters. I. N. ASHESHOV (Biochem. Z., 1929, 211, 202—206).—An account is given of the construction and uses of a simple apparatus to be employed in experiments involving diffusion through semipermeable membranes. Errors due to the employment of membranes of unequal permeability are eliminated by the use of the apparatus.

W. McCARTNEY.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1929.

General, Physical, and Inorganic Chemistry.

Nomenclature and symbolism for the spectra of diatomic molecules. O. W. RICHARDSON (Trans. Faraday Soc., 1929, 25, 628—633).—A notation is described, having regard to existing usages, and those for line spectra, suitable for the quantum treatment of the molecule as a whole, and of the individual electron, and the specification and quantum interpretation of molecular spectra. Standard symbols for important molecular constants are proposed.

N. M. BLIGH.

Detailed electronic structure of diatomic molecules, with special reference to carbon monoxide. R. C. JOHNSON (Trans. Faraday Soc., 1929, 25, 649—668).—The present knowledge of general molecular structure gained from a study of electronic band spectra and the recent extensions of the methods of line spectra interpretation to the study of the electronic structure of molecules by Hund, Mulliken, and others are discussed. The mechanism of molecule formation is investigated from a consideration of atoms in an electric field; the resulting quasi-molecular states are tabulated for atoms of the first short period. The states of a molecule composed of two of these atoms are illustrated for the BeO molecule. About 16 band systems are known for the neutral CO molecule and three for the CO⁺ ion. The known levels and transitions are given diagrammatically. The third positive carbon bands show the first recorded case of a quintuplet level in band spectra. The nature of the ground state is discussed, and the structure of the CO molecule and the interpretation of the electronic states are examined.

N. M. BLIGH.

Band spectra and atomic nuclei. R. S. MULLIKEN (Trans. Faraday Soc., 1929, 25, 634—645).—Mainly mathematical. Alternating intensities and alternate missing lines in band spectra are explained on the assumption that a molecule must be antisymmetrical in all electrons, as confirmed by line spectra, and also in all protons. This rule for protons is examined theoretically for hydrogen and is confirmed by specific heat and band spectrum data. The theory is extended to molecules with complex nuclei, existing data are tabulated, and some difficulties are discussed. In agreement with theory, alternating intensities have not been found in molecules with unequal nuclei.

N. M. BLIGH.

Term representation in complex spectra. O. LAPORTE (Prob. mod. Physik, Debye-Sommerfeld Festschr., 1928, 128—133; Chem. Zentr., 1929, i, 2617).—A discussion.

A. A. ELDRIDGE.

Line structure. D. G. BOURGIN (Physical Rev., 1928, [ii], 31, 704).—A discussion. L. S. THEOBALD.

Second order Stark effect in Balmer lines. M. KIVRI (Z. Physik, 1929, 57, 658—666).—The second order Stark effect for the fine components of the H_γ and H_β lines has been determined quantitatively by Lo Surdo's method in fields up to 575,000 volts/cm. The results are in good agreement with the values required by quantum mechanics.

J. W. SMITH.

Doublet separation of Balmer lines and the molecule of hydrogen in relation to the electromagnetic quantum theory. C. L. SAGUI (Physical Rev., 1928, [ii], 31, 715).—Theoretical. The doublet separation of the Balmer lines of hydrogen has been calculated, using the electromagnetic quantum theory, and good agreement found. The continuous and infra-red spectra have also been studied.

L. S. THEOBALD.

Hydrogen absorption [in the ultra-violet]. J. J. HOPFIELD (Physical Rev., 1928, [ii], 31, 918).—The ultra-violet absorption systems have been extended to include the bands A_n-B and C_{10} , bringing both systems near the converging limit. From the data the heat of dissociation of H_2 with excitation of one of the atoms to the two quantum orbit can be calculated. Further experiments with less hydrogen in the receiver show that the absorption limit previously used by Dieke and Hopfield in connexion with the heat of dissociation of H_2 is not real; it marks the beginning, apparently, of new and stronger absorption band systems probably related to still higher electronic excitation.

L. S. THEOBALD.

Infra-red emission of hydrogen. E. D. MCALISTER (Physical Rev., 1928, [ii], 31, 917).—A shift of intensity as a function of pressure is indicated by thermocouple observations of emission from a long hydrogen tube of the Wood type. At low pressure and with high dispersion the third member of the Brackett series has been observed.

L. S. THEOBALD.

Atomic absorption coefficients. R. M. LANGER (Physical Rev., 1928, [ii], 31, 1114).—The atomic absorption coefficients of normal hydrogen atoms for the first lines of the Lyman and the Balmer series calculated by means of the new mechanics are all high.

L. S. THEOBALD.

Non-metastability of the 2s level in atomic hydrogen. V. ROJANSKY and J. H. VAN VLECK (Physical Rev., 1928, [ii], 32, 327).—Theoretical.

L. S. THEOBALD.

Light excitation in the negative glow of a helium discharge. Y. TAKAHASHI (Ann. Physik, 1929, [v], 3, 49—57).—The different modes of excitation possible for foreign atoms in the negative glow (inside a cylindrical cathode) of a helium glow discharge are discussed. An intensity anomaly is found in the Cd II series, but similar anomalies are much less evident for Zn II and Hg II. In addition to electrons, excitation may be due to metastable 2^3S and 2^1S states of the helium atom and helium ion He^+ .

R. A. MORTON.

Intensity variation at critical points in the helium spectrum. I. CORNOG, J. T. LAY, and C. B. BAZZONI (Physical Rev., 1928, [ii], 31, 1109).—A marked minimum of intensity appears near 54 volts for all lines in general; variations in the rate of change of intensity in different series are recorded.

L. S. THEOBALD.

Effect of pressure and current density on the spectrum of helium. A. C. HODGES (Physical Rev., 1928, [ii], 32, 319).—The intensities of helium lines have been directly compared with the same wave-lengths from a standard tungsten filament. The relative intensities of the higher members of the various series increase with a decrease of pressure or current density.

L. S. THEOBALD.

Structure of the band spectrum of helium. VI. W. E. CURTIS and A. HARVEY (Proc. Roy. Soc., 1929, A, 125, 484—506; cf. A., 1928, 449; this vol., 1).—The rotation term differences for all the states of the He_2 molecule are tabulated, and it appears that in the same electronic sequence for a given value of j they tend towards a definite limiting value as n increases. These limiting values are identical in all cases and are the same for $o\text{-}He_2$ and $p\text{-}He_2$; they must evidently be those characteristic of the He_2^+ ion, since they correspond with the complete removal of an electron. The observed regularities are of great assistance in the further analysis of the spectrum and lead to a classification of the term sequences in agreement with that proposed by Dieke (A., 1928, 677). Details are given of the eight new bands: $4^3S \rightarrow 2^3U$, $4^3Z \rightarrow 2^3U$, $4^3X \rightarrow 2^3U$, $4^3Y \rightarrow 2^3U$, $4^3Y \rightarrow 2^3P$, $5^3Y \rightarrow 2^3P$, $5^3X \rightarrow 2^3P$, and $4^1D \rightarrow 2^1P$. This completes the theoretical term scheme for $o\text{-}He_2$.

L. L. BIRCUMSHAW.

Vacuum spark spectra in the extreme ultra-violet down to 100 Å. B. EDLÉN and A. ERICSON (Nature, 1929, 124, 688—689).—Wave-length standards from 1215.68 to 192 Å. have been determined. In the spectrum of Li II the first three lines of the principal series $1S \rightarrow mP$ have the wave-lengths 199.263, 177.99, 171.54 Å., respectively. Hence the ionisation potential of Li II is 75.282 ± 0.012 volts. The spectrum of Be III has been extended to 100.25 Å.; the ionisation potential of Be III is calculated as 153.10 ± 0.10 volts.

A. A. ELDRIDGE.

Beryllium hydride bands. M. PETERSEN (Physical Rev., 1928, [ii], 31, 1130).—The spectrum of a beryllium arc run in hydrogen at 5—15 mm. pressure shows a strong band group near 5000 Å. This consists of several overlapping sets of three-branch bands, of which the earliest lines are narrow doublets, and apparently embraces part of a band

system attributable to BeH with its origin at 20,032 cm^{-1} , the head of the strongest Q branch. Six P and R branches can be detected. A moment of inertia of 3.53×10^{-40} and, assuming BeH origin, an internuclear distance of 1.54×10^{-8} cm. have been calculated.

L. S. THEOBALD.

New absorption bands in nitrogen. J. J. HOPFIELD (Physical Rev., 1928, [ii], 31, 1131).—Two new band systems or a system of double bands have been observed, together with two prominent isolated bands at λ 1518.8 and 1437.2 Å. The bands are diffuse and appear to be due to a modification of nitrogen.

L. S. THEOBALD.

Alternating intensities in the spectrum of nitrogen. F. RASETTI (Nature, 1929, 124, 792—793).—Results already reported (this vol., 975) have been confirmed. For oxygen the electronic wave function of the normal $^3\Sigma$ state is antisymmetrical, and oxygen nuclei, as expected, satisfy the Bose-Einstein statistics.

A. A. ELDRIDGE.

Absorption of ultra-violet light by oxygen, water vapour, and quartz. L. P. GRANATH (Physical Rev., 1929, [ii], 34, 1045—1048).—Measurements were made in the spectral region 1850—2300 Å. by means of a quartz spectrograph and a recording densitometer. Oxygen at atmospheric pressure in tubes up to 5 metres in length showed the peaks of absorption due to the Schumann-Runge band system below 1970 Å.; from 2000 to 2100 Å. the absorption appeared continuous with no marked peaks, the absorption coefficient α being 0.00025, 0.00032, and 0.0005 at 2100, 2050, and 2000 Å., respectively. Values of α for saturated water vapour at 25° were 0.0005, 0.0013, 0.003 at 2050, 1950, and 1900 Å., and for crystalline quartz 2.5 cm. thick, 0.086, 0.11, 0.13, and 0.17 at 2040, 2000, 1940, and 1870 Å., respectively.

N. M. BLIGH.

Spectra of high-frequency discharge in oxygen and carbon monoxide. R. W. WOOD (Phil. Mag., 1929, [vii], 8, 207—210).—An extension of previous work (A., 1927, 1008) on high-frequency discharges in very highly exhausted tubes. Application of the current by means of a single loop of wire round the tubes gives a bluish discharge exhibiting the secondary spectrum of hydrogen. In a few minutes this gives place to the greenish-yellow discharge of oxygen showing the characteristic four negative bands. After 4—5 min. operation the walls of the tube show a pink fluorescence which becomes ruby-red accompanied by an increase in the oxygen pressure. The luminous gas masses were spherical instead of streamlined and their positions were very sensitive to the position of the electrode. The spectrum of the light from the spheres and the adjacent regions showed both lines and bands, the bands appearing greatly enhanced in the spectral image of the spheres. The appearance of the spheres is therefore associated with gas molecules and not with atoms. The bands have been identified with the "comet tail" bands characteristic of discharges in carbon monoxide at very low pressures.

A. E. MITCHELL.

Corona discharge in neon. L. G. H. HUXLEY (Phil. Mag., 1929, [vii], 8, 128—129).—In reply to

the suggestion by Penning (Phil. Mag., 1928, [vii], 7, 632) that the discrepancies between the results of Penning and of Huxley (A., 1928, 567) were due to impurities in the gas employed by the latter, the methods adopted to assure the purity of this gas are described. Experiments are recorded which claim to show that impurities would tend to accumulate in Penning's apparatus. It is impossible to estimate the effects of these on the potentials required to produce discharges.

A. E. MITCHELL.

Magnetic rotation lines in the red sodium bands. W. R. FREDRICKSON (Physical Rev., 1928, [ii], 31, 1130—1131).—The heads of the red absorption bands of sodium have been remeasured. They can be represented by the formula $\nu = 15006.68 + (115.22n' - 0.384n'^2) - (157.14n'' - 0.423n''^2)$. The magnetic rotation lines have been photographed at high dispersion and many new strong lines accompanied by weak ones have been detected. Absorption and magnetic rotation data have been correlated.

L. S. THEOBALD.

Afterglow spectrum of argon. C. KENTY and L. A. TURNER (Physical Rev., 1928, [ii], 31, 710).—The arc spectrum of argon persists approximately 0.001 sec. after an arc of 0.5 amp. at 0.5 mm. pressure is stopped, but since the *D* lines present in the arc itself are absent in the afterglow the spectrum is not due to direct excitation by electrons. Comparative photographs show that in the afterglow lines involving jumps from high *s* and *d* states are much stronger with respect to *ls-3p* lines than in the arc. It is suggested that the afterglow spectrum results from recombination.

L. S. THEOBALD.

Zeeman effect in the calcium hydride A band. P. S. DELAUP (Physical Rev., 1928, [ii], 31, 1130).—The calcium hydride A band at 7000 Å. has been photographed with field strengths from 9000 to 23,000 gauss. At low fields the $Q_1(1)$, $Q_1(2)$, and $P_1(4)$ lines were resolved into doublets having a separation equal to twice that of the normal Zeeman separation. This agrees with Van Vleck's formula (A., 1927, 87) for the case of loose coupling of the spin axes. At low or medium fields the separation increases linearly with the field.

L. S. THEOBALD.

Intensity relations in the spectra of titanium. III. Intensities in super-multiplets of Ti I. G. R. HARRISON (J. Opt. Soc. Amer., 1929, 19, 109—133; cf. this vol., 860).—The intensities of 93 lines of the complex super-multiplet of Ti I, $^5D'FG' - ^5H'GF'DP'$, arising from the transition $[(3d)^24s]4p - 4d$, parent term a^4F' , have been measured, and also those of 31 lines of the simple super-multiplet $^5D'FG' - ^5F'$ arising from the transition $[(3d)^24s]4p - 5s$, the intensities of which were found to be normal (multiplet ratios 8.95:7.00:5.30, theory requiring 9:7:5). The complex super-multiplet has abnormal intensities; in no multiplet is the summation rule obeyed. For the super-multiplet as a whole no single temperature effects agreement with the rule either horizontally or vertically, the nearest approach being given by a temperature of 2080° Abs. The total intensities of each multiplet after application of the excitation correction agree but roughly with König's formula. Inclusion as far as possible of the corresponding multi-

plets in the triplet system, and of all inter-system lines, effects but little improvement, and it is concluded that at least all the lines originating from the parent term a^4F' by the addition of an electron undergoing the transition $4d - 4p$ must be included. Besides the intensities the intervals are in some cases abnormal, and there is an intermingling of the various levels of the upper states with one another (cf. Houston, this vol., 480).

C. A. SILBERRAD.

Spectra of doubly-ionised vanadium, V III, and triply-ionised chromium, Cr IV. H. E. WHITE (Physical Rev., 1928, [ii], 32, 318).—Doublet and quadruplet terms of the electron configurations $3d^3$, $3d^24s$, and $3d^24p$ have been determined for V III and Cr IV. Terms determined for $3d^24p$ combine with the lowest energy levels in the spectrum, $3d^3$, to give strong lines in the region 1100 Å. for V III and 600 Å. for Cr IV; the ionisation potentials computed for V III and Cr IV are 30 and 52 volts, respectively.

L. S. THEOBALD.

Arc spectrum of nickel, Ni I. H. N. RUSSELL (Physical Rev., 1929, [ii], 34, 821—857).—Tables are given of the energy levels recognised and their designations; terms and their combinations; the terms which have been assigned to each configuration, with the leading energy level and the separations between the remaining components in order of decreasing *j*; the quantum defects, and a table of the wavelength, intensity, and designation of almost all the known lines (1071) of Ni I. Included are 66 lines from the solar spectrum not yet found in the laboratory. The spectrum is regular, and in accordance with Hund's theory. A few of the predicted terms have not been found, but their combinations should be very faint. The principal ionisation potential of the neutral Ni atom is calculated to be 7.606 volts, corresponding with a double electron change from the configuration d^8s^2 to d^9 .

N. M. BLIGH.

Absorption spectrum of nickel vapour. New multiplet of nickel. R. G. LOYARTE and A. T. WILLIAMS (Physikal. Z., 1929, 30, 634—640).—The absorption spectrum of nickel vapour has been studied at 2500° Abs. and earlier results (A., 1927, 5, 395, 396, 607, 910) have been confirmed and extended. Some terms in the arc spectrum of nickel have been classified and five new multiplets recognised. The application to nickel of the equation $N'/N = e^{-E/RT}$ has been considered (N'/N is the ratio of excited atoms to total atoms for deep levels). Atoms like nickel, in which the deep levels show two different configurations the term values of which overlap, require the modified formula $N'/N = e^{-E/RT + \Delta E/RT}$, ΔE being the energy necessary for the transition from one configuration to another (cf. this vol., 366).

R. A. MORTON.

First spark spectra of zinc and cadmium. Y. TAKAHASHI (Ann. Physik, 1929, [v], 3, 27—48; cf. Paschen, A., 1928, 97; this vol., 365).—The spectra of Zn II and Cd II have been photographed with quartz and vacuum grating spectrographs, using the negative glow of a helium discharge, small quantities of the metal vapours being present. Analogies with Cu I and Hg II have assisted in the analysis of the spectra, the liberation of a *d*-electron from the tenth shell playing an important part. Wave-lengths, term

values, and combinations are tabulated. In Cd II the higher terms of series are greatly enhanced, indicating preferential excitation of the metal atom by means of helium ions, whereas the transformation energy of the metastable helium atom in the 2^3S state cannot be drawn on for this purpose (cf. also von Salis, A., 1925, ii, 334). R. A. MORTON.

First spark spectrum of arsenic, As II. C. W. GARTLEIN (Physical Rev., 1928, [ii], 32, 320).—The spark spectrum of arsenic below 2300 Å. has been photographed, using various amounts of inductance in series with the spark. The As II lines were present even with large amounts of inductance, but lines from higher states decreased in intensity with an increase in inductance. The spectrum was also characterised by "long lines" due to glowing arsenic vapour. All terms of $(4p)^2$ and $4p5s$ have been identified as well as some from the configuration $4p4d$, and parts of the terms due to $4p5p$ have been identified by lines in the visible spectrum due to transitions into the levels of $4p5s$. L. S. THEOBALD.

Second spark spectrum of selenium. A. S. RAO (Z. Physik, 1929, 58, 251—254).—The second spark spectrum of selenium has been mapped and analysed. A. J. MEE.

New cadmium hydride bands in the ultra-violet. E. BENGTSSON and R. RYDBERG (Z. Physik, 1929, 57, 648—657).—New CdH^+ bands have been found over the wave-length range 2200—2700 Å., and the conditions under which these bands are excited have been investigated. The separate bands may be divided into simple *P*- and *R*-branches, and the system is ascribed to $^1\Sigma' \rightarrow ^1\Sigma'$ electron jumps of the ionised cadmium hydride. The intensity distribution in these bands is discussed. The dissociation energies of the two electronic states are calculated as 2.5 volts and 1.9 volts, respectively, and the ionisation potential of the neutral cadmium hydride molecule as 7.8 volts. J. W. SMITH.

Carrier of the absorption and fluorescence bands observed in cadmium vapour. W. KAPUŚCINSKI and A. JABLOŃSKI (Z. Physik, 1929, 57, 692—695).—It is claimed that the absorption band system in the region 2590—2825 Å. attributed by Walter and Barratt (this vol., 237) to the CdO molecule is really due to the cadmium Cd_2 molecule, as stated by Jabłoński (this vol., 1) and by Winans (this vol., 481). Experiments carried out on the absorption spectrum of CdO vapour over the temperature range 500—800° showed no signs of these bands. The energy of dissociation of the Cd_2 molecule as calculated from these bands supports the view of the authors. J. W. SMITH.

Doublets and quadruplets of doubly-ionised silver, Ag III. R. C. GIBBS and H. E. WHITE (Physical Rev., 1928, [ii], 32, 318—319).—When for a sequence of isoelectronic systems starting from any element in the periodic table the energy levels representing possible electron configurations are plotted on a Moseley type of diagram, the lines connecting corresponding terms of each successive element will be practically linear. Further, the radiated frequencies resulting from electron transitions involving no change in total quantum number are displaced to higher

frequencies by a constant value. Application of these considerations to the arc spectrum of Rh I and the first spark spectrum of Pd II has enabled some of the doublet and quadruplet terms arising from $4d^9$, $4d^85s$, and $4d^85p$ of the second spark spectrum of silver to be determined. The ionisation potential of Ag III is calculated to be 34 volts approximately. L. S. THEOBALD.

Unclassified lines of the indium arc spectrum. J. G. FRAYNE (Physical Rev., 1928, [ii], 31, 152).—Four of the five unclassified lines previously reported are now classified; the line 2858.30 Å. remains unclassified. L. S. THEOBALD.

Arc spectrum of antimony. J. B. GREEN and R. A. LORING (Physical Rev., 1928, [ii], 31, 707).—The Zeeman effect has been studied for all of the stronger lines between 2500 and 4033 Å., and the *g* values of the terms have been computed. L. S. THEOBALD.

Structure of praseodymium lines. A. S. KING (Physical Rev., 1928, [ii], 32, 319).—The complex structure of praseodymium lines has been examined in greater detail using high dispersion; 400 lines approximately from λ 3100 to 6800 Å. have been listed as complex, the complexity varying from double to six-component lines. Lines compared in furnace, arc, and spark spectra apparently retain their structures unchanged. L. S. THEOBALD.

Platinum term values and classification. P. J. OVREBO (Physical Rev., 1928, [ii], 31, 1123).—Forty new intermediate and upper levels together with three new low levels have been found for platinum. Combinations of these and previous levels give 142 lines; 200 lines remain to be classified, excepting those of low intensity. L. S. THEOBALD.

Quadruplet structure of the first spark spectrum of mercury, Hg II. S. M. NAUDE (Ann. Physik, 1929, [v], 3, 1—26).—Paschen (this vol., 365) in his work on the doublet system of the first spark spectrum of mercury found $^2D_{3/2,5/2}$ terms analogous to those known for Au I and Cu I. The conditions for maintaining a satisfactory discharge in mercury vapour have been worked out so that the unclassified lines are markedly enhanced in intensity. Spectra have been recorded over the range 890—8000 Å. for mercury vapour alone, and in the presence of helium under conditions facilitating the recognition of a number of multiplets belonging to the quadruplet system. The analogous spectrum of copper confirms the classification. Wave-lengths and intensities of lines obtained with or without helium are tabulated together with term schemes and a comparison of excitation potentials corresponding with the strongest lines, with measurements based on electron collisions. R. A. MORTON.

Densitometer curves for the green mercury line. R. W. WOOD (Phil. Mag., 1929, [vii], 8, 205—207).—An examination of densitometer curves for the green mercury line taken from spectrograms made at right angles to and end on to the source show that the satellite at +0.124 is absorbed to a much smaller degree than that at +0.128, which is again less absorbed than that at +0.085. The satellites at

—0.102 and —0.07 are nearly equalised by absorption, whilst that at —0.237, in confirmation of the results of Metcalfe and Venkatesachar (A., 1921, ii, 669), shows no absorption. There is evidence of the unsymmetrical reversal of the main component.

A. E. MITCHELL.

Effect of mercury vapour on the continuous spectrum of hydrogen. H. JEZEWSKI (Spraw. Prace Polsk. Towarz. Fizycz., 1927, 3, 161—173; Chem. Zentr., 1929, i, 2857).—In the presence of mercury vapour the intensity of the continuous spectrum of hydrogen is diminished. Temperature changes do not affect the distribution of the bands. The dissociation potential of hydrogen, 2.5 volts, given by Schuler and Wolf's theory (which is criticised) is too small.

A. A. ELDRIDGE.

Self-reversed lines in the spectrum of mercury. L. H. DAWSON and W. H. CREW (Physical Rev., 1928, [ii], 31, 308; cf. this vol., 1).—Spectrograms of the region 6000—1860 Å. have been made of a mercury arc operating at the ordinary pressure and excited by a condensed discharge. Eleven arc and two spark lines were self-reversed and all of the arc lines, except 2536 Å., represent electron transitions originating on the 2^3P levels, the lowest energy levels of the excited mercury atom. Six of these lines start at 2^3P_1 , two at 2^3P_0 , and two at the 2^3P_2 level, indicating an accumulation of electrons on the supposed least stable orbit. The arc when excited by 4000, 8000, and 16,000 kilocycles at 5, 1, and 0.5 amp., respectively, gives sharp atomic lines as well as molecular bands coincident with those usually observed in fluorescing mercury vapour.

L. S. THEOBALD.

Nature of the production of one of the spark lines of mercury and the determination of mean life. L. R. MAXWELL (Physical Rev., 1928, [ii], 31, 1110).—The variation of intensity of the line 4797 Å., measured for different positive-ion currents, is the same for all points along the line and is approximately proportional to the ion current, indicating that the line results from a single electron collision with the neutral atom. The mean life is of the order 10^{-7} sec.

L. S. THEOBALD.

Voltage-intensity relations of 29 lines of the mercury spectrum. P. B. TAYLOR (Physical Rev., 1928, [iii], 31, 1135).—Data for the variation in intensity with voltage of 29 lines between 2378 and 4108 Å. are given.

L. S. THEOBALD.

Critical potentials below 4.7 volts for negative ion formation in mercury vapour. W. M. NIELSEN (Physical Rev., 1928, [ii], 31, 1134).—The critical potentials observed below 4.7 volts are 0.4, 0.8, 1.4, 1.8, 2.3, and 2.7 volts, and are ascribed to the mercury molecule. The magnitude of such negative-ion currents increases faster than the first power of the vapour pressure.

L. S. THEOBALD.

Continuous spectrum of mercury. L. H. DAWSON and W. H. CREW (Physical Rev., 1928, [ii], 32, 1109).—Band maxima observed in an arc at atmospheric pressure, excited by high voltage and low current density, are at 4500, 3300, and 2350 Å.; no continuous radiation is emitted in the region 2535—2350 Å. under these conditions, but on increas-

ing the current the bands broaden in both directions to fill this gap.

L. S. THEOBALD.

Intensities of the lines of the mercury spectrum. E. O. HULBURT (Physical Rev., 1928, [ii], 31, 1109).—The total radiation measured with a thermocouple in the region 6000—2300 Å. from a quartz mercury lamp filled with vapour at the ordinary pressure was 1.54×10^8 erg sec.⁻¹. This gives about 50 quanta emitted per atom per second. The line intensities were measured. The temperature of the excited atoms derived graphically was of the order of 10^3 degrees.

L. S. THEOBALD.

Turning impulse and effective cross-section in chemical reactions. H. BEUTLER and E. RABINOWITSCH (Z. Elektrochem., 1929, 35, 623—625).—Theoretical. The bands of mercury hydride and the cyanogen spectra are discussed.

H. T. S. BRITTON.

Excitation of radiation by metals by afterglowing mercury vapour. K. NARKIEWICZ-JODKO (Spraw. Prace Polsk. Towarz. Fizycz., 1928, 3, 257—266; Chem. Zentr., 1929, i, 3068).—The following lines were observed with various metals or their salts: sodium 5895.9, 5889.9; potassium 7699, 7665, 4047, 4044; lithium 6707.8, 6104, 4602; caesium 4593, 4555; strontium 6892, 4607; rubidium 7950, 7811, 6298.5, 6206.5, 4215.5, 4201.8; barium 5536; cadmium 6438.5, 4799.9, 4678.1; thallium 3775; calcium 6572, 4226.7 Å.

A. A. ELDRIDGE.

Total emissive power of bismuth. W. DEL REGNO (Atti R. Accad. Lincei, 1929, [vi], 10, 77—83).—Measurements of the total emissivity of bismuth have been made at temperatures between 40° and 250°. The theoretical formulæ which express the emissivity of metals in terms of their specific electrical resistance do not hold in the case of bismuth. The experimental values of the total emissivity are much smaller and of the reflecting power greater than the theoretical values. These differences are due to divergences in the expression for the emissivity $e = K T^m$ of the K term, which is a function of the specific resistance. The experimental and theoretical values of the exponent m show good agreement. The larger experimental value of the reflecting power compared with the theoretical indicates that in the case of bismuth not only the free electrons, but also those in the atoms of the lattice take part in the phenomenon of reflexion.

O. J. WALKER.

Zeeman effect of hyperfine structure and magnetic moment of the bismuth nucleus. E. BACK and S. GOUDSMIT (Physical Rev., 1928, [ii], 31, 1125; cf. A., 1928, 340).—Analysis of the hyperfine structure of the bismuth lines and energy levels shows that the bismuth nucleus probably possesses a mechanical moment of momentum, and an undetected magnetic moment. The nuclear moment is probably not produced by moving or spinning electrons in the nucleus but by positive particles.

L. S. THEOBALD.

High-frequency spark discharge in air. T. NISHI and Y. ISHIGURO (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 817—830).—The characteristics of spark discharges in air between electrodes of various

shapes have been studied at frequencies of 91,000 and 196,000 cycles. At the higher frequency the corona becomes shorter and the sparking potential is in many cases increased. In many ways high-frequency spark discharges resemble low-frequency arc discharges.

H. F. GILLBE.

Mechanism of spark discharge in air at the ordinary pressure. L. B. LOEB (*Science*, 1929, 69, 509—512; *J. Franklin Inst.*, 1928, 205, 305).—Theoretical. Townsend's theory is discussed in the light of recent work and a new mechanism suggested.

L. S. THEOBALD.

Spark spectrum of thallium, Tl II. Term analysis. Fine structure of lines. J. C. McLENNAN, A. B. McLAY, and M. F. CRAWFORD (*Proc. Roy. Soc.*, 1929, A, 125, 570—578; cf. this vol., 366).—The study of the thallium spark spectrum has been extended from the ultra-violet to the visible and near infra-red regions. Spectra of the spark in air between thallium metal electrodes were photographed from 8500 to 1850 Å. with Hilger glass and quartz prism spectrographs, and spectra of a condensed oscillatory discharge between aluminium terminals in an evacuated quartz tube containing heated thallium vapour were photographed also from 7000 to 2100 Å. The wave-lengths in the latter case were exceptionally clear. Many of the Tl II lines showed fine structure, the magnitudes of the line separations in numerous cases being much greater than any hitherto reported in an atomic spectrum. A few fine-structure term intervals are deduced directly by a wave-number analysis of the line components, and a number of fine-structure patterns are interpreted on the basis that the Back-Goudsmit vector relation $F - J + I$ is valid, that the selection rule $\Delta F = \pm 1$ or 0 holds, and that $I = 0.5$ for Tl II; The ionisation potential is estimated to be approximately 20.5 volts.

L. L. BIRCUMSHAW.

Spectra of metals in explosions of gaseous mixtures. S. KALANDYK, L. KOZŁOWSKI, and T. TUCHOLSKI (*Spraw. Prace Polsk. Towarz. Fizycz.*, 1928, 3, 241—255; *Chem. Zentr.*, 1929, i, 3068—3069).—Mixtures of oxygen with hydrogen, carbon monoxide, or coal gas were exploded in presence of finely-divided metallic salts, and the spectra were examined. That of strontium chloride is identical with the spectrum of the salt in the hydrogen-oxygen flame. With calcium chloride the spark lines H and K are increased in intensity and the characteristic bands between 3969 and 3652 Å. disappear. With ferrous sulphate and cupric chloride the spectrum is almost identical with the flame spectrum.

A. A. ELDRIDGE.

Intensity of the Stark effect in the direction of the lines of force. H. MARK and R. WIERL (*Z. Physik*, 1929, 57, 494—500; cf. this vol., 963).—It is shown that the intensity distribution of the electric vector of the light along the electric field is asymmetrical. The longer wave-halves of the components are in good agreement with Schrodinger's theory.

A. J. MEE.

Quantum mechanical problem of ionisation in the Stark effect. J. KUDAR (*Z. Physik*, 1929, 57, 705—709).—Mathematical.

J. W. SMITH.

Explanation of the spectrum of the aurora. V. M. SLIPHER and L. A. SOMMER (*Naturwiss.*, 1929, 17, 802—803).—In photographing the aurora spectrum a new line of wave-length 5206 Å. was found, in addition to the usual lines. This line can be explained in a similar way to the 5577-350 Å. line, viz., as a transition between deep metastable terms. It is a line of the spectrum of the neutral nitrogen atom.

A. J. MEE.

Nucleus as radiator. W. M. HICKS (*Phil. Mag.*, 1929, [vii], 8, 108—114).—A general account is given of radiation phenomena the origin of which is considered to be in the nucleus of the atom. The general considerations are based on the classical electromagnetic theory of light.

A. E. MITCHELL.

Second spark spectrum of lead. A. S. RAO and A. L. NARAYAN (*Nature*, 1929, 124, 794).—Support is adduced for the authors' results (A., 1928, 1067).

A. A. ELDRIDGE.

Total radiation from polished and soot-covered nickel. B. T. BARNES (*Physical Rev.*, 1929, [ii], 34, 1026—1030; cf. Utterback, this vol., 1212).—Total emissivity values for soot-covered nickel range from 0.92 at 400° Abs. to a minimum of 0.81 at 800° Abs., rising to 0.86 at 1100° Abs. The value for polished nickel was 0.205 at 1400° Abs.; at 400° Abs. it was 0.087 before heating to incandescence and 0.063 afterwards. At intermediate temperatures there were similar differences due to surface changes during the initial heating.

N. M. BLIGH.

Single crystal cathodes. K. G. EMELÉUS and J. W. BECK (*Phil. Mag.*, 1929, [vii], 8, 121—125).—It has been shown that a single crystal of pyrites behaves similarly to an ordinary piece of polycrystalline metal when used as the cathode for glow discharges in various gases. It is therefore considered that the work function of a single crystal does not change, as suggested by Linder (A., 1928, 8), from one face to another. From the values of the normal cathode potential fall in various gases the work function of pyrites for electrons is calculated to be 4.8 volts.

A. E. MITCHELL.

X-Ray diffracting power of copper and iron for molybdenum and copper radiation. (Miss) H. ARMSTRONG (*Physical Rev.*, 1929, [ii], 34, 931—936).—Ionisation spectrometer measurements were made of the intensity of reflexion of the $K\alpha$ doublet of molybdenum and copper from copper and iron powders. From the relative intensities of reflexion from the different planes of the powdered crystals the relative atomic scattering factors F for these reflexions were calculated, and referred to an absolute value through the (220) reflexion of sodium chloride. The absolute values of F are shown as functions of $\sin \theta/\lambda$, where θ is the angle of reflexion. The curves for copper and molybdenum are not coincident, which suggests that for sodium chloride is not the same for copper as for molybdenum radiation, and that F is not independent of the wave-length.

N. M. BLIGH.

Short exposure times with X-ray diagrams. H. MARK and G. VON SUSICH (*Naturwiss.*, 1929, 17, 803—804).—Special apparatus is used in order to

obtain X-ray diagrams with the shortest possible exposures. Examples are given of the application of the method to the determination of the structure of the diamond and pentaerythritol, and to following the progress of the action of sodium hydroxide on cellulose.

A. J. MEE.

Total reflexion of long wave-length X-rays. M. SCHON (Z. Physik, 1929, 58, 165—182).—An apparatus is described for measuring the angle of total reflexion of long wave-length X-radiation (3—13 Å.). Results are given for the total reflexion at glass, diamond, quartz, and aluminium surfaces. In the region of normal dispersion the limiting angles of total reflexion agreed with those calculated from the Drude-Lorentz theory. For aluminium in the region of the *K*-level anomalous dispersion was found. No quantitative results can be given in support of Fresnel's reflexion law, although there is qualitative agreement.

A. J. MEE.

Reflexion of the *K* α line of carbon from glass. E. DERSHEM (Physical Rev., 1929, [ii], 34, 1015—1020).—A vacuum spectrographic method is described by which the intensities of the rays of very soft monochromatic X-radiation (the *K* α line of carbon, 44.6 Å.) reflected from a mirror could be compared photographically for glancing angles of incidence from 1° to 8°. The reflected intensity at 8° was less than 4% of that at 1°. The reflexion intensity-glancing angle curve shows no sharp change of slope, indicating that absorption effects so modify the intensity of the reflected ray as to obscure any sudden change at the critical angle for this order of wave-length.

N. M. Blich.

Reflexion of X-rays from platinum films sputtered on glass. H. E. STAUSS (Physical Rev., 1929, [ii], 34, 1021—1025; cf. A., 1928, 574).—Using the method of Edwards (cf. A., 1927, 921) a variation of the critical angle of reflexion with the thickness of the platinum film was found as in the case of nickel. Variations were found in the critical angles of several silver films identically sputtered. On five photographic films corresponding with five sputtered films, four of platinum and one of nickel, the reflected beam was the limit of a much weaker beam. Angles of deviation from the primary beam of 1° 6' to 1° 46' were measured.

N. M. Blich.

Fine structure of X-ray absorption edges. D. COSTER and M. WOLF (Nature, 1929, 124, 652—653).—*K*-Absorption spectra of copper and zinc exhibit considerable differences; the former gives a complex fine structure, whilst the latter does not. With metallic or combined zinc the *M*-shell is complete, whilst this is not the case with copper.

A. A. ELDRIDGE.

***K* X-Ray absorption edge of iron.** H. R. VOORHEES and G. A. LINDSAY (Physical Rev., 1928, [ii], 31, 306).—The iron in crystals of pyrite, hæmatite, arsenopyrite, epidote, or lepidomelane gives the characteristic *K* absorption edge without the use of any other absorbing screen. Screens of iron compounds and of electrolytic iron, using a sylvan crystal reflector, also gave the absorption, a complicated fine structure of the edge extending over 200 volts being observed. It is supposed that a part, at least, of

the fine structure is due to simultaneous ejection of two or more electrons from the atom.

L. S. THEOBALD.

Fine structure in the *K* series of molybdenum. B. DAVIS and H. PURKS (Physical Rev., 1928, [ii], 31, 306).—The fine structures observed with the increased resolving power obtained by proper arrangement of the crystals in the double X-ray spectrometer are described.

L. S. THEOBALD.

Reflexion of soft X-rays from aluminium. S. D. GEHMAN and C. B. BAZZONI (Physical Rev., 1928, [ii], 31, 1117).—Soft X-rays of range 40—300 volts have been passed through a slit system and then reflected from a polished aluminium mirror in a high vacuum. The curves obtained by plotting reflecting power against voltage and against grazing angle are described.

L. S. THEOBALD.

Indices of refraction of platinum for X-rays of long wave-length. E. DERSHEM (Physical Rev., 1928, [ii], 31, 305).—The indices of refraction of platinum measured over the range 1.279—7.01 Å. have values from 27.3×10^{-6} to 663×10^{-6} for 1- μ .

L. S. THEOBALD.

Refractive indices of silver in the wave-length range 2—7 Å. E. DERSHEM (Physical Rev., 1928, [ii], 31, 1117; cf. this vol., 747).—The dispersion curve obtained shows a depression in the values of δ on both sides of the *L_I* absorption limit wave-length, with a greater depression midway between the *L_{II}* and *L_{III}* limit wave-lengths. In all substances so far examined δ rises rapidly with increasing wave-length between 6 and 7 Å.; for silver it increases 54% to a value of 666×10^{-6} at 7 Å.

L. S. THEOBALD.

Absorption coefficient of some gases for short-wave X-rays. K. SCHOCKEN (Z. Physik, 1929, 58, 39—47).—The absorption coefficient of air, oxygen, nitrogen, and argon was measured for different wave-lengths. An apparatus for measuring the absorption of gases at high pressures is described. The results fit a formula only when the scattering absorption coefficient is assumed independent of wave-length.

A. B. D. CASSIE.

Photo-ionisation in liquids and crystals and the dependence of the frequency of X-ray absorption edges on chemical constitution. L. PAULING (Physical Rev., 1929, [ii], 34, 954—963).—A relation is found between the electron affinity *E'*, the average potential energy of a free electron *W₀* in the liquid or crystal, and the diamagnetic susceptibility. The value 3.81 volt-electrons is deduced for the electron affinity of water. Observed values of long wave-length limits for ultra-violet absorption leading to photo-ionisation in crystals of alkali halides give electron affinities for the crystals corresponding with $\alpha=0.8$ in the relation $E=\alpha W_0$, from which it is found that the diamagnetic susceptibilities of the silver halides are of the order of magnitude to give electron affinities of the crystals sufficient to allow photo-ionisation of the halide ions by visible light, as in the primary photo-sensitisation of a photographic plate. Shifts in the *K* edge of chlorine in various crystals and of potassium in its halides are predicted, and found to agree well with those observed in the alkali halides, supporting the view that the main factors in

producing shifts of the edges in these cases are the electrostatic potential and the electron affinity of the crystals.

N. M. BLIGH.

Ionisation of solid dielectrics by X-rays. Investigations on ceresin. D. NASLEDV and P. SCHARAVSKI (Ann. Physik, 1929, [v], 3, 63—90).—The processes occurring in ceresin when exposed to the action of X-rays are probably of ionic origin. The curve intensity/ionisation current is parabolic, indicating that the current is proportional to the square root of the intensity of the incident radiation. Over the range 322—1600 volts the ionisation current is strictly proportional to the voltage, but it is noted that other workers have not observed this strict validity of Ohm's law. Persistent after-effects have been recorded with ceresin and it is thought that the phenomena are due to the slowness of ionic processes in solids. Fatigue phenomena in the irradiation processes have been studied in some detail.

R. A. MORTON.

Photo-ionisation of potassium vapour. E. O. LAWRENCE and N. E. EDLESEN (Physical Rev., 1929, [ii], 34, 1056—1060).—Using a space-charge-neutralisation method (cf. this vol., 1121) the variation with wave-length of the ionisation per unit light intensity in potassium vapour was studied. The ionisation efficiency shows a maximum at the series limit 2856 Å., and another three times as great at 2340 Å.; a minimum value is found near 2700 Å. Good agreement with former results (cf. A., 1925, ii, 831) is shown. Ionisation by wave-lengths longer than the series limit is probably due to the absorption of principal series lines. The increase of ionisation efficiency beyond the series limit is probably not a molecular phenomenon, the observed dependence on wave-length being most likely an atomic property of potassium.

N. M. BLIGH.

Ionisation potential of hydrogen atoms from the point of view of the electromagnetic quantum theory and polarisation of light from canal rays. C. L. SAGUI (Physical Rev., 1928, [ii], 31, 1110).—Theoretical. A hydrogen atom appears to result from a collection of about 1800 electrons distributed in 60 energy levels in which the density of the electrons is proportional to the energy of each level. The electrons of the level $R((1/3)^2 - (1/4)^2)$ would be more easily ejected by bombarding electrons, and 13.78 volts is the ionisation potential found in this case. Polarisation of light from canal rays is attributed to a component of the oscillating electrons parallel to the motion of the hydrogen atoms; this would not be uniform, but would result in a kind of wave.

L. S. THEOBALD.

Critical potentials of metals. H. B. WAHLIN (Physical Rev., 1928, [ii], 31, 155; cf. A., 1928, 1068).—Critical potentials in the vapours of copper, silver, and nickel in the regions 0—11, 0—8, 0—17 volts, respectively, have been found, and some of them identified as optical levels.

L. S. THEOBALD.

Relation between the cathode fall of potential, the length of the dark space, and the current in the electric discharge through gases. (SIR) J. J. THOMSON (Phil. Mag., 1929, [vii], 8, 393—409).—Mainly mathematical. Certain relations between the

electron energy, ionisation potential, pressure, and current density are defined, by means of which the relation between the thickness of the dark space, cathode fall of potential, and current can be found both for the normal and abnormal discharge. In the latter, the *P.D.* increases and the thickness of the dark space diminishes as the current increases. A transverse magnetic field diminishes both the thickness of the dark space and the *P.D.* required to produce a very short spark. An experimental proof of the latter result is described. It is concluded that the electronic collisions, although sufficient to account for the greater part of the ionisation, require to be supplemented by other processes such as radiation. An experiment is described showing the great effect on the discharge produced by radiation from the negative glow.

N. M. BLIGH.

Photo-ionisation of caesium vapour. F. L. MOHLER, C. BOECKNER, R. STAIR, and W. W. COBLENTZ (Science, 1929, 69, 479).—The photo-ionisation of caesium vapour has been redetermined using an ionisation chamber designed to reduce the surface photo-electric effect of the radiation to a minimum. The caesium sensitivity has a maximum at 3184 Å. which falls rapidly to about 15% of this value at 2700 Å. The mercury line 3130 Å. has the greatest effect of all lines giving 78% of the photo-ionisation. The computed value of k_{3130} is 1.85×10^{-19} at pressures ranging from 0.005 to 0.06 mm. (corresponding with temperatures of 146° and 201°) and the value of k_{3184} derived from the spectral sensitivity curve is $2.3 \pm 0.2 \times 10^{-19}$. The disagreement with Little's value of $k_{3130} = 2.2 \times 10^{-21}$ is unexplained.

L. S. THEOBALD.

Talbot's law in photo-electric cells. N. CAMPBELL (Phil. Mag., 1929, [vii], 8, 63—64).—The results of Carruthers and Harrison (*ibid.*, 7, 792) are discussed. It is suggested that the fatigue phenomena observed must be due to temperature changes, since these are mainly responsible for the redistribution of gas and metal films in the cell associated with these phenomena. It is also pointed out that near the sparking potential of a gas-filled cell the form of the voltage characteristic and the magnification due to ionisation by collision vary with the illumination and that under such conditions Talbot's law cannot be general.

A. E. MITCHELL.

Talbot's law in photo-electric cells. T. H. HARRISON and W. S. STILES (Phil. Mag., 1929, [vii], 8, 64—65).—The points raised by Campbell (cf. preceding abstract) are discussed and it is claimed that there is no essential difference in the points of view.

A. E. MITCHELL.

Mechanism of photo-electric emission. J. H. HSU (Physical Rev., 1928, [ii], 31, 311).—Theoretical. On the assumption that when a quantum of radiation strikes an atom its energy content is shared by the valency electron and the core of the atom, a theory to explain the mechanism of photo-electric emission is put forward. According to this theory, the work function, $h\nu_0$, should, in general, be equal to the lowest resonance potential, and for weak illumination and long wave-length, the relation between photo-electric emission and the intensity of incident light should not be linear.

L. S. THEOBALD.

Effect of toluene on the photo-electric behaviour of mercury. D. ROLLER (Physical Rev., 1928, [ii], 32, 323).—The introduction of toluene vapour into an evacuated photo-electric cell containing freshly-distilled mercury increases the sensitivity, and shifts the threshold towards the red. L. S. THEOBALD.

Emission electricity by incandescent tungsten in iodine vapour. S. KALANDYK (J. Phys. Radium, 1929, [vi], 10, 337—344).—Iodine vapour diminishes the positive emission of a new tungsten filament, but does not affect a previously heated one. It increases the negative emission from tungsten particularly at temperatures lower than incandescence. Whilst it diminishes the emission from thoriated tungsten it does not affect that from tungsten oxide.

W. E. DOWNEY.

Influence of outgassing the cathode on the cathode fall. G. BARTH (Ann. Physik, 1929, [v], 3, 253—269).—The gas dissolved in the metal of the cathode is concerned in the processes occurring at the cathode of a glow discharge. The cathode fall increases with diminution of gas and decreases when the cathode is recharged with gas. Photo-electric measurements on heated metal foil indicate a connexion with the capacity of the cathode to emit secondary electrons.

R. A. MORTON.

Effect of canal rays on alkali chlorides. N. EMBIRIKOS (Ann. Physik, 1929, [v], 3, 91—111).—The bombardment of alkali chlorides by means of canal rays gives rise to the emission of both electrons and ions. The ion emission per positive particle increases with increasing velocity of the canal rays. Other things being equal, the ion emission increases with increasing atomic number of the metal. The emission of series lines at the surface of the salts requires a certain minimum current density of positive rays below which only the fluorescence effect for lithium and sodium chlorides can be detected. In addition to arc lines, a few metallic spark lines can be obtained for sodium and potassium chlorides, but the arc lines are much more intense than the spark lines. The arc lines are emitted, although weakly, from the gas space surrounding the brightly luminous layer of vapour, but the spark lines are localised in the glowing vapour. The intensity of the spark lines can be affected by an electric field, a field capable of accelerating the emitted ions enhancing the intensity of the spark lines with respect to the arc lines and a retarding field exerting the opposite effect.

R. A. MORTON.

Polarisation of light from canal rays. F. G. SLACK (Physical Rev., 1928, [ii], 31, 312).—The partial polarisation of light emitted at right angles to a stream of hydrogen canal rays is explained on the theory that an atom, excited to a state characterised by a combination of quantum numbers which places the centre of gravity of the electronic charge well away from the nucleus, favours a transition resulting in light polarised with the electric vector parallel to the axis connecting the nucleus and point of average charge, whilst an atom excited into the state of the same quantum number but with a combination placing the charge closer to the nucleus favours a transition which results in light polarised at right angles to this axis.

L. S. THEOBALD.

Selective absorption and reflexion of slow electrons at metals. E. RUPP (Z. Physik, 1929, 58, 145—164; cf. this vol., 862).—The absorption of slow-moving electrons (4—40 volts) is investigated and it is found that where there is good absorption there is also good reflexion. A selective absorption maximum corresponds, at equal voltage, with a selective reflexion maximum. The results are grouped according to the position of the metal in the periodic table. The shape of the absorption curve is characteristic for elements in each vertical series of the table. In such a series, the position of the maximum shows a progressive displacement with increase of atomic number. The absorption and reflexion decrease rapidly with increasing velocity of radiation. There is, therefore, a larger transmission through metals for slow electrons than for fast ones.

In deciding the shape of the absorption curves, the outer electrons of the atom play a great part, since there is similarity between the curves for elements in the same vertical series and because the number of maxima in the curves depends on the series of the element. Experiment shows that in the copper series there is one maximum, in the magnesium series there are two, and in the arsenic series three. Probably the absorption bands of the outer dispersion electrons of the atom, somewhat modified in their position owing to the shape of the lattice, are concerned.

A. J. MEE.

Diffraction of electrons by a single layer of atoms. C. DAVISSON and L. H. GERMER (Physical Rev., 1928, [ii], 31, 155; cf. A., 1928, 1173).—The scattering of a homogeneous beam of electrons by a crystal of nickel differs from X-ray scattering in that the individual atom scatters the equivalent electron radiation more efficiently, and the radiation is more rapidly extinguished in the metal than is X-ray radiation. The intensity may be reduced by 30 or 40% by passing normally through a single layer of atoms. Diffraction is a result of this.

L. S. THEOBALD.

Investigation of adsorbed layers with electron-waves. E. RUPP (Z. Elektrochem., 1929, 35, 586—590).—A method of investigating crystal surfaces, and layers adsorbed thereon, in which electron-waves are allowed to impinge on the surface and the reflected radiations are received and measured by means of a Faraday cage, is described. The electron-waves emerge from a glowing wire and thence pass through a slit on to the surface. The apparatus is so arranged that the angles of incidence and reflexion are equal, whilst the velocity of the incident waves is varied and the variations in the reflected waves, determined by the space lattice of the crystal surface, are recorded. The method has been tested with pure nickel and iron surfaces and also with adsorbed layers of gases, hydrogen, nitrogen, and hydrogen sulphide, on these metals. The nature of the layers formed when these metals are first subjected to hydrogen and then to nitrogen, and *vice versa*, is demonstrated.

H. T. S. BRITTON.

Electron collisions with molecules and resultant quantum losses. R. WHIDDINGTON (Nature, 1929, 124, 758).—The behaviour of an "electron gun" is described.

A. A. ELDRIDGE.

Properties of the electron. R. D. KLEEMAN (Nature, 1929, **124**, 728).—The electrical field of an electron is shown to decrease during its mean free path. A. A. ELDRIDGE.

Motion of a Lorentz electron as a wave phenomenon. A. M. MOSHARRAFA (Nature, 1929, **124**, 726—727).

Efficiency of quenching collisions and the radius of the excited mercury atom. E. GAVIOLA (Physical Rev., 1929, [ii], **34**, 1049—1051; cf. this vol., 486).—An erroneous interpretation previously given to the reabsorption factor is corrected, and a revised treatment leads to values for the radius of the excited mercury atom of 3.4 and 5.7 Å. for hydrogen and carbon monoxide collisions, respectively. The efficiencies of collisions are 0.4 for water vapour, 0.2 for nitrogen, 0.05 for argon, and 0.005 for helium. N. M. BLIGH.

Reflexion of hydrogen atoms from crystals. T. H. JOHNSON (Physical Rev., 1928, [ii], **31**, 1122).—Evidence for the existence of waves of length $\lambda = h/mv$ associated with the hydrogen atom has been sought by reflecting atomic hydrogen from a Wood tube from crystal surfaces of ice, rock salt, quartz, and calcite. Freshly-cleaved, degassed rock salt reflects intensely with the angle of reflexion equal to that of incidence. The prismatic and hexahedral faces of quartz and freshly-cleaved calcite reflect, but in no preferred direction. L. S. THEOBALD.

Phase theory in thermionics. O. HALPERN (Monatsh., 1929, **53** and **54**, 822—824).—Theoretical. A metal is considered as a two-component system of ions and electrons. L. S. THEOBALD.

Relation between the variations with temperature and density of the coefficient of recombination of gas ions. A. M. CRAVATH (Physical Rev., 1928, [ii], **31**, 912).—On the assumption that the masses of ions do not change with moderate variation in temperature, the density variations of the coefficient of recombination of gas ions with temperature are represented by an equation involving mobilities of positive and negative ions and the gas density. L. S. THEOBALD.

Value of the period of polonium at various places. L. B. BOGOJAVLENSKI (J. Phys. Radium, 1929, [vi], **10**, 321—326).—Determinations of the period of polonium at various places in Russia gave values ranging from 125.6 to 181.6 days. It is concluded that the variation is outside the experimental error. W. E. DOWNEY.

[Value of the period of polonium at various places.] (MME.) P. CURIE (J. Phys. Radium, 1929, [vi], **10**, 327—328; cf. preceding abstract).—It is contended that the author did not exercise sufficient control in obtaining his results. W. E. DOWNEY.

Invariability of radioactive constants. (MME.) P. CURIE (J. Phys. Radium, 1929, [vi], **10**, 329—336).—The attempts made by the author and her collaborators to control radioactive processes with a view of influencing the radioactive constants are summarised. No definite exception to the generally accepted laws

has been found, although some points of detail still require explanation. W. E. DOWNEY.

Application of adiabatic microcalorimeter to measurements of the heats of radiation of uranium, thorium, and radioactive minerals. A. DORABIALSKA (Rocz. Chem., 1929, **9**, 494—503).—Values for heat of radiation in good agreement with those obtained by other authors using different methods, as well as with those theoretically derived, are obtained for the above substances, using Swientoslawski and Dorabialska's adiabatic microcalorimeter (A., 1927, 1163). The entire heat effect of radiation is taken up by the substance examined, so that $Q = c \cdot \Delta t$, where Q represents g-cal./g.hr. and c is the specific heat of the body. R. TRUSZKOWSKI.

Activation in rare gases. M. LAPORTE and L. GOLDSTEIN (Compt. rend., 1929, **189**, 689—691).—To test whether recoil atoms are all positively charged at the moment of formation the yield, i.e., the ratio $(Ra-A+B+C)$ collected: (total active deposit in equilibrium with amount of radon present) was determined in air and in pure argon (cf. A., 1926, 877) for pressures up to 85 cm. of mercury, using 3 millicuries of radon and a voltage of 85 between electrodes. The yield never exceeded 50%, and was uniformly less in argon than in air. Reasons for these results are suggested. C. A. SILBERRAD.

Close collision between an α -particle and a nitrogen nucleus. L. F. CURTISS (Physical Rev., 1928, [ii], **31**, 1128).—Approximately 83,000 α -ray tracks in air have been photographed and recorded. One fork involving a close collision between an α -particle and a nitrogen nucleus has been analysed. The α -particle was deflected through an angle $\phi = 110^\circ$ with its initial direction, and travelled 10.5 mm. after the collision; the nitrogen nucleus travelled 4.7 mm. at an angle $\phi = 26.5^\circ$ to the original direction of the α -particle. The velocity of the latter was 1.1×10^9 cm. per sec. at the moment of impact and 8.7×10^8 cm. per sec. after impact, and it has been calculated that the nearest approach of the α -particle was 0.5×10^{-12} cm. from the centre of the nucleus. No evidence of the ejection of a proton was obtained in spite of the fact that the α -particle penetrated the nuclear structure with sufficient energy. L. S. THEOBALD.

Straggling of β -particles. E. J. WILLIAMS (Proc. Roy. Soc., 1929, A, **125**, 420—445).—Theoretical. A brief account is given of previous experimental work on the loss of energy by fast electrons in traversing matter (e.g., White and Millington, A., 1928, 1302), with special reference to the effect of the complications introduced by "scattering." The inapplicability of Bohr's formula for the straggling of electric particles to β -particles is demonstrated, and a theory is developed whereby the complete curve representing the distribution of the energy losses by β -particles traversing thin foils may be calculated. A theory is also proposed according to which collisions in which a moving electric particle loses energy to an atomic electron are of two distinct types; one involves only the moving particle and the electron which acquires the energy, but in the second the whole atom is involved and the nucleus plays an essential part. L. L. BIRCUMSHAW.

Extreme ultra-violet spectra excited by controlled electron impacts. K. T. COMPTON and J. C. BOYCE (*Physical Rev.*, 1928, [ii], **31**, 708).—Spectra photographed at low pressures and increasing voltages under conditions in which electrons make only one collision with a gas molecule show successive stages of excitation and ionisation brought about by single electron impacts. In helium ten members of the arc series have been observed from 584 to 507 Å. and five members of the spark series from 303 to 234 Å. In neon and argon the results of Dorgelo and Abbink have been generally confirmed and many additional lines observed. L. S. THEOBALD.

Inelastic collisions in mercury vapour. J. D. WHITNEY (*Physical Rev.*, 1929, [ii], **34**, 923—930).—For the study of inelastic collisions through the residual energies of colliding electrons, a narrow beam of electrons from a hot cathode, after undergoing collisions in mercury vapour, passed to a high vacuum region and was separated by a magnetic field into a velocity spectrum. The intensities of components of the spectrum corresponding with energy losses equivalent to 4.9, 6.7, and 8.8 volts were measured as a function of the initial energy of the electrons. The intensity in each case reaches a distinct maximum within a few volts of the excitation potential of that component. Other energy losses were detected of such low intensities that they were not measured. N. M. BLIGH.

Attachment of electrons to neutral molecules. L. B. LOEB (*Phil. Mag.*, 1929, [vii], **98**, 98—102).—The criticisms of Bailey (this vol., 231) of the results of Wahlin (*A.*, 1922, ii, 608) and Loeb (*Phil. Mag.*, 1922, [vi], **43**, 229) are discussed and it is shown that the discrepancies in the results on the formation of negative ions in ammonia attributed to the presence of impurities in the gas used by Wahlin and Loeb are unjustified and that under the different pressure and electrical conditions employed Bailey's results would not be expected to be the same as those of the other observers. A. E. MITCHELL.

Collision process accompanying the combination of nitrogen atoms in active nitrogen. B. LEWIS (*Physical Rev.*, 1928, [ii], **31**, 314).—The necessity for a triple collision in the combination of nitrogen atoms is discarded. The nitrogen molecule may be formed in a two-body collision process. L. S. THEOBALD.

Active nitrogen. Z. BAY and W. STEINER (*Z. Elektrochem.*, 1929, **35**, 733—738).—Spectroscopic evidence is advanced of the existence of unstable intermediate products between the inactive and active forms of nitrogen, the latter being atomic. The concentration of nitrogen atoms and the intensity of the after-glow are inter-related. A mild discharge weakens the intensity of the after-glow. H. T. S. BRITTON.

Change in the electrical state of metallic surfaces on charging with hydrogen ions and by the bombardment of electrons. R. SUHRMANN (*Z. Elektrochem.*, 1929, **35**, 681—686).—If the surface of a metal be illuminated by a beam of light of sufficiently short wave-length, a limiting wave-length is emitted such that the quantity of electrons involved increases per unit of energy of incident light

in the case of most metals as the emitted wave-length decreases. A method is described which enables the nature of a metal surface to be studied when it has been charged with hydrogen, by bombarding it with electrons and measuring the variation in photo-electric sensitivity. Several curves are given illustrating the dependence on the wave-length of photo-electric electron emission of gold and silver under different conditions. It is concluded that hydrogen in the adsorbed state is ionic. The importance of the method in the investigation of the surfaces of catalysts is emphasised and the possibility of "active centres" on metal surfaces is discussed. H. T. S. BRITTON.

Spectroscopic determination of the pressure in the calcium chromosphere. A. UNSOLD (*Astrophys. J.*, 1929, **69**, 209—226).—The average value of the partial pressure of the calcium ion calculated from observations of the emission and absorption spectra of the calcium chromosphere is 4×10^{-15} atm. The average velocity of the ions from Doppler measurements is 15 km./sec. Milne's theory that the radiation absorbed by the *H* and *K* lines is just sufficient to support the mass of the calcium ion in the chromosphere is fulfilled. L. S. THEOBALD.

Is there argon in the corona? H. N. RUSSELL and I. S. BOWEN (*Astrophys. J.*, 1929, **69**, 196—208).—From a critical study of Freeman's work (*A.*, 1928, 210), the authors conclude that he is in error in attributing lines in the solar corona to argon, and that there is no spectroscopic evidence of the presence of argon in the corona or elsewhere in the sun. L. S. THEOBALD.

Scattering of quanta with diminution of frequency. K. K. DARROW (*Science*, 1928, **68**, 488—490).—The four or five cases in which quanta appear to surrender a part but not all of their energy are discussed. L. S. THEOBALD.

General theory of the plasma of an arc. L. TONKS and I. LANGMUIR (*Physical Rev.*, 1929, [ii], **34**, 876—922).—Theoretical. It is assumed that in a plasma each positive ion, instead of having a random velocity, starts from rest and subsequently possesses only the velocity which it acquires by falling through a static electric field which is itself maintained by the balance of electron and ion charges. On this view equations for the plasma-sheath potential distribution are formulated and solved for a number of important cases. The ion current equation gives a new method of calculating the density of ionisation; from the plasma balance equation the rate of ion generation can be calculated. Extensions and calculations from the equations are made and shown to be in agreement with experimental results. N. M. BLIGH.

Role of hydrogen in the oscillating arc. E. Z. STOWELL and H. E. REDEKER (*Physical Rev.*, 1929, [ii], **34**, 978—983).—Attempts to produce radio-frequency oscillations in the Poulsen arc in atmospheres other than hydrogen were unsuccessful, except when this gas could be formed intermediately, and the presence of hydrogen is concluded to be essential. It was found that numerous elements, generally of even atomic number, could be used as cathodes. The spectrum of the oscillating arc shows the Balmer

series and the first spark spectrum of the cathode; when the latter is sufficiently hot the cathode lines disappear leaving a strong Balmer series on a continuous background. All oscillating arcs of the Poulsen type have about the same high-frequency limit of 5×10^6 cycles per sec. N. M. BLIGH.

Connexion between the quantum mechanics "uncertainty" and the structure of elementary particles, and a calculation of the masses of the proton and electron based thereon. R. FÜRTH (Z. Physik, 1929, 57, 429—446).—Theoretical. Whilst the radius of the electron has a definite meaning in the classical electron theory, matters become very complicated on applying quantum mechanics. The Heisenberg "uncertainty" relationship is applied first to a light quantum, and then to protons and electrons. The change of matter into radiation and inversely is considered, and the masses of the electron, proton, and neutron are obtained. Eddington's theory of the elementary quantum, in which it is described in 16-dimensional space, is also considered, and the above calculations are carried out. A. J. MEE.

Electron theory of ferromagnetism and electrical conductivity. F. BLOCH (Z. Physik, 1929, 57, 545—555; cf. Heisenberg, A., 1928, 1300; Dorfman and others, this vol., 751).—Mathematical. The possibility of accounting for ferromagnetism by considering the conductivity electrons is investigated. A. J. MEE.

Synthesis of elements. III. G. I. POKROVSKI (Z. Physik, 1929, 57, 560—565; cf. this vol., 623, 739, 973).—It has already been shown that an electron and a proton can combine together with emission of energy and loss of mass. For elements with atomic numbers greater than 120 the total loss of mass considerably exceeds the mass of a proton. There are, however, a number of facts which go to show that the heavier atomic nuclei are constructed from α -particles. It is shown that the same mechanism as that put forward for the construction of the lighter elements holds for these heavier ones, α -particles taking the place of protons. There is good agreement between the relative loss of mass calculated by this method and Aston's results. An upper limit is found for the loss of mass which enables a limit to be fixed for the number of protons in the nucleus. This number must be less than 240. A. J. MEE.

Electronic structure of some diatomic molecules. J. E. LENNARD-JONES (Trans. Faraday Soc., 1929, 25, 668—686).—Mathematical. The Schrödinger wave-equation is applied to diatomic molecules. N. M. BLIGH.

Wave-mechanical condition for the stability of the atomic nucleus. J. KUDAR (Z. Physik, 1929, 57, 710—712).—Mathematical. J. W. SMITH.

B-State of the hydrogen molecule. C. ZENER and V. GUILLEMIN, jun. (Physical Rev., 1929, [ii], 34, 999—1009).—Mathematical. The *B*-state of the H_2 molecule dissociates adiabatically into a normal and a two-quantum hydrogen atom, the corresponding band system being the Lyman bands. The *B*-state is treated by wave mechanics. The form of the wave

function indicates that the *B*-state is partly, but not wholly, polar. N. M. BLIGH.

Rotational instability and uncoupling of the electronic orbital angular momentum from the axis in diatomic molecules. W. W. WATSON (Physical Rev., 1929, [ii], 34, 1010—1014; cf. this vol., 1136).—Theoretical. The details of several diatomic hydride bands are discussed to illustrate a number of peculiar rotational phenomena exhibited by some molecular spectra, and attributed to uncoupling of the electronic orbital angular momentum from the nuclear axis, which would contribute to a condition of rotational instability. N. M. BLIGH.

Quantum of cosmic radiation and the relative mass of proton and electron. A. K. DAS (Naturwiss., 1929, 17, 841).—If r_0 , the radius of a photon, is equal to c/v the wave-length must be of the order of the radius of an electron. Cosmic radiation has a wave-length of this order, and is therefore regarded as composed of quanta made up of protons and electrons separated by a distance equal to the radius of an electron. It is hence shown that $m_p' + m_e'/m_e = 1839$, m_p' and m_e' being the masses of proton and electron, respectively. Coulomb's law is assumed to be true for a distance of 10^{-13} cm., and if this assumption is valid, the quantum of cosmic radiation would seem to be a miniature hydrogen atom. R. A. MORTON.

Colour efficiency of artificial retina. F. WEIGERT and M. NAKASHIMA (Naturwiss., 1929, 17, 840—841).—Glass plates covered with gelatin layers containing visual purple from frog retinas (artificial retina) have been studied in relation to photodichroism (cf. this vol., 871, 894), the results being quite analogous to those obtained with other light-sensitive dyes and photo-chlorides. The spectral curves for the dichroism with white and monochromatic linearly polarised light are given and it is found that, apart from red light, the same after-effects are obtained in the dark in all cases. The data support Weigert's theory of colour vision and the work indicates a new method of physiological investigation. R. A. MORTON.

Heisenberg's indetermination principle and the motion of free particles. A. E. RUARK (Physical Rev., 1928, [ii], 31, 311).—Theoretical. Heisenberg's principle is concluded to be valid. L. S. THEOBALD.

Atomic structure factor and Fourier analysis. G. E. M. JAUNCEY and W. D. CLAUS (Physical Rev., 1928, [ii], 31, 1118; cf. A., 1928, 938).—Comparison of a *U*-curve obtained from a Fourier integral now derived with a similar curve from Compton's formula for a model Cl' atom shows agreement between the positions of the maxima. A *U*-curve gives the electron distribution relative to a lattice point of a crystal and not relative to the centre of the atom. L. S. THEOBALD.

Rotational distortion and Zeeman effect of diatomic molecules in wave mechanics. C. ZENER (Physical Rev., 1928, [ii], 31, 1115).—Mathematical. L. S. THEOBALD.

Heats of condensation of electrons on platinum in ionised helium, nitrogen, and argon. C. C. VAN VOOERHIS and K. T. COMPTON (Physical Rev., 1928,

[ii], 31, 1122).—The following values for ϕ have been obtained: platinum in argon 5.20, in neon 5.00, and in helium 4.77 volts. Relatively the values are accurate, but the absolute values may be 5% high. The work function of the metal in these gases varies with the gas used; it is the ions rather than the neutral atoms which influence this function.

L. S. THEOBALD.

A gas in crossed fields according to the quantum mechanics. K. F. NIESSEN (Z. Physik, 1929, 58, 63—74).—Mathematical.

Raman effect and hydrogen spectrum. D. B. DEODHAR (Z. Physik, 1929, 57, 570—572).—The Raman effect has been observed in the multiple line spectrum of hydrogen. Allen (cf. this vol., 363) has noted the phenomenon for diminished frequency for five Balmer lines. A further investigation revealed a large number of Raman lines of higher as well as lower frequencies from ten members of the Balmer series. The results obtained are compared with those of Allen. The displacements correspond with the rotation spectrum of hydrogen.

A. J. MEE.

Raman spectrum and geometrical isomerism. The Raman spectrum of the two forms of dichloroethylene. G. B. BONINO and L. BRÜLL (Z. Physik, 1929, 58, 194—199).—The Raman spectra of the *cis*- and *trans*-forms of dichloroethylene were found. The excitation was by mercury arc, apparatus similar to Wood's being used. The *cis*-form has m. p. 60.25°; the *trans*, 48.35°. A number of differences are observed in the Raman spectra of the two forms. For short wave-length infra-red absorption the lines fall almost together. The C-H bands for both forms are at 3.25 μ and 6.30 μ ; the 7.25 μ line also is coincident, but the *trans*-form shows two lines corresponding with 7.85 μ and 13.12 μ which do not appear with the *cis*-form. This is the greatest difference between the two forms in the arrangement of Raman lines below 15 μ . Above 15 μ there are wide differences. The *trans*-form has only one band at 41.1 μ , whereas the *cis*-form has three important bands at 17.60, 24.50, and 58.50 μ . The intensities of the lines were also investigated. The effect of geometrical isomerism in this very simple case is most marked, and differences also appear in the infra-red absorption spectrum.

A. J. MEE.

Scattering of light in crystals at high temperatures. G. LANDSBERG and L. MANDELSTAM (Z. Physik, 1929, 58, 250).—The dispersion spectrum of quartz at high temperatures (800—900°) was investigated.

A. J. MEE.

Raman effect on organic substances. I. Raman spectra of simple benzene derivatives. II. Influence of temperature on Raman lines. Y. FUJIOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 205—222).—I. Tables of the Raman lines are given for benzene, toluene, chlorobenzene, bromobenzene, phenol, nitrobenzene, and anisole. The line corresponding with wave-number difference 3060 cm^{-1} was assigned by Pringsheim and Rosen (A., 1928, 1307) to the fundamental frequency of the CH group. The author contends that, although the 3060 cm^{-1} is the strongest Raman line, Pringsheim

and Rosen's assignment is not in agreement with the results of infra-red spectroscopy, and he prefers to regard it as the first harmonic. The fundamental frequency (6.4 μ) corresponds with a Raman displacement of about 1600 cm^{-1} ; this line, although much more faint than the other, occurs in all the compounds examined. The line corresponding with wave-number difference of 2921.4 cm^{-1} is attributed to the vibration of the CH₃ group. The effect of the coupling force of the substituent group, the sharpness of the lines, and the polarisation of the lines are discussed.

II. The effect of raising the temperature is to make some of the Raman lines more diffuse; others remain unaltered. The diffuseness of Raman lines may be due to quantised motion and the rise in temperature may accelerate this motion and thereby increase the diffuseness.

W. R. ANGUS.

Raman effect from powdered crystals. R. BAR (Nature, 1929, 124, 692).—Powdered naphthalene gives Raman lines at wave-numbers 21541, 21637, 21910, 22170, 22420, 23320, 23682, 23950, and 24195 cm^{-1} , all having been observed previously for the liquid or dissolved material. The mercury line 4358 Å., when scattered by ammonium nitrate, gives rise to two lines of almost equal intensity with wave-numbers 22232 and 21882 cm^{-1} , respectively, by calcium nitrate one line with 21884 cm^{-1} ; with sodium nitrate a strong line at 21864 cm^{-1} was possibly associated with two weaker lines. Sodium nitrite crystal powder gave one line at 21605 cm^{-1} , whilst sodium chloride, ammonium bromide, and solid carbon dioxide gave no lines.

A. A. ELDRIDGE.

Raman effect and electrolytic dissociation. I. R. RAO (Nature, 1929, 124, 762).—Nitric acid (65%) shows nine Raman lines—three for water, three for the HNO₃ molecule, and three for the NO₃ ion; the last group is exhibited also by nitrates. Raman lines belonging to the HNO₃ molecule gradually disappear with dilution; those belonging to the nitrate ion increase in brightness up to a certain dilution and thereafter diminish. The three water bands become sharper with increasing concentration of the acid; one diminishes and one increases in intensity as the concentration of acid is increased.

A. A. ELDRIDGE.

Polarisation of Raman lines. A. C. MENZIES (Phil. Mag., 1929, [vii], 8, 504—515).—Using a small source and a double-image prism the light scattered by some organic liquids at angles of 90° and 180° was investigated. The polarisation can be explained on the assumption that the direction of the initial vibration is parallel to that of the final vibration for plane-polarised lines, and perpendicular for unpolarised lines, with intermediate inclination for partly polarised lines. The Raman spectrum of quartz was measured for three orientations of the optic axis, and the state of polarisation of the lines was investigated. Some of the scattered lines change their direction of polarisation through an angle of 90° as the direction of the optic axis is similarly turned. Two lines remained plane-polarised parallel to, and two others perpendicular to, the direction of the unmodified lines. An energy level diagram co-ordinating the Raman and infra-red observations is given.

N. M. BUGH.

Raman effect of some aqueous solutions. P. PRINGSHEIM and M. YOST (Z. Physik, 1929, 58, 1—6).—Aqueous solutions of sulphuric acid (12%), ammonium sulphate, sodium thiosulphate, sodium dithionate, selenious acid, potassium selenite, and a concentrated solution of uranyl sulphate in sulphuric acid have been investigated. The frequency differences characteristic of the sulphate and thiosulphate ions are nearly the same and are in close agreement with the frequency differences attributed to the sulphite ion by Dickinson and Dillon (this vol., 741). No characteristic wave-number difference can be assigned to the ammonium ion. The binding of the two sulphur atoms in the $S_2O_3^{--}$ and $S_2O_6^{--}$ ions is different and this explains the dissimilarity in Raman spectra of aqueous solutions containing these ions. It is found with both sulphuric and selenious acid that the acid gives a more diffuse spectrum than an aqueous solution of a salt; a salt shows a line not found in the spectrum of the acid. Uranyl sulphate gives a line apparently characteristic of the UO_2 radical. The frequency difference of this line agrees with the results obtained from fluorescence spectra. W. R. ANGUS.

Line absorption spectra of solids at low temperatures in the visible and ultra-violet regions of the spectrum. S. FREED and F. H. SPEDDING (Physical Rev., 1929, [ii], 34, 945—953; cf. this vol., 490).—The absorption spectra of the synthetic uniaxial crystal $GdCl_3 \cdot 6H_2O$ were investigated down to the temperature of liquid hydrogen, and found to consist of very sharp lines, mainly in the ultra-violet; with reduction of temperature the lines showed a slight shift towards the red, and a greater separation between the lines of each multiplet, due primarily to the contraction of the crystal bringing the ions closer together. Complete results are tabulated, and a simple new method for growing crystals from solution is described. N. M. BLIGH.

Molecular scattering of light from solids: crystalline sulphates and their water solutions. A. HOLLANDER and J. W. WILLIAMS (Physical Rev., 1929, [ii], 34, 994—996).—The Raman spectra of the sulphates of calcium, barium, copper, potassium, and aluminium were investigated and results tabulated for the crystalline state and in aqueous solution. For the crystals, lines corresponding with infra-red absorption bands at 4.54, 6.5, and 5.95 μ , and broad and diffuse Raman lines corresponding with the region 14—16 μ were found. For each crystal and solution strong lines were found at 4552 and 4213 Å., corresponding with an infra-red band at 10.2 μ associated with the sulphate ion. N. M. BLIGH.

Proof of the Maxwell-Boltzmann law by intensity measurements of the Raman effect for carbon tetrachloride. L. S. ORNSTEIN and J. REKVELD (Z. Physik, 1929, 57, 539—544).—The method used by Einstein to derive the Planck law is here used to find the intensity ratio of the Stokes-Raman lines and the anti-Stokes-Raman lines. The formula derived is $J_s/J_{as} = (v - v_1)/(v + v_1)e^{h(v - v_1)/kT}$, where J_s and J_{as} are the intensities, and v , v_1 are frequencies corresponding with two states. In order to test this equation intensity measurements were made with the Raman lines shown by carbon tetrachloride. With

this substance the transition frequency is small and this gives rise to relatively strong anti-Stokes lines, so that the ratio J_s/J_{as} is never less than 12. Good agreement was found between experiment and theory. The method also enables the value of h/k to be obtained with accuracy. A. J. MEE.

Absorption of ultra-violet light by some organic substances. L. MARCHELEWSKI and J. MAYER (Bull. Acad. Polonaise, 1929, A, 169—202).—The quantitative spectral absorption of furfuraldehyde, furfuralamide, furyl alcohol, furan-2-carboxylic acid, the three isomeric toluic, nitrobenzoic, aminobenzoic, and hydroxybenzoic acids, the three isomeric nitrotoluenes, α - and β -naphthaquinolines, and benzaldehyde is described. All these substances show complicated selective absorption and follow Beer's law. The *para*-derivatives absorb much more strongly than the corresponding *ortho*- and *meta*-isomerides. A. A. GOLDBERG.

Spectro-chemical study of amino-acid anhydrides. III. Light absorption of some *N*-substituted diketopiperazines and some other amino-acid anhydrides. T. ASAHINA (Bull. Chem. Soc. Japan, 1929, 4, 202—209).—The spectral absorptions of the following substances have been measured, the results being plotted by the older method: *N*-phenylglycine, m. p. 123.5—124.5°, and its ethyl ester, m. p. 55.5—56.5°; *NN'*-diphenyldiketopiperazine, m. p. 265°; ethyl benzylaminoacetate, b. p. 137°/8 mm.; benzylamine, b. p. 182—183°; *NN'*-dibenzyl-diketopiperazine; *NN'*-diacetyldiketopiperazine, m. p. 102.5°, from glycine anhydride and acetic anhydride; *NN'*-dipropionyldiketopiperazine, m. p. 114.5°, obtained by heating glycine anhydride with propionic anhydride at 130—140° for 5 hrs.; *NN'*-dichloroacetyldiketopiperazine, m. p. 169°, best prepared by heating glycine anhydride with chloroacetic anhydride at 100° for 1 hr.; *NN'*-dibenzoyldiketopiperazine, m. p. 137°; hydantoin, m. p. 215°, ethyl hydantoate, m. p. 137.5—138.5°, γ -phenylhydantoin, m. p. 155°, γ -phenylhydantoic acid, m. p. 192°, and phenylcarbamide, m. p. 146—147°; benzaldehyde azlactone, m. p. 164.5°, and furfuraldehyde azlactone, m. p. 170.5°. A. I. VOGEL.

Absorption spectra and the nature of the chemical combination in thallous halides in the vapour state. K. BURKOW (Z. Physik, 1929, 58, 232—249).—The absorption spectra of thallous chloride, bromide, and iodide were investigated over the spectral range from 7000 to 1900 Å. Term tables are drawn up for the chloride and bromide. The convergence limits and heats of dissociation for these two salts are also obtained. The heat of dissociation of the chloride is 87.0 kg.-cal./mol., and that of bromide 73.1 kg.-cal./mol. Considering the nature of the chemical combination of the elements in the thallous halides, it is shown that all the salts are decomposed by absorbed radiation into excited atoms. A decomposition into unexcited atoms which is characteristic of ionic compounds was not observed. The conclusion reached is that in the vapour state the molecules are atomic compounds. The electronic affinity of chlorine and bromine was found to be 91 and 86.5 kg.-cal./mol., respectively. A. J. MEE.

Ultra-violet absorption spectra of benzene and toluene in alcoholic solution. C. V. SHAPIRO and R. C. GIBBS (Physical Rev., 1928, [ii], 31, 310).—Twenty-three new bands in benzene and 21 in toluene are reported in the absorption spectra of these substances in alcoholic solution. Many of the new bands are narrow and resemble those of the vapours, to which, however, they cannot be ascribed. With a possible exception in the case of benzene, all the bands can be arranged in a series by means of a simple mathematical expression derived from the theory of band spectra. The results of Smith, Boord, Adams, and Pease (A., 1928, 152, 1308), indicating a benzene-like structure for the absorption spectra of certain organic compounds, are due to the presence of benzene as an impurity. L. S. THEOBALD.

Absorption of the halogen ions in aqueous solution in the near Schumann ultra-violet (electron affinity spectra). G. SCHEIBE (Z. physikal. Chem., 1929, B, 5, 355—365).—The absorption spectra of the chloride, bromide, and iodide ions in aqueous solution have been determined photometrically from about 1800 to 2100 Å. The extinction coefficient-wave-length curve for the chloride ion exhibits but one maximum, at about 1820 Å., which is, however, probably the result of two adjacent maxima, for the bromide ion two well-defined maxima at 1995 and 1900 Å., whilst for the iodide ion there is a maximum at about 1950 Å. and a minimum at about 2080 Å. The distances between the maxima are in accordance with the view that by separation of the electrons the halogen atoms exist both in the stable 2^2P_2 and the metastable 2^2P_1 states.

H. F. GILLBE.

Rotation-vibration spectrum of ammonia. R. M. BADGER and R. MECKE (Z. physikal. Chem., 1929, B, 5, 333—354).—The absorption spectrum of ammonia has been photographed from 10,000 to 5900 Å. with a dispersion of 216 Å./mm. Of the bands observed, at 8810, 7920, and 6450 Å., the last two are the fourth and fifth of the series arising from the N-H vibration. All the infra-red absorption bands are derived from the three fundamental vibrations $\nu_1=3396-60n$, $\nu_2=1630$, and $\nu_3=966$. Investigation of the fine structure of the band at 7920 Å. indicates that the molecule is somewhat unsymmetrical, probably as a result of nuclear vibration; the three moments of inertia are 2.79×10^{-40} , 2.74×10^{-40} , and 3.40×10^{-40} g./cm.², whilst the distance between the nitrogen and hydrogen atoms is 0.977×10^{-8} cm. and between the hydrogen atoms 1.43×10^{-8} cm.; the height of the pyramidal molecule is 0.517×10^{-8} cm. H. F. GILLBE.

Co-ordination of the potentials of halogen ions and their ultra-violet absorption in aqueous solution. G. SCHEIBE (Z. Elektrochem., 1929, 35, 701—703).—Iodide and bromide ions have two maxima in the ultra-violet absorption spectra of solutions containing them corresponding with an energy difference between the stable and metastable ions. It is argued from theory that there should exist a parallelism between the ultra-violet spectra and the electrode potentials of the various halogen

electrodes. Curves showing the variation in the absorption spectra of halide ions with temperature are compared with the potential measurements of Schmid ("Die Diffusionsgaselektrode," Stuttgart, 1923).

H. T. S. BRITTON.

Molecular spectra. W. E. GARNER and J. E. LENNARD-JONES (Trans. Faraday Soc., 1929, 25, 611—627).—A general survey of the present state of knowledge of molecular spectra with regard to the experimental technique of research in the infra-red, visible, and ultra-violet regions. The theoretical systematisation due to the introduction of wave mechanics, nature and origin of the spectra, notation employed, and results are explained and discussed.

N. M. BLIGH.

Absorption spectrum of nitric oxide. M. LAMBREY (Compt. rend., 1929, 189, 574—576).—Measurements for the band $0 \rightarrow 0$ of the γ -system of nitric oxide (λ 2265 Å.) have shown that the apparent optical density is a function of lp^x , where l is the length of the absorption tube (0.75—1032 mm.), p the pressure, and x equals 1.81 ± 0.03 . Although this is the resonance band of the NO molecule no selective diffusion was observed as in the case of the 2537 Å. mercury line. The effect of change of temperature (-80° to 300°) is in agreement with the classical laws of the distribution of intensities in band spectra.

J. GRANT.

New spectrum of gaseous alkali halides, and its significance. K. SOMMERMEYER (Z. Physik, 1929, 56, 548—562).—Diffuse bands appear at the long-wave limit of the continuous spectrum when the temperature of the salt is sufficiently high. Measurements of minima show convergence towards the red, showing these bands as due to different vibration levels of the unexcited molecule. Different vibration levels in the excited state seem too close to be resolved. This suggests that the normal electronic state always corresponds with ionic binding, the excited state with binding by polarisation; that is, the alkali halides are ionic molecules on Franck's classification.

A. B. D. CASSIE.

Intensities of lines in the ammonia band at 2μ , and the form of the ammonia molecule. E. F. BARKER (Physical Rev., 1928, [ii], 31, 1131).—Intensity computations show the molecule to be oblate, and the distance from the nitrogen atom to the plane of the three hydrogen atoms is 0.06—0.1 of the distance between the hydrogen atoms.

L. S. THEOBALD.

Effect of X-rays on the infra-red absorption of kunzite and hiddenite. P. L. BAXLEY (Physical Rev., 1928, [ii], 31, 1132; cf. A., 1928, 1312).—The range of measurement of the spectral transmission of kunzite and hiddenite, before and after exposure to X-rays, has been extended to 4.5 μ .

L. S. THEOBALD.

Infra-red investigations of molecular structure. III. Molecule of carbon monoxide. C. P. SNOW and E. K. RIDEAL (Proc. Roy. Soc., 1929, A, 125, 462—483).—The vibration-rotation band ($n''=1/2 \rightarrow n'=3/2$) of carbon monoxide has been resolved, the measurements being made with the gas at a pressure of 11 cm. The band consists of P and

R branches only, the *R* branch being convergent, and its centre is at $2144 \pm 0.4 \text{ cm}^{-1}$. The first overtone ($n''=1/2 \rightarrow n'=5/2$), consisting of *P* and *R* branches, has been plotted and the *P* branch partly resolved. The centre of the band is at $4286 \pm 1 \text{ cm}^{-1}$. Almost all the results obtained agree with those calculated for the vibration-rotation bands of a molecule in a 1S state, acting as an anharmonic oscillator, and with the actual experimental values for the vibration frequency and constant of anharmonicity obtained from the electronic bands. The following values are deduced: $\omega_0=2155$, $\omega_0x=11$, $I=1.50 \times 10^{-39} \text{ g.-cm}^2$, and $r=1.15 \times 10^{-8} \text{ cm}$. With a knowledge of the fine structure, the potential function can be completely expressed. The potential function can also be expressed as $V=e^2(C_1/r+C_2/r^4)$, and on this basis it is possible to describe the positions of the lines in the *R* and *P* branches of the fundamental by an expression involving only I , ω_0 , and x . The subject of alternating intensities is briefly considered. It appears certain that there cannot be regular alternating intensities in any bands save those due to a completely symmetrical molecule X_2 (e.g., acetylene and ethylene). L. L. BIRCUMSHAW.

Structure of OH bands. R. S. MULLIKEN (Physical Rev., 1928, [ii], 31, 310).—Each band comprises six main branches, six weak series, and a further weak branch extending towards high frequencies from each band. The main branches ($\Delta j_k = \Delta j$) and four of the weaker agree completely with Hund's predicted structure for $^2S \rightarrow (\text{inverted})^2P$, except that the latter branches are stronger than predicted. The last-mentioned weak branch is identified as an *R* branch ($\Delta j=1$), but $\Delta j_k=2$, and a companion *P* branch, at present unknown, is expected. The occurrence of the *R* branch and the high intensity of the weak series show OH as a transition case between CH 3900 Å. and HgH. The ZnH bands lie between OH and HgH in all these features. Two of the six weak series have $\Delta j_k = \Delta j$ like main branches, but differ by forming the first known exceptions to the usual rules of σ -type doubling. L. S. THEOBALD.

Water absorption band at 9727 Å. J. E. LAMBLY (Physical Rev., 1928, [ii], 31, 706).—The water absorption band in the near infra-red has been located at 9727 Å. for a temperature of 22° (cf. Collins, *ibid.*, 1927, 26, 771). Photographic records of spectral intensity and density measurements have been made, and ratios were computed to determine absorption peaks which have been measured. The average of the three independent determinations made should be accurate to 10 or 12 Å.

L. S. THEOBALD.

Tesla-luminescence spectra. VI. Some phenolic compounds and their ethers. J. C. MACMASTER, A. RUSSELL, and A. W. STEWART (J.C.S., 1929, 2401—2407; cf. McVicker and others, A., 1925, ii, 630).—Photographs were obtained of the spectra emitted under the Tesla discharge by 41 phenols and phenolic ethers, and the wave-length limits of the continuous spectrum, region of maximum brilliancy, occurrence of a glow in the visible region, and the positions of bands are tabulated for each substance. The effect of substitution on the benzene ring, and

similarities for ethers and corresponding chains composed entirely of hydrocarbon radicals, are discussed. Interrupted spectra characterised by a region of non-emission between two regions of emission are shown in the similar spectra of hydrindene and benzyl methyl ether, and of tetrahydronaphthalene and benzyl ethyl ether. This suggests a curving of the ether chains so as to make the ether molecule analogous to the closed-chain compounds. A fresh type of emission, or violet glow, was observed in several ether spectra. A band observed at 4315 Å. in several of the spectra is provisionally attributed to the decomposition of a complex ether with liberation of the alkyl group and a phenol. N. M. BLIGH.

Tesla-luminescence spectra. VII. Some aromatic aldehydes. A. RUSSELL and A. W. STEWART (J.C.S., 1929, 2407—2412; cf. preceding abstract).—Twenty aromatic aldehydes were examined, and out of 17 containing a single benzene nucleus 11 showed no detectable emission. Spectral details are given for benzaldehyde, 3- and 4-methylbenzaldehyde, 3:4-dimethylbenzaldehyde, 4-propylbenzaldehyde, anisaldehyde, and piperonal. All the emitting compounds showed the benzaldehyde blue band type of spectrum. The banding of the spectrum appears to be associated with the benzene ring and is deeply modified by substitution; a methyl group *ortho* to the aldehyde group extinguishes emission in the blue region; *p*-substitution reduces the number of detectable bands. The introduction of a hydroxyl group quenches the emission of the aldehydes, but methoxyl groups do not necessarily extinguish the blue band series. N. M. BLIGH.

High-frequency discharge in organic vapours. P. N. GHOSH and B. D. CHATTERJEE (Nature, 1929, 124, 654).—The striated character of the electrodeless discharge is described. Vapours, e.g., of propyl bromide, when thus ionised give rise to band spectra.

A. A. ELDRIDGE.

Foreign ion content of alkali halide phosphors. W. KOCH (Z. Physik, 1929, 57, 638—647).—It is found that the foreign ion content of crystals of alkali halide phosphors is only 0.5—0.05 of that in the fused mass from which the crystals are prepared. The relation between the heavy metal content, as determined by direct analysis of the crystals, and the absorption at the absorption maximum has been followed. In the case of potassium chloride-thallium chloride phosphor the absorption constant rises almost linearly with the concentration of thallium ion, but potassium chloride-lead chloride was found to be non-homogeneous and no satisfactory data could be obtained. The absorption curves for different concentrations of foreign ion have also been followed. The absorption spectra of aqueous solutions of the chlorides and bromides of lead and thallium have also been investigated. The effect of addition of considerable quantities of potassium chloride on the absorption spectrum of lead chloride solution is also indicated. J. W. SMITH.

Efficiencies in luminescence accompanying electrolysis. R. T. DUFFORD (Physical Rev., 1928, [ii], 31, 157; cf. A., 1928, 994).—The luminescence

at the electrodes accompanying electrolysis has been studied for many solutions with different metals as electrodes, the chief cases being those of aluminium in sodium phosphate or carbonate solutions, and almost any metal in anhydrous ethereal solutions of Grignard reagents. The brightness ranges from 6×10^{-9} to 10^{-5} lambert, and generally increases with applied *P.D.* Efficiency increases and then decreases with an increase in voltage, but is practically unaffected by changes in concentration and is the same for chemically similar solutions. L. S. THEOBALD.

Metallic reflexion from rock-salt and sylvite in the Schumann region. A. H. PFUND (Physical Rev., 1928, [ii], **31**, 315; cf. A., 1928, 934).—The maxima of reflexion lie near 1600 Å. for rock-salt and near 1625 Å. for sylvite, with indications of further maxima near 1000 Å. L. S. THEOBALD.

Dielectric constant and electric moment of some alcohol vapours. J. B. MILES, jun. (Physical Rev., 1929, [ii], **34**, 964–971).—By using a new method of measuring the pressure of the hot vapour, the dielectric constant of the vapours of methyl, ethyl, *n*-propyl, and *n*-butyl alcohols was measured at several temperatures. Good agreement was found with Debye's equation for the dielectric constant of gases at higher temperatures where there is no association. Association is discussed theoretically. The calculated electric moments $\times 10^{-18}$ are respectively 1.68, 1.69, 1.65, and 1.65. N. M. BLIGH.

Dielectric constants and molecular structure of carbon disulphide and nitrous oxide. P. N. GHOSH, P. C. MAHANTI, and B. C. MUKHERJEE (Z. Physik, 1929, **58**, 200–204).—The dielectric constants of carbon disulphide and nitrous oxide determined by the usual balance method are respectively 1.002912 and 1.001050. The electric moments were calculated from the Debye equation, and the Debye function, y , is plotted against temperature. The curves show that neither substance possesses a definite dipole moment, and the Maxwell relationship holds, i.e., the dielectric constant is equal to the square of the extrapolated refractive index for infinitely long waves. The non-polar nature of nitrous oxide is also shown by its relatively weak Kerr effect. The observations show that the molecules of nitrous oxide and carbon disulphide are linearly symmetrical. A. J. MEE.

Dielectric polarisation potential and the law of superposition for hard rubber. H. H. RACE and J. R. CAMPBELL, jun. (Physical Rev., 1929, [ii], **34**, 1031–1034).—A sample of hard rubber (ebonite) was subjected to several similar conditions of charge at a constant potential of 884 volts per cm., and to different conditions of discharge at potentials from 829 to 882 volts per cm. Results indicate that the polarisation potential built up during a long-time charge is approximately equal and opposite to the charging potential. The current-time curve predicted from Curie's law of superposition with data previously obtained for the sample was in close agreement with the actual curve. N. M. BLIGH.

Dielectric constants of benzene, carbon disulphide, and carbon tetrachloride, and of dilute solutions of alcohols in these solvents. J. D.

STRANATHAN (Physical Rev., 1928, [ii], **31**, 156; cf. A., 1928, 576).—The dielectric constants of benzene, carbon disulphide, and carbon tetrachloride have been determined at temperatures between the f. p. and b. p. by means of a high-frequency beat method, and also of dilute solutions of methyl alcohol in benzene and in carbon tetrachloride, and of amyl alcohol in benzene. The electric moments of methyl and amyl alcohols (in benzene) obtained by a graphical method are 1.66×10^{-18} and 1.65×10^{-18} e.s.u., respectively. For methyl alcohol in carbon tetrachloride, the results are inconsistent with the Debye theory, possibly owing to association. The calculated moment of the alcohol molecule in this case is 1.65×10^{-18} , assuming that there is no association at the b. p.

L. S. THEOBALD.

Nature of the general polarisation effect in aromatic molecules. W. A. WATERS (Phil. Mag., 1929, [vii], **8**, 436–441).—The general polarisation effect in aromatic molecules may be correlated with the dipole moment μ of the substituent group. From $\log K_s/K_u \propto \mu$, where K denotes the reaction velocity coefficients of the substituted and unsubstituted compound, the relative orders of magnitude of the reaction velocities of all *meta*-substituted aromatic compounds can be predicted from the electrical dipole moments of the substituent groups, and *vice versa*. The prediction is less certain for *para*-compounds, and is not possible for *ortho*-compounds.

N. M. BLIGH.

Time-lag differences of the Faraday effect in several mixtures and compounds. F. ALLISON (Physical Rev., 1928, [ii], **31**, 313).—The time-lag previously observed (*ibid.*, 1927, **30**, 66) has been studied with mixtures of liquids and with certain chemical compounds. Each liquid retains its own lag on mixing. Lags for various wave-lengths have been measured in ethyl alcohol, acetic acid, and ethyl acetate; the last-named shows two time-lag differences, those of the alcohol and the acid, for each wave-length used. Similar results are obtained with acetic acid, amyl, *n*-butyl, and methyl alcohols, and the corresponding esters, the esters showing no specific lag.

L. S. THEOBALD.

Calculation of the number of dispersion centres in sodium. W. K. PROKOFIEV (Z. Physik, 1929, **58**, 255–267; cf. Sugiura, A., 1927, 1004).—The calculation carried out by Sugiura for the first two doublets of the principal series of sodium is repeated. The calculation is simplified and extended. In the first place the potential energy of the valency electrons of sodium is calculated. The determination of the characteristic function of the Schrödinger wave equation is then carried out, and the probability of switch and number of dispersion centres are obtained from it. The calculation can be applied in an easy way to the third and fourth doublets of the principal series and some of the first doublets of the secondary and combination series.

A. J. MEE.

Magneto-optical dispersion of some organic liquids in the ultra-violet region of the spectrum. C. C. EVANS and E. J. EVANS (Phil. Mag., 1929, [vii], **8**, 137–158).—The magneto-optical rotations of isopropyl alcohol, allyl alcohol, methyl acetate, and

ethyl acetate have been determined for wave-lengths in the violet and longer ultra-violet spectral regions. The refractive indices of isopropyl alcohol, methyl acetate, and ethyl acetate have been determined for the same wave-lengths. The values of $\phi (=n\delta\lambda^2)$ for the respective compounds are given by $5.5526 \times 10^{-3} \{\lambda^2/(\lambda^2 - 0.1137^2)\}^2$, $7.24 \times 10^{-3} \{\lambda^2/(\lambda^2 - 0.1372^2)\}^2$, $4.587 \times 10^{-3} \{\lambda^2/(\lambda^2 - 0.1117^2)\}^2$, and $4.825 \times 10^{-3} \{\lambda^2/(\lambda^2 - 0.1140^2)\}^2$, where n —refractive index, δ —Verdet's constant in minutes per cm. gauss for wave-length λ and the wave-lengths of the absorption bands controlling the magneto-optical rotations of isopropyl alcohol, allyl alcohol, methyl acetate, and ethyl acetate are respectively 0.1137 μ , 0.1372 μ , 0.1117 μ , and 0.1140 μ . A. E. MITCHELL.

Refractive indices of calcite in the wave-length range of 2–6 Å. E. DERSHEM (Physical Rev., 1928, [ii], 31, 916).—For calcite the reflexion method gave $1-\mu = 17.8 \times 10^{-6}$ at 1.98 Å. and 137×10^{-6} at 6.00 Å., in good agreement with the values calculated from the Drude-Lorentz formula. Within 0.2 or 0.3 Å. of the calcium absorption limit the values of $1-\mu$ are depressed on both sides of the absorption edge as required by quantum theories of X-ray dispersion. L. S. THEOBALD.

Interferometric experiments on liquids in an electric field. K. SCHAUM and E. WALTER (Z. wiss. Phot., 1929, 27, 109–112).—An experimental method is devised for the separate determination of the optical changes produced by the thermal and electric effects. With certain organic liquids, such as *tert.*-amyl chloride and *o*-nitrotoluene, the thermal effect is greater than the electric effect from the commencement of excitation by the electric field, or at least after a time of excitation of 1 second. For other substances, however, such as nitrobenzene and ethyl phenylacetate, the electric effect predominates for a certain time. J. W. GLASSETT.

Surface tension. IV. Mechanics of drops pendant from cylindrical tubes. A. W. PORTER (Phil. Mag., 1929, [vii], 8, 180–186).—The mechanics of the formation of sustained drops for cylindrical tubes is discussed. It is shown that assuming conditions such that contact between the drop and a tube of infinitely thin wall is made above the end of the tube, then for a given material one and only one weight of pendant drop can be in equilibrium near the end of a tube of given outside radius of curvature, the weight being determined by the expression $W/\pi a^2 = 1 + a/c$, where W —weight of drop, σ —surface tension, a —radius of tube to the outside, and c —radius of curvature at the point of contact between liquid and tube. Values calculated from this expression are in fair agreement with those determined by Rayleigh and by Harkins and Brown. A. E. MITCHELL.

Interpretation of the temperature coefficient of surface tension. N. K. ADAM (Phil. Mag., 1929, [vii], 8, 539–547; cf. Hunten and Maass, this vol., 252).—On the view that the rate of decrease of surface tension with temperature is the rate of increase of the thermal bombardment pressure exerted by the surface molecules, parallel to the surface on a barrier in the surface, a number of factors, some at present

undeterminable, affecting the value of the Eotvos constant are considered. The temperature coefficient of surface tension of four homologous aliphatic series is considered, and new data are presented for long-chain compounds. There is nearly complete orientation of the surface molecules when the chains are ten carbon atoms or more long, if the molecules have a polar group at one end; the hydrocarbons are probably not fully oriented until double this length of chain. The intensity of vibration of the molecules of the triglycerides appears to be somewhat less than that of three chains separately, although the chains move independently in some degree. N. M. BLIGH.

Determination of the orientation of a crystal from a Laue photograph. K. YAMAGUCHI and S. TOGINO (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 603–608).—Details are given of a "crystallographic globe" by which the orientation of a crystal axis may be obtained mechanically after the type and co-ordinates of the face have been determined from a Laue photograph. With a globe of 6 cm. radius the limit of error is less than 0.1°. F. G. TRYHORN.

Supposed effect of X-rays in crystal rectifiers. S. OBERTO (Atti R. Accad. Lincei, 1929, [vi], 10, 89–92).

Significance of X-ray analysis of alkali sulphates. A. E. H. TURTON (Phil. Mag., 1929, [vii], 8, 195–201).—The classical optical and morphological constants of the series of alkali sulphates are discussed in the light of the results of X-ray analysis, and it is pointed out that in this series of eutropic isomorphous compounds the whole of the morphological and physical properties of their crystals are functions of the atomic numbers and atomic weights of the interchangeable family-group elements giving rise to the series. This result is considered to afford a proof of the law of Haüy that to every definite chemical substance crystallising in any but the cubic system there is a particular crystalline form (or forms if polymorphous) peculiar to and characteristic of the substance. A. E. MITCHELL.

X-Ray analysis of chromium-nickel alloys. F. C. BLAKE, J. O. LORD, W. C. PHEBUS, and A. E. FOCKE (Physical Rev., 1928, [ii], 31, 305; cf. A., 1928, 1313).—Etching, photomicrographs, and X-ray analysis show the presence of a third, rhombohedral phase in nickel-chromium alloys. This rhombohedral lattice, together with the body-centred lattice, is present in alloys containing 65–85% Cr.

L. S. THEOBALD.

Interpretation of X-ray crystal photographs. II. Complete rotation photographs. W. H. GEORGE (Phil. Mag., 1929, [vii], 8, 442–456; cf. this vol., 381).—A mathematical instrument is described which directly interprets the principal axis, and complete rotation of cubic, tetragonal, hexagonal, and trigonal crystals. In combination with the previously described grid method of measuring X-ray photographs, the method is independent of the nature of the spectrometer, the wave-length of the X-rays, or the size of the unit cell of the particular substance. Some applications are described, and some tables of constants are given for use in connexion with reciprocal

lattice methods for interpretation of rotation photographs. N. M. BLIGH.

Fine structure of the absorption bands of crystals. H. M. RANDALL and H. H. NIELSEN (Physical Rev., 1928, [ii], 31, 1131).—A fine structure with the lines spaced approximately 23 Å. apart has been developed in the band of calcium carbonate at 3.5 μ. L. S. THEOBALD.

X-Ray investigation of the structure of naphthalene and anthracene. J. M. ROBERTSON (Proc. Roy. Soc., 1929, A, 125, 542–569).—The crystal structures of naphthalene and anthracene, examined by the rotating-crystal method, are found to be closely similar. The former has a 8.34, b 5.98, c 8.68, β 122° 44', d 1.152; the latter a 8.58, b 6.02, c 11.18, β 125° 0', d 1.250. The space-group is in each case and there are two molecules in the unit cells, which must therefore possess a centre of symmetry. A geometrical structure factor is developed for these conditions. A study of the relative intensities of reflexion at various planes indicates that there is a fundamental periodicity along the c axis of amount 1.28 Å. in both naphthalene and anthracene, and that the scattering centres lie nearer the ac than the bc planes. Since the molecules do not exhibit even an approximate plane of symmetry in the ac planes, it is assumed that the scattering centres lie in two rows parallel to the c axes, forming a chain-like structure. With this limitation, a compact geometrical structure factor is developed for the general case of n scattering centres (each regarded as a carbon atom with its attendant hydrogen atom, if any), and a detailed examination of the parameters leads to values which account for the intensity distribution in the various spectra of the two crystals. The structures are found to be alike, within the limits of experimental error. The dimensions of the molecules differ very little from those of Bragg's tetrahedral structure, and the chain structure, moreover, is shown to be closely related in many of its dimensions to that of the hydrocarbon $C_{29}H_{60}$ (Müller, A., 1928, 1176). This affords strong evidence that the tetrahedral properties of the carbon atom are maintained in aromatic structures.

L. L. BIRCUMSHAW.

Quantitative study of reflexion of X-rays from crystals of aluminium. R. W. JAMES, G. W. BRINDLEY, and R. G. WOOD (Proc. Roy. Soc., 1929, A, 125, 401–419; cf. James and others, A., 1928, 225, 462).—By means of the method previously used for crystals of rock-salt and sylvine (*loc. cit.*), measurements have been made of the intensity of reflexion of X-rays by single crystals of aluminium at the ordinary temperature and at the temperature of liquid air. The temperature factor deduced from the results is in close agreement with that predicted by the Debye-Waller theory, and the absolute values of the atomic scattering power F , corrected by means of the measured temperature factor, agree with those calculated theoretically from the Schrödinger charge-distributions, assuming the existence of zero-point energy. L. L. BIRCUMSHAW.

Precision measurements of X-ray reflexions from crystal powders. M. L. FULLER (Phil. Mag., 1929, [vii], 8, 585–586; cf. Brentano and Adamson,

this vol., 493).—A discussion of the relative accuracy of available data for the lattice parameter of cadmium oxide. N. M. BLIGH.

Spinning target X-ray generator and its input limit. A. MÜLLER (Proc. Roy. Soc., 1929, A, 125, 507–516).—Mathematical. In an ordinary X-ray tube a limit for the specific input is soon reached owing to the intense heating of the focus and the consequent deterioration of the target surface, but by keeping the target moving this limitation may be avoided. An estimate is made of the extent to which the specific input may be increased by this means.

L. L. BIRCUMSHAW.

Systematics of the types of binding of diatomic molecules. H. LESSHEIM and R. SAMUEL (Naturwiss., 1929, 17, 827).—The relations between the two deepest electron terms of diatomic molecules have been investigated with reference to their potential curves. Analysis of the different possibilities indicates a definite correlation between the potential curves and the types of binding. Normal molecules in the chemical sense, whether atom- or ion-molecules, are merely those in which the union of two unexcited atoms or ions leads to a state possessing greater energy of dissociation than that resulting from the combination of one excited and one unexcited entity.

R. A. MORTON.

Term resolution in crystals. H. BETHE (Ann. Physik, 1929, [v], 3, 133–208).—The influence of an electrical field of known symmetry (crystal field) on an atom has been treated by the methods of wave-mechanics. R. A. MORTON.

Chemical binding. F. HUND (Trans. Faraday Soc., 1929, 25, 646–648).—The properties which enable atoms to form bindings are investigated and discussed, and their relation to London's analogy between chemical valency and some quantum properties of atoms is considered. London's work appears to give a quantum theoretical explanation of valency by the energies arising from the disappearance of the exchange degeneracy. N. M. BLIGH.

Structure of diatomic molecules. G. HERZBERG (Z. Physik, 1929, 57, 601–630).—By extensions of the methods of Mulliken (A., 1928, 1067; this vol., 116) and of Hund (this vol., 117) an attempt is made to explain the disagreements obtained when the stable electronic states of a diatomic molecule are calculated by different methods. The theory developed is applied to the calculation of the heats of dissociation of a large number of diatomic molecules for which suitable data are available. J. W. SMITH.

Molecular structure of the silicotungstates and related compounds. L. PAULING (J. Amer. Chem. Soc., 1929, 51, 2868–2880).—The principles previously enunciated (this vol., 748) are used to determine the structures of silicododecatungstic acid and analogous acids. The structures proposed lead to the formula $H_x[MO_4W_{12}O_{18}(OH)_{36}]$, where $x=3, 4, 5, 6$, respectively, when $M=P, Si, B, H_2$. This formula is in complete agreement with the known properties of these complex acids. Structures are also proposed for *isosilico-* and for *isoboro-dodecatungstic acids*, which correspond respectively with the formulae

$H_4[SiW_{12}O_{40}] \cdot 15H_2O$ and $H_5[BW_{12}O_{40}] \cdot 15H_2O$; suggested structures are also given for some unsaturated (or condensed) heteropoly-acids. S. K. TWEEDY.

Structure of crystal hydrates. A. KAPUSTINSKY (Z. physikal. Chem., 1929, 144, 187—196).—A study of the heats of hydration for the addition of successive water molecules to salts which have an odd number of molecules of hydration, and of the molecular heats of these compounds, indicates that the first molecule of water is bound in a different way from the rest. Ions such as those of zinc, magnesium, manganese, copper, lanthanum, iron, and nickel, which form such hydrates, have average ionic radii and charge densities sufficient in general for the attraction of water, and consequently for the formation of crystal hydrates, but insufficient for hydrolysis. The hypothesis here put forward, that in these crystal hydrates the first water molecule is bound constitutionally (*i.e.*, the metal combines with the hydroxyl group and the anion with the hydrogen ion), is in accord with Werner's theory and with the electrostatic theory of chemical affinity. Structural formulae for these and other hydrates are suggested. F. L. USHER.

Chemical combination as an electrostatic phenomenon. II, III. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 114—118, 146—149).—II. The electrostatically stable arrangement of the ions in various types of molecules is described with reference to the periodic classification, and the varieties of ion which can be formed are classified: Six classes of positive ion are recognised: (1) the hydrogen ion; (2) ions with the helium configuration; (3) ions with eight outer electrons, derived from elements following the inert gases by loss of electrons up to eight in number, *e.g.*, ruthenium and osmium; (4) ions with eight outer electrons but containing more electrons than the corresponding inert gas; (5) ions with eighteen outer electrons, derived from elements following nickel, palladium, platinum; (6) ions of a lower degree of symmetry in which the highest valency is not attained, *e.g.*, iron, cobalt, nickel, rhodium, palladium, iridium, and platinum.

III. The space configuration of the ions in molecules containing from 1 to 4 negative ions attached to a positive nuclear ion is discussed. From the similarities of, *e.g.*, lithium hydride with the halides of the alkali metals and of boron hydride, B_2H_6 , with the boron halides it is suggested that in such compounds the hydrogen is present as a negatively charged ion. This view is supported by the behaviour of the hydrocarbons towards substituents and by the contrasts between the properties of halides in various groups of the periodic classification. The manner in which crystal lattices are built up from polar molecules is described. H. F. GILLBE.

Molecular linking and other properties of the hydrogen halides. R. T. BIRGE and O. R. WULF (Physical Rev., 1928, [ii], 31, 917).—Theoretical. Energy level diagrams for hydrogen fluoride, chloride, bromide, and iodide have been devised, using recent data. These substances appear to exist with atomic linking in the non-vibrational state, but a dissociation into ions is also indicated. The heat of dissociation

of these molecules in the ionised condition is approximately zero or negative. L. S. THEOBALD.

Dissociation of molecules by rotation. O. OLDENBERG (Z. Physik, 1929, 56, 563—575).—The curves connecting potential energy with nuclear distance, when modified to include rotational energy, explain the sudden disappearance of rotational levels, and show that the energy of the last discrete level is not the energy of dissociation. Diffuse lines are expected near this critical edge. An example is mercurous hydride. A. B. D. CASSIE.

Gas content, crystal structure, and hydrogen absorption of sputtered nickel films. L. R. INGERSOLL and J. D. HANAWALT (Physical Rev., 1929, [ii], 34, 972—977).—By using a special deposition tube to allow withdrawal of the cathode without altering vacuum conditions, films of nickel were sputtered in hydrogen, helium, nitrogen, and argon, and their gas content was investigated. The gas is emitted just below the baking temperature range for which the films become magnetic and better conducting. In addition to the influence of crystal structure, evidence indicates that the gas, by keeping the atoms apart, is mainly responsible for the abnormal magnetic properties of the films. Evaporated films contained much less gas than the sputtered, even when produced at the same gas pressure, the gas being excited or activated during the sputtering process, and its occlusion promoted; the evidence pointed to the production of nickel hydrides and nitrides. The films showed a high absorption for hydrogen above a critical temperature depending on the previous heat treatment. N. M. BIGH.

Crystal disintegration and formation. P. P. VON WEIMARN (Kolloid-Z., 1929, 49, 149—150).—A summary of previously published work on the conditions of formation and disintegration of small crystals. E. S. HEDGES.

Crystal structure of *m*-iodobenzoic acid. H. P. KLUG, E. MACK, jun., and F. C. BLAKE (J. Amer. Chem. Soc., 1929, 51, 2880—2888).—Assuming β to be $91^\circ 29'5''$ (Groth), the axial ratio of *m*-iodobenzoic acid is $a : b : c = 1.3252 : 1 : 5.5824$, and the unit cell, which contains 4 mols., has a_0 6.206, b_0 4.683, and c_0 26.14 Å. The space-group is C_{2h}^2 , in the monoclinic prismatic group. The parameters of the molecules in the unit cell were determined; the structure embodies a "puckered" benzene ring. The use of absorbing filters in Laue spot X-ray photography is discussed briefly and justified. S. K. TWEEDY.

Crystallographic and optical properties of diaminozinc chloride formed in the Leclanché cell. K. CHUDOKA (Zentr. Min. Geol., 1929, A, 139—143; Chem. Zentr., 1929, i, 2865).—In addition to the compound $ZnCl_2 \cdot 6NH_3$, d 1.50, H 1, n_D 1.539 \pm 0.002, the compound $ZnCl_2 \cdot 2NH_3$, which appears in three habits, was observed.

A. A. ELDRIDGE.

Crystal structure of strontium oxide. T. A. WILSON (Physical Rev., 1928, [ii], 31, 1117).—The pattern of the oxide has been isolated from spectrograms of a mixture of the oxide and carbonate. The

lattice is of the sodium chloride type with 5.073 ± 0.01 Å. length of cube edge, and d 5.235.

L. S. THEOBALD.

Crystal structure of potassium dithionate. M. L. HUGGINS and G. FRANK (Physical Rev., 1928, [ii], 31, 916).—X-Ray spectra from rotating crystals show the space-group to be $D_3^1(3D-1)$ of the hexagonal system. The unit structure has a_0 9.8, c_0 6.45 Å., and contains 6K, 6S, and 18 oxygen atoms. The sulphur atoms are in pairs on the three-fold symmetry axes, each sulphur atom having 3 oxygen atoms placed symmetrically around it. L. S. THEOBALD.

Crystalline structure of bromides of bivalent metals. A. FERRARI and F. GIORGI (Atti R. Accad. Lincei, 1929, [vi], 9, 1134—1140).—The bromides of cobalt, ferrous iron, magnesium, and manganese possess structures of the cadmium iodide type. The characteristics of these substances, in the above order, are: a 3.685, 3.740, 3.815, 3.820 Å.; c 6.120, 6.171, 6.256, 6.188 Å.; c/a 1.66, 1.65, 1.64, 1.62; d 5.072, 4.790, 3.876, 4.549. F. G. TRYHORN.

Vanadium-carbon system. S. OYA and A. OSAWA (J. Study Met., 1928, 5, 434—441).—Vanadium has a body-centred cubic lattice, a 3.024 Å. Vanadium-carbon alloys contain (α) a phase consisting mainly of vanadium, (β) a phase having a close-packed hexagonal lattice with axial ratio 1.59, and (ϵ) a phase having a face-centred cubic lattice. The effect of varying amounts of carbon on the lattice has been examined. The β -phase consists of the compound V_5C , and the ϵ -phase of the compound V_4C . CHEMICAL ABSTRACTS.

Electrical and optical behaviour of half conductors. I. Hall effect and conductivity of silver sulphide. F. KLATBER (Ann. Physik, 1929, [v], 3, 229—253).—The Hall effect has been determined for both modifications of silver sulphide in the form of plates prepared in different ways from pure materials. The Hall constant and the conductivity have been measured at temperatures between 160° and 225°, the results for different specimens agreeing within a few per cent. The transformation: $\beta\text{-Ag}_2\text{S}$ (rhombic) \rightarrow $\alpha\text{-Ag}_2\text{S}$ (regular) at 179° is accompanied by a change in Hall constant from 20 cm.³/amp. sec. to about 0.6 cm.³/amp. sec.; the conductivity of 1.5 ohm⁻¹ cm.⁻¹ increases 310 times, so that $\alpha\text{-Ag}_2\text{S}$ at the transformation point has a conductivity of 4.7×10^2 ohm⁻¹ cm.⁻¹, i.e., about 100 times as great as that of the best molten electrolytes. The product of the Hall constant and the conductivity for both modifications of silver sulphide lies between the limits observed for metals. No Hall effect could be observed for solid, regular silver iodide ($\alpha\text{-AgI}$). The interpretation of the results is discussed.

R. A. MORTON.

Variations of the Hall coefficient, of the thermoelectric power, and of the resistance with the magnetic field in ordinary and compressed bismuth. R. FEDELE (Atti R. Accad. Lincei, 1929, [vi], 10, 83—89).—Measurements of the above three quantities have been made with varying magnetic fields for crystalline bismuth and for bismuth tablets made by compressing the finely powdered metal. Modifications in the structure of the bismuth, even

if these are produced by the magnetic field, have no influence on the variation of the Hall effect, of the thermoelectric power, or of the resistance with the magnetic field. These variations are due solely to electrodynamic action. O. J. WALKER.

Discontinuities of magnetisation in iron and nickel. C. W. HEAPS and J. TAYLOR (Physical Rev., 1929, [ii], 34, 937—944).—The discontinuities of magnetisation (Barkhausen effect) in iron and nickel were recorded photographically, and the dependence of their number on the rapidity of change of the magnetising force was determined. More and smaller discontinuities were found at high than at low speeds of magnetisation. By varying the size of the specimen the length of the portion of material involved in one of the discontinuities was estimated at 2—3 mm., and the volume of the order 10^{-7} c.c. A method for determining the hysteresis loop of very small specimens is described. It is suggested that in different portions of the material different magnetostrictive effects may occur, the strains thus set up, when relieved discontinuously, producing the jumps of induction. N. M. BUGH.

Effective and reversible permeability. G. J. SZOZO (Ann. Physik, 1929, [v], 3, 270—276).—Using an iron-silicon alloy (3% Si) it is shown that as the amplitude of the superposed field becomes increasingly small, the identification of measured effective permeability and reversible permeability becomes increasingly trustworthy. Gans' generalisation, that permeability is a true function of magnetisation, and that the experimental deviations are due to inhomogeneity of material, is valid only in the limiting case of an infinitely small amplitude for the magnetisation process. If Gans' law is a criterion of reversibility, the magnetisation can be reversible only in the limiting case. R. A. MORTON.

Saturation magnetisation of ferro-cobalts and atomic moments of iron and cobalt. P. WEISS and R. FORRER (Compt. rend., 1929, 189, 663—666; cf. A., 1928, 454).—The saturation magnetisation of 25 iron-cobalt alloys (0—100% Co) has been determined at the ordinary temperature, and the variation with temperature down to that of liquid air. From these figures absolute saturation at absolute zero has been calculated. It is deduced that the atoms of iron and cobalt can exhibit magnetic moments of varying multiples of the magneton, usually integral, e.g., 11 and 15 for Fe- α , 14 for Fe- γ , 17 and 9 for Co- α , but sometimes apparently fractional. The revised value 1125.6 is given for the gram-magneton.

C. A. SILBERRAD.

Application of thermomagnetic analysis to the study of oxides and minerals of iron. J. HUGGETT (Ann. Chim., 1929, [x], 11, 447—510; cf. A., 1928, 503, 841).—Apparatus is described by means of which variations in the magnetic properties of oxides of iron with temperature can be employed to establish their presence in mixtures or minerals, and to indicate the occurrence of chemical changes. The results of independent experiments on pure oxides and their mixtures under various conditions have been applied to the investigation of various materials containing iron oxides. Martite and hæmatite are always

found to contain a small quantity of magnetic oxide, whilst goëthite and lepidocrocite give on dehydration a certain amount of Malaguti's oxide, this substance also being formed superficially when magnetite is heated in air. Metallic iron, after long immersion in aerated water, forms a mixture of magnetite and rust, and the latter gives a thermomagnetic curve resembling completely that of lepidocrocite.

F. L. USHER.

Electrical phenomena of crystals floating on a saturated aqueous solution. N. KATO (Nature, 1929, 124, 653—654).—Experiments with acetanilide are described.

A. A. ELDRIDGE.

Electrical resistance and magnetic permeability of iron wire at radio frequencies. G. R. WAIT, F. G. BRICKWEDDE, and E. L. HALL (Physical Rev., 1928, [ii], 31, 303).—No critical change in high-frequency resistance or critical variation in permeability could be observed.

L. S. THEOBALD.

Effect of boundary distortion on the surface energy of a crystal. (Miss) B. M. DENT (Phil. Mag., 1929, [vii], 8, 530—539; cf. this vol., 17).—A method of evaluating the effect of surface distortion on the surface energy of polar crystals is described, and illustrated by results for the halides of sodium and potassium. The distortion decreases the surface energy by about 20%, the effect being due almost entirely to the polarisation of the surface ions.

N. M. BLIGH.

Variation with temperature of the critical stress of cadmium crystals. W. BOAS and E. SCHMID (Z. Physik, 1929, 57, 575—581; cf. this vol., 374).—The initial plastic deformation of cadmium crystals on stretching has been investigated over the temperature range 20—585° Abs. In the lower portion of this temperature range the critical stress of the translation system decreases nearly linearly with rise of temperature, but from about 450° Abs. to the m. p. it is almost constant at about 20.2 g./mm.² The results are compared with those for zinc.

J. W. SMITH.

Slip bands of compressed aluminium crystals. I. Distortion by single slipping and a tentative theory of work-hardening of metal. K. YAMAGUCHI (Sci. Papers Inst. Phys. Chem. Tokyo, 1929, 11, 223—241).—An analysis of distortion when the specimen slips on one plane is made on the assumption that distortion is perfect simple shear on the slip plane to the direction of slip which was obtained from the condition of maximum shear stress. The stress-strain curve obtained is decidedly below the theoretical curve, due probably to inclusion in the sample of small unabsorbed grains. Imperfect slipping influences the direction of the actual slip bands with compression. A tentative theory of work-hardening of metal is put forward based on the mechanism of the self-stopping of the slip.

W. R. ANGUS.

Fracture of iron at low temperatures. F. SAUERWALD and K. A. POHLE (Z. Physik, 1929, 56, 576—578).—Fracture was studied at -10° , -20° , -80° , and -170° .

A. B. D. CASSIE.

Defects in crystal structure and heterogeneous catalysis involving active centres. A.

SMEKAL (Z. Elektrochem., 1929, 35, 567—573).—Defects, e.g., cavities, may be formed in the interior of crystals, depending on the way in which they were prepared, and so give rise to active centres on the surfaces of the crystals. Previous work has shown that these defects affect the physical properties of the crystals (cf. this vol., 753, 871).

H. T. S. BRITTON.

Physical identity of enantiomerides. A. N. CAMPBELL (Nature, 1929, 124, 792).—It appears that chemical combination can take place between dextro- and lævo-forms, and that this action differs from that between molecules of the same form producing association. Hence a difference in chemical, and therefore in physical, nature is to be postulated; measurements of f. p., solubility, and specific rotation, e.g., of the esters of tartaric acid, are desirable.

A. A. ELDRIDGE.

Polymorphism of zinc. W. GUERTLER and L. ANASTASIADIS (Z. Metallk., 1929, 21, 338).—Differential thermal analysis of pure zinc (99.999% Zn) fails to show the presence of any of the three transformation points observed by previous investigators. Their results are attributed to the presence of impurities.

A. R. POWELL.

Effect of iron on the magnetic susceptibility of aluminium. R. B. MASON (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 8 pp.).—Comparative measurements of the magnetic susceptibility of aluminium and its alloys have been made. Pure aluminium (99.97% Al) is shown to be definitely paramagnetic. The susceptibility is increased only slightly by the presence of iron up to 8%. This result is due to the iron existing in the form of an intermetallic compound. On treatment with sodium hydroxide solution to break up the compound and liberate free iron on the surface of the sample, there is a very marked increase in the magnetic susceptibility. The method can be employed for the approximate determination of iron in aluminium in the absence of other impurities. Manganese appears to increase the magnetic properties of aluminium to a greater extent than iron.

H. J. T. ELLINGHAM.

Magnetic susceptibility of halogen ions. K. RIECHENEDER (Ann. Physik, 1929, [v], 3, 58—62).—The magnetic susceptibilities of hydrochloric, hydrobromic, and hydriodic acids in aqueous solution have been determined. Assuming $\chi_{\text{acid}} = (\chi_{\text{a}})_{\text{H}} + (\chi_{\text{a}})_{\text{ion}}$ and putting $(\chi_{\text{a}})_{\text{H}} = 0$, the atomic susceptibilities of the ions are: $\text{Cl}^- = -21.9$, $\text{Br}^- = -32.5$, $\text{I}^- = -50.2 \times 10^{-6}$. The results are in good agreement with Ikenmeyer's data based on measurements with alkali halides (this vol., 247).

R. A. MORTON.

Conductivity of ionised air at high frequency. (FRL.) A. SZÉKELY (Ann. Physik, 1929, [v], 3, 112—132).—The conductivity of ionised air in the negative glow has been determined for frequencies $1-5 \times 10^6$ Hertz (wave-lengths between 242 and 58 m.). In agreement with the requirements of theory the resistance increases as the square of the frequency. The conductivity is due to electrons which are approximately in thermal equilibrium with the gas molecules. The confirmation of the theory concerning the behaviour of ionised gases subjected to

high frequencies in the range of wireless telegraphy is of special interest, since it applies to pressures and ionisation of the type and strength to be expected in the Heaviside layer at 60–80 km. height.

R. A. MORTON.

Ionic magnetic moments. E. C. STONER (Phil. Mag., 1928, [vii], 8, 250–266).—Previous theories of ionic magnetic moments are reviewed in conjunction with the experimental results. The difference in the magnetic behaviour of the first transition series of ions and the rare-earth series is discussed. The difference is attributed to the fact that in the former the incomplete group of electrons belongs to the group of highest total quantum number, whilst in the latter the incomplete group belongs to an inner group and that interaction between an ion and its neighbours affects mainly the electrons of highest quantum number. The rare-earth ions behave magnetically as free, the moment expressed in Weiss magnetons being given by $p=4.97g\sqrt{j(j-1)}$, where g is the Lande splitting factor and j the inner quantum number characterising the state. In the first transition series the orbital moment l and the spin moment s require separate consideration. The orbital moment is partly ineffective owing to the interaction field, which is treated as equivalent to an initial magnetic field the general effect of the character of which on the measured susceptibility is considered. The limits of the value of p for these ions is shown to be between $4.97\sqrt{4s(s+1)}$ and $4.97\sqrt{4s(s+1)+l(l+1)}$, there being a tendency to the former value at low temperatures and to the latter at high temperatures.

A. E. MITCHELL.

Influence of particle size on diamagnetism. V. I. VAIDYANATHAN (Nature, 1929, 124, 762).—The diamagnetic susceptibility of graphite or antimony falls with diminution of particle size.

A. A. ELDRIDGE.

Electroaffinity of gases. M. A. DA SILVA (Ann. Physique, 1929, [x], 12, 99–168).—The ionisation current (produced by α -particles) in pure argon reaches saturation under atmospheric pressure at direct-current voltages much smaller than are needed for air. The negative ions formed in argon consist of free electrons. The ionisation current obtained with alternating current (200–1000 volts) consists of a practically constant flow of negative charges equal to one half the saturation current obtained with direct current. The effects of adding small increasing quantities of oxygen and water vapour have been studied. With oxygen 0.06% of added gas is necessary before the ionisation curve is definitely affected, whilst with water 0.004% suffices. The electronic affinity of water vapour is therefore at least ten times as great as that of oxygen. The mobility of positive ions in argon is 2.2 cm./sec. at atmospheric pressure. Methods which served to show that the electron affinity of argon is zero were applied to nitrogen and hydrogen, and it is found that although the values for these gases are small, the electron affinity is not zero. At the same time, the results for hydrogen might be interpreted by assuming the existence of very rapid (mobility > 11 cm./sec.) positive ions.

The experimental results have been compared with

the hypotheses of J. J. Thomson and of Wellisch to account for the formation of negative ions in gases. It is shown that Wellisch's hypothesis can be rejected. By measuring the ionisation currents in pure argon, the period of decay of polonium is found to be 140.2 days.

R. A. MORTON.

Electrocapillary curve of mercury and its dependence on temperature. Absolute values of electrochemical potentials. O. KOENIG and E. LANGE (Z. Elektrochem., 1929, 35, 686–695).—Theoretical. Reference is made to the contact potential between mercury and metals in *E.M.F.* measurements.

H. T. S. BRITTON.

Aluminium electrolytic condenser. R. E. W. MADDISON (Phil. Mag., 1929, [vii], 8, 29–55).—A general account of the theory and properties of the aluminium electrolytic condenser is given and the bearing of these on its applications is discussed.

A. E. MITCHELL.

Thermoelectric power of selenium crystals. R. M. HOLMES and A. B. ROONEX (Physical Rev., 1928, [ii], 31, 1127).—Crystals of selenium were formed by slow condensation of the vapour in an evacuated tube heated at a constant temperature at one end. The thermal *E.M.F.* in millivolts against copper is given by the equation $E=1.10t+0.00017t^2$ between 0° and 180°. An *E.M.F.* is developed in some crystals by the absorption of light when the circuit is at a uniform temperature.

L. S. THEOBALD.

Absorption of ultrasonic waves by some gases. T. P. ABELLO (Physical Rev., 1928, [ii], 31, 157; cf. A., 1928, 828).—Measurements of the absorption by carbon dioxide and hydrogen using a new method confirm the dependence on concentration previously observed.

L. S. THEOBALD.

Velocity of sound in liquids. L. G. POOLER (Physical Rev., 1928, [ii], 31, 157).—A resonance method for determining the velocity of sound in liquids with a high degree of precision has been developed. The velocity of sound in air-free, distilled water at 25° is found to be 1493.2 ± 2.3 m./sec., and the rate of change of velocity with temperature is 2.2 m./sec. per degree between 25° and 30°, decreasing to 0.4 m./sec. per degree between 60° and 70°.

L. S. THEOBALD.

Physico-chemical properties of ethanesulphonic and methanesulphonic acids. A. BERTHOUD (Helv. Chim. Acta, 1929, 12, 859–865).—The densities at 0–90°, viscosities, refractive indices, heats of dissolution in water, and conductivities in aqueous solution of the above acids have been determined. Surface tension measurements show the acids to be associated in the liquid state. From the f.p. curves of aqueous solutions the existence of the compounds $\text{Me}\cdot\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, m. p. 11°, $\text{Me}\cdot\text{SO}_3\text{H}\cdot 3\text{H}_2\text{O}$, m. p. -51.7° , and $\text{Et}\cdot\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, m. p. 5.4° , is deduced.

R. CUTHILL.

Intensively dried carbon tetrachloride. S. LENHER (J. Amer. Chem. Soc., 1929, 51, 2948–2950).—Intensive drying does not affect the b. p. and mol. wt. (determined by V. Meyer's vapour density method) of carbon tetrachloride.

S. K. TWEEDY.

Superheating and the intensive drying of liquids. S. LENHER (J. Physical Chem., 1929, **33**, 1579—1582; cf. A., 1928, 1189).—Details of results previously announced (this vol., 872) are given and objections are raised to the hypothesis that prolonged drying changes the degree of association of a liquid. The conditions for superheating of liquids are considered.

L. S. THEOBALD.

Specific heat of gases at medium and high pressures. I. [With K. VON LUDE.] Specific heats of air, nitrogen, carbon monoxide, carbon dioxide, nitrous oxide, and methane between 0° and 220°. II. [With G. HOFFMANN.] Specific heat of chlorine between -30° and 180°. A. EUCKEN (Z. physikal. Chem., 1929, **B**, 5, 413—441, 442—451).—I. The specific heats at constant pressures of a number of gases have been determined between 0° and 200° by a modification of the Lummer-Pringsheim method. The observed variations of C_p with temperature for carbon monoxide, carbon dioxide, and nitrous oxide are in good agreement with those calculated from the Planck-Einstein function by employment of spectroscopically determined values for the intramolecular characteristic frequencies, but for nitrogen and oxygen frequencies some 13% greater than the observed values must be employed. In the case of methane the semi-empirical formula of Eucken and Fried is applicable.

II. Application of the Planck-Einstein function yields results for chlorine in good agreement with those experimentally determined with a modified apparatus. Measurements of the vapour pressure of chlorine at -28° have been made and the temperature variation of the second virial coefficient has been calculated from -29° to 184°.

H. F. GILLBE.

Properties of para-hydrogen. K. L. BONHOEFFER and P. HARTECK (Z. Elektrochem., 1929, **35**, 621—623).—At the ordinary temperature hydrogen comprises a mixture of one part of parahydrogen to three parts of orthohydrogen, at the temperature of liquid air the ratio is about 1 : 1, whilst at 20.4° Abs. it is practically pure hydrogen. The m. p. of normal hydrogen at 760 mm. is 20.39° Abs., whereas that of parahydrogen is 20.26° Abs. The triple points of the two forms are slightly different, as also are physical properties such as specific heat and thermal conductivity.

H. T. S. BRITTON.

Metastability of matter and our physical "constants." E. COHEN (Z. Elektrochem., 1929, **35**, 620—621).—The necessity of using physically pure substances, and not mixtures of metastable modifications, for the determination of their physical constants is emphasised.

H. T. S. BRITTON.

Fusion curve of helium. F. SIMON (Z. Elektrochem., 1929, **35**, 618—619).—The fusion curve of solid helium can be represented with considerable accuracy by $\log_{10}(p+171) \text{ kg./cm.}^2 = 1.5544 \log_{10} T + 1.236$, so that at the ordinary temperature the pressure at which melting occurs is of the order of 100,000 kg./cm.²

H. T. S. BRITTON.

M. p. of palladium. F. H. SCHOFIELD (Proc. Roy. Soc., 1929, **A**, 125, 517—531).—The basis of the

"International temperature scale" up to the m. p. of gold is the gas thermometer, and beyond this temperature the Wien or Planck law of radiation. At present, the radiation scale is defined by the values assigned to the constant c_2 and a fixed point on the thermodynamic scale, as given by the gas thermometer, viz., the m. p. of gold. With the object of recording another fixed point on the radiation scale a determination has been made of the m. p. of palladium, the measurements taking the form of a determination of the current in a pyrometer lamp required to give a match in brightness, at a particular wave-length, with a black body held at the m. p. of gold, and a similar measurement in the case of palladium, employing a rotating sector to reduce the brightness to about the same intensity as at the gold point. Full details are given of the experimental procedure used to obtain black-body radiators at the two m. p., three methods of realising a black body being adopted. Taking c_2 as 1.432 cm. degrees and the m. p. of gold as 1063°, the value found for the m. p. of palladium is 1555°, to the nearest 1°, in good agreement with previous determinations.

L. L. BIRCUMSHAW.

Method of reducing heat losses during gaseous explosions and its use in a new method of determining the specific heat of water vapour. K. WOHL and G. VON ELBE (Z. Elektrochem., 1929, **35**, 644—648; cf. Wohl, A., 1924, ii, 600).—A method is described by which the mean specific heat of water vapour, between the ordinary temperature and that at which a mixture of the constituent gases used in the process explodes, can be found. A mixture of oxygen with excess of hydrogen was exploded in a hemispherical vessel of about 10 litres capacity, and the pressures before and after explosion were recorded by means of a membrane indicator. More accurate results were obtained by using wet gases (cf. Pier, A., 1909, ii, 789).

H. T. S. BRITTON.

Entropy and probability. W. S. KIMBALL (J. Physical Chem., 1929, **33**, 1558—1578).—Mathematical.

L. S. THEOBALD.

Molecular forces. II. **Temperature variation of the second virial coefficient of some organic vapours.** A. EUCKEN and L. MEYER (Z. physikal. Chem., 1929, **B**, 5, 452—460).—The second virial coefficients [B in the expression $pV = n(RT + Bp)$] of benzene, carbon tetrachloride, ethyl ether, methyl alcohol, acetone, and nitromethane have been calculated as functions of the temperature from measurements of the vapour pressure in the neighbourhood of 60—110°. The theoretical significance of the results is discussed.

H. F. GILLBE.

Vapour pressure and heat of vaporisation of iron pentacarbonyl. M. TRAUTZ and W. BADSTÜBNER (Z. Elektrochem., 1929, **35**, 799—802).—The vapour pressure of iron pentacarbonyl has been measured between 47.56° and 104.26°, using the apparatus of Trautz, Baisch, and Dechend (A., 1908, ii, 569). Calculations of the heat of vaporisation, using the Clausius-Clapeyron equation, showed that it gradually decreased from 9.65 kg.-cal. at 23.78° to 8.79 kg.-cal. at 98.98°. From the pressures at 0° and 104.2°, a value of 9.38 kg.-cal. is obtained—a

value much higher than that of Dewar and Jones (A., 1906, ii, 89). The lower values corresponding with the higher temperatures are attributed to the presence of $\text{Fe}_2(\text{CO})_9$ dissolved in the pentacarbonyl, reducing its vapour pressure and raising its b. p.

H. T. S. BRITTON.

Vapour pressure of mercury and some mercury compounds at low temperatures. A. STOCK and W. ZIMMERMANN (Monatsh., 1929, 53 and 54, 786—790).—The vapour pressure of mercury has been determined by saturating at the ordinary pressure a large quantity of air with mercury vapour, removing the mercury by means of liquid air, converting it into mercuric chloride, and finally weighing it after electrodeposition on a gold wire or determining its amount colorimetrically. The saturation pressures found are 5.50×10^{-4} , 1.79×10^{-4} , 3.3×10^{-5} , and 4.9×10^{-6} mm. at 10° , 0° , -20° , and -60° , respectively, which are, in general, higher than the values obtained by previous investigators. The corresponding pressures, obtained at 0° in a similar manner, are for mercuric chloride, iodide, and oxide 1.1×10^{-6} , 3.5×10^{-7} , and 4.1×10^{-6} mm., respectively. Mercuric sulphide was not volatilised by this treatment, and mercury should be changed into this compound when it is desirable to avoid any harmful physiological effects of the vapour.

L. S. THEOBALD.

Equation of state of a mixture determined from the equations of state of its constituents, and its application in determining the physical and chemical properties of a mixture in terms of those of the constituents. R. D. KLEEMAN (Physical Rev., 1928, [ii], 31, 311).—The equation of state of a mixture and the equations of the isolated constituents have the functional forms $p = \dots/v$, \dots/v , \dots/v , \dots/v ; $p_a = \psi(A_1 M_a/v, A_2 M_a, \dots)$; $p_b = \psi(B_1 M_b/v, B_2 M_b/v, \dots)$, where M_a, M_b, \dots denote the masses in g.-atoms of the constituents a, b, c, \dots respectively, p, p_a, p_b, \dots the pressures of the mixture and isolated constituents, respectively, and A_1, B_1, \dots are functions of T . The exact form of ψ is unknown. The equations form the theoretical basis for expressing the purely physical properties, such as optical, magnetic, and electric, of a complex substance in terms of those of its constituents.

L. S. THEOBALD.

Volume changes during the solidification of metals and alloys of low m. p. W. E. GOODRICH (Trans. Faraday Soc., 1929, 25, 531—569).—The volume changes which occur during the solidification of tin, lead, bismuth, and zinc and a number of binary and ternary alloys have been investigated. The alloys were prepared and filtered in a vacuum, and the volume changes determined in an atmosphere of nitrogen. Minimal contraction (2.28%) of lead-tin alloys takes place in the alloy containing 48% Pb, 52% Sn. The bismuth in bismuth-tin alloys expands 3.47% during solidification, so that the expansion or contraction of these alloys is determined by the proportion of the constituents. The solidification of any primary antimony-rich crystallites from molten binary antimony alloys containing either zinc or tin is not marked by any sudden volume

changes, neither is there any change in the direction of the specific volume-temperature curve when they begin to solidify. The addition of copper to an alloy of constant tin-antimony ratio increases the contraction, and especially when it has become greater than 1.5%. Pure zinc on solidification contracts 4.48%, and expands on melting by 4.69%. These figures can be considerably increased by alloying small amounts of copper and tin with the zinc, although when aluminium is substituted for the tin the changes in volume are very much reduced.

H. T. S. BRITTON.

Heat capacity of toluene from 14° to 298° Abs. Entropy and free energy of formation. K. K. KELLEY (J. Amer. Chem. Soc., 1929, 51, 2738—2741).—The specific heat of toluene is recorded down to 14° Abs. The molal heat of fusion at the m. p., 177.95° Abs., is 1582 g.-cal. The molal entropy is 52.4 g.-cal./ 1° at 298.1° Abs., and the molal free energy 24,300 g.-cal. For *m*-xylene, the provisional molal entropy of 60.3 g.-cal./ 1° and molal free energy of 24,000 g.-cal. are recorded. These results, taken in conjunction with the values for benzene, support the conclusions previously reached with regard to the entropy and free energy difference in successive members of an homologous series (cf. this vol., 635).

S. K. TWEEDY.

Mass of the normal litre of ammonia. E. MOLES and T. BATUECAS (Monatsh., 1929, 53 and 54, 779—785).—The value of L_0 for ammonia (prepared by three methods) is 0.77170, after the correction for absorption by the glass vessel used has been made. The value is considerably higher than other published values, but agrees with that of Leduc.

H. BURTON.

Movement of gases around electrically heated wires. S. LENHER and G. B. TAYLOR (J. Amer. Chem. Soc., 1929, 51, 2741—2744).—A periodic pressure change occurs in vessels containing an axially-placed electrically heated wire, which change attains a maximum when the vessel is tilted at about 45° . The change is observed with a nearly horizontal wire in air, nitrogen, argon, and carbon dioxide, but not in hydrogen or helium, and the effect decreases in air with a pressure decrease from 2 atm. to 0.25 atm. Introduction of a mist into the gas revealed the formation of a mist-free zone around the wire, which appears to be the conduction zone which has previously been postulated. The size of this zone increases with rising wire temperature. The periodic pressure change synchronises with visible periodic turbulence in the convection currents revealed by the mist.

S. K. TWEEDY.

Intermolecular forces in liquids. J. H. HILDEBRAND (Physical Rev., 1929, [ii], 34, 984—993).—An expression is deduced for the volume energy of liquids, in terms of attractive and repulsive forces, and is tested by the use of thermodynamic data, and energy of vaporisation for a number of liquids. Using the values found for the constants of the expression, the energy-volume coefficient for ether is calculated and plotted as a function of the volume.

N. M. BLIGH.

Azeotropism in binary systems containing hydroxyl compounds. M. LECAT (Atti R. Accad.

Lincei, 1929, [vi], 9, 1121—1128).—A discussion of the nature of the azeotropism in systems in which one component is an alcohol, a phenol, or an acid, and the other a hydrocarbon, halogen derivative, ester, amine, ketone, nitro-compound, or oxide.

F. G. TRYHORN.

Molecular orientation and the partial vapour pressures of binary mixtures. I. Systems composed of normal liquids. II. Systems containing an alcohol. C. P. SMYTH and E. W. ENGEL (J. Amer. Chem. Soc., 1929, 51, 2646—2660, 2660—2670).—I. The vapour pressures below 100° of hexane, ethyl iodide, butyl chloride and bromide, heptane, carbon tetrachloride, and ethyl alcohol and of binary mixtures of some of these with one another and with ethyl bromide were investigated by Same-shima's dynamic method (A., 1918, ii, 429). The data indicate that Langmuir's theory of molecular surface energies is approximately applicable, deviation from the theoretical behaviour being attributed to the presence of electric doublets in the molecules.

II. Binary systems containing either butyl or ethyl alcohol were investigated. Deviation from Raoult's law is very considerable. The results do not conform to Langmuir's theory. The orientation of the alcohol molecules relative to one another appears to be more important in determining the behaviour of the system than their orientation relative to the molecules of the other component or the orientation of the molecules of the other component relative to one another. The deviations from Langmuir's theory are qualitatively explained in terms of the forces acting between the molecular dipoles.

S. K. TWEEDY.

Methods of determining heats of vaporisation of liquid mixtures. V. KIREJEV (Z. Physik, 1929, 57, 403—410).—The heat of vaporisation of liquid mixtures may be derived from the heats of vaporisation of the pure components and the heat of dissolution, and also from the corresponding vapour-pressure data for the mixture. The theories of these methods as well as the definitions of the quantities used have been treated differently by different observers, leading to contradictory results. The results obtained by both the indirect methods are compared with the direct experimental results. The values derived from vapour-pressure data show large deviations. The magnitude of the heat of vaporisation of single components of a mixture may be very different from that of the components in the pure state.

A. J. MEE.

Vaporisation of binary mixtures. I. Method of determining heats of vaporisation of pure liquids and solutions. M. S. VREVSKI (Z. physikal. Chem., 1929, 144, 244—252).—A new method for determining heats of vaporisation at constant temperature has been worked out and applied to water and a solution of sulphuric acid. A knowledge of this constant is essential to the understanding of dissolution processes from an energetic point of view.

F. L. USHER.

Viscosity and m. p. of the system ethylenediamine-water. M. S. ELGORT (J. Russ. Phys. Chem. Soc., 1929, 61, 947—959).—A study of the viscosity

isotherms and m. p. of the above system shows the existence of *ethylenediamine dihydrate*, m. p. -10° . The eutectic point is -53° at 83.2 mol.-% H_2O .

R. TRUSZKOWSKI.

M. p. of mixtures of cyclohexane and benzene. I. SETO (Bull. Centr. Res. Inst. S. Manchuria Rly. Co., 1928, 13, 123—125).—Maximal expansion was observed at 55.56% of cyclohexane. The m.-p. curve shows the existence at -41.9° of a eutectic containing 74.44% of cyclohexane. CHEMICAL ABSTRACTS.

Refraction of alcohol-water mixtures. N. SCHOORL (Pharm. Weekblad, 1929, 66, 905—920).—The data recorded in the literature for the refractive indices of absolute alcohol and of alcohol-water mixtures are found to be unsatisfactory for the analysis of mixtures. Tables are given of data obtained with the Eykman and Pulfrich-*Zeiss* refractometers. For analytical purposes the mixture should contain about 30 wt.-% of alcohol, as in this region the refractive index alters most rapidly with the composition.

S. I. LEVY.

X-Ray investigation of palladium-silver-hydrogen alloy. I. Å. OSAWA (J. Study Met., 1928, 5, 443—454).—Palladium and silver both have a face-centred cubic lattice with lattice constant 4.069 and 3.86—3.874 Å., respectively, and form a solid solution for all ranges of composition. Saturation of palladium with hydrogen increases the lattice constant by 3.6—3.87%. Palladium-silver alloys absorb hydrogen well. The expansion coefficient increases from an alloy containing 30% Pd to a maximum at 100% Pd. CHEMICAL ABSTRACTS.

Elastic constants, lattice constants, and densities of metallic solid solutions. Z. NISHIYAMA (J. Study Met., 1929, 6, 17—41).—Binary solid solutions of nickel, silicon, aluminium, cobalt, vanadium, tungsten, chromium, and manganese with iron; of aluminium, tin, zinc, manganese, and nickel with copper; of iron and copper with nickel; and of zinc and manganese with aluminium were studied.

CHEMICAL ABSTRACTS.

Special properties of eutectic and eutectoid alloys in binary metallic systems. P. J. SALDAU (J. Russ. Phys. Chem. Soc., 1929, 61, 837—882).—Reheated eutectic alloys of the pairs tin-zinc, tin-antimony, tin-zinc, gold-zinc, and gold-cadmium, as well as reheated eutectoid carbon steel, show greater hardness and a smaller electrical conductivity and temperature coefficient than alloys of different composition. It follows that the physical and mechanical constants of reheated eutectic alloys do not lie on the curves obtained for mechanical mixtures which would be obtained by the fusion together of the given components of a system. Eutectic and eutectoid alloys show either a maximum or a minimum value. This relation persists at all temperatures below the m. p. in the case of eutectic alloys or below the transition point in the case of eutectoid alloys, and is restored on cooling should the alloys have been heated above these temperatures. The presence in excess of one of the eutectic phases is essential for the process of coalescence in reheated eutectic alloys.

R. TRUSZKOWSKI.

Systems formed by certain tetrahalides. P. A. BOND and W. R. STEPHENS (J. Amer. Chem. Soc., 1929, **51**, 2910—2922).—The miscibility of the tetrachlorides of titanium and of silicon with liquid sulphur dioxide has been examined. The results accord with theory as regards polarity etc. The solubility of zirconium tetrachloride in liquid sulphur dioxide between 0° and 20° was determined by a method specially adapted for measuring solubility in highly volatile solvents; the results agree with the principles governing solubility where there is a large difference of polarity. The compound $\text{ZrCl}_4 \cdot \text{SO}_2$ was isolated in the form of colourless plates, stable at and below 0°.

S. K. TWEEDY.

Solubility of ethylene glycol. H. M. TRIMBLE and G. E. FRAZER (Ind. Eng. Chem., 1929, **21**, 1063—1065).—Ternary systems of ethylene glycol and acetone with xylene (25°), toluene (27°), chlorobenzene (23°), bromobenzene (25°), nitrobenzene (22°), and benzene (27°), and of glycol and alcohol with xylene (26°), toluene (25°), benzene (25°), and nitrobenzene (29°), have been investigated at the temperatures indicated. In each case a single binodal curve is obtained. Tie-lines are shown for all the systems containing acetone.

C. W. GIBBY.

Solubility of ether in concentrated solutions of mineral acids. C. MARIE and G. LEJEUNE (Monatsh., 1929, **53** and **54**, 69—72).—The solubility curves for ether in various concentrations (2—11*M*) of perchloric, hydrochloric, sulphuric, and phosphoric acids have been determined at 18° and 25°. The solubility is greatest in perchloric acid; a maximum is shown at 6.5—7*M*. In general, an increase in the concentration of the acid of 1 mol. per litre (at the concentrations where solubility is of a measurable order) causes an increase of the solubility of ether by 20, 1.8, 2.25, and 7.5 mols., respectively, for the above order.

H. BURTON.

Limit of solubility of copper in reversible ferro-nickels. P. CHEVENARD (Compt. rend., 1929, **189**, 576—578).—Dilatometric observations show that ternary austenite is formed in the presence of small amounts of copper. A second constituent rich in copper appears in the austenite when the proportion of copper is increased, but this disappears on tempering. The logarithmic contraction-time curve (cf. A., 1923, ii, 166) associated with the precipitation of Mg_2Si from hyper-tempered aluminium-magnesium-silicon alloys (isothermal recovery) has been confirmed.

J. GRANT.

Solubility of nitric oxide in carbon tetrachloride, benzene, and nitrobenzene. A. KLEMENC and E. SPITZER-NEUMANN (Monatsh., 1929, **53** and **54**, 413—419).—Determination of the Ostwald solubility coefficients for nitric oxide in benzene and carbon tetrachloride at 8.8—34.6° shows that these rise with the temperature for each solvent. With nitrobenzene at 20—90° the coefficient is the same at all temperatures. The free energy of the dissolution process decreases with rising temperature. Nitric oxide dissolves in benzene and carbon tetrachloride with a small negative heat of dissolution.

H. BURTON.

Solubility of sodium thiocyanate in water and in organic solvents. O. L. HUGHES and T. H. MEAD (J.C.S., 1929, 2282—2284).—The solubility of sodium thiocyanate in water has been measured between 10.7° and 101.4°; a hydrate $\text{NaCNS} \cdot \text{H}_2\text{O}$ is formed below 30.4°. The solubilities have also been determined in methyl alcohol from 15.8° to 52.3°, in ethyl alcohol from 18.8° to 70.9°, and in acetone from 18.8° to 56° (compound $\text{NaCNS} \cdot \text{COMe}_2$).

C. W. GIBBY.

Solubility of sodium ferrocyanide in water between 0° and 104°. J. A. N. FRIEND, J. E. TOWNLEY, and R. H. VALLANCE (J.C.S., 1929, 2326—2330).—The solubility of sodium ferrocyanide in water has been determined by a gravimetric method. Above 65° the results diverge from those of previous workers (cf. Conroy, A., 1899, i, 2; Farrow, A., 1926, 236).

C. W. GIBBY.

Hydrates of lithium sulphate and their solubility in water between —16° and 103°. J. A. N. FRIEND (J.C.S., 1929, 2330—2333).—The solubility of lithium sulphate in water has been determined between —16° and 103°. A break in the curve was found at —8°. A dihydrate is possibly formed at lower temperatures.

C. W. GIBBY.

Solubility of benzidine sulphate and benzidine hydrochloride in hydrochloric acid solutions. W. B. MELDRUM and I. G. NEWLIN (Ind. Eng. Chem. [Anal.], 1929, **1**, 231).—The solubility of benzidine sulphate in hydrochloric acid at 25° increases rapidly with the acidity, and attains a maximum of about 1.93 g. per litre in 3.5*N*-acid, thereafter decreasing slowly. The solubility of benzidine hydrochloride under similar conditions decreases rapidly from 5.34 g. per litre in pure water to 1.24 g. per litre in 5.6*N*-acid, remaining constant at this value for higher concentrations of acid up to 10*N*.

H. F. HARWOOD.

Connexion between velocity of dissolution and solubility. General equation for solubility. I. W. JACEK (Rocz. Chem., 1929, **9**, 472—492).—If k is the thickness of the layer of saturated solution which would be obtained by the concentration of the dilute solution formed in unit time by the immersion of the solute, the surface of which is taken as constant, and ρ' the thickness of the layer of solute dissolved in unit time by the pure solvent, then $\rho'\delta/k\Delta = C'$, where δ is the density of the solute, Δ that of the saturated solution, and C' the solubility expressed per unit weight of saturated solution. A further expression, $s = \rho'\delta/\xi\delta'$, is derived, in which s is the solubility per unit weight of solvent, δ' the density of the solvent, and ξ is the thickness of the layer of pure solvent corresponding with ρ' . The value of ρ' is determined for sylvine, sodium chloride, alabaster, potassium sulphate and dichromate, alum, tartaric acid, and sucrose, for temperatures between 0° and 50°. The relation between ρ' and temperature, T , is given by $\rho'\delta = e^{-A_1/T+B_1}$, where the constant B_1 depends on the rate of stirring. A general equation for the solubility is given by $s = e^{-A_1/T+B_1}$ (9a). The terms $(A_1 - A_2)$, $(B_1 - B_2)$, $(C_1 - C_2)$, and $(G_1 - G_2)$ depend on the heat of dissolution of the given solute and on the nature of both components of the solution,

and may have positive, negative, or zero values, and the differences observed between the solubility curves of various substances are due to the differential nature of these terms.

R. TRUSZKOWSKI.

Adsorption of air and water vapour on rock-salt surfaces. J. H. FRAZER (Physical Rev., 1929, [ii], 34, 644—648).—By a method previously used (cf. this vol., 503) the adsorption of air on rock-salt surfaces has been measured at various temperatures, and the temperature at which complete outgassing occurs determined. The thickness and approximate speed of formation of the film are estimated. Exposure to water vapour has no permanent effect on the surface so long as the partial pressure of the water vapour is less than that of the saturated solution at the same temperature. This is true only of cleavage surfaces; polished surfaces are less stable against the action of water vapour.

N. M. BLIGH.

Sorption of vapours from circulating gas by solid absorbents and the adaptation of activated charcoal and silica gel to the determination of small quantities of vapours in exhaled breath. W. PONNDORF and H. W. KNIPPING (Beitr. Klin. Tuberk., 1928, 68, 751—806; Chem. Zentr., 1929, i, 2904).—The principle of the process is discussed, and curves illustrate the effect of the form of the absorbent layer, the temperature, and the pressure. Silica gel is preferable for the absorption of water and active charcoal for that of acetone and other organic substances. Acetone can be quantitatively absorbed from large volumes of moist air.

A. A. ELDRIDGE.

Temperature coefficient of the saturation maximum in gaseous adsorption. F. J. WILKINS and A. F. H. WARD (Z. physikal. Chem., 1929, 144, 259—268).—Theoretical. The temperature variation of the value of the saturation maximum expected from Langmuir's and other theories is discussed. The basis of the alteration is to be sought, not in a change of the adsorbing surface, as Zeise supposes, but rather in the adsorbed gas layer. From the conception of lateral diffusion of the adsorbed unimolecular gas layer, the saturation pressure is found to be independent of the temperature, whilst the temperature coefficient of the adsorption maximum is equal to the coefficient of expansion of a gas at constant pressure. This conclusion is supported by the available experimental data.

F. L. USHER.

Linear adsorption. R. S. BRADLEY (Phil. Mag., 1929, [vii], 8, 202—204).—The thermodynamic surface activity is given by the expression $RT \log a_s = F' - F'_0 - RT \log F + BF$, where a_s is the surface activity, B is a constant and the standard state for F' , the free energy per g.-mol. in the surface being defined by the limits $F' \rightarrow F'_0$ when $A \rightarrow B/A \rightarrow 1$, $A \rightarrow RT/F$, and $a_s \rightarrow F$, where A is the area per g.-mol. Applying this to a two-dimensional gas the Langmuir isotherm becomes constant/ $p = 1/s$ —constant, where p is the pressure and s is the surface concentration, the substance distributing itself between the two regions according to the distribution law $p/[s/(1-SB)] = \text{constant}$, $S/(1-SB)$ being the effective surface concentration. Similar application to adsorption at a line gives $RT \log a_l - RT \log$

$RTL' + RTB^2L'$, where a_l is the linear activity and L' is the effective linear concentration $= L/(1-LB^2)$, where L is the linear concentration. The approximate distribution law between a line and a surface then becomes $L'/S' - \text{constant} = e^{\Delta F_0/RT}$, where $S' = S/(1-SB)$ and ΔF_0 is the free energy increase for the change line \rightarrow surface in the standard states.

A. E. MITCHELL.

Heat of adsorption of gases by solids. K. F. HERZFELD (J. Amer. Chem. Soc., 1929, 51, 2608—2621).—Theoretical. On the assumption that the adsorbing forces are purely of electrical nature, the adsorption of a gas without permanent dipoles on the surface of a heteropolar salt is investigated mathematically and it is shown that the positive or negative increase in the heat of adsorption with the amount adsorbed can be explained by the interaction of the dipoles set up in neighbouring molecules by the adsorbing forces. The association of a large free energy change during adsorption with a small total energy change is best explained (but not with complete satisfaction) by assuming that the adsorbed molecules cohere together into groups. The extent of the difference between the amounts of two gases (having the same heat of adsorption) adsorbed on the same adsorbent under the same external pressure is discussed briefly.

S. K. TWEEDY.

Mixed adsorbents. N. SCHILOV, M. DUBININ, and S. TOPOROV (Kolloid-Z., 1929, 49, 120—126).—A method for the preparation of an intimate mixture of silica and wood charcoal for adsorption purposes is described. This mixed adsorbent is more active than wood charcoal alone in the adsorption of ammonia, chlorine, steam, and benzene vapour and in the adsorption of iodine from solution in water, alcohol, or benzene. The maximum activity is attained when the adsorbent contains 60—70% of carbon. Although silica gel adsorbs iodine negatively, it increases the adsorption by carbon. Coarse mixtures of silica and wood charcoal have less adsorbent capacity than wood charcoal alone.

E. S. HEDGES.

Adsorption velocity of water and benzene vapours. H. ISOBE and S. MORI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 801—804).—Activated charcoal adsorbs more benzene than water from air saturated with both substances, whereas for acidic clay the reverse is true; with both adsorbents the adsorption of benzene is more rapid than that of water. Density measurements indicate that activated charcoal possesses a greater surface than non-activated charcoal.

H. F. GILLBE.

Adsorption and gas-friction. C. DRUCKER (Z. Elektrochem., 1929, 35, 640—644).—Expressions are obtained by which the coefficient of friction of mixtures of gases, e.g., helium and hydrogen, carbon dioxide and hydrogen, hydrogen chloride and hydrogen, can be calculated with fair accuracy. With the help of these formulæ, it is possible to determine the adsorption of the gases by the glass walls of the containing vessel.

H. T. S. BRITTON.

Process of adsorption. H. KALBERER, H. MARK, and C. SCHUSTER (Z. Elektrochem., 1929, 35, 600—602).—The adsorbing surfaces of silica gel and

aluminium oxide have been calculated from an expression involving the heat of adsorption, the thickness of the adsorbed layer, and the volume occupied by the adsorbed gas. The different values obtained for the surface of an adsorbent when different gases are used is attributed to differences in the adsorption potential which the active places in the surface have for the particular gases (see Kalberer and Schuster, this vol., 757). The dependence of the volume of adsorbed gas on the temperature is also discussed. H. T. S. BRITTON.

Adsorption of complex platinum compounds by carbon. I. I. SHUKOV and O. P. SCHIPULINA (Kolloid-Z., 1929, 49, 126—133).—The adsorption of a number of complex platinum compounds by wood charcoal has been studied. The compounds were decomposed on adsorption and the adsorbability depends on the electronic configuration of the compound, no relation being found between adsorbability and solubility. The adsorbability is influenced by isomerism only so long as a change in electrical configuration is involved. Of the compounds examined, the non-electrolytes were adsorbed more strongly than the electrolytes. Optically active complex platinum compounds cannot be resolved into their isomerides by adsorption on charcoal.

E. S. HEDGES.

Precipitation and adsorption of small quantities of substances. III. The adsorption law, applications, results, and conclusions. O. HAHN and L. IMRE (Z. physikal. Chem., 1929, 144, 161—186; cf. A., 1926, 1092).—The authors distinguish between the co-precipitation of small amounts of a substance with a bulky precipitate and the adsorption of the substance by the precipitate, and the two laws previously put forward are restated and confirmed by new data. In the present work the adsorption of hydrolysing and non-hydrolysing cations by two types of lattice, polar and non-polar, is considered. The polar lattices studied were those of the silver halides, the non-polar those of the mercurous halides. The adsorbed substances were the short-lived radio-elements thorium-B, thorium-C, and polonium (hydrolysing ions), radium and thorium-C' (non-hydrolysing), chosen for convenience in detecting small amounts, but the results are generally applicable. The difference between the behaviour of non-hydrolysing and hydrolysing cations is striking, inasmuch as the latter show "colloid adsorption," and an excess of the precipitating anion is not necessary for considerable adsorption to occur. Appreciable adsorption occurs only under special conditions on non-polar precipitates such as the mercurous halides, since they lose their charge much more readily than the analogous silver compounds, but under these conditions Hahn's adsorption law is followed. The results of ionic and colloid adsorption on polar and non-polar lattices are summarised. The earlier results of Fajans are in agreement with the authors' views on adsorption processes. A possible extension of the adsorption law to readily soluble but weakly dissociating compounds is indicated. F. L. USHER.

Influence of adsorbed ions on the absorption spectrum of metal halides. K. FAJANS and

G. KARAGUNIS (Z. physikal. Chem., 1929, B, 5, 385—405).—Measurements with silver iodide analogous to those previously conducted with silver bromide (this vol., 625) show that adsorbed silver ions produce up to 40% increase in the intensity of the band with its maximum at 4200 Å., without, however, influencing the position of the maximum. Adsorbed iodine ions produce a decrease of absorption on the long wavelength side of the maximum. These results are in accordance with the colour variations exhibited by the iodide when precipitated in presence of an excess of iodide or of silver ion. Mercuric iodide emulsions show a general decrease of absorption when treated with a solution of a mercuric salt or of a soluble iodide on account of the formation of non-absorbing complex ions. The energy quantum of the primary process of the photochemical decomposition of silver iodide is not altered by the presence of adsorbed silver ions, but the number of elementary processes is increased.

H. F. GILLBE.

Lyosorption. WO. OSTWALD and W. HALLER (Kolloidchem. Beih., 1929, 29, 354—395).—When powders are shaken with liquids in which they are insoluble and are then allowed to settle, the volume of the sediment varies with different liquids. A technique for the examination of this phenomenon is developed, the essential conditions being constant temperature and a long duration of experiment. The sedimentation volumes of powdered talc, fuller's earth, alumina, silica, magnesium oxide, calcium carbonate, ferric oxide, graphite, and norit stand in the same order for all the liquids tested, being greatest for carbon tetrachloride and decreasing in the order hexane, benzene, chloroform, ether, acetic acid, alcohol, acetone. Some irregularities can be traced to chemical reaction or some other secondary influence. The variation in sediment volume is caused by the binding of a layer of liquid by the surface of the powder. The volume can be reduced by mechanical pressure or by centrifuging, and is smaller at higher temperatures. By centrifuging the sediment a constant final volume is attained, which, although smaller than the sedimentation volume, varies in the same order throughout the series of liquids. Lyosorption produces an increase in viscosity of the suspension, which is dependent on the velocity of flow, the viscosity falling with increasing velocity. The influence of moisture and of heating the powder has been examined and the result varies with the different systems; graphite and norit give smaller sedimentation volumes after heating, but talcum gives the same volume after heating at 350°. In an investigation of the relation between lyosorption and chemical constitution of the liquid, experiments have been carried out with two powders and about 50 different organic liquids and a relation between lyosorption and the dielectric properties of the liquid has been established. Lyosorption values and the dielectric constants of the liquids vary antipathetically and it is inferred that the force involved in lyosorption is of electronic nature.

E. S. HEDGES.

Activation process at boundary surfaces. M. POLANYI (Z. Elektrochem., 1929, 35, 561—567).—Theoretical. H. T. S. BRITTON.

Ring method for determining surface tension.

A. H. NIETZ and R. H. LAMBERT (J. Physical Chem., 1929, **33**, 1460—1467).—The influence of the thickness and diameter of the ring and of the contact angle on determinations of surface tension has been investigated. The pull on the ring for a given diameter is a linear function of the size of the wire, and *vice versa*. The classification of the ring method as one independent of the angle of contact is erroneous, since it has been shown that the pull on the ring is related to the angle of contact between the material of the ring and the liquid. The relationship $F = 2lT(1 + \cos \theta)^{1/2}$, where F is the force in dynes required to remove the ring, l is the average perimeter of the ring, and θ is the angle of contact, holds over a limited range of size of wire. L. S. THEOBALD.

Calculation of surface tension from drop weight. T. IREDALE (Z. physikal. Chem., 1929, **144**, 158—159).—Comments on a paper by Palitzsch (this vol., 257). F. L. USHER.

Unimolecular films of cyclic ketones. E. H. BÜCHNER, J. R. KATZ, and P. J. P. SAMWEL (Z. physikal. Chem., 1929, **B**, 5, 327—332).—Unimolecular films on water of a number of cyclic ketones have been prepared and their thicknesses per molecule determined. The results indicate that the molecules of these substances are formed of two parallel carbon chains, in accordance with the view of Ruzicka (cf. A., 1928, 642, and earlier abstracts).

H. F. GILLBE.

Structural changes produced in colloidal films by stretching. J. TRILLAT (J. Phys. Radium, 1929, [vi], **10**, 370—384).—The structural changes produced when films of cellulose nitrate and acetate are stretched have been followed by means of X-ray diffraction photographs taken in three directions: along the axis of stretching and also the two axes perpendicular to this. When the extension of the film is slight normal circular diffraction haloes are obtained which are more or less intense in certain directions. As the extension is increased the film becomes anisotropic, for the haloes obtained from two of the three directions studied possess a marked increase in intensity at the equator. The long molecules constituting the film appear therefore to arrange themselves in a direction parallel to the axis of stretching. At very great extensions the haloes are deformed into ellipses. A comparison of these diffraction patterns with those given by the substances in the crystalline state indicates that in these highly stretched films incipient crystallisation is taking place. A nematic phase is therefore transformed by stretching into a pseudocrystalline phase. These results are applied to the consideration of the properties of "cold-worked" films. F. J. WILKINS.

Electrical conductivity caused by insoluble unimolecular films of fatty acid on water. J. W. MCBAIN and C. R. PEAKER (Proc. Roy. Soc., 1929, **A**, **125**, 394—401).—The possibility of the dissociation of unimolecular films of insoluble fatty acids on water with formation of free hydrogen ions in the latter is investigated. A special form of conductivity cell is described which enables measurements to be made of (a) the conductivity of the

water alone, (b) that of the water after introduction of the fatty acid but with the surface far removed from the electrodes, (c) that of the water when the surface is brought to the level of the tops of the electrodes, and (d) that of the water with the surface in the same position after the introduction of the fatty acid. A modified form of the conductivity bridge described by Jones and Josephs (A., 1928, 595) is employed. The specific surface conductivity (*i.e.*, the conductivity in reciprocal ohms between two parallel electrodes 1 cm. long placed 1 cm. apart on the surface) at 25° in the region of the unimolecular film of stearic acid is 3.5×10^{-8} mho. This corresponds with a dissociation of about one ninth of the total stearic acid in the unimolecular layer on water of conductivity 1.2×10^{-6} mho. The surface conductivity is ascribed to the presence of independent mobile hydrogen ions dissociated from the fatty film, which is thus left with an equal and opposite electric charge. This conception lends support to the view that the Helmholtz double layer is not responsible for the electrokinetic phenomena, and that the classical formulæ are not strictly applicable owing to the existence of unbalanced charges on the interface. L. L. BIRCHUMSHAW.

Stability of sub-microns. Dissolution of crystals and their formation. J. TRAUBE (Z. Elektrochem., 1929, **35**, 626—627).—The dissolution of crystalline substances begins at definite points on their surfaces, leading thereby to pearl-like cellular structures, which subsequently collapse to form sub-microns, and finally dissolve. The rate of dissolution can be decreased in the presence of gelatin. The reverse order has been observed in the building-up of crystals from sub-microns. A cinematograph was used in the experimental part of the work.

H. T. S. BRITTON.

Insoluble sulphates and passivity. L. McCULLOCH (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 4 pp.).—Attention is directed to the difficulty with which anhydrous chromic, ferric, and nickel sulphates dissolve in dilute sulphuric acid and it is suggested that passivity may be due to films of these anhydrous salts. H. J. T. ELLINGHAM.

Periodic precipitations with diffusion. H. RYAN and R. J. DOYLE (Nature, 1929, **124**, 762).—The authors' objection to Ostwald's theory (this vol., 1144) is invalid. A. A. ELDRIDGE.

Velocity of transference of water through a semi-permeable wall by osmotic pressure. S. RAY (Z. anorg. Chem., 1929, **182**, 351—352).—An expression for the rate of osmotic flow of solute through a semi-permeable membrane is derived.

H. F. GILLBE.

Penetration of electrolytes. W. J. V. OSTERHOUT (Proc. Soc. Exp. Biol. Med., 1928, **26**, 192—197).—For a time-curve of penetration (of living cells by weak electrolytes) of the first order, the high electrical resistance of the protoplasm in *Nitella* and *Valonia* suggests that when a binary electrolyte is largely ionised there is very little penetration. If the external concentration remains constant while the p_H value changes so as to decrease the concentration of undissociated molecules, the rate of penetration

will diminish even when the protoplasm is permeable to ion pairs only. Strong electrolytes may enter largely as undissociated molecules formed at the surface by collision of ions. **CHEMICAL ABSTRACTS.**

Electro-stenolysis and electrolytic membrane processes. K. SOLLNER (Z. Elektrochem., 1929, 35, 789—799).—The effects produced when currents are passed through certain porous membranes and precipitates, on each side of which are solutions of salts of heavy metals, may be divided into two classes, viz., (1) membranes to which only small *P.D.* may be applied (2—3 volts), resulting in the deposition within the membrane of a precipitate containing the metal, e.g., the oxide, (2) membranes to which a *P.D.* of at least 20 volts must be applied to effect the precipitation of the metal itself within the pores of the membranes ("electro-stenolysis"). Hypotheses to account for these effects are advanced. **H. T. S. BRITTON.**

Unequal distribution of ions in a collodion cell. J. H. NORTHROP (J. Gen. Physiol., 1929, 13, 21—25).—A "dry" collodion membrane containing sodium thiosulphate solution immersed in a solution of iodine in potassium iodide gradually becomes richer in iodine ions until all the free iodine outside has been converted into iodide ions within the cell. As the membrane, although permeable to iodine, is impermeable to iodide ions, comparatively high concentrations of iodide ions inside the membrane may be attained. With a membrane containing sodium chromate immersed in a solution of mercuric chloride and sodium sulphate, the mercury is gradually precipitated as mercuric chromate. In this case the membrane is permeable to mercuric chloride, but not to sodium or other chlorides. Acetate ions are concentrated in a cell originally containing a suspension of calcium carbonate and immersed in acetic acid. These experiments show that artificial systems may be made which resemble living cells.

W. O. KERMACK.

Preparation of colloidal gold solutions by the use of alkaloids. M. O. CHARMANDARJAN (Kolloid-Z., 1929, 49, 133—135).—Colloidal solutions of gold are obtained when small quantities of brucine or nicotine are added to a boiling dilute solution of chloroauric acid acidified with hydrochloric acid. Brucine gives a yellowish-orange sol and nicotine a blue sol. **E. S. HEDGES.**

Viscosity of hydrophilic colloids. H. FICKENTSCHER and H. MARK (Kolloid-Z., 1929, 49, 135—148).—The relation between mol. wt. of colloids and viscosity is discussed and leads to the rule that at constant temperature and in solutions of polymeric homologous series of the same viscosity the square of the mol. wt. varies inversely as the concentration. In Einstein's modified equation, $z = 1 + a \cdot cb / (100 - cb)$, where *b* is the volume in which 1 g. of substance is dispersed, it is shown that \sqrt{b} is proportional to the mol. wt. The values calculated by the two methods show good agreement and are independent of temperature. **E. S. HEDGES.**

Nephelometric study of colloidal solutions of metallic sulphides. M. WATANABE and C.

NAKAU (J. Petrol. Min. Ore Dep., 1929, 1, 61—64).—When dilute solutions of metallic salts are precipitated with an excess of sodium sulphide in dilute solution the colloidal sulphide does not easily coagulate. A study of the relation between the coagulation time and the relative concentrations shows that at an initial period the turbidity increases, is then constant for a time, and on coagulation decreases suddenly.

CHEMICAL ABSTRACTS.

Scattering of light in colloidal solutions and gels. K. KRISHNAMURTI (Nature, 1929, 124, 690—691).—In the ageing of silicic acid sols formed by the hydrolysis of methyl silicate the primary particles form larger aggregates after some time, the rate of formation being determined by an increase in the number of effective collisions between the particles and a decrease in the number of the original particles. An explanation of similar results obtained with gelatin sols is offered. With sodium oleate solutions supersaturation with formation of colloidal particles is observed on cooling. **A. A. ELDRIDGE.**

Electrolytic dissociation of colloidal solutions. I. K. TAKATA (Hokkaido J. Med., 1928, 6, 577—586).—In 0.00001—0.001*N*-hydrochloric acid or sodium hydroxide solution containing mastic sol there is a discrepancy between the calculated and experimental *p_H* values which shows that hydrogen or hydroxyl ions are combined with the mastic. The electrical conductivity decreases with addition of mastic. **CHEMICAL ABSTRACTS.**

Organophilic colloids. G. S. WHITBY, J. G. McNALLY, and W. GALLAY (Coll. Symp. Mon., 1928, 6, 225—236).—The smaller the amount of solvent bound in a sol, the smaller is the quantity of precipitant needed to produce separation. Various properties are considered. **CHEMICAL ABSTRACTS.**

Influence of electrolytes and non-electrolytes on optical activity and relative resistance to shear of gelatin systems. J. R. FANSELOW (Coll. Symp. Mon., 1928, 6, 237—252).—The behaviour of gelatin systems can be better explained by the laws for highly dispersed heterogeneous systems than by the classical laws of stoichiometry.

CHEMICAL ABSTRACTS.

Emulsions. II. System xylene-phenol-sodium oleate-water. J. WEICHERZ (Kolloid-Z., 1929, 49, 158—173; cf. this vol., 260).—A study has been made of the phase relations between water and a mixture consisting of 79.94% of xylene, 12.91% of phenol, and 7.15% of sodium oleate. With increasing amounts of water, the initial homogeneous phase is followed by a heterogeneous region of water-in-oil emulsions, then by a second homogeneous region, and finally by a heterogeneous region of oil-in-water emulsions. Rise of temperature displaces all the regional limits in the direction of smaller quantities of water: the first homogeneous region and the region of water-in-oil emulsions become narrower, whilst the second homogeneous region and the region of oil-in-water emulsions become more extensive. The transformation of the system sodium oleate dispersion in xylene-phenol into the system sodium oleate dispersion in water occurs at a lower water content the higher the temperature. Measurements were made of

the viscosity of the system xylene-phenol-sodium oleate-water at different temperatures. With increasing water content, the viscosity rises to a maximum, then falls, and again rises. E. S. HEDGES.

Rôle of dielectric constants, polarisation, and dipole moment in colloid systems. VII. Swelling of cellulose acetate in binary mixtures. III. I. SAKURADA (Kolloid-Z., 1929, 49, 178-184; cf. this vol., 1234).—Experiments have been conducted on the swelling of cellulose acetate in binary liquid mixtures where both the components are polar. No simple relation between swelling and polarisation, such as is observed where only one component is polar, could be recognised. The curves are greatly influenced by the presence of small amounts of additional polar substances. Data are listed in an attempt to show the relations between swelling, molecular polarisation, vapour pressure, and viscosity of solutions of cellulose acetate in binary liquid mixtures where one or both of the components are polar. E. S. HEDGES.

Wo. Ostwald's solid-phase rule and the solubility of casein in sodium hydroxide. A. VON BUZAGH (Kolloid-Z., 1929, 49, 185-188).—An explanation is given of the different results obtained by Sorensen and Sládek (this vol., 1230) and by von Buzagh (A., 1927, 310) on the solubility of casein in solutions of sodium hydroxide. E. S. HEDGES.

Solid-phase rule in the production of protein sols. Wo. OSTWALD (Kolloid-Z., 1929, 49, 188-209).—The essential differences in the solubility relations of colloids and molecularly dispersed substances are defined. The dependence of the solubility of molecularly dispersed tartaric acid in sodium hydroxide solutions on the amount of the solid phase (Sorensen and Sládek, this vol., 1230) is shown to bear no analogy with the solid-phase rule recognised in colloid systems. The maximum of solubility in this system is caused by the formation and precipitation of a new solid phase consisting of an acid tartrate. The solubility of globulin in solutions of neutral salts is discussed from the same point of view. Numerous other arguments are advanced against Sorensen's views on the molecular relations of protein sols. E. S. HEDGES.

Theory of colloid osmosis. W. HALLER (Kolloid-Z., 1929, 49, 74-83).—The osmotic pressure of colloidal solutions does not conform to the law $P=cRT$. Secondary influences causing deviation are discussed, but it is also shown on theoretical grounds that molecular-kinetic processes must lead to deviations from van 't Hoff's equation, which only represents a special case. Whilst in the case of the osmotic pressure of molecular solutions only a translatory motion of the molecule is concerned, in the treatment of colloids it is necessary also to consider movements of oscillation and rotation. The following equation for total osmotic pressure is developed: $P=c'RT+c'^2RT(0.46N_A v \phi)$, where c' is the concentration in g.-mol. per litre, v is the number of degrees of freedom of oscillation of a micelle, and ϕ is the amplitude. E. S. HEDGES.

Action of sodium hydroxide on stannic acid sol. I, II. B. N. GHOSH (J.C.S., 1929, 2290—

2297, 2298-2304).—I. Measurements have been made on the membrane equilibria and osmotic pressures of stannic hydroxide sols containing sodium hydroxide. In mixtures in which the ratio $\text{SnO}_2:\text{Na}_2\text{O}$ varied from 17.2 to 0.5 the amount of diffusible stannic oxide never exceeded 19%. The membrane potential calculated on the assumption that all the diffusible ions are univalent agrees with the observed value. The dissociation of the colloidal complex of the two oxides is small.

II. Measurements have been made of the hydroxyl-ion concentration, f.p. lowering, and conductivity of five sols in which the ratio $\text{Na}_2\text{O}:\text{SnO}_2$ varied from 2 to 0.25. At higher values of the ratio the greater part of the added alkali is uncombined, but this fraction diminishes as the ratio becomes smaller. The f.p. depressions are due mainly to the free sodium hydroxide, and diminish as the ratio $\text{Na}_2\text{O}:\text{SnO}_2$ diminishes. The degree of dissociation of the colloid diminishes rapidly as the proportion of stannic oxide increases. Conductivity measurements indicate that the greater part of the conductivity is due to the free sodium hydroxide. C. W. GIBBY.

Acidity-dilution and neutralisation curves for a sol of arsenious sulphide and a suspension of gamboge. A. BOUTARIC and (Mlle.) G. PERREAU (Bull. Soc. chim., 1929 [iv], 45, 701-706).—In the determination of the acidity-dilution curves a sol containing 18.6 g. of arsenious sulphide per litre was diluted with water up to 32 vols., and a suspension of 6.124 g. of gamboge up to 4 vols. For neutralisation the sol contained 1.55 g. per litre, the suspension 1.225; in both cases equal volumes of a solution of potassium hydroxide of normality varying from 2 to 200×10^{-4} for the sol, and from 1 to 100×10^{-4} for the suspension were added. The p_H was determined with a quinhydrone electrode—for the sol immediately, and after 3 days, for the suspension after 3 days only. The intermicellary liquid of the sol, obtained by filtration through collodion, was similarly examined; the dilution curve was quite similar, but that of neutralisation indicated that the presence of the granules increased the buffer effect in the mixture of sol and base. In both cases the behaviour is that of a weak acid such as acetic, but the equilibrium takes some time to establish itself, the change on keeping being consistent with the hypothesis of a slight dissociation of the "acid."

C. A. SILBERRAD.

Physico-chemical behaviour of lecithin. I. Capillary activity of lecithin as a function of p_H . H. I. PRICE and W. C. M. LEWIS (Biochem. J., 1929, 23, 1030-1043).—The capillary behaviour of egg-lecithin has been studied and the surface tension- p_H curves for aqueous dispersions and aqueous-alcoholic dispersions are compared. According to these curves the isoelectric point is 2.6 in both sets of dispersions. An explanation of the surface tension- p_H curves is offered on the basis of simple orientation. The influence of salts such as sodium chloride and calcium chloride on the surface tension- p_H relation for dispersions of lecithin has been examined. The effects are of a complex character. The mol. wt. of egg-lecithin is found to be 797 in ethyl alcohol and 3388

in benzene. The egg-lecithin was prepared by Levene and Rolf's method. S. S. ZILVA.

Osmotic pressure of crystalline egg-albumin. J. MARRACK and L. F. HEWITT (Biochem. J., 1929, 23, 1079—1089).—In moderate concentrations of sodium acetate and sodium chloride, isoelectric egg-albumin has the same osmotic pressure as in medium concentrations of ammonium sulphate. Different values are obtained in concentrated solutions of sodium chloride and in dilute solutions of sodium acetate, but the deviations are less than those shown by ammonium sulphate solutions. The mol. wt. calculated from the authors' figures and from those of Sorensen is 43,000. Electrodialysed egg-albumin gives a slightly higher figure. There is no fall of osmotic pressure on the acid side of the isoelectric point in the presence of sodium chloride and sodium acetate. At p_H 6.7—8.0 the osmotic pressure-concentration curve of egg-albumin resembles that of serum. The influence of ammonium sulphate on the activity of egg-albumin cannot be explained entirely in terms of the salting-out effect. S. S. ZILVA.

Lyophilic colloids. III. Gum arabic sol. H. R. KRUYT and H. J. C. TENDELOO (Kolloidchem. Beih., 1929, 29, 396—412).—Sols of gum arabic exhibit the properties typical of lyophilic colloids. Measurements were made of the viscosity of the sol at different concentrations and in presence of varying amounts of electrolytes. Poiseuille's law is obeyed. The effect of electrolytes is to lower the viscosity, and the first small amounts produce the greatest effect; at higher concentrations of electrolyte the particles of sol become partly dehydrated, and when dehydration and electrical discharge occur simultaneously (as by adding alcohol and an electrolyte) the sol is coagulated. Small quantities of electrolyte raise the charge on the particles. It is maintained that the stability of lyophilic colloids is conditioned by capillary electric charge and hydration of the particles.

E. S. HEDGES.

Lyophilic colloids. IV. Charge, hydration and particle-size in sols of starch, gum arabic, gelatin, and casein. H. R. KRUYT and H. J. C. TENDELOO (Kolloidchem. Beih., 1929, 29, 413—431).—A method for measuring the cataphoretic migration velocity of the particles of colourless sols is described. Measurements of the viscosity, electrical conductivity, and cataphoretic migration velocity of starch sols give a mean particle size of $9\ \mu\mu$ for the hydrated particles and $4\ \mu\mu$ for the dehydrated particles. In sols of gum arabic the ζ -potential passes through a maximum with increasing electrolyte concentration, whilst the viscosity falls continuously. Hydration and electric charge vary simultaneously in sols both of gum arabic and of gelatin. E. S. HEDGES.

Lyophilic colloids. V. H. R. KRUYT (Kolloidchem. Beih., 1929, 29, 432—435).—A discussion of previously published work having a bearing on the four preceding parts of the series. E. S. HEDGES.

Lyophilic colloids. VI. Electroviscous effect with two hydrophilic sols which do not obey Poiseuille's law: linseed and carrageen. H. G. B. DE JONG and O. S. GWAN (Kolloid-

chem. Beih., 1929, 29, 436—453).—Sols of linseed and carrageen possess an unusually high viscosity even at low concentrations. Poiseuille's law does not hold either for the sols alone or in presence of electrolytes. The sols are very sensitive to traces of electrolytes, 1 milliequiv. of electrolyte lowering the viscosity considerably, but similar concentrations of a non-electrolyte such as alcohol produce no effect. The valency of the cation determines the type of viscosity lowering. Electrolytes with ter-, quadri-, and sexa-valent cations fall into two groups: complex salts, which lower the viscosity in the normal sequence, and cations the salts of which are readily hydrolysed (lanthanum, aluminium, thorium) which in low concentrations produce much less lowering of viscosity than is to be expected. E. S. HEDGES.

Lyophilic colloids. VII. Capillary electric charge and hydration as characteristics of hydrophilic gels: reversible volume changes of agar gel. H. G. B. DE JONG (Kolloidchem. Beih., 1929, 29, 454—482).—An apparatus for the measurement of small dimensional changes in a gel is described. At the ordinary temperature, a 2.2% gel of agar does not swell in distilled water, but undergoes syneresis. All neutral electrolytes in small concentrations cause the gel to shrink, the maximal linear change being 1%. Non-electrolytes have no influence. The shrinkage is a capillary electrical phenomenon which is determined solely by the valency of the cation; the nature of the cation or the valency and nature of the anion have no influence. Sexavalent cations produce their maximal effect at so low a concentration as 1.5 milliequiv. per litre and the contraction produced at higher concentrations is less, although whether this is due to a reversal of charge is not clear. The contraction is reversible, for the gel increases in volume again when the electrolyte is washed out; exchange-adsorption of the cations can also take place. Alcohol in high concentrations causes a linear contraction of 7%, which is reversible and is due to dehydration of the units of the structure. High concentrations (up to 5N) of magnesium chloride do not cause greater shrinkage than small amounts, but with magnesium sulphate a greater shrinkage (4%, linear dimensions) is observed the higher is the concentration; the difference is that magnesium chloride is unable to dehydrate the particles of gel, whilst magnesium sulphate does so readily.

E. S. HEDGES.

Slow change in mixtures of colloidal solutions recalling anaphylactic effects. A. BOUTARIC and M. DUPIN (Compt. rend., 1929, 189, 754—757; cf. A., 1928, 360).—Contrary to the effect of repeated additions of small quantities of an electrolyte to a colloidal solution, the successive addition of small quantities of a second sol causes complete flocculation with a smaller total amount of the second sol than when this is added in one lot. The phenomenon is illustrated by the addition of a sol of arsenious sulphide to one of ferric hydroxide and *vice versa*. The possible bearing of this result on the phenomenon of anaphylaxis is pointed out. C. A. SILBERRAD.

Electrical excitation and the possible structure of the plasmatic membrane. H. H. DIXON and

T. A. BENNET-CLARK (*Nature*, 1929, **124**, 650—651).—In electrical excitability there is a marked similarity between oil-in-water emulsions, *e.g.*, olive oil 50 c.c., water 25 c.c., oleic acid 1 c.c., sodium hydroxide 0.08 g. (or calcium oxide 3.0 g.), and living tissues. The relation between the voltage applied to a given emulsion and the change of resistance produced is of the same type as that obtained with living tissues. It is believed that the plasmatic layer of the living cell is a water-in-oil emulsion close to its inversion point. A. A. ELDRIDGE.

Growth of colloidal silver in gelatin layers. H. ARENS and J. EGGERT (*Z. Elektrochem.*, 1929, **35**, 728—733).—The growth of silver particles embedded in gelatin layers has been investigated in its dependence on the initial size of particles and also on the silver concentrations, and this has been compared with the growth occurring in the blackening of a photographic plate. H. T. S. BRITTON.

Reactions between hydrophilic sols. I. Gelatin and silicic acid. W. J. LESLEY (*Trans. Faraday Soc.*, 1929, **25**, 570—579).—Determinations of the p_H values of acid and alkaline solutions of gelatin or silicic acid, or both, were made under varying conditions. Co-precipitation of the two colloidal substances appears to be at a maximum at the isoelectric point of the gelatin. Addition of silicic acid sol to an acid solution of gelatin causes practically no change in p_H value, although precipitation occurs in many cases. Various precipitates obtained from hydrochloric acid solutions in the neighbourhood of the gelatin isoelectric point were of approximately constant composition, although in all cases the silicic acid was completely precipitated. A series of experiments with decreasing ratio of gelatin to silicic acid showed that when the ratio was less than about 0.07 the precipitation of silicic acid ceased to be complete and, instead of precipitation, opalescence alone ensued. H. T. S. BRITTON.

Coagulation of hæmoglobin. I. S. L. PUPKO (*Kolloid-Z.*, 1929, **49**, 150—153).—The coagulation of aqueous hæmoglobin solutions in presence of ethyl alcohol and potassium chloride and bromide has been investigated viscosimetrically. The greater is the amount of added electrolyte, the smaller is the amount of alcohol required for coagulation. The product of the volume of alcohol just insufficient to cause coagulation and the concentration of the electrolyte is constant. Potassium chloride and bromide have equal effects. E. S. HEDGES.

Coagulation and separation into two liquid layers. Systems gum arabic-gelatin. H. G. B. DE JONG and W. A. L. DEKKER (*Biochem. Z.*, 1929, **212**, 318—336).—In mixtures of some hydrophilic sols, *e.g.*, gum arabic and soluble starch, gum arabic and agar, the viscosity relationships are almost exactly additive. With gelatin-gum arabic mixtures, additive relationships are obtained outside the p_H range 4.8—1.2, but within this range the additivity curve shows a minimum corresponding with optimal separation into two layers. Capillary electric charges also have an influence on the separation into liquid layers. At p_H 4.7, gelatin is faintly positively and

gum arabic strongly negatively charged; as the p_H decreases the charges are reversed, gelatin becoming strongly positively and the gum weakly negatively charged. At p_H 1.2 when the gelatin has lost much of its positive charge and the gum arabic is very slightly negatively charged, separation into liquid layers ceases. Over the same p_H range in presence of 0.15N-potassium chloride, the viscosity again shows additive relations. In equivalent concentrations the return to additivity is the more pronounced the greater is the valency of the anions, increasing, *e.g.*, with KCl, $\frac{1}{2}$ K₂SO₄, $\frac{1}{3}$ K₃Fe(CN)₆, and the same holds for increasing valency of cations. The same behaviour is obtained with gelatin and mucilages of linseed, Iceland moss, althæa root, tragacanth, and carrageen as with gum arabic. P. W. CLUTTERBUCK.

Effect of proteins on the coagulation of bentonite suspensions by electrolytes. B. N. GHOSH (*J.C.S.*, 1929, 2285—2290).—The addition of small quantities of gelatin accelerates the coagulation of bentonite suspensions by sodium or barium chloride, but larger quantities retard coagulation and finally cause protection. The protective action of a given weight of gelatin is the greater the more dilute is the suspension. Casein and egg-albumin behave similarly, but the protective action of the latter is less than that of the two former. On the acid side of their isoelectric points the proteins coagulate the suspensions without addition of electrolytes.

C. W. GIBBY.

Precipitations in gels. I. Influence of an electric field on rhythmic precipitation. II. Single ring precipitation. B. KISCH (*Kolloid-Z.*, 1929, **49**, 154—156, 156—158).—I. Experiments are described on the formation of Liesegang rings of silver chromate under the influence of an electric field. When a P.D. of 0.1 volt was applied, the anode being in the centre of the drop of diffusing silver nitrate and the cathode in the gelatin beyond the edge of the drop, more rings are formed in the direction of the cathode and they are more strongly marked and broader. If instead of a point-cathode a platinum ring is used so as to encircle completely the drop, diffusion occurs more quickly and broad rings are formed, but if the outer circular electrode is made the anode, the diffusion field is much smaller and no rings are formed.

II. When a drop of a concentrated solution of potassium iodide is placed on a gelatin or agar gel containing 1% of mercuric chloride, a single ring of mercuric iodide is produced instead of the usual series of concentric rings, and the boundary of the drop moves as the potassium iodide diffuses outwards. This is because the ring of precipitate is soluble in excess of the reagent. E. S. HEDGES.

Effect of potassium alum on gelatin. A. LOTTERMOSER and W. MATTHAES (*Kolloid-Z.*, 1929, **49**, 103—118).—The changes in certain properties of gelatin after treatment with solutions of potassium alum have been examined. The gelatin was allowed to swell in water, a solution of the alum was added, and the viscosity of the mixture measured 5 min. after the addition. These values of the "initial viscosity" increase with the amount of swelling

undergone by the gelatin before the addition of alum and also reach a maximum at a concentration of 11% of potassium alum. The high initial viscosity falls with time, ultimately reaching a value close to that of untreated gelatin solutions. Heating the solution reduces the initial viscosity and this change is irreversible. The viscosity of gelatin solutions treated with alum is also reduced by pressure, although such a change is not observed in untreated solutions. The m. p. of gelatin gels is at a maximum after treatment with 3% of potassium alum and the value is reduced by heating the mixture; when the gel is kept, the m. p. rises. The temperature of setting increases with the concentration of both the gelatin and the alum. The "Abschwimmtemperatur," at which a gelatin film ceases to adhere to the base on which it has been formed, increases with the amount of alum added: for ordinary gelatin solutions this value lies below the m. p., but for solutions treated with alum it is always above the m. p. and is more readily reproducible; the value also depends on the drying treatment. The surface tension of the solutions, as determined by a stalagmometric method, is raised by the addition of alum, but is reduced when the solution is heated. The addition of potassium alum reduces the swelling of gelatin. The mechanical strength of gelatin gels is at a maximum after addition of 3% of potassium alum, coinciding with the maximum of m. p. E. S. HEDGES.

Diffusion of methylene-blue in gelatin gels. K. SCHULTZE (Kolloid-Z., 1929, 49, 118—120).—The gradual disappearance of colour at the boundary of a gelatin gel and a solution of methylene-blue which is allowed to diffuse into it, described by Mokruschin (A., 1928, 238), does not occur when all the apparatus and materials used are carefully sterilised, but may be brought about by the subsequent addition of certain bacteria. It is inferred that the explanation given by Mokruschin is not valid, and that the disappearance of colour is due to some reducing substance in the gelatin which may be produced by bacterial decomposition. E. S. HEDGES.

Effect of hydrogen carbonate ions on the swelling of gelatin. E. G. MILLER, jun. (Biochem. J., 1929, 23, 876—879).—The influence of hydrogen carbonate concentration and p_H on gelatin swelling (over a limited range) is of the same order of magnitude as the corresponding influence of the chloride ion. S. S. ZILVA.

Vapour-pressure diminution of rubber jellies. P. STAMBERGER (J.C.S., 1929, 2318—2326).—Measurements have been made of the vapour pressure of rubber jellies in benzene, chloroform, and carbon disulphide, particularly at low concentrations. Up to a certain concentration the vapour-pressure lowering is inappreciable, but increases rapidly above that. The solvation of the jellies is discussed. C. W. GIBBY.

Ionisation currents from zinc oxide smokes. H. P. WALMSLEY (Phil. Mag., 1929, [vii], 8, 553—568; cf. A., 1927, 287; this vol., 869).—Using the method previously described (cf. A., 1926, 654) the ionisation currents from clouds or smokes of zinc

oxide particles were investigated. The smoke was produced in a cistern from an electric arc between zinc electrodes, whilst in a second case zinc oxide was dispersed by the decomposition of diluted zinc ethyl vapour passed into the cloud chamber. The initial ionisation and its changes with time were measured. The cloud particles in both cases are crystalline, with the internal structure of zincite. The clouds from the arc are ionised on formation; those from the zinc ethyl are not. There is a spontaneous production of ions in the clouds as they age; in those from zinc ethyl, ionisation increases from zero to a maximum and then diminishes. Qualitatively the intensity increases with the amount of material dispersed and with the degree of dispersion. The initial ionisation in clouds from the arc is attributed to thermoelectric emission of charges at the high temperature of formation. With arc clouds of low concentration this diminishes with time. The coefficient of recombination of these ions is of the same order of magnitude as the coagulation constant of similar clouds. With increasing concentration of dispersion the two effects are superposed.

N. M. BLYTH.

Derivation of the law of mass action. R. D. KLEEMAN (Phil. Mag., 1929, [vii], 8, 267—269).—Further to a previous paper (cf. A., 1928, 1315) in answer to Goldstein's criticism of the derivation of the modified law of mass action (this vol., 881), it is pointed out that the ordinary (and Goldstein's) derivation of the law involves constraints which do not allow of molecular dissociation, whilst in the revised derivation no constraints are applied. It is pointed out that under conditions of constraint the process of the van 't Hoff cycle cannot be considered as isothermal. A. E. MITCHELL.

Velocity law of gas molecules. G. JAGER (Monatsh., 1929, 53 and 54, 199—202).—Mathematical. For values between u and $u+du$ the velocity component of a gas molecule depends only on u and not on any other arbitrarily-assumed quantities.

L. S. THEOBALD.

Derivation of the Boltzmann entropy law by means of the conception of material waves. A. HAAS (Monatsh., 1929, 53 and 54, 165—174).—Mathematical. The Boltzmann entropy law can be deduced from the Gibbs formula for energy distribution. It is now shown that the logarithm of the probability equals $E-\Psi/\Theta$, where E is the total energy and Θ the distribution modulus which is proportional to T ; by using the conception of material waves the function Ψ is identified with the free energy F . From these results the Boltzmann entropy law is derived and applied to vibrating quantum systems. L. S. THEOBALD.

Equilibrium between the mono-, di-, and tri-oxides of nitrogen. E. ABEL and J. PROISL (Z. Elektrochem., 1929, 35, 712—715).—The equilibria involved in the decomposition of nitrogen trioxide at 8.1° and 34.8° have been investigated: from the results it is calculated that nitrogen trioxide at 25° and 760 mm. is 89.5% dissociated into the monoxide and dioxide, at 50°, 94.2%, and at 100°, 98.8%.

H. T. S. BRITTON.

Equilibrium of carbon dioxide decomposition of formic acid and its potential. G. BREDIG, S. R. CARTER, and M. ENDERLI (Monatsh., 1929, 53 and 54, 1023—1030).—The equilibrium constants for the formation of formic acid from carbon dioxide and hydrogen in presence of water and palladium-black (cf. Bredig and Carter, A., 1914, i, 377) at 20—90° and 60—117 atm. have been determined. From these constants and those for the water-gas reaction (*loc. cit.*) the equilibrium constants for the formation of formic acid from carbon monoxide and water in aqueous solution are calculated; these agree with the values obtained by Branch (A., 1915, ii, 742). The vapour pressures of 0.0306—0.0641*M*-solutions of formic acid in water at 20—90° have been determined by Zawidzki's method (A., 1901, ii, 6). From these results the equilibrium constants for the formation of formic acid from either carbon dioxide and hydrogen or carbon monoxide and water were calculated for the gaseous phase. The normal potential for the formation of aqueous formic acid in *N*-hydrogen-ion solution from carbon dioxide at 1 atmosphere pressure is calculated to be approximately -0.12 volt at 20° and -0.18 volt at 90°.

H. BURTON.

The p_H value of water. A. KLING and A. LASSIEUR (Compt. rend., 1929, 189, 637—639; cf. this vol., 240, 355).—The p_H of water determined by means of the cell $H_2|Aq-Hg_2Cl_2|Hg$ and a Moulin quadrant electrometer is "about 5.6." A more accurate method, using two hydrogen electrodes, one containing the water under examination, the other a liquid of known p_H adjusted until the *E.M.F.* of the combination vanishes, gave p_H 5.8.

C. A. SILBERRAD.

Ebullioscopic determination of equilibrium constants. W. SWIENTOSLAWSKI, Z. BLASZKOWSKA, and E. JÓZEFOWICZ (Bull. Acad. Polonaise, 1929, A, 149—167).—See this vol., 396.

Electrolytic dissociation. C. DRUCKER (Monatsh., 1929, 53 and 54, 62—68).—The saturation concentrations of benzoic, *o*-nitrobenzoic, oxanilic, and picric acids in dilute sulphuric, hydrochloric, and nitric acids decrease with increasing concentration of the inorganic acid. The specific conductivity of the solutions increases with diminishing values of the saturation concentrations. With benzoic, *o*-nitrobenzoic, and oxanilic acids in dilute picric acid solution, the saturation concentration first diminishes and then increases with increasing concentration of picric acid. This increased solubility is doubtless due to the formation of additive compounds. The anionic mobilities of the above organic acids in the same acid solutions have been determined electrometrically, using either hydrogen-iridium or quinhydrone-gold electrodes, and are found to be approximately the same. The results given for picric acid alone do not agree with those of von Halban and Ebert (A., 1924, ii, 826). All measurements were carried out at 25°.

H. BURTON.

Dissociation constant of nitrous acid. A. KLEMENC and E. HAYEK (Monatsh., 1929, 53 and 54, 407—412).—When carbon dioxide is passed through a 0.06*M*-solution of sodium nitrite at the

rate of 170 c.c. per min. at 12.5°, the amount of nitrite decomposed in accordance with $3NaNO_2 + 2CO_2 + H_2O = 2NaHCO_3 + NaNO_3 + 2NO$ reaches a limiting value (cf. Baur, A., 1906, ii, 649). If sodium hydrogen carbonate is first added to the nitrite solution no decomposition occurs on passing carbon dioxide. The conductivities of dilute solutions of nitrous acid (from barium nitrite and sulphuric acid) have been determined at 0° and 12.5°, using platinum electrodes. The equivalent conductivities (λ) at $v=411.2$ and 822.4 litres are 84.3 and 106.5 at 0° and 122.7 and 155.1 at 12.5°, respectively. Extrapolation of the values of λ for potassium nitrite gives $\lambda_\infty=115.7 (\pm 0.5)$ at 12.5°. From the above data, the accessible transport numbers, and the heat of dissociation ($\Delta H=4480$ g.-cal.) the dissociation constants of nitrous acid at 0°, 12.5°, and 30° are found to be $3.2(\pm 0.3) \times 10^{-4}$, $4.6(\pm 0.4) \times 10^{-4}$, and $6.0(\pm 0.6) \times 10^{-4}$, respectively.

H. BURTON.

Ionisation constant of *p*-cyanobenzoic acid. E. P. VALBY and H. J. LUCAS (J. Amer. Chem. Soc., 1929, 51, 2718—2720).—An improved method of preparing *p*-cyanobenzoic acid is described. The conductivity at 25° of solutions of the acid up to 0.007446 mol./litre is recorded. Assuming the limiting conductivity to be 377 ohm⁻¹, *i.e.*, the same as that of *m*-cyanobenzoic acid, the Ostwald ionisation constant is 3.1×10^{-4} . The electron attraction of the $\cdot CN$ radical appears to exceed that of the $\cdot SO_2 \cdot NH_2$ group and to be less than that of the $\cdot NO_2$ group. The equivalent conductivity of the *p*-cyanobenzoic ion is 27.

S. K. TWEEDY.

Dissociation constants of valine and glutamic acid. L. J. HARRIS (J. Biol. Chem., 1929, 84, 179—181).—The criticism by Kirk and Schmidt (this vol., 397) of the values obtained by the author for the dissociation constants of valine and glutamic acid is based on a mistaken reference.

C. R. HARRINGTON.

[Physico-chemical] study of bromosuccinic acid. I. Ionic product of water and some other dissociation constants. A. ÖLANDER (Z. physikal. Chem., 1929, 144, 49—72).—When bromosuccinic acid is hydrolysed two simultaneous reactions occur, giving as end-products fumaric and maleic acids. Fumaric acid can be accurately determined in the presence of the other constituents by precipitation as mercurous fumarate dihydrate. Analytical details are given. Existing data for the ionic product of water, the p_H of standard buffer mixtures, and dissociation constants as determined conductometrically are critically discussed. The value 2.093 is selected as being the most trustworthy for the p_H at 18° of the mixture 0.01*N*-HCl+0.09*N*-KCl, which has been used as a standard in conjunction with a quinhydrone electrode in the potentiometric determination of the dissociation constants of acids, for which the following values are given, in the form of negative logarithms: succinic acid, 4.22; bromosuccinic acid, 2.69; phthalic acid, 3.00; acetic acid, 4.79. The above are the first dissociation constants at 50°. The second dissociation constant of succinic acid is $pK_2=5.73$ at 50°. The apparent second dissociation constant of sulphuric acid at ionic strength 0.25

is $pk_2=1.68$ at 50° . Activity coefficients at various ionic strengths have been determined for acetate, primary phthalate, and primary and secondary succinate ions. A table of values of the ionic product of water between 0° and 50° , calculated from the formula of Lewis and Randall, is given.

F. L. USHER.

Acidity of mannitol. P. TERECHOV (Coll. Czech. Chem. Comm., 1929, 1, 551—559).—It is suggested that mannitol (M) behaves as a weak acid and that in the presence of hydroxyl ions a complex $M\cdot OH'$ is formed thus: $M+OH'=M\cdot OH'$. The constant of the reaction has been determined (a) from cryoscopic measurements with sodium hydroxide solutions of concentrations varying between 0.1401*N* and 0.4102*N* and found to be 4.2 at 0° , (b) from the solubility in sodium hydroxide of various concentrations, the value found being about 8 in dilute solutions and decreasing in more concentrated solutions, the variation being attributed to the salting-out effect, (c) from potentiometric measurements with mercuric oxide and platinum electrodes of the activity of hydroxyl ions in the presence of mannitol, which lead to a value of 4.2 at 0° and 5.0 at 22° , and (d) from conductivity measurements of ammoniacal solutions containing mannitol which lead to values of 4.20 and 4.24 at 0° and 25° , respectively. The fact that the constant appears to be independent of the temperature is claimed to support the view of complex formation. The mass law constant is calculated to be 0.42 and 2.4×10^{-4} at 0° and 25° , respectively, when the values 0.1 and 1.0×10^{-14} , respectively, are employed for the ionic product of water at these two temperatures.

A. I. VOGEL.

Viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. G. JONES and M. DOLE (J. Amer. Chem. Soc., 1929, 51, 2950—2964).—The viscosity, η , at 25° of barium chloride solutions varying in concentration from 0.005 to 0.99*M* was determined in a Washburn viscosimeter. The results are given to within 0.03% by the equation $\eta_{\text{BaCl}_2}/\eta=1-0.02013\sqrt{c}-0.20087c$. Equations of this general type are shown to represent accurately the available trustworthy viscosity data for salt solutions. The coefficient of \sqrt{c} is negative for strong electrolytes and zero for non-electrolytes. It represents the stiffening effect on the solution of the electric forces between the ions which tend to maintain a space-lattice structure; this effect is the cause of the negative curvature in viscosity-concentration curves. The coefficient of c is negative for those salts which increase the viscosity of water at all concentrations; the equation of the given type is then valid up to M . For salts which decrease the viscosity of water this coefficient is positive and the type of equation is valid only up to 0.2*M*. It is predicted from the equation type that at very low concentrations the viscosity of solutions of all strong electrolytes will be greater than that of water.

S. K. TWEEDY.

Dependence of the molecular refraction of acids in aqueous solutions on concentration. H. KOHNER and M. L. GRESSMANN (Z. physikal. Chem., 1929, 144, 137—146; cf. A., 1928, 477, 1320; this

vol., 258).—Measurements of the molecular refraction of sulphuric, acetic, perchloric, and benzenesulphonic acids are recorded. The occurrence of a well-defined maximum at 18 mol.-% of perchloric acid is confirmed. The molecular refraction of benzenesulphonic acid increases regularly with dilution within the range 22.6—3 mol.-%, and no indication of the attainment of a constant value at 12.5 mol.-%, as recorded by Hantzsch and Düringer, has been observed (cf. following abstract). F. L. USHER.

Chemical changes of acids and salts in solution based on refractometric data. II. A. HANTZSCH and F. DÜRINGER (Z. physikal. Chem., 1929, 144, 147—157; cf. A., 1928, 834, 1089).—Polemical against Fajans and co-workers (cf. preceding abstract). The authors' theoretical conclusions are in no way invalidated by the fact that other workers have based different interpretations on data obtained by the use of more refined methods. The scale used by Fajans and others in illustrating their results is adversely criticised, as is also their practice of making dilutions from a standard concentrated solution without checking the final concentrations by analysis.

F. L. USHER.

Landolt and Oudemans' law in non-aqueous solutions. P. WALDEN (Monatsh., 1929, 53 and 54, 14—38).—The rotatory powers of tetraethylammonium α -bromocamphor- π -sulphonate, the free acid, and the acid chloride in non-aqueous solvents have been determined at dilutions varying from 10 to 500 litres per mol. of solute. The values of $[M]_{\text{D}}^{25}$ for the camphorsulphonate in methyl, ethyl, *n*- and *iso*-butyl alcohols, acetonitrile, chloroform, chloroform+benzene, acetic anhydride, and ethylene dichloride vary from 297° to 332° (water, 273°), but dilution has no effect on the value for any one solvent. For the acid chloride the values vary from 390° to 438° (same solvents), and dilution has no effect. The ratio $[M]_{\text{chloride}}/[M]_{\text{salt}}$ for all the solvents is approximately 1.31. The values do not appear to be related to the dielectric constants of the solvents; in acetonitrile and chloroform almost identical values are obtained. An approximate parallelism between rotatory power and refractivity in individual solvents is noticed. The values of $[M]$ for the free acid in various solvents are the same as the values for the camphorsulphonate. From the results it is concluded that not only free ions in the salt (or acid), but also the latent or not yet dissociated ions in the heteropolar linking, are responsible for the constant values.

H. BURTON.

Alteration of the optical absorption in the visible and ultra-violet regions through aggregation processes in alkaline and acid solutions of amphoteric hydroxides. G. JANDER and T. ADEN (Z. physikal. Chem., 1929, 144, 197—212).—When aqueous solutions of alkali stannates or tungstates are gradually acidified, the formation of the final product is preceded by that of anions of progressively higher mol. wt. In the case of stannic, tungstic, chromic, or vanadic acid this process is accompanied by a displacement of the beginning of the optical absorption towards the longer wavelengths. At the same time any maxima or minima

tend to become flattened and are usually shifted in the direction of shorter wave-length.

F. L. USHER.

F.-p. measurements in very dilute solutions of strong electrolytes in cyclohexanol. E. SCHREINER, O. E. FRIVOLD, and F. ENDER (Phil. Mag., 1929, [vii], 8, 669—680).—Deviations from the ideal values of the f. p. of very dilute solutions of uni-univalent salts in cyclohexanol (A., 1926, 1208) are in close agreement with the Debye-Hückel theory, in spite of the low dielectric constant, 15.0, of cyclohexanol. Similar experiments have now been carried out with uranyl acetate, lanthanum nitrate, and mixtures of lanthanum nitrate and lithium chloride. So far as it is possible to judge from the experiments the deviations do not conform so closely with the Debye-Hückel law as in the case of a uni-univalent salt alone. The discrepancies, however, appear to be in the direction indicated by the modifications introduced into the theory by Müller (A., 1927, 626; 1928, 590), and by Gronwall, LaMer, and Sandved (A., 1928, 841).

M. S. BURR.

Dielectric constants of electrolytic solutions for various concentrations. A. P. CARMAN and C. C. SCHMIDT (Physical Rev., 1928, [ii], 31, 157).—The dielectric constants of solutions of sodium, potassium, and barium chlorides, and of copper sulphate have been measured for equivalent concentrations up to 0.02, 0.01, 0.022, and 0.026, respectively. The graph of ϵ against concentration shows for sodium chloride a decrease in ϵ up to a concentration of 0.012, followed by an abrupt increase, and for concentrations greater than 0.016, the value of ϵ is greater than that of water. Solutions of potassium chloride give a similar curve, but the curves for barium chloride and copper sulphate show two minima, the values for ϵ in each case being greater in the more concentrated solutions than that for water. Walden (A., 1925, ii, 773) predicted part of these results, but not the occurrence of the minima.

L. S. THEOBALD.

Static balance electrometer method for measuring dielectric constants of electrolytes. A. P. CARMAN, O. B. YOUNG, and K. O. SMITH (Physical Rev., 1929, [ii], 34, 1040—1041).—Carman's differential electrometer method (cf. A., 1928, 106) has been adapted to take readings with conducting electrolytes by static balance, the thermal disturbances being controlled by a special cooling water-jacket round the vessel containing the tested solution.

N. M. BLIGH.

Dielectric constants of three electrolytes by a static balance electrometer method. A. P. CARMAN and K. O. SMITH (Physical Rev., 1929, [ii], 34, 1042—1044; cf. preceding abstract).—Values of the dielectric constants of solutions of potassium chloride, copper sulphate, and barium chloride were measured for concentrations from 0.001*N* to 0.024*N*, at temperatures between 25° and 26°, in fields of about 26.7, and were found to increase at first above that of water, and later to decrease; in the case of copper sulphate, the values are greater than that of water.

N. M. BLIGH.

Thermodynamic requirements of concentrated solutions. R. FRICKE and J. LUKE (Z. Elektrochem., 1929, 35, 631—640).—To test the validity of Kirchhoff's equation connecting the heat of dilution with the vapour pressures of solvent and of solution, an improved method was used for determining vapour pressures (cf. Fricke and Havestadt, A., 1928, 134). Solutions of the following were investigated: thorium nitrate, ammonium nitrate, glycerol, carbamide, sodium hydroxide, sodium acetate, magnesium chloride, and zinc chloride.

H. T. S. BRITTON.

Activity of hydrogen ion in concentrated hydrofluoric acid. E. R. B. PRIDEAUX and J. N. MILLOTT (Trans. Faraday Soc., 1929, 25, 579—581).—Measurement at 18° of the *E.M.F.* of cells of the type: quinhydrone|HF sol.|sat. KCl, Hg₂Cl₂|Hg, in which the acid is 33.5*M* and 3.485*M*, respectively, give 0.179 and 0.106 for the activity coefficient. Taken in conjunction with the data of Wynne-Jones and Hudleston (A., 1924, ii, 470), it appears that the graph of the activity coefficient of hydrofluoric acid against concentration passes through a minimum at about 1.5*M*.

H. T. S. BRITTON.

Activity coefficients of cadmium chloride and bromide. W. W. LUCASSE (J. Amer. Chem. Soc., 1929, 51, 2597—2604).—*E.M.F.* measurements at 25° on cells of the type Hg, Cd|CdX₂, *xM*|AgX|Ag are recorded, with *x*=0.01—6 when X=Cl, and *x*=0.01—3 when X=Br. The data do not fit the functions of Bronsted and of Hückel, probably owing to complex ion formation. The activity coefficients, γ , of the cadmium halides have been computed by utilising the standard potential of the cadmium electrode. These are given by $\log \gamma = aM - bM^c$, where *a*, *b*, and *c* are 0.6, 1.75, and 0.38, respectively, for the chloride and 0.2, 1.48, and 0.308 for the bromide. The activity coefficients of these salts decrease with increase in concentration much more rapidly than the coefficients of typical strong electrolytes; the results indicate that cadmium chloride and bromide cannot be regarded as completely dissociated in solution.

S. K. TWEEDY.

Activity coefficients of electrolytes. III. Principle of specific interaction in mixtures of high valency electrolytes. V. K. LAMER and R. G. COOK (J. Amer. Chem. Soc., 1929, 51, 2622—2632).—The validity of Bronsted's principle of specific interaction (A., 1922, ii, 699) has been tested for salts of higher valency by measuring the effects of various salts (e.g., nitrates and chlorides of potassium, magnesium, and lanthanum) on the solubility at 25° of two ter-univalent and two uni-univalent cobalt-ammines. The principle holds for solvents of higher valency provided that comparisons are restricted to types in which the ratio of the ionic strengths remains unaltered when changes are made in the common solvent ion at the same equivalent concentration. Even at very low concentrations, the Debye limiting law is not obeyed by these solvent salts (cf. LaMer and Mason, A., 1927, 314, whose work is confirmed).

S. K. TWEEDY.

Activity coefficients of electrolytes. IV. Solubilities of lanthanum and thallous iodates

in aqueous salt solutions and the principle of specific interaction. V. K. LAMER and F. H. GOLDMAN (J. Amer. Chem. Soc., 1929, **51**, 2632—2645).—The solubility of lanthanum iodate and of thallos iodide in aqueous salt solutions (e.g., magnesium sulphate, lanthanum nitrate, etc.) has been determined. The Debye-Hückel limiting law is not obeyed, so that this disagreement is not peculiar to the cobaltammines. The conclusions stated in the preceding abstract with regard to the validity of Bronsted's theory of specific interaction are substantiated. The individual specific interactions appear to be restricted to the ions of opposite sign at least up to 0.1*N*. The solubility ratios for thallos chloride and for thallos iodate in various salt solutions conform to Bronsted's principle up to 0.3*N*. The data of Harkins and Pearce (A., 1917, ii, 77) for the solubility of lanthanum nitrate in ammonium nitrate solutions, recalculated according to modern theory, show excellent agreement with the principle of ionic strength.

S. K. TWEEDY.

Perylene and its derivatives. XXVI. Heats of combustion of perylene and its derivatives. A. PONGRATZ and F. GRIENGL (Monatsh., 1929, **53** and **54**, 256—262).—The heats of combustion of several perylene derivatives have been determined using the micro-apparatus described by Roth, Ginsberg, and Lassé (A., 1924, ii, 748). The molecular heats of combustion (kg.-cal. 15°), the values being based on that for benzoic acid [6324 g.-cal.¹⁵/g. (air)], are: perylene, 2333.0; 3:9-diacetyl-, 2780.5; 3:9-dipropionyl-, 3079.6; 3:9-dibutyl-, 3395.4; 3:9-dibenzoyl-, 3878.0; 3:9-di-*o*-toluoyl-, 4213.0, and 3:9-dicyano-perylene, 3156.0. Perylene-3:10- and -1:12-quinones give values of 2158.8 and 2213.3, respectively.

H. BURTON.

Thermochemistry of the compounds in the system CaO-Al₂O₃-SiO₂. I. Heat of dissolution of calcium oxide in hydrochloric acid. T. THORVALDSON, W. G. BROWN, and C. R. PEAKER (J. Amer. Chem. Soc., 1929, **51**, 2678—2682).—The heat of dissolution of calcium oxide in the solution HCl, 200H₂O at 20° is 828.9 g.-cal. (20°) per g., independent of the ignition temperature of the oxide between 800° and 1200°.

S. K. TWEEDY.

Solubility and energy of reciprocal transformation of different forms of calcium sulphate. P. N. LASCHTSCHENKO and A. I. MOROZOVA (J. Russ. Phys. Chem. Soc., 1929, **61**, 962—976).—The solubility at 25° of gypsum is 2.209 g./litre. That of anhydrite, as expressed by the electro-conductivity of the solution, rises to a maximum in 6—7 days as a result of hydration. The solubility of polyhydrate falls from 7.48 g./litre 10 min. after dissolution to 2.15 g./litre 48 hrs. later, whilst constant values for the conductivity of saturated polyhydrate solutions are attained 7 hrs. after their preparation. The process of setting of plaster of Paris is supposed to consist of a rapid process of hydration of anhydrite with the formation of metastable β-gypsum (dihydrate), which is then gradually converted into ordinary gypsum. The initial conductivity of saturated solutions of gypsum rises from 26.5 × 10⁻⁴ in the case of gypsum previously heated at 110° to 62.4 × 10⁻⁴ for material

heated at 230°; when higher temperatures are used, the initial conductivity gradually falls to 13.1 × 10⁻⁴ for 1100°. The final conductivity is 22.8—22.3 for gypsum heated at 110—285°; above 285° it rises to 29.4 for 600°, falling again to 24.5 for 1100°. These results indicate a maximum formation of soluble anhydrite at 230°, following which the yield of insoluble anhydrite becomes increasingly large. The energy of transformation, *E*, of one form of calcium sulphate into another is given by $E - 2RT \log K_2/K_1$, where *K*₁ and *K*₂ are the specific conductivities of saturated solutions of the respective forms. The results obtained by substitution in this formula of values for the interconversion of the various forms are in good agreement with those obtained by using van 't Hoff's formula.

R. TRUSZKOWSKI.

Formation of gaseous gold hydride. A. FARKAS (Z. physikal. Chem., 1929, **B**, **5**, 467—475).—The vapour pressure of gold at 1400° is 9.1 × 10⁻³ mm., and of the hydride AuH 7.8 × 10⁻² mm. The equilibrium constant of the reaction 2Au + H₂ → 2AuH + Q is 1.04 × 10⁻², whilst *Q* has the value 43,500 kg.-cal. At 1100° the vapour pressure of silver is 3.8 × 10⁻² mm. and of silver hydride 1.1 × 10⁻² mm. The equilibrium constant of the reaction 2Ag + H₂ → 2AgH is 14.5, and the heat of dissociation of the hydride 67,500 ± 6300 kg.-cal. The absorption spectra of gold and silver hydrides at 1400° and 1100°, respectively, have been examined and the results compared with those given by Birge and Sponer's extrapolation method.

H. F. GILLBE.

Decomposition of thallic oxide. A. B. F. DUNCAN (J. Amer. Chem. Soc., 1929, **51**, 2697—2705).—From the oxygen pressures set up in the decomposition of thallic oxide between 670° and 770° the amount, *x*, of thallos oxide present in the fused mass has been derived. The m. p. of thallic oxide is 717° ± 5°; this cannot be determined in air, since *p* is 25.5 cm. at 720°. For a given temperature *p* is a linear function of *x*, the isotherms being inclined to the composition axis. Raoult's law is apparently obeyed. The heat and free energy of the reaction Tl₂O₃ = Tl₂O + O₂ are calculated from the equilibrium constant of the reaction.

S. K. TWEEDY.

Hydrates of lithium thiocyanate. V. I. NIKOLAEV (J. Russ. Phys. Chem. Soc., 1929, **61**, 939—945).—The equilibrium diagram for the system lithium thiocyanate-water shows two hydrates, LiCNS, H₂O, m. p. 60.5°, and LiCNS, 2H₂O, m. p. 34°; the existence of a trihydrate is excluded. The eutectic point of the system is -33° at 88% of water.

R. TRUSZKOWSKI.

Additive compounds of lithium halides with methyl and ethyl alcohols. Existence rule in homologous series of complex compounds. G. F. HURTIG [with F. OSCHATZ] (Monatsh., 1929, **53** and **54**, 299—304).—The heats of formation (kg.-cal.) of the following alcoholates are: LiCl, MeOH, 13.4; LiCl, 3MeOH, 13.2; LiCl, EtOH, 12.9; LiCl, 4EtOH, 12.8; LiBr, MeOH, 14.6; LiBr, 3MeOH, 14.15; LiBr, EtOH, 14.05; LiBr, 4EtOH, 13.45; LiI, MeOH, 14.8; LiI, 3MeOH, 13.4; LiI, 4MeOH, 13.2. The three halides form mono-, di-, and tri-hydrates; the

iodide gives also a hemihydrate. Revised values for the heats of formation of lithium halide amines are given (cf. Biltz and Hansen, A., 1923, ii, 760), and also the values for the analogous compounds with mono-, di-, and tri-methylamine (Simon and Glauner, this vol., 431). In a homologous series the tendency towards the formation of additive compounds diminishes with increasing mol. wt. of the addendum.

H. BURTON.

Dissociation of the compounds $\text{HgBr}_2 \cdot 2\text{NH}_3$ and $\text{HgCl}_2 \cdot 2\text{NH}_3$. M. FRANÇOIS (Compt. rend., 1929, 189, 583—585).—The temperatures at which the dissociation pressures are equal to 760 mm. are 186° and 239° , respectively.

J. GRANT.

System leucite-diopside. N. L. BOWEN and J. F. SCHAIRER (Amer. J. Sci., 1929, [v], 18, 301—312).—Leucite (m. p. $1686 \pm 5^\circ$) and diopside (m. p. 1391.5°) form a eutectic at $1300 \pm 2^\circ$ containing 61.5% of diopside. The liquidus curve of leucite is concave upwards at high temperatures and convex at lower temperatures.

C. W. GIBBY.

System water-carbon dioxide-ammonia. E. JÄNECKE (Z. Elektrochem., 1929, 35, 716—728).—The binary systems ammonium hydrogen carbonate-ammonium carbamate, ammonium carbamate-ammonia have been investigated. Solubility determinations at various temperatures have also been carried out on the ternary systems: ammonium hydrogen carbonate-ammonia-water, and ammonium carbamate-ammonia-water. The solubilities of ammonium hydrogen carbonate in ammonia solutions are recorded for temperatures below 0° . The solubilities of carbon dioxide in concentrated solutions of ammonia at 1 atm. and over an extensive range of temperature are also given.

H. T. S. BRITTON.

Equilibrium in the reduction of silver sulphide by hydrogen. M. WATANABE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 708—713).—The reduction of silver sulphide by hydrogen between 453° and 704° has been studied. The equilibria can be represented by the equation $\log K_p - 125.44/T - 0.6499$.

C. W. GIBBY.

Equilibrium between water and the nitrates and chlorides of sodium and potassium. E. CORNEC and H. KROMBACH (Caliche, 1928, 10, 153—161; Chem. Zentr., 1929, i, 2740—2741).—The limits of the sodium nitrate field only have been investigated, and the results include solutions saturated with respect to this salt as well as potassium nitrate or sodium chloride or both at temperatures from 0° to 100° . The deviations from earlier work are considerable. The four saturation fields of the nitrates and chlorides meet at the two ternary points KNO_3 – NaNO_3 – NaCl and KNO_3 – KCl – NaCl . The diagrammatic representation of the results is described. The ternary point shows a minimum solubility for sodium chloride at 75° .

L. S. THEOBALD.

Equilibrium between water and the nitrates, chlorides, and sulphates of sodium and potassium at 75° . E. CORNEC and H. KROMBACH (Caliche, 1928, 10, 250—259; Chem. Zentr., 1929, i, 2741; cf. preceding abstract).—The equilibria which obtain between water and these salts at 75° have been inves-

tigated. Their representation in a geometrical manner is described. Thirty invariant points occur.

L. S. THEOBALD.

Quaternary system water-sodium nitrate-sodium chloride-sodium sulphate. A. CHRÉTIEN (Ann. Chim., 1929, [x], 12, 9—155).—The binary systems sodium nitrate-water, sodium chloride-water, and sodium sulphate-water have been investigated, with results in general agreement with those of other workers. The system sodium nitrate-sodium chloride-water has been studied at various temperatures between -24.3° and 119.8° . No double salts are formed. In the system sodium sulphate-sodium chloride-water, of which isotherms have been determined between -10.6° and 100° , no solid phases other than the simple salts and their hydrates have been found. The system sodium sulphate-sodium nitrate-water was investigated between -18° and 120° . Darapskite, $\text{Na}_2\text{SO}_4 \cdot \text{NaNO}_3 \cdot \text{H}_2\text{O}$, is stable between 13° and 74° ; solutions in contact with it are incongruently saturated. The preparation of darapskite is discussed. Dehydration of darapskite between 92° and 112° gives rise to an anhydrous double salt, $\text{Na}_2\text{SO}_4 \cdot \text{NaNO}_3$. The quaternary system has been investigated between -24.4° , the temperature of the quaternary eutectic, and 121.7° . No further complex salts are formed.

C. W. GIBBY.

System AlCl_3 – FeCl_3 – KCl – HCl – H_2O at 25° . G. MALQUORI (Gazzetta, 1929, 59, 556—563).—Phase studies have been made of the systems FeCl_3 – KCl – HCl – H_2O and AlCl_3 – KCl – FeCl_3 – H_2O and the results applied to the elucidation of the system AlCl_3 – FeCl_3 – KCl – HCl – H_2O . In the latter, the following sets of solid phases are capable of independent existence: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ – KCl ; $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ – KCl – $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ – KCl ; $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ – $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ – $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ – $\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ – $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ – $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ – $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ – $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ – $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ – $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$. The study of the above system shows the possibility, exemplified in the practical application of the Blanc process, of obtaining good yields of potassium and aluminium chlorides of high purity from the fractional crystallisation of the liquors resulting from the treatment of leucite with hydrochloric acid.

F. G. TRYHORN.

Heat of formation of sulphur dioxide. J. R. ECKMAN and F. D. ROSSINI (Bur. Stand. J. Res., 1929, 3, 597—618).—Since a variable small quantity of sulphur trioxide is formed when sulphur burns in an excess of oxygen the heat of formation of sulphur dioxide has been determined by causing oxygen to react with an excess of hot sulphur vapour in a specially-designed reaction chamber. No trace of trioxide is formed and difficulties associated with the analysis of the combustion gases are thereby obviated. The mean value of the heat of formation from solid rhombic sulphur and gaseous oxygen at 25° is $70,940 \pm 50$ g.-cal.

A. R. POWELL.

Energy of hydration of hydroxyl ion and the lattice energies of alkali hydroxides. F. J. GARRICK (Phil. Mag., 1929, [vii], 8, 102—107).—The total energy of hydration of the ions of water is deter-

mined from the cycle $Aq \rightarrow (H_2O)_{gas} \rightarrow (H^+ + OH^-)_{gas} \rightarrow (H^+_{aq} + OH^-_{aq}) \rightarrow Aq$, employing accepted values for the heat of evaporation of water and the heat of neutralisation of strong acids and bases and the mean of the values of Senftleben (A., 1926, 768) and Hund (Z. Physik, 1925, 32, 1) for the work of ionisation of water vapour. The existence of H_3O^+ as postulated by Volmer is accepted and it is assumed that H_3O^+ and OH^- have nearly the same energy of hydration. Then taking the mean of the values of Hund (*loc. cit.*) and of Grimm (Z. Elektrochem., 1925, 31, 474) for the heat of formation of H_3O^+ from water vapour and a proton, the heat of hydration of OH^- is found to be 94 kg.-cal., whilst that of H^+ becomes 255 kg.-cal., in good agreement with the results of Fajans and Webb. A similar cycle is employed to calculate the lattice energies of alkali hydroxides, the results obtained being in agreement with those obtained by the method of Hund (*loc. cit.*). These values combined with those of Fajans and Born and of Webb for the heat of hydration of H^+ lead to the mean value of 92 kg.-cal. for the heat of hydration of OH^- .

A. E. MITCHELL.

Vapour pressure and heat of dilution. VI. Heat of dilution of hydrochloric acid, sodium hydroxide, and acetic acid. R. C. PAYN and E. P. PERMAN (Trans. Faraday Soc., 1929, 25, 599—610).—The heats of dilution of aqueous solutions of hydrochloric acid, acetic acid, and sodium hydroxide over wide ranges of dilution have been measured at temperatures ranging from 20° to 70° by means of the apparatus of Harrison and Perman (A., 1927, 207). Hydrochloric acid solutions gave no positive values, but small positive heats were observed in the case of dilute sodium hydroxide solutions at the lower temperatures. The higher concentrations of acetic acid gave large positive values, but these became slightly negative in the more dilute solutions. The heat of dilution of acetic acid at any particular concentration is found to be a linear function of the temperature. It is not possible to correlate the heats of dilution with the nature and constitution of the solutions.

H. T. S. BRITTON.

Individuality of the integral heats of dilution of strong electrolytes. E. LANGE and J. MEIXNER (Physikal. Z., 1929, 30, 670—678).—The Debye-Hückel theory has been examined by reference to integral heats of dilution, and certain simplifications in the formulæ have been introduced. A more exact calculation of the heats of dilution, which takes account of the higher terms, leads to the conclusion that the heat of dilution is equal to the difference of the electrical potential energies at the initial and final concentrations multiplied by a factor $1 + TdD/DdT$ which depends on the solvent (D =dielectric constant). The case of a symmetrical z - z -valent electrolyte with equal apparent cross-sections for both ions is discussed in relation to theoretical equations and experimental data, the degree of agreement for small concentrations showing an improvement as compared with previous work. Alternative methods for considering the case of unsymmetrical valencies are suggested.

R. A. MORTON.

Revision of thermal data. I. W. A. ROTH (Z. physikal. Chem., 1929, 144, 253—258).—The need for a thorough revision of existing thermochemical data by means of fresh and more trustworthy experiments is pointed out. The connexion between atomic number and heat of formation furnishes a convenient check on the results. The heats of formation of silicon and aluminium oxides have been found by the calorimetric bomb method to be 204.0 ± 2.1 and 380.8 ± 0.4 kg.-cal. per g.-atom, respectively, at constant pressure. These results are higher than the values generally accepted.

F. L. USHER.

Thermochemistry of iron, manganese, and nickel. W. A. ROTH (Z. angew. Chem., 1929, 42, 981—984).—The following heats of formation derived from combustion experiments in a bomb calorimeter are recorded: $FeO = +64.0$, $Fe_3O_4 = +265.7$, $Fe_2O_3 = +197.6$, $Fe_3C = -5.4$, $Fe(CO)_5 = +54.4$, $NiO = +58.6$, $Ni_3C = -9.2$, $Mn_3O_4 = +343.8$, $MnO = +96.2$, $Mn_3C = +23$ (kg.-cal./mol. at constant volume). The values are higher than those usually recorded.

C. IRWIN.

Heat of decomposition and of activation of some oxides and sulphides. K. FISCHBECK (Z. Elektrochem., 1929, 35, 607—610).—The work involved in the various stages of the formation of oxides and sulphides, *e.g.*, the formation of oxygen atoms from oxygen molecules and their transference to the surface of the oxide layer and subsequent diffusion through the oxide layer to, and reaction with, the metal, is discussed. A method, in which metal oxides are allowed to react with liquid sulphur between 150° and 200° and so to produce sulphur dioxide at measurable velocities, is described; from these observations the heats of activation of oxides may be derived.

H. T. S. BRITTON.

Heat of dissociation of some strong electrolytes in benzonitrile and their calculation from molecular structure. A. R. MARTIN (Phil. Mag., 1929, [vii], 8, 547—552).—The dissociation constants of strong electrolytes in benzonitrile can be calculated from measurements of the dielectric constant of the solvent and from conductivity data (*cf.* this vol., 143); values are tabulated for the iodides of lithium, sodium, and potassium, lithium bromide, and silver nitrate. The heat of dissociation of an electrolyte in any solvent can be calculated, the dissociation being regarded as taking place in three stages, for each of which the energy changes are found from the dielectric constant of the solvent and the ionic and molecular constants of the solute. Values are tabulated for sodium and potassium iodide.

N. M. BLIGH.

Heats of hydrolysis of the amides. Acetamide. E. CALVET (Compt. rend., 1929, 189, 530—533).—The heat change in the hydrolysis of acetamide is derived from the thermal values of $Me \cdot CO \cdot NH_2 + NaOH = Me \cdot CO_2Na + NH_3 + x$ cal., and $Me \cdot CO_2Na + NH_3 + H_2O = Me \cdot CO_2NH_4 + NaOH + y$ cal.

J. GRANT.

Inner friction of electrolytic solutions and its interpretation according to the Debye theory. H. FALKENHAGEN and M. DOLF (Physikal. Z., 1929, 30, 611—622).—Theoretical. The relation $\eta_\mu = \eta_0(1 + A\sqrt{\mu})$ (η_μ being the viscosity coefficient at a

concentration μ expressed in equivalents per litre of solution, γ_0 that obtained when $\mu=0$) applies to solutions of strong electrolytes. The mathematical development of Debye's theory is considered for the simplest case of binary electrolytes with ions of the same mobility, discussion of the general case for simple electrolytes being deferred. The square root relationship is placed on a firm theoretical basis.

R. A. MORTON.

Conductivity measurements in liquid ammonia. L. SCHMID and M. K. ZACHERL (*Monatsh.*, 1929, 53 and 54, 498—507).—Solutions of glycogen or inulin in liquid ammonia have the same conductivity as the solvent, thus showing that neither compound undergoes molecular change. Mannitol and extrose show practically no change. H. BURTON.

Conductivity measurements in acetonitrile. P. WALDEN and E. J. BIRR (*Z. physikal. Chem.*, 1929, 144, 269—315; cf. A., 1926, 1104; this vol., 401).—Conductivities of solutions in acetonitrile of 11 salts of quaternary ammonium bases, 15 salts of primary, secondary, and tertiary amines, and 9 inorganic salts have been determined at 25° and at dilutions up to 5×10^4 litres/mol. A comparison of the measured and calculated values of Λ_{∞} for tetraethylammonium picrate confirms the square root law. The influence of the nature of both solvent and salt on the strength of the salt solution is discussed. The behaviour of the solvent depends much more on its chemical character than on such physical quantities as dielectric constant or electric moment. The salts investigated fall into three classes: (1) strong salts, including those of quaternary ammonium bases, silver picrate and perchlorate, and potassium picrate and iodide, for which the Kohlrausch square root law holds even in concentrated solution; (2) a group of very weak salts consisting of the chlorides of incompletely substituted amines, where Λ increases greatly with dilution, and (3) an intermediate group consisting of picrates, bromides, and iodides of incompletely substituted ammonium bases. Kohlrausch's law of the additivity of conductivities holds good for several quaternary ammonium bases, and Stokes' law for tetraethylammonium picrate. Λ_{∞} has the value 0.563 for the last-named salt, as in other solvents. Ionic mobilities and solvation numbers for alkali and halogen ions in acetonitrile have been calculated. F. L. USHER.

Electrical conductivity of organic acids in water, alcohols, and acetone, and the electronic structures of the acids. H. HUNT and H. T. BRISCOE (*J. Physical Chem.*, 1929, 33, 1495—1513; cf. this vol., 401).—The molecular conductances of mono-, di-, and tri-chloro- and cyano-acetic acid and of glycollic acid in methyl, ethyl, and butyl alcohols and in acetone have been determined at 30°. The solution of an acid in acetone has a conductance between that in ethyl and propyl alcohols, except in the case of trichloroacetic acid, which falls between those in propyl and butyl alcohols at most dilutions. The CH_3 radical attached to hydroxyl forms molecules of a solvent weaker in ionising power than water, and the separation of CH_3 from OH by CH_2 does not greatly alter the ionising power of the medium. The addition of a second CH_2 group, however, is accompanied by a

pronounced decrease in ionising power. The presence of the methyl, ethyl, and other radicals appears to affect the basicity or hydrogen-accepting properties of the solvent.

The molecular conductances and dissociation constants of 26 organic acids, chiefly derivatives of benzoic acid, have been calculated from the limiting conductivities of hydrochloric acid, sodium chloride, and the sodium salts of the acids at 30°. The results are interpreted in terms of the electronic theory of valency and current views on molecular structure.

L. S. THEOBALD.

Transport numbers and ionic mobilities in mixed solutions of electrolytes and their interpretation in terms of the Debye-Hückel-Onsager theories. K. BENNEWITZ, C. WAGNER, and K. KUCHLER (*Physikal. Z.*, 1929, 30, 623—634).—Onsager's formulæ derived from the Debye-Hückel theory and applied to the ionic mobilities of strong electrolytes have been extended to solutions containing two electrolytes, one ion of which is present in very small amount in a ternary mixture of ions. In order to test the theory, conductivities, transport numbers, and ionic mobilities have been determined for mixtures of barium chloride and potassium chloride, barium chloride and hydrochloric acid, and potassium chloride and hydrochloric acid, the total concentration in each case being 0.01*N*. The mobility of the hydrogen ion in the mixtures was found to be considerably smaller than that observed in pure hydrochloric acid containing the same concentration of chlorine ions. On the other hand, the mobilities of barium and potassium ions in the acid solutions were somewhat greater than in the pure salt solutions. The results are qualitatively in accord with the theory. It must be remembered, however, that the data refer to solutions which are too concentrated for the Onsager theory to be applied quantitatively, and moreover that the components are present in definite amounts, so that the condition of a vanishingly small concentration for one ion is not fulfilled. The experimental results are, however, at variance with the classical theory. The conductivity of mixtures is discussed with special reference to the non-additivity of potassium chloride-hydrogen chloride mixtures.

R. A. MORTON.

Conductivity and transport number of the chloride ion in mixtures of sodium and potassium chlorides. D. A. MACINNES, I. A. COWPERTHWAIT, and T. SHEDLOVSKY (*J. Amer. Chem. Soc.*, 1929, 51, 2671—2676).—The transport number of the anion in mixtures of sodium and potassium chloride at a total volume concentration of 0.1*N* at 25° has been determined by the moving boundary method, the initial formation of the boundary being produced by an automatic device. The conductivity of the solutions was also determined. There is no evidence of complex ion formation (cf. Braley and Rippie, A., 1927, 733).

S. K. TWEEDY.

Transport numbers of cadmium chloride and bromide. W. W. LUCASSE (*J. Amer. Chem. Soc.*, 1929, 51, 2605—2608).—From *E.M.F.* measurements at 25° on the cell $\text{Ag}|\text{AgX}|\text{CdX}_2(0.1M)|\text{CdX}_2(xM)|\text{AgX}|\text{Ag}$, with $x=0.01$ —6 when $\text{X}=\text{Cl}$ and 0.01—3 when $\text{X}=\text{Br}$, and with the aid of results from a pre

vious paper, the transport numbers of the cadmium ion have been calculated (A., 1925, ii, 399). The values pass through zero at about $1.5M$ for the bromide and $4.25M$ for the chloride; in the case of the chloride there is also a minimum at about $0.03M$.

S. K. TWEEDY.

Thermolysis of solids (Ludwig-Soret effect). H. REINHOLD (Z. Elektrochem., 1929, 35, 627—631).—A wandering of ions through mixed crystals of the iodides, bromides, and sulphides of silver and univalent copper, when these are compressed into cylinders, and the two ends subjected to a difference in temperature, has been found to occur; the phenomenon appears to be similar to the Ludwig-Soret effect in solutions. The ends of compressed cylinders, 3 cm. long, of the mixed crystals were placed in electric furnaces at various temperatures such that the temperature fall in each case was 100° and allowed to remain for 8 days. The hotter end increased and the cooler end decreased in weight, due to the migration of silver to the former and copper to the latter. The thermolytic equilibrium bears no relation to the temperature difference, but rather to the temperatures employed. Previous work by the author (A., 1928, 846) on thermoelectric cells is discussed in the light of the results obtained.

H. T. S. BRITTON.

Potential difference: metal-solution. A. E. BRODSKY (Physikal. Z., 1929, 30, 665—669).—The idea that electrode potentials can be resolved into a summation of two terms, one depending only on the nature of the electrode and the second on the properties of the solution, has been placed on a thermodynamic basis with the aid of the Debye-Hückel theory. For the second term a linear relationship with the reciprocal of the dielectric constant of the solvent is found to be in agreement with experimental data. Neutral salt effect and concentration effects are discussed in relation to the theoretical considerations.

R. A. MORTON.

Measurement of *E.M.F.* in dilute aqueous solutions. I. Lead electrode. W. R. CARMODY (J. Amer. Chem. Soc., 1929, 51, 2905—2909).—A small electrode cell is described which can be operated so as to yield reproducible potential results for solutions below $0.001M$. From *E.M.F.* measurements with the cell $Pb(Hg)|PbCl_2|AgCl|Ag$ the normal potential of lead is found to be 0.1263 volt (? at 25°). The activity coefficients of lead chloride in solution are calculated.

S. K. TWEEDY.

Silver chloride electrode. W. R. CARMODY (J. Amer. Chem. Soc., 1929, 51, 2901—2904).—Directions are given for preparing a silver chloride electrode having a constant potential and perfect reproducibility. To ensure the latter desiderata the electrode must be free from cyanide and protected from light, both of which increase the potential. The electrode described, when the prescribed precautions are observed, exhibits no ageing phenomena.

S. K. TWEEDY.

Electromotive properties of rare-earth metals and their amalgams. I. Lanthanum. R. MÜLLER (Monatsh., 1929, 53 and 54, 215—223).—Lanthanum amalgams are prepared from the metal turnings and mercury at 800 — 900° ; those containing 20—50 at.-% of the metal are obtained only with

difficulty. The amalgams rich in lanthanum undergo oxidation readily in air forming the hydroxide.

[With F. KREINER and H. J. SCHMIDT.]—The potentials of lanthanum and its amalgams have been determined at 25° , using a Dolezalek electrometer. A silver electrode in a $0.1N$ -solution of silver nitrate in pyridine was used for the reference electrode and the lanthanum electrode was in a saturated solution of lanthanum bromide in pyridine. The potentials of the pure metal and the 5% amalgam are -0.71 and -0.932 volt, respectively. In an aqueous solution of the bromide the values for the metal and its 1.5% amalgam are -0.71 and -0.932 volt, respectively. The potential-temperature curve for lanthanum shows three maxima (at 19° , 26 — 29° , and 0°), being analogous to the curve for aluminium (A., 1926, 1105). The potentials of amalgams containing 5—96% of the metal are of the same order (limits, -0.908 and -0.944) at 25° .

H. BURTON.

Electromotive properties of rare-earth metals and their amalgams. II. Cerium. R. MÜLLER and H. J. SCHMIDT (Monatsh., 1929, 53 and 54, 224—230).—Cerium amalgams (prepared by heating the metal at 600° in an atmosphere of mercury vapour) are very sensitive to air and moisture. Amalgams containing 15—75% of the metal could not be obtained. The amalgams are stored under paraffin, connexions for potential measurements being made with copper wire. The potentials of the metal and its 5% amalgam in a saturated solution of cerium bromide in pyridine are -0.721 and -0.965 volt, respectively, at 25° . In aqueous cerium bromide the values for the metal and its 1.5% amalgam are -0.739 and -0.946 volt, respectively. The potential-temperature curve shows chief maxima at 26° and 34° . The 0.25—8 and 75—99% amalgams show variations in potential of less than 0.1 volt at 25° .

H. BURTON.

Amount of hydrogen and oxygen present on the surface of a metallic electrode. F. P. BOWDEN (Proc. Roy. Soc., 1929, A, 125, 446—462).—With the apparatus previously described (Bowden and Rideal, A., 1928, 1088), a quantitative investigation has been made of the potential changes which occur during the discharge of small quantities of electricity at a bright platinum electrode in air-free $0.2N$ -sulphuric acid saturated with either hydrogen or oxygen. The quantity of electricity required to change the potential from that of oxygen to that of hydrogen, or *vice versa*, is 9×10^{-4} coulomb per sq. cm. of accessible area, *i.e.*, 9×10^{-9} g.-ion per sq. cm. At high current densities, when the rate of deposition is so rapid that natural loss from the surface by dissolution and evaporation is inappreciable, this quantity is independent of the current density and the direction of the change, and is in agreement with that calculated on the assumption that the potential change involves the removal of a surface layer of one gas adsorbed on or between the accessible metal atoms and its replacement by the other gas. It is not sufficient to form a complete gas envelope (*cf.* Johnson, this vol., 639). The quantities of electricity required to establish hydrogen and oxygen overvoltage, in solutions saturated with hydrogen and oxygen, respectively,

are 6×10^{-7} and 11×10^{-6} coulomb per 100 millivolts. It is suggested that the adsorbed gas on the electrode surface is deformed with formation of oriented dipoles (which might be ions, atoms, or molecules), and that the *P.D.* across the interface is controlled by the number and electric moment of these dipoles. Further changes in the potential, with the establishment of hydrogen or oxygen over-potential, are due to an increased deformation of the dipoles with consequent increase in electric moment. There is considerable evidence, supported by experiments with oxidised platinum foil, for the formation of a layer of platinum oxide on the surface of a platinum anode on which oxygen is being deposited. The catalytic activity of the platinum surface may be markedly enhanced by the alternate oxidation and reduction of even a unimolecular layer, although this treatment causes little increase in the accessible area.

L. L. BIRCUMSHAW.

Evidence of protons in metals. A. COERN (Z. Elektrochem., 1929, 35, 676—680).—Three methods are described to show that electrolytically generated hydrogen diffuses through a palladium cathode, and thereby imparts to the various points on the electrode the potential which would be assumed by a hydrogen electrode. In the first experiment 0.1*N*-sulphuric acid solution was electrolysed between a platinum and a bent palladium cathode, and after stopping electrolysis the potential at different points on the latter was compared with that of the calomel electrode. At first certain points on the wire showed the oxygen electrode potential as a result of exposure to air, but after 80 hrs. the potential became equal to that of the hydrogen electrode. The second method was to observe the variation in electrical resistance of the palladium wire electrode as a result of the diffusion through it of hydrogen. In the third method advantage was taken of the ready oxidation of hydrogen contained in palladium by oxygen to form hydrogen peroxide.

H. T. S. BRITTON.

Crystalline mercurous sulphate and the Weston normal standard cell. D. B. SUMMERS and W. C. GARDINER (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 19 pp.).—In view of conflicting reports as to the effect of the size of the mercurous sulphate crystals on the *E.M.F.* of the Weston element, cells with crystals of various sizes produced under different conditions have been examined over a period of several months. The crystals were prepared by recrystallisation of electrolytic mercurous sulphate from solutions of sulphuric acid, potassium hydrogen sulphate, or cadmium sulphate, and several forms of apparatus were devised to make the recrystallisation process continuous. The size of the crystals varied from 30 to 1000 μ as against an average value of 1 μ for the original electrolytic product. Photographs of typical crystals are given. It is found that the larger the crystals the higher is the initial value of the *E.M.F.* above the normal, but the more rapid is the decrease of the *E.M.F.* with time. Crystals prepared by recrystallisation from cadmium sulphate solution show exceptionally high initial values of the *E.M.F.* which decrease comparatively slowly with time. The

explanation of the results is that with large crystals the surface exposed to the solution is relatively small, so that this surface is readily coated with basic salt produced by hydrolysis, whilst the acid produced by hydrolysis readily diffuses away through the loosely granular mass and thus permits further hydrolysis to occur (cf. following abstract).

H. J. T. ELLINGHAM.

Hydrolysis of mercurous sulphate by cadmium sulphate solution in the Weston normal cell. W. C. GARDINER and G. A. HULETT (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 18 pp.; cf. preceding abstract).—The extent to which mercurous sulphate in contact with mercury can be hydrolysed by means of a saturated solution of cadmium sulphate has been examined by rotating the cathode limb of a Weston cadmium cell and measuring the change in *E.M.F.* and determining the mercury content of the solid phase. When the *E.M.F.* measurements indicate that the solution contains only the basic salt, analysis shows only a comparatively slight hydrolysis of the solid mercurous sulphate, proving that a coating of basic salt forms around the crystals and prevents further action. Experiments using large crystals of mercurous sulphate confirm this view and indicate that the hydrolysis is a very slow process. It is shown that the p_H value of a saturated cadmium sulphate solution is reduced from 4.5 to 4.2—4.0 by rotating with mercury and mercurous sulphate, whereas water rotated with these substances assumes a value of 2.2, which is increased to 4.1 when cadmium sulphate is dissolved in it, so that the resulting solution can still hydrolyse mercurous sulphate. As a result of the observations made, a method of preparing the depolariser for standard cells so as to avoid hydrolysis and increase the constancy of the *E.M.F.* is suggested.

H. J. T. ELLINGHAM.

Oxidation of the depolariser in preparing standard cells. W. C. GARDINER and G. A. HULETT (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 12 pp.).—An investigation has been made of the effect of variations in the method of preparation and washing of the mercurous sulphate, of the composition of the electrolyte, and of the conditions of setting up, on the *E.M.F.* of the Weston cadmium cell over periods of several months. It is confirmed that cells with a neutral cadmium sulphate electrolyte show a gradual decrease of *E.M.F.* On the other hand, the setting up of the cell in an atmosphere containing oxygen has no apparent effect on the *E.M.F.* of neutral or acid cells (cf. A., 1925, ii, 672; B., 1928, 528). The use of solutions saturated with oxygen gave high initial values which decreased to normal values in about a month and continued to decrease, but some cells prepared in an atmosphere of an inert gas showed decreases of a similar magnitude. It would seem that cells show a greater tendency to decrease in *E.M.F.* when the mercurous sulphate is washed with a large volume of cadmium sulphate solution in an inert atmosphere. This effect is attributed to the formation of a basic mercurous sulphate. The presence of a small amount of sulphurous acid in the electrolyte has a beneficial effect owing to its preventing this hydrolysis.

H. J. T. ELLINGHAM.

Potential of solutions of sugars. II. R. WURMSER and J. GELOSO (J. Chim. phys., 1929, 26, 424—434; cf. A., 1928, 846).—When the concentration of the sugars used (dextrose and levulose) is varied between 0.55*M* and 0.0055*M* the limiting potential is not affected. The temperature coefficient valid between 40° and 90° also holds down to 10°. It is further concluded that the limiting potential attained by an electrode in a sugar solution, when air is excluded, depends only on the temperature and is independent of the nature of the sugar, nature of the electrode (platinum, gold, or mercury), and the nature and concentration of the buffer.

F. L. USHER.

Tyrosinase. I. Oxidation and reduction potentials of the tyrosinase system. D. OKUYAMA (J. Biochem. Japan, 1929, 10, 463—479).—Tyrosinase gives a high reduction potential with *p*-cresol and glycine in nitrogen. The high reduction potential of tyrosine is not increased by tyrosinase even in presence of glycine. The reduction potential of pyrocatechol or quinol, but not that of resorcinol, is increased by tyrosinase in presence of glycine.

CHEMICAL ABSTRACTS.

Polarographic studies with the dropping mercury cathode. VI. Influence of fatty acids on the maximum of current due to atmospheric oxygen. J. RASCH (Coll. Czech. Chem. Comm., 1929, 1, 560—570).—A study has been made by the dropping mercury cathode method of the influence of formic, propionic, *n*-butyric, *n*-valeric, isovaleric, palmitic, and stearic acids on the development and the suppression of the maximum, assumed to be due to atmospheric oxygen, in the current-voltage curves. The maximum is greatest when the ionic concentration is about $0.5 \times 10^{-3}N$, as is the case for strong electrolytes; the undissociated molecules exhibit a suppressive effect on the maximum which is greater the higher the acid is in the homologous series. Experiments in alkaline solutions show that the anions of the lower fatty acids have little suppressive action, whilst the palmitate and stearate ions possess a very large suppressive activity. The suppressive activity is assumed to be due to the adsorption of the acids at the mercury cathode interface; the following concentrations represent the values for half suppression of the maximum: formic, 0.5*N*; propionic, 0.24*N*; *n*-butyric, 0.06*N*; *n*-valeric, 0.016*N*; isovaleric, 0.03*N*; palmitic and stearic acids, $<10^{-5}N$. A. I. VOGEL.

Overvoltage on metals. P. SEDERHOLM and C. BENEDICKS (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 15 pp.).—The potential of a platinised platinum electrode fully saturated with hydrogen and half immersed in dilute sulphuric acid changes only very slightly and in a practically linear manner with the strength of current, up to 0.4 milliamperes/cm.², which is passed through it in either direction. If the electrode is completely immersed in the solution, anodic treatment with much smaller current densities causes considerable polarisation and the potential remains at relatively positive values during step-wise decrease of the anodic current density. With increasing cathodic current density, however, the potential soon returns to more negative values. A

totally immersed platinum gauze electrode was subjected to several cycles of step-wise increase and decrease in cathodic current density, and increase and decrease in anodic current density. It was found that after anodic oxygen evolution, subsequent cathodic treatment caused practically reversible hydrogen evolution and on reducing the cathodic current density this reversibility could persist up to small anodic current densities. Similarly, after cathodic hydrogen evolution, subsequent anodic treatment led to oxygen evolution at a potential which changed little with current density over a certain range extending somewhat into the cathodic region. It is claimed that this nearly constant potential represents the true equilibrium value for an oxygen electrode. The difference between this value and that of the hydrogen electrode in the same solution is 1.48 volts, which represents, according to the above view, the reversible *E.M.F.* of the hydrogen-oxygen cell. The significance of these results and their bearing on the nature of overvoltage are discussed. H. J. T. ELLINGHAM.

Kinetics of passivity phenomena. W. J. MÜLLER (Z. Elektrochem., 1929, 35, 656—670).—From a discussion of current-time and -potential curves, it appears that whether passivation is due to the formation of a surface film or to a chemical process, the passivation of an electrode depends on the attainment of a certain effective current density which always accompanies the formation of a surface film. H. T. S. BRITTON.

Effect of addition agents on the conductivity, cathodic polarisation, and grain size of deposits obtained from the cell: $Cu|CuSO_4, H_2SO_4|Cu$. B. CLARK and E. O. JONES (Trans. Faraday Soc., 1929, 25, 583—590).—The cathodic polarisation of a cell containing as electrolyte 0.5*M*-copper sulphate and 0.1*N*-sulphuric acid and one of the following substances: gelatin, dimethylaniline, dextrose, starch, lactic acid, peptone, camphor, was measured by Haring's method at current densities ranging up to 2.5 amp./dm.² The added substances increase the cathodic polarisation and decrease the conductivity of the electrolyte. From a series of electro-depositions using 2 amp./dm.², it was found that the added substances give rise to a smaller grain size of the deposits, except in the case of peptone, which causes the formation of an unsatisfactory powdery deposit. H. T. S. BRITTON.

Action of atmospheric oxygen on photo-electric cells containing a coloured liquid. A. GRUMBACH and S. SCHLIVITZ (Compt. rend., 1929, 189, 753—754).—Two platinum electrodes were immersed in a solution of sodium fluorescein and one of them was exposed to light from a mercury arc, with arrangements for working in air or in a vacuum. With a solution of 5 g. of fluorescein and 0.1 g. of sodium hydroxide per litre, an *E.M.F.* of 5 millivolts was obtained in air, but in a vacuum the *E.M.F.* was zero; the effect is attributed to partial oxidation of the fluorescein in air. With a solution containing 3 g. per litre of sodium fluorescein in 40% glycerol, the Becquerel effect in air is negative and the absorption effect positive; in a vacuum both effects are negative and much greater (—50.2 millivolts after

20 min. compared with +8.7 in air). The essential difference between the two effects is thus emphasised.

C. A. SILBERRAD.

Reaction velocities. J. J. VAN LAAR (Chem. Weekblad, 1929, 26, 506—510).—A mathematical exposition of the errors involved by considering total energies instead of free energies in various systems.

S. I. LEVY.

Relative critical energy of isokinetic reactions. H. DAMIANOVICH (Gazzetta, 1929, 59, 568—570).—The author's deduction that the critical energy in isokinetic reactions is proportional to the absolute temperature of the reaction holds satisfactorily for the decomposition of nitrous oxide, hydrogen iodide, and chlorine monoxide, and the relation is most rigidly satisfied when the values of the critical energy are calculated from the ratio of effective to total molecular collisions.

F. G. TRYHORN.

Effects of magnetic field on certain chemical reactions. S. S. BHATNAGAR, R. N. MATHUR, and R. N. KAPUR (Phil. Mag., 1929, [vii], 8, 457—473).—The influence on chemical reactions to be expected from a magnetic field is discussed theoretically. An investigation was made for a number of inorganic reactions and one organic reaction having very small reaction velocities and large changes in the susceptibilities of the initial and final products. It is concluded that the rate of reaction is accelerated, retarded, or uninfluenced by the field according as the sum of the molecular susceptibilities of the final products is greater, less than, or equal to those of the initial products. Weigle's mathematical relation (cf. A., 1928, 577) for the concentration of the solution within and without the field is applied to the reduction reaction of chromic acid by phosphorous acid; it indicates that the concentration of the more paramagnetic ions will be greater in the stronger field near the poles.

N. M. BLIGH.

Explosions with parahydrogen. F. GOLDMANN (Z. physikal. Chem., 1929, B, 5, 305—306).—After explosion of a mixture of hydrogen and air rich in hydrogen and containing parahydrogen, the whole of the residual hydrogen is present in the normal state. This phenomenon furnishes a characteristic example of the rapid establishment of equilibrium in the explosion zone, and is ascribed to the impulse of particles of high energy content produced during the combustion.

H. F. GILLBE.

Ignition of intersecting streams of oxygen and combustible gas. F. GOLDMANN (Z. physikal. Chem., 1929, B, 5, 316—326).—The minimum temperature of a stream of oxygen which when intersecting a similar stream of hydrogen, carbon monoxide, ethylene, methane, or ether vapour will cause ignition has been determined as a function of the temperature of the combustible gas, and curves constructed showing the variation of the ignition temperature T_i with the composition of the gaseous mixture. Dilution of the hydrogen or oxygen with nitrogen does not influence the ignition temperature, but in presence of carbon dioxide T_i is markedly increased. The ignition curve of oxygen-carbon monoxide mixtures exhibits a minimum at which

T_i is 200° and 130° below the values for 100% oxygen and 100% carbon dioxide, respectively.

H. F. GILLBE.

Diffusion phenomena at the lower explosion limit of hydrogen-oxygen mixtures. F. GOLDMANN (Z. physikal. Chem., 1929, B, 5, 307—315).—The variation of the lower explosion limit of hydrogen-oxygen mixtures according to whether the ignition takes place at the upper or lower end of the explosion tube is due to diffusion phenomena, which have been studied by introducing into the mixture finely-divided platinum or palladium particles, formed by sparking between two electrodes placed at the end of the tube.

H. F. GILLBE.

Influence of water vapour on the heat radiation of exploding gas mixtures. Specific heat of water vapour at high temperatures. K. WOHL and G. VON ELBE (Z. physikal. Chem., 1929, B, 5, 241—271; cf. this vol., 973).—The maximum pressures attained by exploding mixtures of hydrogen and oxygen diluted with varying quantities of hydrogen, water vapour, or argon have been measured and used to calculate the loss of heat by radiation. Although in dry mixtures the loss amounts to several parts % of the heat of combustion, in the presence of water vapour it is reduced to considerably less than 1%. It is concluded that the loss in "dry" explosion is due to emission of light by freshly-activated reaction products (probably OH), and that water vapour absorbs this radiation and converts it into heat in the reaction vessel. The authors consider that the occurrence of a similar effect in the carbon monoxide-oxygen mixtures studied by Garner and Johnson is to be attributed to catalytic action shortening the time of explosion, and consequently the loss by radiation, rather than to chemi-luminescence; in the present experiments the time of explosion was unaffected by the introduction of water vapour. Values of the specific heat of water vapour between 1760° and 2400° are deduced, which are in good agreement with those calculated by means of Einstein functions from optically-determined atomic vibration-frequencies.

F. L. USHER.

Thermal reaction between chlorine and ozone. M. BODENSTEIN, E. PADEL, and H. J. SCHUMACHER (Z. physikal. Chem., 1929, B, 5, 209—232).—The velocity of decomposition of ozone in the presence of chlorine has been measured at 35° and at 50° and found to be proportional to $[\text{Cl}_2]^{1/2}[\text{O}_3]^{3/2}$, after the completion of a period of induction which varies inversely with the concentration of ozone. Although under the conditions of the experiments no intermediate product could be detected, when moist chlorine was used crystals of perchloric acid monohydrate were found, indicating the production of an oxide of chlorine; on mixing ozonised oxygen with diluted chlorine dioxide, chlorine hexoxide (Cl_2O_6) was obtained. In the light of these observations the following scheme is proposed for the mechanism of the reaction: (1) $\text{Cl}_2 + \text{O}_3 = \text{ClO} + \text{ClO}_2$; (2) $\text{ClO}_2 + \text{O}_3 = \text{ClO}_3 + \text{O}_2$; (3) $\text{ClO}_3 + \text{O}_3 = \text{ClO}_4 + 2\text{O}_2$; (4) $\text{ClO}_3 + \text{ClO}_2 = \text{Cl}_2 + 3\text{O}_2$; (5) $\text{ClO} + \text{ClO} = \text{Cl}_2 + \text{O}_2$. The velocity coefficients and heats of activation of reactions (1), (3), and (4) are calculated. From the ratio of the

velocity coefficients of reaction (1) and of the whole reaction, the length of the "chain" is shown to be of the order 10^4 units. The absolute velocities deduced for the partial reactions account satisfactorily for the periods of induction observed. F. L. USHER.

Thermal reaction between bromine and ozone. B. LEWIS and H. J. SCHUMACHER (*Z. Elektrochem.*, 1929, **35**, 648—652).—The decomposition of ozone, at pressures ranging from 56.5 to 102.2 mm., by means of bromine vapour, at 0.30—9.0 mm. pressure, was studied at 7° by following the variations in pressure. The rate of decomposition was unaffected by additions of oxygen and the temperature coefficient at 0° was 3.05 for 10°, corresponding with a heat of activation of 16.5 kg.-cal. The reaction, after an induction period, in the presence of a definite amount of bromine becomes one of zero order. The material of the reaction vessel, viz., glass, quartz, had no measurable effect on the reaction. This type of decomposition probably depends on the intermediate formation of an oxide of bromine, which the authors prepared in two modifications, both of which catalyse the decomposition of ozone with equal intensity. It was prepared at -5° to +10° by allowing 3—15 mm. of bromine and 5—10 times the amount of ozone to react, when after the elapse of about 1 hr. at -5°, or 5—20 min. at 10°, a white, flocculent substance separated on the walls. At -80° the oxide can be kept for a day. It is essential that the reactants should be employed in the above amounts, otherwise no oxide may form, and also should the temperature be too high there is a risk of a severe explosion. Prolonged cooling of the oxide at -40° causes the formation of fine white needles, the transition temperature of which is $35 \pm 3^\circ$. Its formula is $(Br_2O_8)_n$.

H. T. S. BRITTON.

Inflammability of mixed gases. G. W. JONES.—See B., 1929, 930.

Nitryl chloride: formation and thermal decomposition. H. J. SCHUMACHER and G. SPRENGER (*Z. Elektrochem.*, 1929, **35**, 653—655).—By passing ozone through nitrosyl chloride until the yellow colour is destroyed and then by lowering the temperature to -115° nitryl chloride can be separated. Its composition corresponds with the formula NO_2Cl . Its m. p. is below -115° and b. p. -15° (cf. this vol., 1155). Its decomposition into nitrogen tetroxide and chlorine was investigated at 130°, 140°, and 150°. Up to about 90% decomposition the reaction appears to be unimolecular, but afterwards becomes bimolecular. The rate is appreciably affected by additions of the products of decomposition.

H. T. S. BRITTON.

Homogeneous oxidation of acetylene. G. B. KISTIAKOWSKY and S. LENHER (*Nature*, 1929, **124**, 761).—The oxidation of acetylene by oxygen at 250—315° proceeds by way of glyoxal, formaldehyde, formic acid, carbon dioxide, and water; all the reaction products have been isolated. The rate of reaction is proportional to the square of the acetylene concentration and is almost independent of that of the oxygen. In packed vessels a heterogeneous oxidation direct to carbon dioxide and water takes place, the rate being proportional to the product of

the acetylene and oxygen concentrations (cf. also Thompson and Hinshelwood, this vol., 1243).

A. A. ELDRIDGE.

Inflammability of mixtures of ethyl alcohol, benzene, furfuraldehyde, and acetone. G. W. JONES and J. R. KLUICK.—See B., 1929, 930.

Physical chemistry of "knock" and "anti-knocks." P. LAFFITE (*J. Chim. phys.*, 1929, **26**, 391—423).—A general discussion of the phenomenon of "pinking" in internal-combustion engines and an examination of theories put forward in explanation of it.

F. L. USHER.

Effects of knock-suppressing and knock-inducing substances on the ignition and partial combustion of certain fuels. R. E. SCHAAD and C. E. BOORD.—See B., 1929, 930.

Flame characteristics in "pinking" and "non-pinking" fuels. II. G. B. MAXWELL and R. V. WHEELER.—See B., 1929, 878.

Autoxidation of hydrazine. E. C. GILBERT (*J. Amer. Chem. Soc.*, 1929, **51**, 2744—2751).—When oxygen is bubbled through an alkaline solution of hydrazine, hydrogen peroxide is formed but no nitrate, nitrite, or azoimide. The rate of oxidation passes through a maximum with increasing concentration of alkali hydroxide, the optimum concentration of the latter corresponding with that for the maximum rate of decomposition of hydrogen peroxide by colloidal materials. This fact, and the temperature coefficient of 1.75, indicate that the reaction is micro-heterogeneous; the reaction is governed by the rate of adsorption of hydrazine on the active surface available (possibly dark particles). The maximum rate of oxidation is accompanied by the minimum formation of peroxide. The amount of the latter appears to be the resultant of two reactions, a formation and a decomposition. Ammonia and azoimide when added to the solution have no effect, but, as in the case of other autoxidations, acetanilide, aniline, etc. influence the reaction.

S. K. TWEEDY.

Period of induction in chemical reactions: action of hypophosphorous acid on copper salts. P. NEOGI and S. MUKHERJI (*J. Indian Chem. Soc.*, 1929, **6**, 529—545).—A study of the action of hypophosphorous acid on copper sulphate and cupric chloride, producing copper hydride and cuprous chloride, respectively, shows that the period of induction observed is increased by increasing the dilution, and also by adding alcohols, glycerol, chlorides, sulphates, nitrates, oxalates, citrates, tartrates, some sugars, etc. It is, however, decreased by rise in temperature, and by the presence of acids. The period of induction is probably due to the following successive intermediate reactions: (1) formation of copper hypophosphite, $Cu(H_2PO_2)_2$; (2) decomposition of this salt into a compound, $CuH(H_2PO_2)$, and phosphorous acid, as deduced from a study of the p_H values; (3) decomposition of the copper compound by water in the first case and cupric chloride in the second to form the hydride and cuprous chloride, respectively. The reactions are not influenced by light. The influence of added

substances is probably catalytic. The preparation of pure copper hypophosphite solution is described. It has not been found possible to prepare the pure solid. Hypophosphorous acid is a stronger acid than has generally been supposed. M. S. BURR.

Induced reactions. W. G. VANNOY (J. Physical Chem., 1929, 33, 1593—1624; cf. Bancroft, this vol., 1019).—The induced reaction, chromic, arsenious, and tartaric acids, has been investigated. A reaction of an autocatalytic nature occurs between tartaric and chromic acids, whilst the extent and velocity of the direct oxidation of sodium tartrate are dependent on time, temperature, concentration of acid and of oxidising agent. The induction factor for this reaction, after correcting for the oxidation of the tartrate by the chromic acid, is found to be 4 and not 2.8 as determined by Schilow (A., 1903, ii, 276). The mechanism is explained on Bancroft's theory (*loc. cit.*), by the formation of Cr_2O_5 as the lower stage of the actor, but alternative views are possible. The reaction between permanganic, arsenious, and tartaric acids has also been studied. The induction factor increases with concentration of the tartrate and acid present in the solution and could not be followed beyond a value 3 owing to oxidation of the tartrate by the permanganate at higher concentrations. Indications of complex formation between arsenious acid and undissociated sodium tartrate were obtained. L. S. THEOBALD.

Kinetics of the reaction between bromic and hydrobromic acids. F. POLLAK (Monatsh., 1929, 53 and 54, 914—925).—The reaction between bromic and hydrobromic acids in aqueous solution in the presence of phenol proceeds according to the scheme $-d[\text{BrO}_3']/dt = k[\text{BrO}_3'][\text{Phenol}][\text{H}^+]^2$ and k has the value 3.2×10^{-2} at $25 \pm 0.04^\circ$. Bromous acid is an intermediate product. In the presence of phenol the reaction $\text{BrO}_3' + 2\text{Br}' + 3\text{H}^+ \rightarrow 3\text{HBrO}$ takes place with a measurable velocity, and it is a stage of the chief reaction $\text{BrO}_3' + 5\text{Br}' + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$ which occurs in the absence of phenol. In both cases, however, the actual velocity is determined by the reaction $\text{BrO}_3' + \text{Br}' + 2\text{H}^+ \rightarrow \text{HBrO}_2 + \text{HBrO}$. L. S. THEOBALD.

Hydrolysis of methyl acetate with alkali carbonates. A. MUSIL (Monatsh., 1929, 53 and 54, 367—406).—The hydrolysis of methyl acetate with varying concentrations (0.001—1M) of rubidium, caesium, lithium, sodium, and potassium carbonates has been studied at 25° . The reaction mixtures are fixed by the addition of barium chloride solution, boiled to expel carbon dioxide, the barium carbonate is collected, dissolved in standard hydrochloric acid, and titrated back. The calculated velocity coefficients are not always constant, and are generally smaller with M-alkali carbonate than with more dilute (0.01—0.1M) solutions. For 0.01—0.1M-solutions the coefficients increase in the order Li, Na, K, Rb, Cs. H. BURTON.

Water hydrolysis of ethyl acetate. A. SKRABAL and A. ZAHORKA (Monatsh., 1929, 53 and 54, 562—576).—The rate of hydrolysis of ethyl acetate has been studied in acetate buffers at 25° . When the observed minimum reaction velocity is corrected for the

effects due to the hydrogen and hydroxyl ions it is assumed that the residual velocity represents the effect of the uncatalysed reaction or the catalytic effect of the water molecule. This residual velocity ($k_w = 1.48 \times 10^{-8}$ mol./litre/min.) agrees with the value derived from similar measurements by Karlsson (A., 1925, ii, 877). The result is said to show that 36% of the ester is hydrolysed spontaneously or by the action of undissociated water when the total reaction velocity is a minimum. The relative importance of k_w in its dependence on the nature of the hydrolyte is discussed in reference to available data. H. BURTON.

Rates of saponification of commercial oils, fats, and waxes and pure triglycerides by aqueous alkali. J. W. MCBAIN, C. W. HUMPHREYS, and Y. KAWAKAMI (J.C.S., 1929, 2185—2197).—The rates of saponification by aqueous alkali of 25 oils and triglycerides have been determined under comparable conditions at 25° , the rate of change of the hydroxyl-ion concentration being followed by means of a hydrogen electrode. The rates differ considerably for the different oils and are explained as being determined mainly by their varying degrees of emulsification. Small quantities of acid in the oil have no effect, but larger quantities have a very marked effect on the rate. The ease of emulsification of the oils is not related to the emulsifying powers of the corresponding soaps. There is no relation between mol. wt. and rate of saponification, but the time required for saponification increases with the degree of unsaturation. J. A. V. BUTLER.

[Physico-chemical] study of bromosuccinic acid. II. Decomposition of bromosuccinic and acetoacetic acids in aqueous solution. III. Bimolecular reactions in dilute solution. A. ÖLANDER (Z. physikal. Chem., 1929, 144, 73—133; see this vol., 1384).—II. The rate of decomposition of bromosuccinic acid in alkaline solution has been measured at various ionic strengths. The decomposition is shown to take place only in two ways, represented by the equations: (1) $\text{CO}_2' \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CO}_2' = \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2' + \text{Br}'$; $\text{OH}' + \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2' = \text{CO}' \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2'$, and (2) $\text{CO}' \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CO}_2' + \text{OH}' = \text{CO}_2' \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2' + \text{Br}' + \text{H}_2\text{O}$. The first reaction is not appreciably influenced by salts, whereas the second shows a marked positive primary salt effect which, at low ionic strengths, is in accordance with Bronsted's formula, and at greater ionic strengths is due mainly to cations. The acid decomposition of acetoacetic acid is completely analogous to the foregoing, the bimolecular reaction $\text{Me} \cdot \text{C}(\text{O})' \cdot \text{CH} \cdot \text{CO}_2' + \text{H}_2\text{O} = 2\text{Me} \cdot \text{CO}_2'$ being catalysed by hydroxyl ions, and showing a similar positive salt effect. The decomposition of bromosuccinic acid in neutral and acid solution in the presence of buffers has also been investigated, and the velocity coefficients of the decomposition of both the primary and secondary ions have been determined. The undissociated acid is relatively stable. From these measurements the second dissociation constant of bromosuccinic acid has been found, viz., $pK_2 = 4.69$ at 50° . Experiments on the decomposition in concentrated solutions in the

absence of buffers indicate that fumaric acid is formed from lactone-maleic acid or one of its condensation products, and not directly from bromosuccinic acid.

III. Theoretical. For the velocity coefficient of a bimolecular reaction in dilute solution the following expression is derived: $k = \pi RT(r_1 + r_2)^2(\alpha/kT + 1)^{m/2-1} e^{-\alpha/kT} / 100\eta r_1 r_2 \cdot \Gamma(m/2)$, where r_1, r_2 are the radii of the two molecules considered, m is the sum of their degrees of freedom, α the total energy of activation, η the coefficient of viscosity of the solution, and k the Boltzmann constant. The coefficient calculated by means of this expression is greatly in excess of that observed in a number of reactions, indicating that actually only a small fraction of the fully-activated molecules reacts on collision. The non-reactivity of a large proportion of the molecules may be explained on the ground that only a small part of the surface of a large molecule may be reactive, and that attached molecules of the solvent may exercise a protective action. F. L. USHER.

Hydrolysis of organic compounds in neutral and acid solutions. S. C. J. OLIVIER (Chem. Weekblad, 1929, 26, 518—523).—A review of the influence of the position and nature of substituent groups on the rates of hydrolysis of substituted benzyl chlorides and acid chlorides. S. I. LEVY.

Autoxidation of quinol. R. DUBRISAY and A. SAINT-MAXEN (Compt. rend., 1929, 189, 694—696).—The solutions examined contained 25 g. of quinol per litre together with either varying amounts of an alkali or alkaline earth or a buffer solution prepared according to Sorensen's formulae. The amount of oxidation of the quinol being at first proportional to time, the rate thereof has been taken as measuring the catalytic activity of the various solutions. The results indicate that for alkalis and alkaline earths the activity is proportional to the hydroxyl-ion concentration with an approximately uniform coefficient of proportionality. With buffer solutions the activity varies in the same direction as the ionic concentration, but with very varying coefficients of proportionality. C. A. SILBERRAD.

Kinetics of cell fermentation treated from the point of view of a reaction in a closed space.

V. Mechanism of enzyme action. F. F. NORD and J. WEICHERTZ (Z. Elektrochem., 1929, 35, 612—618).—The rate of fermentation of dextrose by yeast has been investigated under various experimental conditions. When the reaction vessel was revolved at higher rates the rate of fermentation increased, the outer liquid being enabled to pass more rapidly through the cell membrane. With more concentrated solutions of dextrose the rate of fermentation attained a maximum value in a longer time, and afterwards diminished more slowly (cf. Sclator, J.C.S., 1906, 89, 133; 1910, 97, 922). Photomicrographs of yeast cells before and after immersion in 30% dextrose solution for 20 min. show that they undergo appreciable shrinking, which thereby leads to the compression of the cell pores and a reduction in the active membrane surface. H. T. S. BRITTON.

Corrosion of metals. II. General theory. W. PALMAER and others.—See B., 1929, 921.

Effect of anions on the rate of dissolution of aluminium. M. CENTNERSZWER and W. WITTAND (Z. Elektrochem., 1929, 35, 695—701).—The anions F' , Cl' , Br' , and ClO_4' accelerate the dissolution of aluminium in hydrochloric acid solution, whilst I' , SO_4'' , and NO_3' retard it. The action of the anions appears to be independent of the cations present. The accelerating effect of anions is greater at low concentrations of hydrogen ions. The accelerating action of chloride ions, and probably of other anions, increases with concentration, reaching a maximum at about 3*N*. Passivity in nitric and sulphuric acid solutions is reduced by those anions which accelerate the rate of dissolution, and those anions which retard dissolution increase the passivity of aluminium.

H. T. S. BRITTON.

Topochemical reactions showing adlineation. E. PIETSCH, A. KOTOVSKI, and [FRL.] G. BEHREND (Z. Elektrochem., 1929, 35, 582—586).—The following reactions between a solid and a solution visibly exhibit adlineation, in that the attack on the crystal begins along the edges and at the corners: potassium dichromate crystals and concentrated sulphuric acid solution, crystals of either copper or nickel sulphate and an alcoholic or alcohol-etheral solution of hydrogen sulphide, the dissolution of copper sulphate crystals in alcohol, copper sulphate crystals and an alcoholic or alcohol-etheral solution of potassium thiocyanate, copper sulphate crystals and an aqueous-alcoholic solution of potassium cyanide, potassium dichromate crystals and an ethereal solution of hydrogen peroxide, bismuth nitrate crystals and an ether-alcohol mixture, crystalline sodium thiosulphate and an ethereal solution of ferric chloride, decomposition of manganic alum, dehydration of crystalline copper sulphate with concentrated sulphuric acid, sodium acetate crystals and an ethereal ferric chloride solution, crystalline nickel sulphate and dimethylglyoxime in alcohol, potassium ferrocyanide crystals and ferric chloride in hydrochloric acid and ether.

H. T. S. BRITTON.

Chemical equilibrium in autoxidation. A. GILLET and D. GUIRCHFELD (Compt. rend., 1929, 189, 691—694).—Anthracene oil (free from products volatile below 350°) in which 25% of its weight of coal dust had been dispersed was submitted to the action of oxygen or of oxygen and nitrogen in varying proportions, at varying rates at 350°, and (a) the amount of oxygen absorbed and (b) the concentration thereof in the issuing gases determined; (a) is practically nil for this temperature when the concentration is below 75%, whilst (b) is independent of the rate at which the gas is passed into the mixture. Similar results were obtained for the oil and coal separately, and for alizarin. It is hence concluded that for any substance liable to autoxidation for each temperature there is an equilibrium pressure of oxygen below which it is not absorbed. C. A. SILBERRAD.

Quantum-mechanical explanation of activation. F. LONDON (Z. Elektrochem., 1929, 35, 552—555).—Theoretical. H. T. S. BRITTON.

Decomposition of ozone catalysed by chlorine. M. BODENSTEIN (Sitzungsber. Preuss. Akad. Wiss.

Berlin, 1929, 23, 367—369).—The velocity of the thermal decomposition of ozone in the presence of chlorine is given by the equation $-d[O_3]/dt = k[Cl_2]^{1/2}[O_3]^{3/2}$. The following reaction chain is proposed: (1) $Cl_2 + O_3 = ClO + ClO_2$, (2) $ClO_2 + O_3 = ClO_3 + O_2$, (3) $ClO_3 + O_3 = ClO_2 + 2O_2$, (4) $ClO_3 + ClO = Cl_2 + 3O_2$, (5) $ClO + ClO = Cl_2 + O_2$. The velocity coefficients of the individual reactions are estimated to be $k_1 = 1.83 \times 10^{-7}$, $k_2 = 9.2 \times 10^2$, $k_3 = 1.70 \times 10^3$ at 50° . That of reaction 2 is much greater.

J. A. V. BUTLER.

Mechanism of the catalytic action of molybdic acid on the reduction of nitric acid by ferrous chloride in a hydrochloric acid medium. R. HÁČ and V. NEFUKA (Coll. Czech. Chem. Comm., 1929, 1, 521—527).—Molybdic acid acts as a powerful catalyst in the reduction of nitric acid by ferrous chloride. The catalytic action of molybdic acid in the presence of a large excess of ferrous chloride can be suppressed by adding the appropriate quantity of ferric chloride (about 3.0 g. $FeCl_3$ per 0.1—0.2 g. MoO_3). Molybdenum pentachloride in 6*N*-hydrochloric acid rapidly reduces nitric acid to nitric oxide even at the ordinary temperature; with molybdenum trichloride the reduction is also very rapid, but the two main products are ammonia and nitric oxide. The catalytic behaviour of molybdic acid in the reduction of nitrates in the presence of hydrochloric acid with ferrous chloride is attributed to the molybdenum pentachloride produced by the partial reduction of the molybdic acid by the ferrous chloride.

A. I. VOGEL.

Reactivity of iodine in organic solutions. II. F. FEIGL and A. BONDI (Monatsh., 1929, 53 and 54, 508—549; cf. A., 1928, 1131).—The effect of addition of various activators to the inactive violet solution of iodine in carbon disulphide (cf. *loc. cit.*) and the reactivity of the resulting solutions towards silver saccharin have been studied. Thus, addition of benzyl sulphide causes increased production of silver iodide, provided the added sulphide is above a certain concentration; with a relatively large amount of activator quantitative formation of silver iodide is observed. Similar activation of the inactive solutions of iodine in carbon tetrachloride, tetrachloroethylene, and trichloroethylene occurs with benzyl sulphide. Benzyl sulphide also increases the activity of the partly active solutions of iodine in dichloroethylene, chloroform, and toluene (the results with toluene alone vary greatly with the specimen; in pure toluene silver iodide is formed quantitatively). The brown solution of iodine in ether is not so reactive as the activated carbon disulphide solution; benzyl sulphide increases the activity of the ethereal solution. Phenyl sulphide has practically no activating effect on carbon disulphide solutions. Phenyl benzyl sulphide is intermediate in its activating effect. The following substances are all activators (to varying extents) for carbon disulphide solutions: phenyl triphenylmethyl sulphide, methyl and ethyl sulphides, tetramethyl-tetrathioethylene, the isomeric methyl dithio-oxalates, pyridine, quinoline, tetramethyldiamino-benzophenone, and *N*-phenylbenzaldoxime. Little or no activating effect is given by thiophen, dibenzyl ether, dimethylpyrone, diphenyl and dibenzyl di-

sulphides, acetophenone, benzophenone, diphenyl ether, and azobenzene.

The above activators are all known to form polyiodides; *benzyl sulphide tetraiodide* and *phenyl triphenylmethyl sulphide tetraiodide* are new. The iodine in these polyiodides is determined directly by titration. The activators are considered to serve as co-ordination centres for the iodine to take part in the reaction.

The compound formed during the action of iodine on silver saccharin is *N-iodosaccharin*. This has not been obtained in the pure state, but it is shown that no reaction occurs between the silver and *N*-iodo-derivatives in presence of benzene. With silver phthalimide and the inactive carbon disulphide solution of iodine, little silver iodide is formed; silver succinimide gives a larger amount of the iodide. Benzyl sulphide has an activating influence with both metallic derivatives.

H. BURTON.

Mechanism of oxidation processes. XVIII.

Activation of hydrogen peroxide by iron. H. WIELAND and W. FRANKE (Annalen, 1929, 475, 1—19; cf. A., 1927, 944).—The oxidising action of hydrogen peroxide on arsenious, phosphorous, and hypophosphorous acids in presence of bivalent and trivalent iron has been studied with results similar to those previously observed with organic acids (*loc. cit.*). In the presence of ferrous ions there is a primary oxidation impulse, after which the rate of oxidation is much the same whether ferrous or ferric ion is present. Variation of concentration of hydrogen peroxide does not appreciably influence the primary effect until high concentrations are reached, when a slight diminution of the primary oxidation impulse is observed. Cupric salts have an inhibiting effect on the oxidation of hypophosphorous acid in presence of ferrous salts. Cuprous salts have no activating action similar to ferrous salts. It is probable, therefore, that the effect of the cupric salt is to oxidise ferrous salt to ferric with formation of a cuprous salt. The influence of a change in the p_H value of the hypophosphite solution was also examined. The primary oxidation at p_H 0.6 was greater than at p_H 7.0, but both were less than that at p_H 4.6. The presence of dihydroxymaleic acid increases the activation by ferrous salts, and, at lower concentrations, the increase in effect is approximately proportional to the amount added, but becomes much less as the concentration increases. This behaviour is comparable with that observed in the activation of oxygen by ferrous ions (A., 1928, 965). Dihydroxy-tartaric acid also catalyses the activation by ferrous salts, but not to the same extent as dihydroxymaleic acid, so that activation by the latter cannot be attributed to the dihydroxytartaric acid formed. Thioglycollic acid also causes marked acceleration of the primary oxidation impulse. The action of hydrogen peroxide on linolenic acid, in presence of ferrous and ferric salts, is similar to that previously observed for other organic acids (A., 1927, 944). The extent of activation obtained supports the conclusion that, contrary to the opinion of Manchot and Lehmann (A., 1928, 261), the effect is not due to the formation of a peroxide of iron, but to the formation of a complex between the ferrous ion and the compound to be oxidised. The latter becomes more readily oxidisable,

whilst oxidation of the iron is delayed. The extent of the primary oxidation impulse will depend on the rate of formation of the complex, its degree of dissociation, and the rate of oxidation of the acid in the complex.
M. S. BURR.

Mechanism of oxidation processes. XIX. Combined autoxidation systems. H. WIELAND and W. FRANKE (*Annalen*, 1929, 475, 19—37).—The accelerating influence of small quantities of certain organic acids on the autoxidation of hypophosphite in presence of iron, previously observed (A., 1928, 965), has been further investigated. The following acids have been found to be active: acetoacetic, oxalacetic, acetonedicarboxylic, benzoylacetic, dihydroxytartaric, and thioglycollic acids. Salicylic and malonic acids are without action, and, although in the case of mesoxalic and benzoylformic acids there is a catalytic increase of oxygen consumption in the system iron-hypophosphite, the effect is due to oxidation of the acid. The organic acid catalysis at first increases with increasing quantity of acid, but ultimately diminishes again. Substitution of the corresponding ethyl ester for the acid reduces the effect very considerably. It is probable that even the small effect that is observed is due to very small quantities of acid set free by hydrolysis of the ester. By measuring the carbon dioxide evolution in presence and absence of hypophosphite, it has been shown that a considerable amount of oxidation of the organic acid takes place in the presence of the hypophosphite. The behaviour of mesoxalic and benzoylformic acids mentioned above, and also of pyruvic acid previously observed, represents an extreme case of this catalysis of the oxidation of the organic acid by the hypophosphite. These experiments were all carried out in solutions of p_H 4.7 buffered by sodium acetate and acetic acid. The influence of copper salts has been studied in solutions of p_H 0.6, 4.7, and 7.3, respectively. Copper sulphate alone causes practically no autoxidation of hypophosphite. In strongly acid solution it exercises a decelerating action on the catalytic effect of ferrous sulphate at first, but after about 15 min. the behaviour of the solution is not appreciably different from that of the solution containing ferrous sulphate alone. In the slightly alkaline solution copper sulphate definitely inhibits the action of ferrous sulphate. In the solution of p_H 4.7 the influence of copper sulphate is very slight. In the presence of the enolic carboxylic acids previously employed both cuprous and cupric ions are practically as active, catalytically, as the ferrous ion, but do not bring about the primary oxidation impulse characteristic of the latter. If ferrous sulphate and copper salts are added to the same solution, the combined effect is greater than the sum of the separate effects, and is greater for the cuprous ion than for the cupric. Experiments employing acetonedicarboxylic acid in presence of iron; and a substrate other than hypophosphite, namely, formic acid, alanine, thioglycollic acid, acetylenedicarboxylic acid, pyrogallol, levulose, or dextrose, indicated no acceleration of the autoxidation process. In the most favourable cases the total effect scarcely reached that to be expected from the sum of the separate reactions. The different behaviour

of hypophosphorous acid is no doubt due to its ability to form complexes.
M. S. BURR.

Catalytic decomposition of ammonia. G. M. SCHWAB and (FRL.) H. SCHMIDT (*Z. Elektrochem.*, 1929, 35, 605—607).—See this vol., 890.

H. T. S. BRITTON.
Heterogeneous catalysis. F. HABER (*Z. Elektrochem.*, 1929, 35, 533—535).—A discussion.

H. T. S. BRITTON.
Role of walls of vessels in gas reactions. M. BODENSTEIN (*Z. Elektrochem.*, 1929, 35, 535—539).—A discussion.

H. T. S. BRITTON.
Topochemistry of contact catalysis. III. Localisation of catalytic activity. G. M. SCHWAB and E. PIETSCH (*Z. Elektrochem.*, 1929, 35, 573—582).—Arguments are adduced to show that increased catalytic activity arises from an increase in field and reactivity, through the existence of crystal edges, boundary lines in a grain surface, and surface derangements.
H. T. S. BRITTON.

Particle formation and particle action as a special case of heterogeneous catalysis. M. VOLMER (*Z. Elektrochem.*, 1929, 35, 555—561).—The reactions occurring at phase boundaries in giving rise to new phases are considered to be autocatalytic, and use is made of this view to account for the separation and aggregation of particles.
H. T. S. BRITTON.

Orientation of molecules in the adsorption layer and heterogeneous catalysis. H. R. KRUYT (*Z. Elektrochem.*, 1929, 35, 539—549).—Adsorption alone does not account for the catalysis of organic reactions between large molecules, but instead a definite orientation of the reacting molecules at the surface of the catalyst must be postulated.

H. T. S. BRITTON.
Influence of catalysts and of heating the silicon on solubility of silicon in hydrofluoric acid. C. BEDEL (*Compt. rend.*, 1929, 189, 643—644; cf. this vol., 756, 997).—The solubility of silicon (96%) in hydrofluoric acid is very markedly increased by a small addition of copper to the acid, markedly so by additions of silver or iron, but is practically unaffected by zinc, lead, or aluminium. Heating the silicon to 300° or 550° and suddenly chilling it [which should according to Koenigsberger and Schilling (A., 1910, ii, 481) have transformed it into allotropic modifications] had no effect on the solubility.

C. A. SILBERRAD.
Uniform distribution of catalysts throughout porous solids. H. N. HOLMES and R. C. WILLIAMS (*Coll. Symp. Mon.*, 1928, 6, 283—285).—Porous silica gel was soaked in a salt solution and dried; a water-soluble gas was then admitted to the gel, which was subsequently immersed in water to allow reaction within the capillary pores to take place.

CHEMICAL ABSTRACTS.
Behaviour of gaseous hydrogen halides and unsaturated hydrocarbons in the presence of contact substances. J. P. WIBAUT (*Z. Elektrochem.*, 1929, 35, 602—605).—Reactions between ethylene and propylene, respectively, and hydrogen chloride and hydrogen bromide are described. Of the two hydrocarbons propylene is the more reactive. No

reaction took place between propylene and hydrogen chloride when passed over asbestos at 18°, but on impregnating the asbestos with bismuth chloride a vigorous reaction ensued with the evolution of heat and the formation of isopropyl chloride. Antimony trichloride may be used in place of the bismuth salt, but not in the case of the reaction of hydrogen chloride with ethylene. Bismuth chloride in the dissolved state, either in water or in benzene, has no catalytic properties. If ethylene and hydrogen chloride are passed over anhydrous aluminium chloride a complicated reaction occurs. Propylene and hydrogen bromide react in presence of asbestos alone, but for ethylene an addition agent is necessary (cf. Tilman, Diss., Amsterdam, 1928). Brief reference is also made to the reactions with acetylene, an account of which is about to be published.

H. T. S. BRITTON.

Oxidation of physiological substances by animal charcoal. O. FÜRTH and H. KAUNITZ (Monatsh., 1929, 53 and 54, 127—145; cf. Warburg and others, A., 1921, i, 230; 1924, ii, 466).—Various substances have been treated with an active charcoal (Carbo medicinalis, Merck) in boiling aqueous solution. With amino-acids up to 70% of the nitrogen may be eliminated as ammonia. The decomposition of alanine is studied in detail; the effects of concentration, time of heating, and presence of oxygen are considered. The change occurring is the formation of ammonium lactate (cf. Baur, A., 1923, i, 97; Wunderly, A., 1924, ii, 841). The charcoal adsorbs some amino-acid but no ammonium salt. Inactivation of the charcoal occurs during the process; addition of fresh charcoal to the filtrate causes renewed decomposition. Amino-acids of high mol. wt. (tyrosine, leucine) are hydrolysed more readily than alanine, but histidine and proline are only slowly attacked. Amides are not affected and proteins only slightly so. Phenols are decomposed readily, but dextrose is not affected (adsorption occurs). Dihydroxyacetone, acetone, and lactic acid are partly decomposed, but β -hydroxybutyric acid is destroyed almost completely. Sugar charcoal is almost as active towards alanine as is an iron-rich animal charcoal (cf. Warburg, *loc. cit.*); addition of iron, copper, manganese, or vanadium salts diminishes the formation of ammonia nitrogen.

H. BURTON.

Catalytic power of active carbons, before and after exhaustion, towards hydrogen peroxide. G. MEZZADROLI and E. VARETON (Annali Chim. Appl., 1929, 19, 415—420).—Activated carbons act as physical catalysts towards hydrogen peroxide, the decomposition of which is most rapid with appula, this being followed in order by animal charcoal, norit supra neutral, norit supra acid, industrial norit, suchar, nuchar W, antichromos, and carboraffin. After being exhausted by mixing with raw sugar solution and filtering, appula, bone-black, norit supra, and industrial norit lose, but suchar, antichromos, and carboraffin gain, in catalytic activity, a mean value for which is approached with all the materials.

T. H. POPE.

Oxidation of ammonia to calcium nitrate at a calcium oxide surface. K. LESCHEWSKI and K. A. HOFMANN [with H. GALOTTI] (Ber., 1929, 62, [B],

2509—2514; cf. A., 1926, 370; B., 1927, 600).—In the oxidation of ammonia to nitrate at an alkaline surface, fluctuations in the yield are observed owing to conversion of ammonia into nitrogen. The last-named change occurs exclusively in the gaseous phase and on the walls of the furnace and can be eliminated by causing intimate contact between the gas and alkaline surface and maintaining the temperature of the entering and emergent gas below 300°. The reacting ammonia is then converted exclusively into nitrate, and nitrogen oxides are not produced provided that the temperature is below that of the decomposition of the alkaline nitrate. As alkaline surface, slaked lime containing a small proportion of the activating heavy metal oxide (*loc. cit.*) is very suitable. The maximum yield of nitrate, calculated on ammonia oxidised, is obtained at 300°, but under these conditions there is a partial dehydration of the calcium hydroxide to oxide, which acts adversely, but can be overcome by suitable addition of water vapour to the gas mixture when the yield attains 93.9%; addition of excessive moisture diminishes the yield. The absorption of ammonia by the lime and its immediately following dehydrogenation to imide are influenced greatly by the activator, whereas the union of imide with oxygen to nitrite and nitrate is conditioned essentially by the alkaline medium. To obtain maximal yield it is necessary, owing to the lower alkalinity of the material, to use smaller concentrations of ammonia with calcium hydroxide than with soda-lime. With a rapid current of gas, a portion of the imide appears to be removed from the contact before oxidation to nitrite can occur and subsequently to be decomposed in the gas phase into nitrogen and hydrogen.

H. WREN.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. IV. Decomposition and synthesis of methyl alcohol by catalysts composed of zinc and chromium oxides. D. S. CRYDER and P. K. FROLICH.—See B., 1929, 934.

Catalytic decomposition of carbon monoxide. III. Is the so-called X-carbide really formed in the iron catalyst? H. TUTIYA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 609—613).—The X-ray spectrograms of specimens of iron, iron carbide, and ferric oxide used as catalysts in the decomposition of carbon monoxide gave no evidence of the formation of new compounds. The photograms of samples of ferric oxide taken at suitable stages of the reaction showed evidence of the successive reduction to the oxides Fe_3O_4 and FeO , and later to Fe_3C . It was found that almost all the lines of strong intensity which Hofmann (A., 1928, 853) ascribed to the X-carbide agreed with those of Fe_3O_4 , not only in position, but also in order of intensity; one of the weak lines which was not common to Fe_3O_4 was due to FeO , and two were shown by Fe_2O_3 .

F. G. TRYHORN.

Catalysis of hydrogen peroxide by tungstic oxide. A. LOTTERMOSER [with W. EICHLER] (Z. Elektrochem., 1929, 35, 610—612).—The decomposition of hydrogen peroxide in the presence of tungstic oxide satisfies the expression: $dx/dt = Kx(a-x)$, and is due to the formation of the autocatalyst, $\text{WO}_3 \cdot \text{H}_2\text{O}_2$.

which afterwards decomposes. The rate of the reaction depends on (1) the mass of catalyst used and its size of grain—the greater the mass and the finer the particles, the greater is the catalysis; (2) the presence of foreign substances, *e.g.*, a trace of oil has a strong retarding action. Gelatin, if in sufficient quantity, can arrest action; salts and especially acids also hinder, and the effect of sodium hydroxide depends on its concentration.

H. T. S. BRITTON.

Catalytic oxidising action of platinum. J. DALIETOS and K. MAKRIIS (Prakt. Acad. Athenes, 1928, 3, 569; Chem. Zentr., 1929, i, 3063).—Alcohol vapour is readily oxidised by sodium chloroplatinate, but not, under the conditions employed, by the potassium compound.

A. A. ELDRIDGE.

Catalytic decomposition of hydrogen peroxide by metallic compounds. H. VON EULER and B. JANSSON (Monatsh., 1929, 53 and 54, 1014–1022).—The velocity coefficient ($k \times 10^3$) (for the first quarter of the reaction) for the decomposition of 0.004*N*-hydrogen peroxide by a mixture of 0.01*N*-sodium hydroxide and 0.00001*N*-copper sulphate solutions is 47 at 17°; k decreases if more dilute copper solutions are used with the same concentration of alkali. Addition of glycine to a mixture of 0.002*N*-copper and -sodium hydroxide solutions (stabilisation of the copper) decreases the value of k from 34 (mean) to <0.2. Addition of pyridine, however, causes an increase in the velocity coefficient; with pyridine in absence of copper there is no measurable decomposition of the peroxide. Silver salts in presence of ammonia or pyridine have a more powerful action than copper salts.

H. BURTON.

Catalytic decomposition of aqueous solutions of formic acid by platinum metals. IV. E. MULLER and W. LOERPABEL (Monatsh., 1929, 53 and 54, 825–851).—The effect of addition of potassium osmate, sodium chloroiridate, chloroplatinic acid, ruthenium, rhodium, and palladous chlorides to aqueous formic acid solutions (containing a little sodium formate) at 100° has been studied. The rate of gas evolution varies greatly with the metal used, but osmium and ruthenium show similarities (induction period, then rapidly increasing gas evolution to a maximum, and then decrease). The induction period is not observed if finely-divided osmium metal is used in place of the salt; those metal salts not showing induction periods are readily reduced to the metal. The time necessary for the formic acid-potassium osmate mixture to reach the hydrogen potential decreases with rise of temperature. Addition of titanous chloride to the mixture at 60° causes a rapid alteration in the potential (a similar change is observed at 70° when active osmium is added); this is ascribed to partial reduction of the osmate to metal, which then catalyses the reduction of the rest of the salt by formic acid. The time necessary for the formic acid-salt mixture to attain the hydrogen potential at 100° varies from 0.5 min. (Pd) to 22 min. (Ru). The effect of addition of various salts on the acid-osmate mixture is studied. The induction period at 100° is lowered by large amounts of sodium formate and acetate, but is increased by sodium and potassium chlorides. The addition of a protective

colloid (gelatin) to the acid-osmate mixture causes a marked diminution in the rate of evolution of gas; with the other metallic salts used, an increased gas evolution occurs, varying from 7% (Pd, Ru) to 730% (Rh). Palladous and platinum hydroxides on barium sulphate are more active than when used alone.

The mechanism of the decomposition, namely, adsorption of hydrogen by the metal whereby carbon dioxide is first liberated, and subsequent liberation of hydrogen, is discussed electronically.

H. BURTON.

Gaseous combustion in electric discharges. IV. Effect of moisture on the cathodic combustion of carbon monoxide detonating gas. G. I. FINCH and D. L. HODGE (Proc. Roy. Soc., 1929, A, 125, 532–542).—By using the apparatus previously described (this vol., 890), a study has been made of the combustion of moist detonating gas (a mixture of carbon monoxide and oxygen in equivalent proportions) in the cathode zone of a direct-current discharge. Platinum, silver, gold, palladium, tantalum, and tungsten were employed as cathodes. Other conditions remaining unchanged, the rate of cathodic combustion, c , is determined solely by the current, i , passed by the discharge. At freely sputtering cathodes the rate is practically independent of the total gas pressure and is retarded by the presence of moisture, the maximum retarding effect being attained when the partial pressure of moisture is about 3 mm. Higher concentrations of moisture, up to 15 mm., have no additional effect. Combustion at non-sputtering cathodes, on the other hand, is accelerated by moisture, and for any given partial pressure of moisture the ratio c/i is hyperbolically related to the total gas pressure, combustion increasing with decrease of pressure. It is inferred from the above facts that combustion of moist “detonating gas” mixtures is determined by a prior ionisation of both constituent gases, that at freely sputtering cathodes steam molecules form clusters on sputtered metal atoms, and that such clusters promote combustion by neutralising the electrostatic forces of repulsion existing between similarly charged ions. At non-sputtering cathodes combustion is proportional to the number of separate moisture clusters in the cathode zone, and is effected by the neutralising of electrostatic forces of repulsion between positively-charged ions by negatively-charged water.

L. L. BIRCUMSHAW.

Active form of oxygen. L. C. COPELAND (Physical Rev., 1928, [ii], 31, 1113).—An active form of oxygen is produced by the passage of oxygen, saturated with water vapour, through a discharge tube. Density measurements indicate the presence of a dissociated gas and association to a heavier molecule. Platinum and nickel wires glow in this gas, but copper and tungsten appear to be unaffected. Luminescence results when iodine or sulphur vapour is mixed with the gas.

L. S. THEOBALD.

Decomposition of carbon monoxide in the silent electric discharge. E. OTT (J.C.S., 1929, 2422–2423; cf. Lunt and Mumford, this vol., 1150).—Malonic anhydride forms different polymerides under different conditions, and the evidence that the product of the discharge is a mixture is not conclusive.

J. A. V. BUTLER.

Effect of electric discharges on chemical reactions. R. SCHWARZ and W. KUNZER (*Z. anorg. Chem.*, 1929, 183, 376—383).—The combination of sulphur dioxide and chlorine is accelerated by the passage of electric discharges. The observation of Odling that sulphur dioxide and bromine unite in sunlight was not confirmed by irradiation by a mercury arc. The action of the Tesla discharge on certain reactions has been studied. No union of bromine with nitrogen or oxygen was observed. The union of silver and bromine was hindered owing to the passivation of the silver or to the removal of traces of water by the electric discharge.

The influence of electric discharges in various gases on the catalytic activity of contact platinum has been investigated. Activated oxygen and hydrogen reduce the activity of the platinum owing to the formation of oxides and hydrides at its surface.

J. A. V. BUTLER.

Gas absorption during electric discharges. M. PAWLOW (*Sprawoz. Prace Polsk. Towarz. Fizycz.*, 1927, 3, 101—116; *Chem. Zentr.*, 1929, i, 2859).—When an electric discharge is passed between iron or mercury electrodes at a *P.D.* greater than 600 volts in nitrogen at a low pressure the gas pressure is diminished and nitrides are formed; when the discharge is passed between iron electrodes in nitrogen admixed with mercury vapour only iron nitride is produced. The formation of metallic nitrides is associated with cathodic sputtering.

A. A. ELDRIDGE.

Electrolytic production of fluorine from fused potassium fluoride. K. FREDENHAGEN and O. T. KREFFT (*Z. Elektrochem.*, 1929, 35, 670—676).—The attack of graphite electrodes by a solution of potassium fluoride in hydrofluoric acid or a fused mass of potassium fluoride containing an excess of the acid is not a chemical process, but one of mechanical disintegration which occurs during electrolysis. If the amount of hydrofluoric acid is about 1.8 mols. to 1 mol. of potassium fluoride, moistened anodes of graphite or carbon could be used. Details of the apparatus used are given. The current-potential curves show that the electrolysis depends largely on the water content of the fused mass. Employing a dry fused mass fluorine could be obtained with a current density of 0.3 amp./cm.² at 10 volts, whilst with 1% of water and using a current density of 0.1 amp./cm.² and 4 volts the water alone undergoes decomposition. With a water content less than 0.7% the potential increases rapidly. Water causes the cell to become polarised even at 250° and destroys the anode, and the fluorine obtained is contaminated with oxygen. The behaviour of platinum and nickel anodes is discussed. The *E.M.F.* of the cell $H_2|HF, (KF)|F_2$, using platinised platinum electrodes at 0°, is 2.768 volts (Krefft, *Diss.*, Greifswald, 1928), from which the heat of formation of hydrogen fluoride, 62.630 kg.-cal., is calculated. H. T. S. BRITTON.

Formation of zinc nitride in the electric arc. K. MASLOWSKI and H. REGULSKI (*Sprawoz. Prace Polsk. Towarz. Fizycz.*, 1927, 3, 87—89; *Chem. Zentr.*, 1929, i, 2865).—Zinc nitride is formed by the electric discharge between zinc electrodes in nitrogen at a pressure below 25 mm. The substance, which

probably has the formula Zn_3N_2 , is decomposed in a vacuum at 500°.

A. A. ELDRIDGE.

Separation of chromium from solutions of chromic acid. E. LIEBREICH and V. DUFFEK (*Ber.*, 1929, 62, [B], 2527—2538).—The processes of reduction, which occur during the deposition of metallic chromium from chromic acid have been investigated by a U-tube method which permits the elucidation of the individual stages in a sharply-defined cathode space without the use of a diaphragm. Bivalent chromium is certainly produced and it appears probable that deposition of the metal occurs by discharge of the chromous ions. During electrolysis in ordinary vessels a similar cathode zone is formed around the cathode within which the reduction processes occur.

H. WREN.

Effect of current density on the hardness of electro-deposited chromium. R. J. PIERSOL.—See B., 1929, 944.

Electrolytic deposition of molybdenum at a mercury cathode. J. L. MERRILL and A. S. RUSSELL (*J.C.S.*, 1929, 2389—2393).—The conditions for the electrolytic deposition of molybdenum have been investigated. The most suitable cathode is mercury and the optimum conditions are: current density 0.6—1.0 amp. per cm.²; acidity, 1.2—1.4*N*-sulphuric acid. Under these conditions 0.1 g. of molybdenum is completely deposited in about 50 min. and the use of a rotating anode does not shorten this time. In sulphuric acid solutions complete deposition is obtained at very low current densities, whereas in hydrochloric acid no deposition occurs at current densities below 2.84 amp. per cm.²

J. A. V. BUTLER.

Electrolytic deposition of tungsten at a mercury cathode. K. S. JACKSON, A. S. RUSSELL, and J. L. MERRILL (*J.C.S.*, 1929, 2394—2398).—The conditions for the electrolytic deposition of tungsten from hydrofluoric acid solutions, at a mercury cathode, have been investigated. The optimum conditions are: temperature 95°; acid concentration about 4.6*N*; current density 0.65—1.0 amp. per cm.² Hydrochloric or sulphuric acid must not be present.

J. A. V. BUTLER.

Order of removal of metals from amalgams. A. S. RUSSELL (*J.C.S.*, 1929, 2398—2401).—The order of removal of molybdenum, tungsten, and bismuth from mercury by oxidising agents has been redetermined with respect to other metals the positions of which are known (A., 1926, 911). The revised order is: zinc, cadmium, manganese, thallium, tin, lead, bismuth, copper, chromium, iron, molybdenum, cobalt, mercury, nickel, tungsten. Molybdenum and cobalt, and also mercury and nickel, lie close together in this series.

J. A. V. BUTLER.

Electrolysis of molten ternary alloys. R. KREMANN [with B. KORTH, E. I. SCHWARZ, and W. PIVETZ] (*Monatsh.*, 1929, 53 and 54, 203—214).—Using a modified form of the apparatus described by Kremann and Gruber-Rehenburg (A., 1925, ii, 678) the effect of current density on a copper-tin alloy (29:71) has been investigated. With increasing current density the "relative effects" (maximal

differences in the concentration of the metals at the anode and cathode) and "absolute effects" (the values of the relative effects referred to 100 parts of the metals) increase up to a limiting value of about 6 amp./mm.² The addition of small amounts of a third metal causes an increased electrolysis effect; this does not increase with larger amounts of added metal. With silver-copper-tin alloys an increase in current density again causes an increase in the relative effect. A limiting value (at 3.6 amp./mm.²) is reached with 10.84% Ag (31.7% Cu; 57.4% Sn); this does not occur with lower concentrations of silver. Similar results are obtained with lead-copper-tin alloys, a limit in the absolute effect for lead being shown at 6 amp./mm.² and 2.9% Pb (28% Cu; 69.2% Sn). The absolute effects at maximal current density decrease with increase of silver and lead in bronze or lead and tin in brass, and limiting values are again reached. Metallographic examinations of various lead-copper-tin anodes and cathodes show that lead and tin move to the anode (silver and copper move to the cathode). H. BURTON.

Electrochemical behaviour of gold and platinum in hydrochloric acid solution. G. GRUBE [with J. HELFER and G. LUZ] (Z. Elektrochem., 1929, 35, 703—709).—The following reduction potentials have been determined: ${}_0E_h$ of Au|AuCl₂' at 40° is 1.13±0.02 volt; at 60°, 1.04±0.03 volt; ${}_0E_h$ of AuCl₄'|AuCl₂' at 40°, 0.95±0.01 volt, at 60°, 0.96±0.02 volt; ${}_0E_h$ of Au|AuCl₄' at 40°, 1.01±0.01 volts, at 60°, 0.99±0.01 volt. Curves are given connecting the anode potentials with increasing current densities of gold and platinum anodes, for temperatures ranging between 20° and 80°, the former in solutions containing auric chloride and hydrochloric acid and the latter in hydrochloric acid solution. Similar curves are given for gold cathodes. Gold undergoes anodic dissolution at ϵ_h =+1.1 to +1.3 volts, the amount of polarisation depending on the acid content of the electrolyte and the temperature. It becomes passive at about ϵ_h 2.0 volts, the precise voltage again depending on the previous conditions.

H. T. S. BRITTON.

Electrolytic chlorination of benzene in methyl alcohol. P. JAYLES (Compt. rend., 1929, 189, 686—689).—A solution of 532 g. of benzene in 2 litres of methyl alcohol saturated with hydrochloric acid, electrolysed with no diaphragm at 15—20° for 28 hrs. by a current of 8 amp. (density 12 amp./dm.², total quantity 180 amp.-hrs.), gave a yield of 10.6% of chlorobenzene and 0.3% of benzene α -hexachloride, with current efficiency 10.5%. With a diaphragm, but otherwise similarly, 250 g. of benzene in 1.5 litres of a similar solution electrolysed for 38 hrs. by a current of 6 falling to 3 amp. (total quantity 141 amp.-hrs.) gave 35.3% of chlorobenzene and 0.9% of benzene α -hexachloride, with current efficiency 20%. The poor yield is due to the action of the chlorine on the methyl alcohol producing formaldehyde and carbon monoxide and dioxide. C. A. SILBERRAD.

Electrochemical oxidation of anthracene to anthraquinone. C. H. RASCH [with A. LOWY].—See B., 1929, 886.

Electrolysis of salts of organic acids. F. FICHTER (Z. Elektrochem., 1929, 35, 710—712).—A review. H. T. S. BRITTON.

Luminescence during electrolysis. N. HARVEY (J. Physical Chem., 1929, 33, 1456—1459; cf. Albrecht, A., 1928, 1307).—Luminescence occurs at the anode during the electrolysis of aminophthalic hydrazide, at fresh metallic surfaces of aluminium, zinc, cadmium, and tin when placed in a solution of aminophthalic hydrazide in 0.1N-sodium hydroxide, and at the surface of such solutions when played on by oxy-hydrogen or oxy-carbon monoxide flames. Luminescence also occurs when oxidising phosphorus is placed in a solution of aminophthalic hydrazide, and is connected with the formation and decomposition of ozone. It is suggested that this hydrazide is a test for active oxygen and that the term "galvanoluminescence" be used for luminescence associated with electrolysis. L. S. THEOBALD.

Quanta-yield and "Chemismus" in light reaction. J. PLOTNIKOV (J. Indian Chem. Soc., 1929, 6, 635—640).—Theoretical. It is suggested that the method of representation of the primary stage of photochemical action as $M+h\nu=M'$ (activated molecule) has neither a real nor a symbolical significance. The energy $h\nu$ of the light quantum may transform itself into one or more of the following: heat radiation, kinetic energy of the molecule, chemical energy, new radiations of lower energy, photo-electric effect, etc. The percentage ratio of the different forms of light energy distribution depends, not only on the reacting wave-length, but also on the "Chemismus," i.e., the combined effect of the chemical properties of each particular compound individually, the medium, the temperature, added catalysts, and other active and inactive components. In exceptional cases only, and under definite conditions of experiment, $h\nu$ may be converted approximately completely into any one of the above given forms of energy. M. S. BURR.

Mechanism of formation of chlorine hexoxide. M. BODENSTEIN and H. J. SCHUMACHER (Z. physikal. Chem., 1929, B, 5, 233—236; cf. A., 1925, ii, 991).—When a mixture of chlorine and ozone is exposed to light of such wave-length as to be absorbed by the ozone rather than by the chlorine, it is suggested that the following reactions occur: (1) $O_3+E=O_3^*$; (2) $O_3^*+Cl_2=ClO+ClO_2$; (3) $ClO_2+O_3=ClO_3+O_2$; (4) $ClO_3+O_3=ClO_2+2O_2$; (5a) $ClO_3+ClO_2=Cl_2+3O_2$; (5b) $ClO_3+ClO_3=Cl_2O_6$; (6) $ClO+ClO=Cl_2+O_2$. Since (5a) has a large heat of activation, it should become less important in comparison with (5b) as the temperature is lowered, and it is in fact found that under these conditions more chlorine hexoxide is formed; the yield is also increased by increasing the surface of the containing vessel. The formation of the hexoxide from a mixture of the dioxide with ozone takes place in the two stages (1) $ClO_2+O_3=ClO_3+O_2$, (2) as in (5b) above. The mechanism of the photochemical formation of the hexoxide from the dioxide alone is less certain, the most probable sequence being (1) $ClO_2+E=ClO_2^*$; (2) $ClO_2^*=ClO+O$; (3) $ClO_2+O=ClO_3$; then as (5a) and (5b) above. This would lead to a yield of

1 mol. of hexoxide per 2 einsteins, which is compatible with the observations.

F. L. USHER.

Mechanism of the photochemical decomposition of chlorine monoxide and of the chlorine-sensitised decomposition of ozone. H. J. SCHUMACHER and C. WAGNER (*Z. physikal. Chem.*, 1929, B, 5, 199—208; cf. Bodenstein and Kistiakowski, A., 1925, ii, 883).—The fact that the absorption of 1 light-quantum by a molecule of chlorine in the neighbourhood of 430μ gives rise to a direct dissociation into 2 atoms enables a simple mechanism of the chlorine-sensitised decomposition of chlorine monoxide by light of this wave-length to be formulated, on the assumption that ClO is formed as an intermediate product. The complete scheme is: (1) $\text{Cl}_2 + E = 2\text{Cl}$; (2) $\text{Cl} + \text{Cl}_2\text{O} = \text{Cl}_2 + \text{ClO}$; (3) $\text{ClO} + \text{ClO} = \text{Cl}_2 + \text{O}_2$. If it is further assumed that recombination of chlorine atoms takes place only at the surface of the containing vessel, but that reaction between the ClO molecules occurs at each collision; this mechanism leads to a quantum yield of 2, in agreement with observation. A minimum value of 58 kg.-cal. for the reaction $\text{Cl} + \text{O} = \text{ClO}$ is deduced. It is considered probable that ClO is also an intermediate product in the non-sensitised decomposition of chlorine monoxide by light. The lower quantum yield (1) observed when the decomposition takes place in carbon tetrachloride solution (cf. Bowen, J.C.S., 1923, 123, 1199) is attributed to the presence in the solvent of impurities which use up the chlorine atoms, which are then no longer available for reaction (2) above. The intermediate formation of ClO is further shown to explain the chlorine-sensitised photochemical decomposition of ozone.

F. L. USHER.

Photochemical formation of carbonyl chloride. V. Reaction between intensively dried gases. G. SCHULTZE (*Z. physikal. Chem.*, 1929, B, 5, 368—384).—The photochemical formation of carbonyl chloride from intensively dried chlorine and carbon monoxide at 1 atm. total pressure follows the same law as when moist gases are used, no appreciable retardation of the reaction being observed; the temperature coefficient from 15° to 50° is 0.9 per 10° . Under these conditions also oxygen retards the reaction on account of carbon dioxide formation, which appears to proceed more rapidly when the gases are intensively dried.

H. F. GILLBE.

Photochemical action of complex and intermittent light. A. BERTHOUD (*J. Chim. phys.*, 1929, 26, 435—446; cf. Padoa and Vita, A., 1928, 378, 1102).—The oxidation of potassium nitrite by iodine in aqueous solution has been studied in yellow and blue light separately and when mixed, and the effect shown to be purely additive, contrary to the statement of Padoa and Vita. It is considered that in cases where the law of additivity is not followed the causes are the same as those which give rise to departure from the Grothius-Draper law. In the bromination of cinnamic acid and the oxidation of hydriodic acid the effect of increasing the distance of the source of light, or of interposing solutions of nickel sulphate or of ammoniacal copper sulphate, is perfectly regular. The effect of intermittent light on the oxidation of hydriodic acid previously studied

(cf. A., 1928, 485) has been re-examined, and found to be in agreement with theory. The velocity maximum reported by Padoa and Vita was not observed.

F. L. USHER.

Photometric and spectrophotometric studies. VIII. Measurements with the König-Marten spectrophotometer. K. SCHAUM, L. HOCK, and W. DANNEFELSER (*Z. wiss. Phot.*, 1929, 27, 145—168).—A method is described for calibration of the König-Marten spectrophotometer whereby the number of measurements is so far reduced that investigation of changing systems may be effected. Study of the reaction between sodium hydroxide and sodium picrate indicates the existence of a light-sensitive reaction which results in the formation of ammonia, but a similar reaction has not been observed with *o*- or *p*-nitrophenol nor with 2:4- or 2:6-dinitrophenol.

H. F. GILLBE.

Photochemical studies. IX. Uranyl sulphate as sensitiser for the photochemical decomposition of oxalic and malonic acids. W. C. PIERCE (*J. Amer. Chem. Soc.*, 1929, 51, 2731—2738).—The temperature coefficient of the photolysis, in presence of uranyl sulphate, of oxalic acid is unity and of malonic acid 1.13. The rate of reaction is independent of the concentration of the uranyl sulphate when the latter is between 0.0025*M* and 0.01*M*, but depends on the concentration of malonic acid. In view of these results possible mechanisms for these reactions are discussed. Reaction may be due to the decomposition of an intermediate uranyl ion-acid complex, or to collisions of the second kind between activated uranyl ions and acid molecules.

S. K. TWEEDY.

Influence of [light] intensity on the velocity of photochemical reaction. A. K. BHATTACHARYA and N. R. DHAR (*J. Indian Chem. Soc.*, 1929, 6, 473—487; cf. A., 1926, 1216; 1928, 378, 1198).—Experiments have been made to test the conclusion that the velocity of a true photochemical reaction, of which the dark velocity is negligible, is proportional to the square root of the intensity of the incident radiation. By the use of accelerators or retarders it has been found possible to vary the velocity of the dark reactions between the following pairs of reagents: potassium oxalate and iodine, Rochelle salt and bromine, quinine sulphate and chromic acid, sodium formate and iodine. By increasing the velocity of the dark reaction, and exposing it to radiation which is only slightly absorbed by the reacting system, a truly photochemical reaction, proportional to the square root of the intensity of the incident radiation, or to the amount of energy absorbed, becomes directly proportional to the intensity of the incident radiation. On the other hand, a photochemical reaction directly proportional to the intensity of the incident radiation, or proportional to its square, can be made proportional to the square root of the intensity by decreasing the dark reaction velocity and increasing the photochemical velocity. On the basis of these results, the divergent data relating to the photochemical reaction between hydrogen and chlorine may be explained. Other known photochemical reactions are also shown to be in agreement with the authors' results. The

mechanism of photochemical reaction is discussed. It is pointed out that those photochemical reactions which obey Einstein's law of photochemical equivalence need not follow Draper's law, and conversely.

M. S. BURR.

Relation between the intensity [of incident radiation] and the velocity of the reaction between potassium oxalate and bromine in visible and infra-red radiations. A. K. BHATTACHARYA and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 523—527; cf. preceding abstract).—By retarding the dark reaction between potassium oxalate and bromine by potassium bromide, it has been shown that the relation between the velocity of reaction and the intensity of incident radiation, or the amount of energy absorbed, can be varied approximately from the fourth root to unity as the ratio of the thermal and photochemical velocities increases. Since the reaction is markedly accelerated by wave-lengths in the region of 7304 Å., which cannot atomise bromine molecules, it is concluded that, contrary to Berthoud's conception (A., 1924, ii, 327), the halogens are not, as a general rule, atomised by the absorption of radiation, but the molecules are activated and then react.

M. S. BURR.

Photosynthetic reaction. R. B. GORDON (Ohio J. Sci., 1929, 29, 131—132).—The scheme: $6C_{55}H_{70}O_6N_4Mg$ (chlorophyll-*b*) + $6H_2O \longrightarrow 6C_{55}H_{72}O_5N_4Mg$ (chlorophyll-*a*) + $6O_2$; $6C_{55}H_{72}O_5N_4Mg + 6CO_2 \longrightarrow 6C_{55}H_{70}O_6N_4Mg + C_6H_{12}O_6$ does not require the assumption of the intermediate formation of formaldehyde.

CHEMICAL ABSTRACTS.

Irradiated proteins. III. Velocity of coagulation by light of various proteins. M. SPIEGEL-ADOLF [in part with O. KRUMPEL and FERNAU] (Strahlenther., 1928, 29, 367—374; Chem. Zentr., 1929, i, 2898—2899).—The velocity of coagulation of proteins in the light of the mercury lamp is markedly affected by the presence of traces of electrolytes and by the age of the solution after electro-dialysis. The ultra-spectrograms of the freshly-dialysed and the aged serum-albumin solutions showed no difference. The effect of previous history is also observed in the denaturation of proteins by radium, and may depend on the autolytic production of traces of electrolytes, e.g., ammonia. Below a certain concentration the exposure necessary for visible change increases with the dilution; in more concentrated solutions the outer layers protect the inner. The coagulation of protein solutions by radium is arrested by salts. Salts also inhibit the appearance of turbidity when serum-albumin solutions are exposed to light. The velocity of coagulation diminishes in the order: pseudoglobulin, ovalbumin, serum-albumin.

A. A. ELDRIDGE.

Action of polarised light on photographic plates prepared from colloidal silver. A. COTTON (Compt. rend., 1929, 189, 599—603).—The Weigert phenomenon (A., 1928, 1103) is obtainable with plates prepared by dipping a plate coated with gelatin containing collargol into a solution of cupric bromide, chloride, or iodide. Such a plate exposed for 1 hr. to polarised light from an ordinary arc lamp can be

examined in the green light of mercury without fixing, or (especially an iodide plate) with shorter exposure after development. A chloride plate can also be rendered dichroic by exposure for 18 hrs. to polarised monochromatic light (366 mμ from a mercury arc with nickel oxide screen). The author prefers to attribute the phenomenon to anisotropy of distribution, rather than (Weigert's theory) to anisotropy of shape of the ultra-microscopic silver grains. The dichroism is, however, not affected by a magnetic field. This, whilst not negating the preferred explanation, does not support a suggested mechanism thereof.

C. A. SILBERRAD.

Asymmetric synthesis and the combined action of polarised light and a magnetic field on certain photographic plates. A. COTTON (Compt. rend., 1929, 189, 657—660).—The effect of circularly polarised light on plates prepared as previously described (*supra*) is nil, as it is also on plates prepared as described by Zoehrer and Coper (A., 1928, 573) if formaldehyde be the reducing agent. The effect described was, however, obtained equally whether reduction was effected by *lævo*- or *dextro*-tartrate of potassium and sodium, and is thus shown to be due to the incident light, which must in some way modify the micelles of silver according to the character of its polarisation. Further, the resultant rotatory power being the same if the plate be turned over, the arrangement assumed must resemble that of a screw which progresses as it turns. Lastly, it is pointed out that there has been no synthesis of active molecules, but merely production of an active arrangement of molecules in a medium. The action of a magnetic field previously described (*loc. cit.*) should produce double refraction in a sensitive layer of appreciable thickness, but even so there would be no production of active molecules.

Weak points in the crystal lattice and the speck concentration theory of photographic sensitivity. A. STEIGMANN (Z. wiss. Phot., 1929, 27, 76—78).—The close connexion between these two theories of photographic sensitivity is discussed.

J. W. GLASSETT.

Blackening surfaces of two slightly sensitive emulsions. H. ARENS and J. EGGERT (Z. wiss. Phot., 1929, 27, 79—84).—The blackening surfaces, obtained from the three-dimensional figure formed by plotting the blackening against the logarithms of the intensity and the time of exposure, have been determined for the Agfa diapositive and kine-positive emulsions. Over normal ranges of times of exposure the Schwarzschild exponent *p* remains approximately equal to unity, but at very low intensities and long times of exposure, as was previously noted with desensitised rapid emulsions, the value of *p* falls considerably and approaches zero.

J. W. GLASSETT.

Photochemistry of the silver halides. VIII. Silver values and the process of fixation with sodium sulphite. H. H. SCHMIDT and F. PRETSCHNER (Z. wiss. Phot., 1929, 27, 173—176).—Sodium sulphite does not dissolve the silver particles to any appreciable extent, and complexes formed in solution with the silver halides are very stable; the fixing solution may thus be readily washed out of the

gelatin film. About 85% of the silver in a silver chloride-gelatin emulsion may be extracted by 10% sodium sulphite solution, whilst the remainder is present possibly as atomic silver or as silver sulphide. Sodium sulphite appears to be the most satisfactory fixing agent yet studied. H. F. GILLBE.

Function of gelatin in photographic emulsions. S. E. SHEPPARD.—See B., 1929, 959.

Photographic sensitivity of photographic layers. F. WEIGERT.—See B., 1929, 959.

Theory of photographic light sensitivity. A. STEIGMANN.—See B., 1929, 959.

Mechanism of latent image formation. F. C. TOR.—See B., 1929, 960.

Oxidation of ferrous sulphate in aqueous solution by X-rays of different wave-lengths. Determination of Compton absorption. H. FRICKE (Physical Rev., 1928, [ii], 31, 1117; cf. this vol., 408).—The amount of ferrous sulphate oxidised by X-rays is independent of concentration (0.01—0.00004*N*). The change is considered to be due to a primary production of activated water molecules and it is calculated that for each activated water molecule approximately 8 ferrous ions are oxidised and 2.05 oxygen molecules are reduced; in gas-free solutions, 4.1 ferrous ions are oxidised. With solutions containing added salts of light elements, the amount of ferrous sulphate transformed is independent of wave-length when the mass coefficient of photoelectric absorption of the solution is equal to that of air, but when this coefficient is larger the effect of the shorter wave-lengths becomes increasingly smaller. This is due to the Compton effect, and for λ equal to 0.204 the mass coefficient of absorption due to the production of Compton electrons equals 0.0158, in agreement with Compton's theoretical value of 0.0156.

L. S. THEOBALD.

Ozonisation and interaction of oxygen with nitrogen under α -radiation. S. C. LIND and D. C. BARDWELL (J. Amer. Chem. Soc., 1929, 51, 2751—2758).—Ozonisation in oxygen flowing past an α -ray bulb is higher per ion pair the faster is the rate of flow and the lower is the intensity of ionisation (cf. D'Olieslager, Bull. Acad. Roy. Belg., 1925, 12, 719). The yield per ion pair is between 1.5 and 2—2.6 and probably could never exceed 3—4. The yield is controlled by secondary deozonisation caused, not by direct collision of α -particles and ozone molecules, but by a deozonising action of activated oxygen, either as ions or as atoms. Ozone, acidic nitrogen oxides, and nitrous oxide are formed when mixtures of nitrogen and oxygen flow past an α -ray bulb, and the amount of acidic oxides formed diminishes with decrease in the proportion of nitrogen in the mixture, although the total oxidising power towards potassium iodide is practically uninfluenced. This is explained on the basis of ionisation by collision of the second kind proceeding only in the direction $N_2^+ + O_2 = N_2 + O_2^+$.

S. K. TWEEDY.

Chemical effects of penetrating radium radiation. XVIII. Action on acetyl and benzoyl chlorides. A. KAILAN (Monatsh., 1929, 53 and 54,

153—164).—Prolonged action of penetrating radiation from radium on acetyl chloride causes no change in the density, but the specific conductivity increases. The number of mols. of acetyl chloride undergoing chemical change (m) is of the same order as the number of ion pairs (n) formed, and $m/n = 0.5$. In benzene or toluene solution the density increases only slightly, but the conductivity is unaltered; m/n varies from 0.3 to 0.9. Acetophenone or benzyl methyl ketone is not formed. The specific conductivity of benzoyl chloride is 30 times as high after irradiation, whilst the density is decreased slightly. Benzoic acid is produced and the ratio m/n varies from 0.4 to 1.6.

H. BURTON.

Chemical inertia of the rare gases. I. Action of helium on platinum. H. DAMIANOVICH (Gazetta, 1929, 59, 571—577).—By passing an electrical discharge through helium at low pressures between platinum electrodes a diminution of pressure corresponding with an absorption of helium was obtained. Simultaneously a loss in weight of the electrodes corresponded with the deposition in small vessels shielding the electrodes of traces of a substance notably different from platinum. This product contained helium in a fairly stable condition and in considerable amounts. The ratio of the amount of helium absorbed to the amount of platinum lost tended asymptotically to a maximum in the different experiments.

F. G. TRYHORN.

Preparation of dithiophosphates and some new dithiophosphates. P. NEOGI and M. G. GHOSH (J. Indian Chem. Soc., 1929, 6, 599—605).—Magnesium dithiophosphate, $Mg_3P_2S_4O_4 \cdot 2H_2O$, has been obtained by the action of powdered phosphorus pentasulphide on magnesium oxide suspended in ice-cold water. The soluble dithiophosphates, sodium, $Na_3PS_2O_2 \cdot 11H_2O$, potassium, $K_3PS_2O_2 \cdot 4H_2O$, ammonium, $(NH_4)_3PS_2O_2 \cdot 2H_2O$, and calcium, $Ca_3P_2S_4O_4 \cdot H_2O$, have been prepared by double decomposition of the corresponding hydroxides with the magnesium salt. The insoluble dithiophosphates of barium, $Ba_3P_2S_4O_4 \cdot 10H_2O$, zinc, $Zn_3P_2S_4O_4 \cdot H_2O$, thallous, $Tl_3P_2S_4O_4$ [?], and lead, $Pb_3P_2S_4O_4 \cdot 4H_2O$, have been prepared by precipitation of a soluble salt of the corresponding metal with sodium dithiophosphate. Manganese, mercuric, thorium, and lanthanum dithiophosphates were also obtained, but were decomposed on washing with ice-cold water. Dithiophosphates of bismuth, mercurous mercury, copper, silver, cobalt, nickel, cadmium, and ferrous iron were probably obtained, but decomposed within a few seconds of precipitation. Attempts to obtain the dithiophosphates of aluminium, zirconium, and molybdenum were unsuccessful.

M. S. BURR.

Formation of aminothiocyantes in aqueous solution. I. Simple amines with hexamethylenetetramine. R. RIPAN and L. DIMA (Bul. Soc. Stiinte Cluj, 1929, 4, 413—430; Chem. Zentr., 1929, i, 2993—2994).—Treatment of a solution of a metallic nitrate with alkali thiocyanate and aqueous hexamethylenetetramine (X) leads to the formation of two types of salt, $[MX_2(H_2O)_4](SCN)_6$ and $[MX_2(H_2O)_2](SCN)_2 \cdot 2H_2O$, respectively. The following compounds were prepared:

$[\text{CoX}(\text{H}_2\text{O})_4](\text{SCN})_2 \cdot \text{H}_2\text{O}$; $[\text{ZX}(\text{H}_2\text{O})_4](\text{SCN})_2$, where $\text{Z} = \text{Zn}$ or Co ; $[\text{CuX}_2](\text{SCN})_2 \cdot \text{H}_2\text{O}$; $[\text{CdX}(\text{H}_2\text{O})_2](\text{SCN})_2$; $[\text{NiX}_2(\text{C}_5\text{H}_5\text{N})_3](\text{SCN})_2 \cdot 7\text{H}_2\text{O}$; $[\text{NiX}(\text{H}_2\text{O})_3](\text{SCN})_2 \cdot 2\text{H}_2\text{O}$; $[\text{MnX}_2(\text{C}_5\text{H}_5\text{N})_2](\text{SCN})_2 \cdot 3\text{H}_2\text{O}$; $\text{Mn}(\text{SCN})_2 \cdot 2\text{X} \cdot 4\text{H}_2\text{O}$; $[\text{ZnX}(\text{C}_5\text{H}_5\text{N})_4](\text{SCN})_2 \cdot 3\text{H}_2\text{O}$; $[\text{ZnX}(\text{C}_5\text{H}_5\text{N})_3](\text{SCN})_2 \cdot 7\text{H}_2\text{O}$; $[\text{FeX}(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{H}_2\text{O}](\text{SCN})_2 \cdot 2\text{H}_2\text{O}$; $[\text{FeX}_3(\text{H}_2\text{O})_4](\text{SCN})_2$; $[\text{CuX}_2(\text{C}_5\text{H}_5\text{N})_2](\text{SCN})_2 \cdot 5\text{H}_2\text{O}$; $[\text{CdX}(\text{C}_5\text{H}_5\text{N})_4](\text{SCN})_2 \cdot 2\text{H}_2\text{O}$. A. A. ELDRIDGE.

Influence of cations of the alkali metals on the precipitation of zinc ferricyanide. F. ČUTA (Coll. Czech. Chem. Comm., 1929, 1, 538—550).—A study has been made of the precipitation of zinc ferricyanide under various experimental conditions with especial reference to its precipitation in the presence of alkali halides. Brown zinc ferricyanide, when precipitated from slightly acid (hydrochloric) solution of zinc chloride with potassium ferricyanide in the cold, has the composition $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$, whilst the yellow substance precipitated and washed in boiling solution is anhydrous. The transition point, determined dilatometrically, is 69—70°. The solubility of zinc ferricyanide at the ordinary temperature, determined iodometrically, is 1.24×10^{-4} mol. per litre. Precipitation from zinc chloride solution by lithium, sodium, potassium, and rubidium ferricyanides in the cold and in hot solution led to the conclusion that less of the alkali ferricyanide is occluded from the hot solution than in the cold and that the proportion of occluded alkali ferricyanide increases with the rise in the atomic weight of the alkali metal. With rubidium the precipitate formed has approximately the composition $\text{Rb}_3\text{Fe}(\text{CN})_6 \cdot 4\text{Zn}_3[\text{Fe}(\text{CN})_6]$. Zinc ferricyanide is very soluble in alkali chloride solutions, especially on warming. These solutions deposit crystalline compounds, which, for rubidium and potassium chlorides, have the composition $\text{Rb}_3[\text{Fe}(\text{CN})_6] \cdot \text{Zn}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_3\text{Fe}(\text{CN})_6 \cdot 4\text{Zn}_3[\text{Fe}(\text{CN})_6]$ (hydrated) respectively. The substance obtained from lithium chloride solutions consists of zinc ferricyanide containing a little lithium ferricyanide; the compounds deposited from sodium and ammonium chloride solutions have no simple composition. Warm water decomposes these double salts into the alkali ferricyanide and zinc ferricyanide, the reaction being reversible. Cadmium and zinc ferricyanides also dissolve in alkali halide solutions. A. I. VOGEL.

Additive compounds of mercuric cyanide and hydrated metallic azides. B. RICCA and F. PIRRONE (Gazzetta, 1929, 59, 564—568).—The compound $\text{Hg}(\text{CN})_2 \cdot \text{Na}_3\text{N}_3 \cdot 2\text{H}_2\text{O}$ was obtained as colourless crystals by mixing solutions of mercuric cyanide and sodium azide. By the action of suitable metallic salt solutions on a solution of this compound, the following products were obtained: $\text{Hg}(\text{CN})_2 \cdot \text{AgN}_3$; $\text{Hg}(\text{CN})_2 \cdot \text{Cu}(\text{N}_3)_2$; $\text{Hg}(\text{CN})_2 \cdot \text{Zn}(\text{N}_3)_2$; $\text{Hg}(\text{CN})_2 \cdot \text{Co}(\text{N}_3)_2$; and $\text{Hg}(\text{CN})_2 \cdot \text{Ni}(\text{N}_3)_2$. When heated these compounds decompose with ignition but without explosion. F. G. TRYHORN.

X-Ray examination of the effect of heat on aluminium hydroxide, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. H. P. ROOKSBY (Trans. Ceram. Soc., 1929, 28, 399—404).—

The composition of precipitated aluminium hydroxide and the changes occurring when crystalline $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is heated were studied by the X-ray powder method. The crystalline hydrate of alumina, prepared from sodium aluminate, has the composition $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and its X-ray pattern differs from that of the natural hydrate, gibbsite. Alumina precipitated from aluminium chloride solution with ammonia solution varies in composition and consists of a mixture of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, the latter being usually in excess. Crystalline $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ loses water when heated at 200°, and at 250° a definite hydrate, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, is formed; its X-ray pattern differs from that of diaspor, but is the same as those of certain bauxites. Between 250° and 500° the hydrate $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ loses water and γ -alumina is formed. At 1000° γ -alumina begins to change to corundum and at 1150° the change is complete. F. SALT.

Rhythmic crystallisation of alum in a metastable system. C. HRYNAKOVSKI (Bull. Soc. Amis Sci. Poznan, 1927, B, 49—52; Chem. Zentr., 1929, i, 2854).—The isothermal crystallisation of alum at the surface of separation of saturated and supersaturated solutions is described.

A. A. ELDRIDGE.

Europium halides. G. JANTSCH, H. ALBER, and H. GRUBITSCH (Monatsh., 1929, 53 and 54, 305—311).—Anhydrous europium chloride, m. p. $623 \pm 1^\circ$, is obtained by passing dry hydrogen chloride over the hydrated salt at 320°; it is not necessary to carry out the process under diminished pressure (cf. Kleinheksel and Kremers, A., 1928, 603). Reduction to europous chloride occurs readily in a current of hydrogen at about 500° (cf. Urbain and Bourion, A., 1912, ii, 162). Reduction of europium iodide (hydrated), alone or mixed with ammonium iodide, occurs with hydrogen iodide. Reduction of europium chloride with a mixture of hydrogen and hydrogen iodide gives mainly europous iodide. A cold solution of europous iodide is stable; the oxyiodide separates only after a long time. The electrical conductivity of the solution gradually diminishes on keeping. H. BURTON.

Order of fractionation of rare-earth bromates, and a search for illinium. J. K. MARSH (J.C.S., 1929, 2387—2389).—Discrepancies in the order of separation of the rare-earth bromates recorded by previous workers are ascribed to variations in the final temperatures of the cooled fractions. Below 20° the order of increasing solubility is found to be: samarium and europium, gadolinium, neodymium, terbium, praseodymium, dysprosium, holmium, yttrium. The possibility that illinium might be present in unusual abundance in Joachimsthal pitchblende has been disproved. J. A. V. BUTLER.

Germanium. I. R. SCHWARZ (Ber., 1929, 62, [B], 2477—2483).—Dehydration of germanium dioxide, obtained by hydrolysis of germanium tetrachloride, proceeds continuously at 10° until at tension 0 mm. a product remains containing 3.2% of water, corresponding with a compound, $5\text{GeO}_2 \cdot \text{H}_2\text{O}$. The product is not further dehydrated when preserved over phosphoric oxide. The water is regarded as firmly adsorbed and not chemically united, since more water is attracted when it is exposed to moist air.

Desiccation by the acetone method yields a similar product containing 3.3% of water. Topochemical decomposition of crystalline sodium germanate by acids does not afford a suitable method of examining the system $\text{GeO}_2\text{--H}_2\text{O}$, since the dioxide is appreciably soluble in water and dilute acids.

Thermal analysis of the system $\text{Li}_2\text{O--GeO}_2$ discloses the existence of *lithium metagermanate*, Li_2GeO_3 , m. p. 1239° , d_4^{25} 3.53, n 1.70, and *lithium orthogermanate*, Li_4GeO_4 , m. p. 1298° . *Sodium metagermanate*, m. p. 1078° , d_4^{25} 3.31, n 1.59, is similarly identified in the system $\text{Na}_2\text{O--GeO}_2$, but there is no evidence of the existence of the compound $\text{Na}_2\text{Ge}_2\text{O}_5$. Measurement of the degree of hydrolysis of sodium metagermanate in dilute aqueous solution shows that germanic is appreciably stronger than silicic acid. *Barium metagermanate*, obtained by precipitation from sodium metagermanate, has the composition $\text{BaGeO}_3 \cdot 5\text{H}_2\text{O}$ after remaining for some hours in contact with the solution. A basic copper salt, $2\text{CuO} \cdot \text{GeO}_2 \cdot \text{H}_2\text{O}$, is described.

H. WREN.

Various modifications of ammonia. L. TRONSTAD (Z. physikal. Chem., 1929, B, 5, 365—367).—The differences of behaviour exhibited by the two modifications of ammonia postulated by Baly and Duncan (J.C.S., 1922, 121, 1008) are, by analogy with recent observations on ortho- and para-hydrogen, not necessarily due to variations of reactivity, but to differences of specific heat and heat conductivity.

H. F. GILLBE.

Double sulphates of bismuth with alkali metals. II. Double sulphates of bismuth and ammonium. V. CAGLIOTI and L. MALOSI (Atti R. Accad. Lincei, 1929, [vi], 10, 97—100; cf. A., 1927, 951).—When ammonium sulphate solution is added to a concentrated solution of bismuth nitrate containing nitric acid in the proportions required to give the 1:1 and 1:3 bismuth ammonium double sulphates the compound $\text{Bi}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$ slowly crystallises out. In a study of the system $\text{Bi}_2(\text{SO}_4)_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ at 25° , however, this compound was not found. Only one perfectly anhydrous compound is formed, viz., $(\text{NH}_4)_3\text{Bi}(\text{SO}_4)_3$.

O. J. WALKER.

Action of certain dioxides on very dilute aqueous solutions of [potassium] permanganate. G. RAFIN (Compt. rend., 1929, 189, 699—701).—The powdered dioxides of manganese, lead, or tin decompose dilute solutions (of the order of 1 g. per litre) of potassium permanganate in mutually similar fashion, very rapidly at first, and then much more slowly. The rate is proportional to the weight of dioxide added, and is increased by rise in temperature; addition of acid increases, or of alkali decreases it. It further varies with the physical and chemical nature of the dioxide. As no evolution of gas occurs, the action is attributed to the oxide passing into colloidal solution. Calcined alumina, being completely insoluble, is without action.

C. A. SILBERRAD.

Preparation of a gram of rhenium. J. NODDACK and W. NODDACK (Z. anorg. Chem., 1929, 183, 353—375).—A gram of pure rhenium has been prepared from 660 kg. of Norwegian molybdenite having a rhenium content of $2\text{--}4 \times 10^{-6}$. Eight methods of

separating rhenium from molybdenum were tested. In the method adopted the greater part of the molybdenum was removed by five successive treatments with disodium hydrogen phosphate in nitric acid solution, whereby molybdenum is precipitated as ammonium phosphomolybdate and the whole of the rhenium remains in the solution. After each treatment the molybdenum and rhenium remaining in the solution were precipitated as sulphides by the addition of yellow ammonium sulphide, followed by acidification with sulphuric acid, and the sulphides dissolved in nitric acid. The final product was reduced in hydrogen at 1000° , and nickel, copper, cobalt, and iron were eliminated by fusion of the reduced substance with sodium hydroxide and sodium nitrate, followed by washing with water. The sulphide precipitated from the filtrate now contained 1.9% of rhenium. It was reduced by hydrogen and the easily volatile oxide Re_2O_5 was distilled by heating in a stream of oxygen at 150° . The rhenium content in the reduced product was 93.5%. The final purification was effected by repeated reductions of the sulphide with hydrogen at 1000° followed by distillation in oxygen at 150° . The total impurities in the metallic rhenium finally obtained are estimated to be less than 10^{-4} .

J. A. V. BUTLER.

Finely-divided iron of atomic dimensions. W. FRANKENBURGER and K. MAYRHOFER (Z. Elektrochem., 1929, 35, 590—600; cf. Mittasch and Frankenburg, this vol., 282).—Extremely fine particles of iron may be deposited on the walls of a vessel, cooled by immersion in either liquid nitrogen or a pentane cold bath, by condensation of iron vapour obtained from an iron spiral, which is heated by means of an electric current, in an atmosphere of nitrogen the pressure of which is of the order of 0.1—0.01 mm. No evidence could be obtained of any combination occurring between the nitrogen and the iron under the conditions of experiment, but it occurred with hydrogen, when that gas in either the perfectly dry or wet state was substituted for the nitrogen. The effect of the presence of water was to tend to lower the hydrogen content of the particles to that required by the formula FeH_2 .

H. T. S. BRITTON.

Stability of iron-complexes. W. FRANKE (Annalen, 1929, 475, 37—42).—An attempt has been made to obtain experimental evidence of the existence of the ferrous iron complexes regarded by Wieland and Franke (cf. this vol., 1398) as the cause of the iron activation phenomena in oxidation. Pyruvic acid and ferrous sulphate form a brown solution which has been examined colorimetrically under conditions of varying p_H value. The relative complex formation apparently diminishes with increasing p_H . Under the conditions of optimum acidity for autoxidation, p_H 4, about 70% of the complex present at p_H 6.5 remains, whilst at the p_H of a $M/4$ solution of the acid alone, i.e., 1.5, nearly 20% is left. In the same way the stability of ferric iron-acetic acid and ferric iron-glycollic acid complexes was also examined. The stability of the former decreases with increasing acidity, and more rapidly than that of the ferrous iron-pyruvic acid complex. The maximum colour

effect in the ferric iron-glycollic acid solution is at p_H 1.5 and decreases with both increasing and decreasing acidity. This behaviour is probably to be ascribed to the existence of a complex acid.

M. S. BURR.

Formation of a carbide, Fe_3C , by reduction of iron oxide with carbon monoxide at a lower temperature. W. GLUUD, K. V. OTTO, and H. RITTER (Ber., 1929, 62, [B], 2483—2485).—If ferric oxide is heated in a current of carbon monoxide at 275° , reduction to triferrous tetroxide rapidly occurs followed by simultaneous deposition of carbon and formation of carbide. If the percentage of carbon is plotted against the time, a graph is obtained of which the latter portions are rectilinear, showing that deposition of carbon is proportional to the time and independent of the nature and amount of substrate. Extrapolation of the curve indicates the existence of a carbide, Fe_3C . Confirmation is found by study of the volatilisation of carbide carbon in hydrogen at 275° , which is arrested at a point when the loss of carbon corresponds exactly with the formula Fe_3C . If a decarbonised product is again treated with carbon monoxide for a shorter period than is required for the production of the carbide, Fe_3C , and then with hydrogen, almost exactly only the newly-added carbon is removed. If, however, more carbon is deposited than corresponds with the compound Fe_3C , only so much of it is volatilised as corresponds with Fe_3C .

The experimental results of Fischer and Bahr (Ges. Abhand. Kenntn. Kohle, 8, 265) coincide with those of the authors, and, if their graphs are treated as indicated above, the existence of the carbide Fe_3C (instead of Fe_3C_4) is demonstrated.

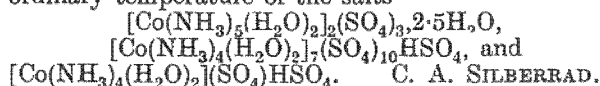
H. WREN.

Oxidation and reduction of silicates of iron by gases. B. BOGITCH (Compt. rend., 1929, 189, 581—583).—The method previously employed (this vol., 400) has been used to investigate the oxidising or reducing effects at 1300° of oxygen, nitrogen, carbon dioxide, carbon dioxide-monoxide mixtures, hydrogen, and illuminating gas (containing methane) on iron silicates. The colours of the silicates were found to vary in intensity with the percentage of iron (0.1—10%), but it is considered that they are made up of combinations in varying proportions of the two yellow and two blue silicates. There are no silicates corresponding with the oxides Fe_2O_3 or Fe_3O_4 , but one of the blue compounds corresponds with a suboxide.

J. GRANT.

Aquopentammino- and diaquatetrammino-cobaltic sulphates. F. JOB and L. O. TAO (Compt. rend., 1929, 189, 641—642).—Examination by Schreinemakers' method of a solution of aquopentamminocobaltic sulphate to which sulphuric acid has been added shows that for concentrations of 0—0.5 mol. of acid per litre the solid phase is the salt itself, and for 2—4.5 mols. of acid per litre it is $[Co(NH_3)_5H_2O](SO_4)_2 \cdot H_2O$ in the cold and at 56° $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$. For other concentrations the tie-lines are not concurrent, although nearly so for concentrations of 4.5—8.5 mols. of acid per litre. A similar method applied to diaquatetrammino-

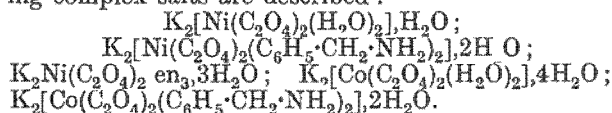
cobaltic sulphate indicates the formation at the ordinary temperature of the salts



New cobaltites of the spinel type. S. HOLGERS-SON and A. KARLSSON (Z. anorg. Chem., 1929, 183, 384—394).—A series of cobaltites of the type RO, Co_2O_3 (where R is Cu, Mg, Zn, Mn, Ni) has been prepared by mixing solutions of cobalt nitrate and the nitrate of the metal, evaporating to dryness, and heating the product to 800 — 850° . The X-ray spectra of the products, examined by the Debye-Scherrer method, were all of the spinel type. The unit cell contains eight molecules. The oxide Co_3O_4 prepared in three different ways gave similar spectra and is therefore CoO, Co_2O_3 . It is possible that some mixed crystal formation occurs; e.g., in manganese cobaltite the bivalent manganese may be partly replaced by bivalent cobalt and tervalent cobalt by tervalent manganese, giving $(Mn, Co)O, (Mn, Co)_2O_3$.

J. A. V. BUTLER.

Double salts. XVIII. Ammino-oxalates. G. SPACU and O. VOICU (Bul. Soc. Stiinte Cluj, 1928, 4, 154—164; Chem. Zentr., 1929, i, 3080).—The following complex salts are described:



A. A. ELDRIDGE.

Double salts. XIX. Amines of double bromides. G. SPACU and J. DICK (Bul. Soc. Stiinte Cluj, 1928, 4, 187—210; Chem. Zentr., 1929, i, 3080—3081).—Three groups of compounds were differentiated according to the solvents used in their preparation: (1) The compounds (Bzd=benzidine) $[MnBzd_6][SnBr_6] \cdot 2H_2O$; $[NiBzd_6][SnBr_6] \cdot 8$ or $4H_2O$; $[CoBzd_6][SnBr_6] \cdot 4H_2O$; (2) the compounds $[MnBzd_5(COMe_2)][SnBr_6] \cdot 2H_2O$; $[NiBzd_5(COMe_2)][SnBr_6] \cdot 8H_2O$; $[CoBzd_5(COMe_2)][SnBr_6] \cdot 6H_2O$; (3) $[NiBzd_5(C_6H_5N)][SnBr_6] \cdot 8H_2O$; $[MnBzd_5(C_6H_5N)][SnBr_5(OH)]$; $[CoBzd_5(C_6H_5N)][SnBr_5(OH)] \cdot 5H_2O$; $[NiBzd_5(C_6H_5N)][SnBr_5(OH)] \cdot 4H_2O$.

A. A. ELDRIDGE.

Applications and limits of emission spectrographic analysis. G. SCHEIBE (Z. angew. Chem., 1929, 42, 1017—1022).—The principles and practice of the quantitative spectrographic analysis of alloys are discussed, and the special value of this method for ascertaining the purity of metallic copper, lead, zinc, aluminium, and magnesium is emphasised.

H. F. HARWOOD.

Segregation of analysed samples. G. F. SMITH, L. V. HARDY, and E. L. GARD (Ind. Eng. Chem. [Anal.], 1929, 1, 228—230).—Mixtures of arsenic trioxide with mercuric oxide or potassium sulphate, ferric oxide and silica, and ferrosferro oxide and magnesia were filled into a brass column and subjected to mechanical jarring for 90 hrs.; in the last case the difference in density was artificially augmented by means of an electromagnet. Samples

taken from different parts of the column were then analysed. The results indicate that mixtures of materials of different densities if once mixed to uniformity following grinding to pass a 200-mesh sieve cannot be segregated by jarring or storage under vibration, irrespective of the actual densities of the components. Hence in referee analyses of supposedly identical samples if different analysts disagree the fault cannot be ascribed to segregation of the samples, provided that these have been ground to pass a 200-mesh sieve.

H. F. HARWOOD.

Extension of methods of gravimetric analysis.

L. MOSER (Monatsh., 1929, 53 and 54, 39—47).—A *résumé* of the following methods, which have been applied by the author and his co-workers to the determination of metals during the past 10 years. (1) Temporary hydrolysis (cf. A., 1923, ii, 438), (2) repression of hydrolysis (A., 1922, ii, 315), (3) formation of sparingly soluble adsorption compounds with tannic acid, (4) formation of complexes with sulphosalicylic acid (A., 1925, ii, 329), and (5) thermal dissociation of ammonium halides (A., 1926, 814; 1927, 435).

H. BURTON.

Determination of dilute aqueous solutions of "argyrol" by photographic nephelometry. F. RIMATTEI (J. Pharm. Chim., 1929, [viii], 10, 349—363).—An apparatus for the nephelometric determination by photographic means of very dilute colloidal solutions, *e.g.*, "argyrol," is described. Monochromatic light is used and is usually produced by passing a beam from an electric arc through a green filter (Wratten 74 E), exposures being made on Lumière orthochromatic plates. The determinations may be made either by the nephelometry of absorption or of diffusion, the latter being the more sensitive; both methods are considerably more accurate than visual nephelometry. The difference in the density of the deposit on the photographic plate, produced by light passing through solutions of different titre, can be easily seen by the unassisted eye, whereas no difference can be detected in the solutions themselves. A "metoquinone" developer is used, the time of development varying from 10 to 15 min. The results obtained by the more accurate nephelometric diffusion method agree with those obtained by weight to within 4%, using aqueous solutions of argyrol containing between 1 and 2 mg. per litre.

P. G. MARSHALL.

Measurement of hydrogen-ion concentration in unbuffered solutions. I. Adsorbent properties of platinised platinum. I. M. KOLTHOFF and T. KAMEDA (J. Amer. Chem. Soc., 1929, 51, 2888—2900).—The adsorption capabilities of platinised platinum in various salt solutions were investigated. In a hydrogen atmosphere the cation is adsorbed from a neutral salt solution and an equivalent amount of free acid is formed in the solution (cf. Frumkin and Donde, A., 1927, 1021). Zinc sulphate solutions, in an atmosphere of hydrogen, increased in acidity to an extent equivalent to the amount of zinc adsorbed by the platinum. Ammonium chloride likewise became slightly acid, but in oxygen such solutions became very distinctly acid, and the acidity increased the longer the oxygen

was passed. This is attributed to the formation of hexa-aquo-platinic acid, which reacts with the ammonium ions present: $\text{H}_2\text{Pt}(\text{OH})_6 + 2\text{NH}_4^+ \longrightarrow (\text{NH}_4)_2\text{Pt}(\text{OH})_6 + 2\text{H}^+$. Similar results were obtained with trimethylammonium and potassium chlorides. No acid adsorption from hydrochloric acid occurs in a hydrogen atmosphere, but in an oxygen atmosphere there is equivalent adsorption of hydrogen and chlorine ions. Sodium hydroxide is strongly adsorbed in a hydrogen atmosphere; maximum adsorption occurs at a concentration of 0.0007*N*. This adsorption is increased by addition of sodium chloride and in presence of large amounts of the latter the maximum disappears. In the presence of oxygen the hexa-aquo-platinic acid formed neutralises some of the alkali and only apparent adsorption of the latter, therefore, takes place.

S. K. TWEEDY.

Application of differential potentiometric titration to the determination of weak acids in dilute solution. B. L. CLARKE and L. A. WOOTEN (J. Physical Chem., 1929, 33, 1468—1480).—An apparatus and method for the differential potentiometric titration of weak acids in concentrations of the order 0.0004*N* are described. The theory of the method is developed and methods for determining the end-point are deduced. Data for 0.0004*N*-acetic acid titrated with 0.001*N*-barium hydroxide are given. No indication of a second end-point in the presence of quinuhydrone such as that observed by MacInnes and Jones (A., 1927, 35) has been observed.

L. S. THEOBALD.

Indicators. XVI. Sensitivity and stability of phthaleins and sulphonephthaleins to alkali. A. THIEL (Monatsh., 1929, 53 and 54, 1008—1013).—Comparison of a series of analogous phthaleins and sulphonephthaleins shows that the latter are the more stable at 18—20°; the velocity coefficients for decolorisation (cf. this vol., 445) are in the ratio of about 1000:1. In general, the sulpho-derivatives are also more sensitive; this is probably due to the existence of a secondary lactonic ion (cf. *loc. cit.*). The absorption maxima (lower limiting curve) of the sulphonephthaleins are about 5—10 μ greater than for the analogous phthaleins.

H. BURTON.

Determination of hydroxide and carbonate in solutions. J. LINDER.—Sec B., 1929, 895.

Determination of chlorine and carbonyl chloride in mixtures. S. PLETNEV (Lab. Praktika, 1928, 4, No. 2).—The free chlorine is determined in one sample with potassium iodide solution, and the total chlorine is determined in another sample which is collected in sodium hydroxide solution and treated with arsenious oxide and sodium carbonate.

CHEMICAL ABSTRACTS.

Micro-determination of iodine in organic material. J. F. REITH (Pharm. Weekblad, 1929, 66, 829—845; cf. this vol., 337).—The limits of sensitiveness in micro-determinations of free iodine in aqueous solutions are indicated for various conditions, and the effects of foreign ions are examined. The benzene method is not sufficiently sensitive for general use. Very good results are obtained by oxidation to iodate by means of bromine, and subsequent titration with thiosulphate of iodine liberated by the iodate;

the presence of bromides interferes seriously. Nitrites must first be destroyed by means of sodium azide. The colorimetric determination of a chloroform extract is very suitable for small quantities, but laborious, and much affected by foreign ions. A colorimetric method based on oxidation to iodate, liberation of iodine by this, and addition of starch is also very accurate. For determination of iodine in potable and other waters, 0.5–3 litres after addition of about 2 c.c. of saturated potassium hydroxide solution are evaporated to 50 c.c., filtered, and the solution evaporated to dryness with potassium nitrate. The residue is ignited, taken up in water, and the filtration, evaporation, and ignition are repeated. The white residue is extracted with alcohol, the extract evaporated, and iodine determined in the residue by the bromine oxidation method. The necessary precautions are described in detail. Methods of determination for soils are discussed. For urine, it is recommended to ignite the evaporation residue with a mixture of potassium nitrate and carbonate; nitrite is destroyed before the determination of iodine in the final mass.

S. I. LEVY.

Stabilised starch indicator. M. S. NICHOLS (*Ind. Eng. Chem. [Anal.]*, 1929, 1, 215).—50 G. of potato starch, mixed to a thin paste with 250 c.c. of cold water, are added gradually to 20 litres of boiling water, and the solution is boiled with continual stirring for a further 15 min. After partial cooling, 25 g. of salicylic acid are added, and dissolved by stirring. The reagent thus prepared keeps almost indefinitely, even although exposed to air, and is very sensitive. 2 C.c. are required for a 200 c.c. titration.

H. F. HARWOOD.

Titration of soluble iodides in colloidal silver iodide. R. B. SMITH and W. G. CHRISTIANSEN.—See B., 1929, 909.

Reduction reactions with calcium hydride. I. Rapid determination of sulphur in insoluble sulphates. W. F. CALDWELL with F. C. KRAUSKOPF (*J. Amer. Chem. Soc.*, 1929, 51, 2936–2942).—Heating with calcium carbide will not quantitatively reduce sulphates to sulphides. By observing certain precautions non-volatile sulphur compounds free from metals which form acid-insoluble sulphides may be quantitatively reduced to sulphides by fusion with calcium hydride; the sulphur may be determined in the fused mass by iodometric titration: $\text{MSO}_4 + 2\text{CaH}_2 = \text{MS} + 2\text{CaO} + 2\text{H}_2\text{O}$; $\text{MSO}_4 + 4\text{CaH}_2 = \text{MS} + 4\text{CaO} + 4\text{H}_2$; $\text{CaH}_2 \rightleftharpoons \text{Ca} + 2\text{H}$; $\text{MS} + \text{Ca} = \text{CaS} + \text{M}$. With regard to the last two of these equations it was found that fusion of sodium thiosulphate with calcium hydride yields some metallic sodium.

S. K. TWEEDY.

Potentiometric titration of sulphuric acid. S. LINDA and J. ETTINGER (*Rocz. Chem.*, 1929, 9, 504–522).—Sodium hydroxide solution and not acid should be used in the burette in the potentiometric titration of sulphuric acid, as the error due to carbon dioxide is thereby minimised, and the solution should be strongly agitated in order to reduce the time necessary for supervention of equilibrium. The disturbing influence of carbon dioxide is considerably less than in using calorimetric methods of titration, and the

potentiometric method has the further advantage of permitting the accurate titration of 0.01*N*-solutions. Identical results are obtained using calomel or zero electrodes. It is of importance that the alkali solution be standardised under the same temperature conditions as are applied during titration.

R. TRUSZKOWSKI.

New isomorphous series of fluorine compounds. H. CARON and L. VANBOCKSTAEL (*J. Pharm. Chim.*, 1929, [viii], 10, 301–308).—A more detailed account of work already reviewed (this vol., 526). Micro-methods for the detection of small quantities of sulphuric acid in hydrofluoric acid and of sulphuric acid and aluminium in hydrofluosilicic acid are given.

A. A. GOLDBERG.

Turbidimetric determination of sulphate in chromium-plating baths. L. E. STOUT and A. W. PETCHAFT.—See B., 1929, 901.

Determination of sulphate in chromic acid and in chromium-plating baths. H. H. WILLARD and R. SCHNEIDEWIND.—See B., 1929, 895.

Determination of small quantities of selenium in ores. E. T. ERICKSON.—See B., 1929, 899.

Rapid determination of nitrogen. F. M. WIENINGER and M. LINDEMANN.—See B., 1929, 939.

Micro-determination of nitrates and nitrites. K. WOLDICH (*Oesterr. Chem.-Ztg.*, 1929, 32, 183).—Devarda's reduction method has been adapted for micro-chemical purposes, a determination requiring only 20 min. A special form of apparatus used for the reduction and distillation is described, the ammonia formed being collected in 0.02*N*-sulphuric acid, and titrated with 0.02*N*-sodium hydroxide. In the determination of nitrates and nitrites in water, the total ammonia formed by reduction is collected in water and determined colorimetrically in the usual way, the nitrite being subsequently determined colorimetrically in a separate sample.

H. F. HARWOOD.

Molybdenum-blue method for micro-determination of phosphate and arsenate ions. G. DENIGES.—See B., 1929, 939.

Determination of carbon dioxide in gases containing acetylene. H. FRIEDRICH.—See B., 1929, 877.

Determination of alkalis in minerals by the interferometer. G. BURGER (*Monatsh.*, 1929, 53 and 54, 985–988).—Using Lowe's interferometer with distilled water as a comparison liquid the curve for the system 4% sodium chloride–4% potassium chloride has been determined. The minerals studied (potash feldspar, sanidine, natrolite, deep-sea earth, and kainite) are ignited with ammonium chloride and calcium carbonate, the calcium is removed as carbonate or oxalate, and the residue ignited repeatedly with small amounts of hydrochloric acid (if sulphate is present this is removed as barium sulphate). The dry residue is dissolved in water to a 4% solution and its composition determined gravimetrically and interferometrically. The two sets of values are in good agreement.

H. BURTON.

Determination of true sodium content of calcium carbonate intended for use in the Lawrence Smith method for alkalis. E. R. CALEY (*Ind. Eng. Chem. [Anal.]*, 1929, **1**, 191—192).—The usual method of weighing the residue obtained by extracting the calcium carbonate with water gives untrustworthy results. It is preferable to dissolve 2 g. of the material in hydrochloric acid, evaporate the solution to dryness, take up the residue with 2 to 3 c.c. of water, and determine the sodium directly by precipitation with magnesium uranyl acetate solution (this vol., 900). H. F. HARWOOD.

Determination of calcium and magnesium in aluminium containing other alloying elements. K. STEINHÄUSER.—See B., 1929, 899.

Rapid detection of the metals of group II: arsenic, antimony, tin, mercury, bismuth, lead, copper, and cadmium, by means of organic reagents. G. SENSI and S. SEGHEZZO (*Annali Chim. Appl.*, 1929, **19**, 392—396).—For separating the sulphides of the metals of group II, a reagent prepared by adding 10 g. of sodium hydroxide to 100 c.c. of 20% sodium sulphide solution free from sulphates is recommended. The separate metals may then be detected by organic reagents.

T. H. POPE.

Use of phenolic acids in the detection, separation, and determination of metals. I. Separation of 2A group (analytical) metals. P. N. DAS-GUPTA (*J. Indian Chem. Soc.*, 1929, **6**, 627—633).—The action of tannic, gallic, and 2:4-dihydroxybenzoic acids on the nitrates, chlorides, acetates, and sulphates of the metals of group 2A has been studied, and, as a result, alternative methods for the qualitative separation of the metals, using gallic acid when the metals are first precipitated as sulphides, and 2:4-dihydroxybenzoic acid when precipitation of sulphides is unnecessary, have been devised. These methods are based on the following experimental data: (1) in dilute nitric acid solution gallic acid completely precipitates bismuth, whilst lead, copper, and cadmium are unaffected; (2) in neutral or faintly acid (nitric) solution gallic acid and sodium acetate precipitate lead and copper completely; (3) in neutral or dilute nitric acid solution hydrogen peroxide and ammonia precipitate lead completely, whilst copper remains in solution; (4) in dilute nitric acid solution of the metals 2:4-dihydroxybenzoic acid precipitates completely mercury alone of all the group, the remaining metals then being separable by (1), (2), and (3).

M. S. BURR.

[Use of hexamethylenetetramine in] micro-chemical analysis. I. M. KORENMAN (*Pharm. Zentr.*, 1929, **70**, 709—714; cf. this vol., 286).—A 10% solution of hexamethylenetetramine yields crystalline precipitates with many phenols, such as resorcinol and pyrogallol; 0.0003 mg. of the latter may thus be detected under the microscope. A mixture of hexamethylenetetramine with an equimolecular amount of ammonium thiocyanate, potassium bromide, or potassium iodide forms a more sensitive reagent for the micro-chemical detection of the heavy metals than hexamethylenetetramine alone, the iodide mixture giving the best results. This

reagent is especially sensitive for antimony and bismuth, somewhat less so for mercury, lead, copper, cadmium, and tin. Oxidising agents must be absent, as these cause precipitation of periodides of hexamethylenetetramine. H. F. HARWOOD.

Detection of heavy metals by means of "dithizone" (diphenylthiocarbazon). H. FISCHER (*Z. angew. Chem.*, 1929, **42**, 1025—1027).—Dithizone forms coloured complex compounds with many metals, all of which, except manganese and the metals of the eighth group, belong to the sub-groups of the periodic classification. These compounds are characterised by insolubility in water and ammonia solution, and ready solubility in many organic solvents such as carbon tetrachloride and carbon disulphide (except in the case of the silver and gold compounds). Dithizone is soluble in carbon tetrachloride or disulphide to a bright green solution, and if a very dilute solution of the reagent be shaken with an almost neutral aqueous solution of one of the above metals a sharp change of colour in the non-aqueous layer results; 0.001 mg. of metal per c.c. of solution can thus be detected. The metal may be identified by comparison of the colour produced with that of known standards. Owing to the varying affinities of the metals for the reagent, it is possible to detect certain metals in the presence of others, e.g., silver in presence of all other metals except gold, mercury, and the platinum metals, and zinc in presence of iron, cobalt, and nickel. Addition of an excess of potassium cyanide to the aqueous solutions of the metals prevents the reaction with dithizone except in the case of lead and tin. Traces of cobalt in presence of nickel may be detected by the addition of a very dilute ammoniacal solution of the reagent to a similar solution of the two metals; if cobalt be present an intense reddish-violet coloration results. H. F. HARWOOD.

Determination of zinc. G. SPAOU and J. DICK (*Bul. Soc. Stiinte Cluj*, 1928, **4**, 177—181; *Chem. Zentr.*, 1929, **i**, 2905).—A modification (cf. A., 1928, 608) consists in weighing the complex salt $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2](\text{SCN})_2$ after washing it with alcohol or ether and drying it in a vacuum. A. A. ELDRIDGE.

Rapid gravimetric determination of cadmium as oxalate. J. DICK (*Z. anal. Chem.*, 1929, **78**, 414—417).—The cadmium is precipitated by the addition of a slight excess of ammonium oxalate to the cold, neutral solution of the sulphate or nitrate, followed by one third the volume of 95% alcohol. After 15 min. the precipitate is filtered, and washed successively with 50% alcohol, 95% alcohol, and ether. It is then dried for 2 to 3 min. in a vacuum and weighed as $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$. The method is not available in the presence of alkalis, chlorides, or large amounts of ammonium salts. H. F. HARWOOD.

Cadmium as reducing agent in chemical analysis. H. EGNER (*Svensk Kem. Tidskr.*, 1929, **41**, 240—243).—The use of electrolytically prepared cadmium as a reducing agent in quantitative analysis is advocated, and a suitable form of reductor is described. Cadmium offers the advantages over zinc that reduction takes place readily in the cold and is complete after a few minutes, and the quantity

of reducing agent required is much less than when zinc is used. The following procedure is recommended for the determination of phosphoric acid. The phosphoric acid is precipitated by Lorenz' method (A., 1901, ii, 278), filtered through a glass filter crucible, washed with a sulphuric acid solution of ammonium sulphate, and redissolved in ammonia. An excess of sulphuric acid is added, and the solution passed through the reductor and received in a solution containing iron alum and sulphuric and phosphoric acids which prevents reoxidation of the reduced molybdenum. The liquid is then titrated with permanganate solution which has been standardised against a pure phosphate. H. F. HARWOOD.

Micro-chemical reactions of salts of certain heavy metals. I. M. KORENMAN (Pharm. Zentr., 1929, 70, 693—695).—Meurice's test for cadmium with potassium bromide and brucine sulphate (A., 1926, 703) has been applied to the micro-chemical detection of that element, and the action of the reagents on other heavy metals investigated. Cadmium, mercury, bismuth, and antimony salts all yield characteristic crystalline precipitates under the microscope, and 0.0003—0.0005 mg. of these metals may thus be detected; metals which form insoluble sulphates or bromides and substances which react with brucine sulphate, such as nitrous acid or potassium hydroxide, must be absent. H. F. HARWOOD.

Rapid determination of lead. P. F. THOMPSON.—See B., 1929, 943.

Gravimetric macro- and micro-chemical determination of copper. G. SPACU and G. SUCIU (Z. anal. Chem., 1929, 78, 329—334).—The complex compound $[\text{HgI}_4](\text{Cu en}_2)$ which has been previously utilised for the determination of mercury (cf. this vol., 901) may also be employed in the determination of copper. The copper solution is neutralised with ethylenediamine, and a slight excess is added, together with 2 g. of ammonium thiocyanate and 2 g. of potassium iodide. The solution is heated to boiling and the copper precipitated with a hot, concentrated solution of potassium mercuric iodide. The whole is kept until cold, being frequently stirred meanwhile, the precipitate transferred to a Gooch crucible with a dilute solution of the precipitants, washed with alcohol and ether, and dried for 10 min. in a vacuum. The method gives excellent results in the micro-chemical determination of copper, as the final precipitate contains only 7.127% of the metal.

H. F. HARWOOD.

Potentiometric titration of mercurous ion with ammonium oxalate and its application to the determination of chromate. C. MAYR and G. BURGER (Monatsh., 1929, 53 and 54, 493—497).—Electrometric titration of mercurous nitrate with ammonium oxalate in presence of metallic mercury gives values which are in good agreement with the electrolytic measurements. The titration is not sharp if the acid or salt (e.g., sodium nitrate) concentrations are too large. For the determination of chromate the neutral chromate solution is treated with an excess of slightly acid mercurous nitrate solution, whereby the basic salt, $\text{HgO} \cdot 6\text{Hg}_2\text{CrO}_4$, is precipitated (cf. Fichter and Oesterheld, A., 1912, ii, 66). The

mercurous ions remaining in the filtrate are titrated potentiometrically. The results agree well with those determined gravimetrically. The application of the method to the determination of chromium in a chrome-iron mineral is described. H. BURTON.

Determination of mercuric iodide by iodate reactions. F. G. BROCKMAN.—See B., 1929, 909.

Titration of mercurial preparations used in pharmacy. A. WØHLK.—See B., 1929, 957.

Determination of aluminium in plants. I. Use of aurintricarboxylic acid for the colorimetric determination of aluminium. O. B. WINTER, W. E. THURN, and O. D. BIRD (J. Amer. Chem. Soc., 1929, 51, 2721—2731).—The colorimetric determination of aluminium by means of aurintricarboxylic acid has been modified so that samples containing 0.005—0.07 mg. of aluminium may be compared against the same standard, the amount of aluminium present being read directly from a curve. The maximum colour intensity is attained when the p_H of the solution is 4; the p_H is advantageously controlled by the use of ammonium acetate and chloride as buffers. The excess of the dye is preferably decolorised by addition of ammonium carbonate.

S. K. TWEEDY.

Detection of aluminium, iron, chromium, manganese, zinc, nickel, and cobalt with organic reagents. Application to systematic qualitative analysis. G. SENSI and R. TESTORI (Annali Chim. Appl., 1929, 19, 383—391).—The reactions of the following metals with organic reagents are summarised: Iron. Chromium: the salt is oxidised to chromate, which, in presence of free hydrochloric acid, gives a violet-red coloration with a reagent made by dissolving 2 g. of diphenylcarbazide in 10 g. of glacial acetic acid and making up to 200 c.c. with 90% alcohol. Aluminium: the solution is treated with one fifth of its volume of 1% alcoholic commercial alizarin solution, then made alkaline with ammonia, heated, and allowed to cool; formation of a red lake, insoluble in dilute acetic acid, indicates aluminium. Manganese: the very dilute solution is treated with alkali and a few drops of a solution of benzidine in 50% acetic acid; a deep blue coloration, disappearing on shaking and reappearing on addition of further reagent, and so on, indicates manganese. Cobalt gives a similar colour, but only in very concentrated solutions. Zinc: addition of alcoholic resorcinol solution to a slightly ammoniacal zinc solution gives a straw-yellow coloration, changing in turn to golden yellow, brownish-yellow, olive-green, and deep opaque blue, slowly in the cold, but rapidly on heating. Addition of a zinc salt solution to alkaline uric acid solution (5 g. of potassium hydroxide and 2 g. of uric acid in 100 c.c. of water) gives a gelatinous white precipitate which, after separation, turns greenish-blue in the air and light or when dusted with potassium persulphate. Nickel: Feigl's modification (Z. anal. Chem., 1925, 66, 176) of Tschugaev's reaction is recommended. Cobalt: the acid solution, mixed with ammonium thiocyanate solution, is treated with a few c.c. of concentrated aqueous ammonium acetate solution and then, drop by drop, with 5% tartaric acid solution, which destroys the red coloration of ferric

thiocyanate; when the liquid is then shaken with amyl alcohol, the latter becomes blue if cobalt is present. Nickel, cobalt, and zinc together may be detected by Feigl and Tustanowska's procedure (*Z. anal. Chem.*, 1925, 66, 177).
T. H. PORE.

Volumetric determination of manganese as dioxide. I. M. KOLTHOFF and E. B. SANDELL (*Ind. Eng. Chem. [Anal.]*, 1929, 1, 181—185).—Von Knorre's persulphate method for the determination of manganese has been examined, and the following procedure is recommended. To 50 c.c. of solution containing 20—100 mg. of manganese, and from 1 to 30 times this quantity of iron, sufficient sulphuric acid is added to make the acid concentration 0.5—1*N*. After addition of 3—4 g. of potassium persulphate the whole is boiled for 10 min.; if much iron is present a further quantity of persulphate must be added, and the boiling prolonged for 15 min. more. The liquid is filtered, the precipitate washed free from persulphate, and the manganese dioxide present determined either iodometrically or with ferrous sulphate and permanganate. To obtain correct results the figures obtained must be multiplied by an empirical factor, 1.024. A better method consists in substituting potassium bromate for the persulphate. In the absence of zinc or iron the results are from 3 to 5% low, but in the presence of an amount of iron from 1 to 70 times that of the manganese correct results are afforded by multiplying the percentages obtained by 1.01. Chromium, cobalt and small amounts of nickel, lead, and bismuth do not affect the method, but molybdenum, tungsten, and large quantities of phosphoric acid interfere. The method is not suitable for the determination of small amounts of manganese in presence of a large excess of iron, hence if a steel is under examination the iron should be previously removed by means of zinc oxide.

H. F. HARWOOD.

Diisonitrosoacetone as a sensitive reagent for ferrous iron. J. DUBSKY and M. KURAS (*Chem. Listy*, 1929, 23, 496).—1 c.c. of a 1% alcoholic solution of diisonitrosoacetone added to 5 c.c. of a ferrous salt solution gives an intense blue coloration with more concentrated solutions of iron, and a violet-rose coloration with very dilute ferrous salt solutions. The colour develops 2 hrs. after addition of the reagent to *N*/10⁵ solutions, and 3 hrs. after addition to *N*/10⁶ solutions. This reagent may also be used for the detection of ferric iron, which should previously be reduced by alkaline hydrazine. The reaction is weakened by the presence of manganese, and inhibited in the presence of nickel or cobalt. The reagent is more sensitive than those of Slavikov [Slawik] (*A.*, 1912, ii, 299) or of Tschugaev and Orelkin (*A.*, 1915, ii, 489), which are not sensitive to concentrations of less than *N*/10⁴ of ferrous iron.

R. TRUSZKOWSKI.

Sensitivity of some colorimetric reactions as determined by an electrochemical method. H. FRITZ (*Z. anal. Chem.*, 1929, 78, 418—427).—The sensitivity of various colorimetric reactions of iron, nickel, copper, and silver has been determined by an electrochemical method. A wire of the metal under examination was employed as anode in contact with

a revolving cylinder of paper soaked in a solution of the reagent; a thermionic valve and suitable circuit served to regulate the current. The method may be utilised conversely for the colorimetric determination of the strength of weak currents (0.01—5 millamp.) and for the determination of the periodicity of alternating currents of low frequencies.

H. F. HARWOOD.

Determination of cobalt by titration of [the precipitate of] potassium cobaltinitrite. A. A. VASSILIEV (*Z. anal. Chem.*, 1929, 78, 439—442).—The glass filter crucible containing the washed precipitate is placed in a 600-c.c. flask, and 250 c.c. of water, 50 c.c. of 0.1*N*-permanganate, and 35 c.c. of 50% sulphuric acid are added in the order named. The whole is heated at 50° for 30—40 min. until the precipitate is completely decomposed. The solution is cooled, 2—3 g. of potassium iodide are added, and the flask is stoppered and shaken until all the manganese dioxide has redissolved, when the liberated iodine is titrated with 0.1*N*-thiosulphate. The cobalt present may be calculated from the formula $\text{Co} = (\text{c.c. of } 0.1\text{N-permanganate} - \text{c.c. of } 0.1\text{N-thiosulphate}) \times 0.0005361$.

H. F. HARWOOD.

Colorimetric determination of cobalt. W. HEINZ (*Z. anal. Chem.*, 1929, 78, 427—439).—The various methods for the colorimetric determination of cobalt have been studied, a Duboscq colorimeter being employed for the purpose, and the results obtained are tabulated.

H. F. HARWOOD.

Phenylthiohydantoic acid for determination and separation of cobalt. V. CUVELIER (*Natuurwetensch. Tijds.*, 1929, 11, 131—150).—In order to test the accuracy of the determination, electrolytic cobalt, containing less than 0.02% of lead, was employed in a series of tests, which showed errors of the order of 0.1—0.2% on quantities of 1—200 mg. The precipitate is ignited at a temperature not exceeding 650°, the residue taken up in the minimum quantity of concentrated hydrochloric acid, sulphuric acid added, the whole dried carefully and then ignited, the temperature being raised gradually to 550°; the anhydrous sulphate is cooled and weighed with precautions to prevent access of moisture. The conclusion of Willard and Hall (*A.*, 1922, ii, 874, 875) that in the presence of iron small quantities of that metal are carried down in the precipitate is confirmed, but the amount may be reduced by boiling the finely divided precipitate with concentrated hydrochloric acid. A procedure is described whereby in the precipitation of 25 mg. of cobalt in presence of 1 g. of iron, only 1.4 mg. of the latter is left with the cobalt. Nickel if present is best separated by means of dimethylglyoxime before precipitation of cobalt; no other metals interfere if the procedure is suitably modified.

S. I. LEVY.

Cyanates. VI. Detection of cobalt. Test for cobalt in presence of iron. R. RİPAN (*Bul. Soc. Stiinte Cluj*, 1928, 4, 144—154; *Chem. Zentr.*, 1929, i, 2905).—The following salts have been prepared: $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_4](\text{NCO})_2$, $\text{K}_2[\text{Co}(\text{NCO})_4]$, $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2](\text{NCO})_2$, $[\text{Cu}(\text{C}_5\text{H}_7\text{N})_2](\text{NCO})_2$, $[\text{Cu}(\text{C}_{14}\text{H}_{15}\text{N})_2](\text{NCO})_2$, $\text{K}[\text{Cd}(\text{NCO})_3]$, $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_2](\text{NCO})_2$. The formation of the blue salt $\text{K}_2\text{Co}(\text{NCO})_4$ from a solution of a cobalt salt,

potassium cyanate, and a drop of acetic acid in presence of acetone permits the detection of 0.02 mg. of cobalt. Iron is precipitated by hot potassium cyanate solution, whilst cobalt remains dissolved if ammonium salts are present. A. A. ELDRIDGE.

Rapid potentiometric determination of nickel. T. HECZKO (Z. anal. Chem., 1929, 78, 325—329).—4 G. of citric or tartaric acid are added to the nickel solution, followed by an excess of ammonia and a little ammonium nitrate or chloride. The solution is then titrated with 0.4*N*-potassium cyanide, a silver wire immersed in a mixture of potassium iodide and silver nitrate solutions in an Emich filter tube being employed as comparison electrode. The solution must be kept well stirred during the titration. Iron and manganese do not influence the results, but trivalent chromium must be absent.

H. F. HARWOOD.

Determination of uranium and thorium with 8-hydroxyquinoline. F. HECHT and W. REICH-ROHRWIG (Monatsh., 1929, 53 and 54, 596—606).—When soluble uranyl salts are treated with 8-hydroxyquinoline in approximately neutral media the sparingly soluble, non-hygroscopic compound $\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2 \cdot \text{C}_9\text{H}_6\text{ON}$ is precipitated. The hydroxyquinoline content of this is determined by bromide-bromate titration and the metal as U_3O_8 by igniting with oxalic acid. In presence of acetic acid (5—10%) an excess of 8-hydroxyquinoline must be used to ensure complete precipitation of the complex. Any mineral acid present is removed by ammonium (not sodium) acetate. The method can be used for the determination of small amounts of uranium. The compound $\text{Th}(\text{C}_9\text{H}_6\text{ON})_4$ exists in hydrated and anhydrous forms. Dehydration is best carried out at 160—170°. Precipitation of the thorium complex is quantitative only in dilute acetic acid solution. The thorium solution is treated with sodium or ammonium acetate, neutralised to phenol-red, and treated at 50° with twice the calculated amount of 8-hydroxyquinoline in dilute acetic acid to give a concentration of 2—4% of acetic acid. The mixture is heated to 70° and then treated with 2*N*-sodium hydroxide to give an acetic acid concentration of 0.3%. The complex is filtered and washed with alcohol (water causes hydrolysis); the anhydrous form is obtained. The method can be used for the determination of small amounts. H. BURTON.

Thermoelectric temperature scales. W. F. ROESER (Bur. Stand. J. Res., 1929, 3, 343—358).—The differences between four thermoelectric temperature scales based on the m. p. of (a) antimony, silver, and gold, (b) zinc, antimony, silver, and gold, (c) zinc, aluminium, and copper, and (d) zinc, antimony, and copper as calibration points have been determined. The maximum difference between (a) and (b) was 0.1°, between (a) and (c) 0.2°, and between (a) and (d) 0.3°. Any one of these temperature scales is reproducible to within 0.1°. The f. p. of the copper-silver eutectic alloy (71.9% Ag) was found to be $779.4^\circ \pm 0.1^\circ$ and the difference between the m. p. of gold and copper $20^\circ \pm 0.1^\circ$. For calibrating thermocouples the following m. p. temperatures are recommended: copper

1083°, gold 1063°, silver 960.5°, aluminium (99.81%) 659.23°, antimony 630.52°, zinc 419.57°.

A. R. POWELL.

Laboratory apparatus for continuous circulation of liquids and vapours. R. S. HUGHES-DON, G. J. ROBERTSON, and J. READ (J.S.C.I., 1929, 48, 263—264t).—Descriptions are given, with figures, of two types of circulatory apparatus which have been used in work on the catalytic hydrogenation and dehydrogenation of piperitone, menthone, isomenthone, etc. (cf. J.C.S., 1923, 123, 2924). The substance, in a thin liquid film or as vapour, is brought repeatedly into contact with the catalyst at a known temperature and in the presence of any desired gaseous medium. The action is continuous and automatic.

Dropping bottle for reagents. P. FUCHS (Z. anal. Chem., 1929, 78, 411—414).—A simple form of dropping bottle, constructed on the siphon principle, is described. H. F. HARWOOD.

Accurate drop recorder. O. S. GIBBS (Science, 1929, 69, 649—650).—An apparatus giving an accuracy of 600 drops per c.c. is described (cf. J. Lab. Clin. Med., 1927, 12, 686). L. S. THEOBALD.

Simple method of providing a burette with an automatic zero adjustment. J. FISCH (Chem.-Ztg., 1929, 53, 799).—The lower part of the burette is clamped to the neck of a stock bottle provided with a stopper bored with three holes into which pass the stem of a stoppered funnel for filling, a soda-lime tube, and a long tube passing from the bottom of the bottle above the top of the burette and bent in the shape of an inverted U so that the other limb passes through a stopper in the top of the burette. This stopper also carries a short tube terminating in a length of rubber tubing; by applying gentle suction to the latter the liquid is drawn up from the bottle into the burette. A. R. POWELL.

Burette clamp and holder. M. HOLLINGSWORTH (Ind. Eng. Chem. [Anal.], 1929, 1, 233).—A new form of burette holder for use with burettes connected to stock bottles of volumetric solutions is described. H. F. HARWOOD.

Filtering vessel. J. MIRA (Z. anal. Chem., 1929, 78, 334—340).—The special flask described is provided with a narrow side tube containing an asbestos filtering mat, resting on a platinum spiral. After carrying out a precipitation in the flask the precipitate may be collected and washed by connecting the side tube to a filter-pump; the flask and precipitate are finally weighed together after being dried.

H. F. HARWOOD.

Thermostat to work off A.C. mains. J. HUME (J. Opt. Soc. Amer., 1929, 19, 158—161).—The thermostat and relay are figured and described. To expose a larger surface for heating or cooling the toluene tube is made zigzag; there is an improved method of adjustment to give the desired temperature. To reduce sparking in the thermoregulator a condenser of capacity 0.002 microfarad is inserted in parallel therewith. A thermostat thus constructed has worked continuously for 5 months with maximum variation of 0.001°. To construct a glass-fronted

metal tank pressure tubing is employed as a seal between the glass and the metal.

C. A. SILBERRAD.

Automatic regulation of temperatures up to 600° by means of a platinum resistance regulator. E. A. COOKE and J. C. SWALLOW (*J. Sci. Instr.*, 1929, 6, 287—293).—The change in temperature of the windings of a 15-ohm platinum wire, wound in the form of a resistance thermometer and forming one arm of a Wheatstone bridge in balance at the required temperature, destroys the balance and allows a current to operate a moving-coil relay which controls an additional heating current. A device to avoid sticking contacts is described. The accuracy is ± 0.1 at 350°, and ± 0.2 at 600°.

J. GRANT.

Simple air thermometer. J. E. SHRADER (*J. Opt. Soc. Amer.*, 1929, 19, 162—163).—The instrument employs a short scale. The bulb is protected by being placed inside a metal reservoir which may be filled with steam or ice-packed; the reservoir has also an opening into which a constant-pressure thermometer may be placed for a simultaneous experiment therewith.

C. A. SILBERRAD.

High vacuum technique. Effect of ionisation on pump speeds. C. T. KNIPP and P. C. LUDOLPH (*J. Opt. Soc. Amer.*, 1929, 19, 152—157).—Two new designs of mercury-vapour pumps with internal water cooling are figured and described, with details of their performance. It is also shown that the effect of ionisation of the air pumped is to increase the speed if the direction of flow of the electrons is with the air stream, or to decrease it if opposed thereto.

C. A. SILBERRAD.

Vacuum arc. V. M. ALBERS (*J. Opt. Soc. Amer.*, 1929, 19, 146—147).—The essential points of the apparatus are: (i) a rack and pinion inside the vacuum chamber, worked from outside, to move one electrode so as to strike the arc; (ii) a water-cooling arrangement for each electrode so as to prevent the material used to make the joints air-tight from melting, and (iii) the placing of the window through which the light of the arc passes at the end of a side tube so as to prevent its being affected by vapours from the arc. The apparatus was used to examine the spectrum of a beryllium arc in hydrogen.

C. A. SILBERRAD.

[Extractor.] JALADE.—See B., 1929, 909.

Simple micro-mol. wt. determination. K. SCHWARZ (*Monatsh.*, 1929, 53 and 54, 926—930).—The apparatus consists of two bulbs in series joined in \cap -formation to one bulb which can be evacuated at the top of the \cap . A substance of known mol. wt. (0.05 g.) is placed in the two-bulb arm and the substance (1—5 mg.) the mol. wt. of which is to be determined in the other. A solvent (benzene, carbon tetrachloride, or acetone) is added to both substances (5 and 0.5 c.c., respectively), the apparatus evacuated and sealed. After keeping for 24—48 hrs. at 15° (whereby solutions of equal vapour pressure result) the bulbs are cut off and the weights of solvent in each arm determined. The mol. wts. calculated from these weights of substances and solvents are in good agreement with the calculated values.

H. BURTON.

Study of hydration changes by a volume change method. H. A. NEVILLE and H. C. JONES (*Coll. Symp. Mon.*, 1928, 6, 309—318).—The dilatometer consists of a petrolatum mould enclosed in a bottle and covered with a layer of oil which can rise in a capillary tube. The method was applied to a study of the course of hydration of plaster of Paris, Portland cement, and gelatin. After elimination of thermal effects the curves obtained with the first two substances closely resemble that for the third, indicating that adsorption of water in hydration occurs in the gel structure, rather than by the formation of definite hydrates.

CHEMICAL ABSTRACTS.

Laboratory rectifying columns with non-siphoning bubbling-cap plates. J. H. BRUNN (*Ind. Eng. Chem. [Anal.]*, 1929, 1, 212—213).—Five types of laboratory rectifying columns for fractional distillation are described. Their construction obviates the possibility of liquid in the column siphoning back into the still when cold liquid is added to the latter, or if the distillation is interrupted. Test distillations using a 1:1 mixture of benzene and chloroform showed that the bulk of the latter could be recovered with a purity of 98—99%.

H. F. HARWOOD.

Device for maintaining a constant rate of flow of liquids [for leaching purposes]. J. D. SULLIVAN (*Ind. Eng. Chem. [Anal.]*, 1929, 1, 233).—A wooden float in the vessel containing the liquid carries a glass siphon which can be adjusted with reference to the liquid surface to any desired hydrostatic head; if a very small outflow be desired the end of the siphon under the liquid may be constricted. This device ensures delivery of a constant stream of solution at a uniform rate so long as any liquid remains in the container.

H. F. HARWOOD.

Crucibles with handles for use in ignitions and fusions. KÖNIG (*Chem.-Ztg.*, 1929, 53, 851).—The crucible is provided with a handle at one side for lifting with crucible tongs.

H. F. HARWOOD.

Combination electrochemical switchboard. W. F. MUNN (*Ind. Eng. Chem. [Anal.]*, 1929, 1, 208—209).—A type of laboratory switchboard adapted for use in a number of different fields of work is described.

H. F. HARWOOD.

Electrolytic [switch]board for determination of lead. O. W. HOLMES and D. P. MORGAN (*Ind. Eng. Chem. [Anal.]*, 1929, 1, 210—212).—A form of switchboard for use in the electrolytic determination of lead in low-grade tailings is described, and the procedure for carrying out the analysis is discussed. The same apparatus may also be employed for copper.

H. F. HARWOOD.

Simple thermionic valve (audion) potentiometer for p_H determinations. G. LJUNGGREN and R. ELMQVIST (*Svensk Kem. Tidskr.*, 1929, 41, 213—216; cf. A., 1922, ii, 307; 1925, ii, 1196).—A portable apparatus constructed entirely from standard "wireless" components is described. A compensation method is employed in making the determinations, the grid being first of all given zero potential by connexion with the cathode, and the strength of the anode current measured. The unknown *E.M.F.* is then introduced between grid and cathode, and by

means of a variable resistance the anode current is brought back to its former value, when the desired potential can be read directly on a millivoltmeter. An accuracy of ± 1 millivolt is attainable.

H. F. HARWOOD.

Simple thermionic valve apparatus for carrying out electrometric titrations. V. EHRHARDT (Chem. Fabr., 1929, 443—445, 455—457, 463—465).—A convenient form of apparatus for electrometric titrations is described in detail. The solution to be titrated forms one of a pair of half elements, the other being a calomel electrode. The latter is connected to the negative end of the valve filament circuit, the former to the grid. A milliammeter, reading from 0 to 0.5 milliamp., is inserted in the anode circuit, and shows a sudden deflexion when the end-point is reached. In order to increase the sensitivity, a constant current is passed through the instrument in the reverse direction by means of a 4-volt accumulator in series with an 800-ohm resistance, a 60-volt accumulator being used in the main anode circuit. A difference of only 0.2 volt in the titration potential at the end-point will then cause a difference of 0.44 milliamp.

in the anode current. An efficient mechanical stirrer is employed in the solution under titration. Electrometric titrations of ferrous salts in presence of hydrochloric acid invariably show an end-point several tenths of a c.c. before that obtained by titration in the ordinary way, and in the former case the end-point is perfectly sharp, even with 0.01*N*-permanganate. An advantage of the apparatus described above is that it permits the determination of one oxidising or reducing substance in the presence of another, e.g., chromic acid can be titrated in the presence of nitric acid or chlorates, which is not possible when the compensation method is employed. The presence of minute amounts of oxidising or reducing constituents in gases can also be detected if these latter are allowed to bubble through the liquid in the titration vessel. By employing a second electrode and suitable modification of the circuit the apparatus may also be employed for titrations where the end-point is denoted by the change in conductivity of the solution; examples of a number of typical curves obtained in this way are given.

H. F. HARWOOD.

Geochemistry.

Ions and electric currents in the upper atmosphere of the earth. E. O. HULBERT (Physical Rev., 1929, [ii], 34, 1167—1183).

Diurnal and nocturnal measurements of the quantity of ozone in the upper atmosphere. D. CHALONGE and F. W. P. GÖTZ (Compt. rend., 1929, 189, 704—706).—Measurements were made by day at Arosa (1856 m.), where the clearness of the sky allows of this all the year round, with the Chalonge spectrograph (A., 1928, 389), and also with that of Dobson (A., 1926, 493), and a constant difference in their indications was determined, those of the latter being uniformly lower. Measurements were also made with the former instrument on a series of consecutive days and nights. Coupling these results with those previously obtained it is concluded that in these latitudes the presence or absence of the sun has no effect on the thickness of the layer of ozone.

C. A. SILBERRAD.

Reaction-regulating power of sea-water. R. MARGARIA (Atti R. Accad. Lincei, 1929, [vi], 10, 123—128).—Titration curves show that, when acid or slightly alkaline, sea-water changes its reaction appreciably on addition of comparatively small proportions of acid or alkali. When, however, the p_H value reaches 10 or 11, the opposite is the case, but the buffering influence thus exhibited is only apparent, being due to the gradual precipitation of magnesium hydroxide. At p_H 7.4, this buffering power is only 0.0016, whereas that of blood-serum is 0.0206.

T. H. POPE.

Characteristics of the Red Sea with regard to the nitrogen cycle. G. BINI (Atti R. Accad. Lincei, 1929, [vi], 9, 1128—1133).—Determinations of nitrogen compounds in samples of water from various localities in the Red Sea have been made, and the

bearing of the analyses on the nitrogen cycle is discussed. The absence of nitrates is probably due to the large numbers of denitrifying bacteria in these waters and to the scarcity of inflowing fresh-water. The scanty vegetation in the Red Sea is a consequence of the absence of nitrates.

F. G. TRYHORN.

Phthalein reaction of certain mineral waters. O. BAUDISCH and H. VON EULER (Biochem. Z., 1929, 212, 149—157).—A discussion of the possible relationships between the geological sources of certain mineral waters and the state of combination of the iron which they contain.

W. MCCARTNEY.

Occurrence of silicates in natural waters. O. W. REES (Ind. Eng. Chem. [Anal.], 1929, 1, 200—201).—The silica obtained in the analysis of natural waters should be expressed as SiO_2 and reckoned with the acidic radicals, especially where the alkalis are not determined directly, but are calculated from the difference between the sum of the positive and negative ions present.

H. F. HARWOOD.

Spectrochemistry of Portuguese mineral waters. The water of Cambres. A. P. FORJAS (Compt. rend., 1929, 189, 703—704; cf. A., 1928, 730).—Spectrochemical examination of the mineral waters of Cambres (Corredoura) shows the presence of radium, lead, uranium, vanadium, zinc, copper, germanium, and probably thallium, in addition to sodium, potassium, lithium, calcium, strontium, barium, magnesium, aluminium, manganese, titanium, and iron also detected chemically.

C. A. SILBERRAD.

Iodine survey of Nebraska. W. H. ADOLPH and F. J. PROCHASKA (J. Amer. Med. Assoc., 1929, 92, 2158—2160).

CHEMICAL ABSTRACTS.

Iodine in S. Carolina. J. H. MITCHELL (Science, 1929, 69, 650—651).—The iodine content at depths of soil up to 18 in. from six different localities in S. Carolina has been determined together with that of 8 rivers and 36 foodstuffs and vegetables. A marked increase in iodine content from the surface to a depth of 18 in. is reported. L. S. THEOBALD.

Petrography of the Alpi Aurine and Vedrette Giganti regions. A. BIANCHI (Atti R. Accad. Lincei, 1929, [vi], 9, 1145—1150).

Petrographic studies on the zone of Canavese. Granite of Belmonte. H. FENOGLIO (Atti R. Accad. Lincei, 1929, [vi], 9, 1141—1145).—A microscopical and chemical examination has been made of granite from Belmonte. An analysis gave as the percentages of the main constituents: SiO_2 69.91, TiO_2 0.51, Al_2O_3 15.20, Fe_2O_3 3.24, CaO 1.21, Na_2O 2.77, K_2O 4.79; the percentages of TiO_2 , ZrO_2 , FeO , MnO , MgO , SrO , BaO , H_2O , F , and S (in all cases less than 1%) were determined. F. G. TRYHORN.

Nontronite from Chenlo, Pontevedra. I. P. PONDAL (Arq. Seminario Est. Galegos, 1929, 2, 9—14).—The composition of the nontronite of Pontevedra corresponds with the formula $\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The material readily absorbs and loses water as the atmospheric temperature and humidity vary, and the large number of varieties of the material described in the literature is ascribed to this phenomenon.

H. F. GILLBE.

Tungsten-bearing minerals of Galicia. I. Analysis of wolframites from La Brea, Corpiño, and Carboeiro, Pontevedra. I. P. PONDAL and J. VÁZQUEZ-GARRIGA (Arq. Seminario Est. Galegos, 1929, 3, 1—5).—Various tungsten ores from the neighbourhood of Lalin have been analysed; X-ray analysis indicates the presence of about 6% of tantalum pentoxide in the residue insoluble in hydrochloric acid.

H. F. GILLBE.

Pyrites of Galicia. Pyrites from La Mañoca, Santiago. I. P. PONDAL (Arg. Seminario Est. Galegos, 1929, 2, 3—5).—The iron pyrites from La Mañoca contains Fe 46.25, S 30.83, Cu 0.28, Ni 0.02, As 0.08, residue insoluble in hydrochloric acid 21.91%.

H. F. GILLBE.

Elastic properties of certain basic rocks and of their constituent minerals. L. H. ADAMS and R. E. GIBSON (Proc. Nat. Acad. Sci., 1929, 15, 713—724).—Determinations of the compressibility of labradorite, jadeite, grossularite, and almandite, and of diabase rocks, combined with others previously known, enable a list of compressibilities at various pressures of all important constituents of basic rocks to be given. The maximum velocity at which longitudinal elastic waves can travel through basaltic rocks is 7.4 km. per sec. It is concluded that the possible components of the earth below 60 km. and above the core are in the following ascending order of probability: holocrystalline basalt, eclogite, peridotite.

A. J. MEE.

Geologic relations of the diaspore and flint fire clays of Missouri. H. S. McQUEEN (J. Amer. Ceram. Soc., 1929, 12, 687—697).—The general geology of the north-central Ozark region of Missouri

is described. In this area, diaspore, flint clay, "burley" clay (a high-alumina clay containing oolites or "burls"), and plastic clay are found in inverted, cone-shaped, sink-hole type deposits in the Pennsylvanian sandstone. The diaspore clay is characterised by the presence of oolites composed of the mineral diaspore, which occur in a porous ground-mass of fine-grained clay. The origin and mode of occurrence of the clays are briefly discussed.

F. SALT.

Origin of nickel silicates at Webster, N.C. C. S. ROSS, E. V. SHANNON, and F. A. GONYER (Econ. Geol., 1928, 23, 528—552). CHEMICAL ABSTRACTS.

Mineralogical composition of tripoli of Kaluga district, U.S.S.R. E. M. YANISHEVSKI (Trans. Inst. Econ. Min. Met., Moscow, 1929, No. 42, 32—50).—The diatomaceous earth contains SiO_2 75.59—78.76, TiO_2 0.27—0.94, Al_2O_3 9.67—10.57, Fe_2O_3 3.15—3.74, CaO 0.69—1.05, MgO 1.46—1.72, K_2O 0.56—0.78, Na_2O 0.27—0.54, SO_3 0.11—0.29, loss on ignition 4.41—4.70%.

CHEMICAL ABSTRACTS.

Orthites of certain massive rocks of the Transbaikal region. B. Z. KOLENKO (Bull. Acad. Sci. Leningrad, 1929, 243—260).—Although in small quantities, orthite is of widespread occurrence in the massive rocks of the Transbaikal region. It is found mostly in rocks of acid character, particularly the granite-gneisses, but occasionally in basic rocks such as diorite and gabbro.

T. H. POPE.

Radioactive mineral deposits, and the present output of radium. R. THORGEUS (Svensk Kem. Tidskr., 1929, 41, 216—222).—The principal commercially exploitable deposits of radioactive minerals are briefly described, and statistics of radium production given.

H. F. HARWOOD.

Analysis of a peat profile. R. THIESSEN and R. C. JOHNSON (Ind. Eng. Chem. [Anal.], 1929, 1, 216—220).—The changes occurring in peat after deposition have been studied by carrying out a series of analyses of samples taken at intervals from a peat bed 10 ft. thick. The results show that the lignin and cellulose decrease with depth, and hence with age, whilst the humus and insoluble matter increase. Owing to the varying nature of the plants which gave rise to the peat at different periods it cannot be decided from the analyses whether the humus is mainly derived from lignin or from cellulose, but the former is probably the principal source. Details are given of the methods of analytical investigation employed.

H. F. HARWOOD.

Composition of peculiar clinkers found in snags after forest fires. D. T. ENGLIS and W. N. DAY (Science, 1929, 69, 605—606).—Analyses of samples from various localities show close agreement in composition and the view of their meteoritic origin is disproved.

L. S. THEOBALD.

Meteorite stone of Hinojo, Buenos Aires. E. H. DUCLOUX (Rev. fac. cienc. quim. La Plata, 1929, 5, [2], 1—7).—The material, d 3.407—3.411, contained: (magnetic fraction) insol. 41.525, $(\text{Al}, \text{Fe})_2\text{O}_3$ 23.885, CaO 0.266, MgO 9.000, NiO 1.489, Fe 21.482, Ni 0.908, Co 0.046, S 1.766—1.853, P

0.104%, Cr and Mn traces; (stony fraction) SiO_2 37.320, Al_2O_3 2.410—2.425, FeO 13.360, Fe_2O_3 17.975, MnO 0.652, Cr_2O_3 trace, NiO 1.516—1.614, CoO 0.046, CaO 2.475, MgO 21.787, K_2O 0.207, Na_2O 1.653, P_2O_5 0.480, H_2O and loss 0.119%.

CHEMICAL ABSTRACTS.

El Mocovi meteorite. E. H. DUCLOUX (Rev. fac. cienc. quim. La Plata, 1929, 5, [2], 9—12).—The meteorite, *d* 7.632—7.716, contained: siliceous material 0.210, Fe 93.135, Ni 5.680, Co 0.304, graphite 0.239, S 0.141, P 0.166, Cr trace, Mn 0.010, (Ir, Ru, Os) 0.035—0.087%.

CHEMICAL ABSTRACTS.

Cachari meteoric stone. E. H. DUCLOUX (Rev. fac. cienc. quim. La Plata, 1929, 5, [2], 13—23).—Average analytical results for the meteorite, *d* 3.13 (values for portions soluble or insoluble in hydrochloric acid are also recorded), are: loss on ignition 0.196, SiO_2 48.475, Al_2O_3 13.945, Fe_2O_3 0.237, FeO

19.803, MnO 0.783, Cr_2O_3 0.062, CoO none, TiO_2 0.072, CaO 8.617, MgO 6.840, K_2O 0.127, Na_2O 0.919, P_2O_5 0.058, SO_3 0.056%, NiO and S traces.

CHEMICAL ABSTRACTS.

Renca (San Luis) meteorite. E. H. DUCLOUX and F. PASTORE (Rev. fac. cienc. quim. La Plata, 1929, 5, [2], 111—120).—The meteorite, *d* 3.410, contained: SiO_2 38.392, Al_2O_3 3.030, FeO 20.802, MnO 0.778, Cr_2O_3 0.464, CaO 1.441, MgO 20.047, NiO 1.128, K_2O 0.577, Na_2O 2.367, SO_3 0.062, S 2.588, Fe 7.788, Ni 0.787, Co 0.048, P 0.008%. Analytical results for the magnetic and stony fractions, respectively, are also recorded.

CHEMICAL ABSTRACTS.

Elements in the sun. C. E. ST. JOHN (Proc. Nat. Acad. Sci., 1929, 15, 789—793).—The principles underlying the identification of lines in the solar spectrum are outlined. Fifty-eight elements have been found in the sun.

C. W. GIBBY.

Organic Chemistry.

Application of the Abbé number to the refractometric determination of the constitution of organic liquids. W. BIELENBERG (Z. angew. Chem., 1929, 42, 972—975).—Calculations of the Abbé number $v = (n_D - 1)/(n_F - n_C)$ for a large number of organic compounds show that, for all the different members of each type of compound, the Abbé numbers fall within a certain range which is specific for that type. Ethylenic linkings, especially when conjugated, depress the value of the Abbé number in a manner strictly parallel to the exaltation of the molecular refractivity. The Abbé number is therefore a function which throws considerable light on the constitution, state of unsaturation, relative position of double linkings, and the presence of conjugation in liquid organic compounds. It is particularly valuable, since it does not require knowledge of the mol. wt. In cases where the Abbé number assigns a compound to one of two or more classes then the values of n_D and $(n_F - n_C)$ are decisive. A. A. GOLDBERG.

Oxidation mechanisms of the paraffin hydrocarbons. G. EGLOFF, R. E. SCHAAD, and C. D. LOWRY, jun.—See B., 1929, 930.

Action of aluminium chloride on certain saturated aliphatic hydrocarbons. J. JURKIEWICZ and K. KLING (Przemysł Chem., 1929, 13, 481—492).—Above 370—390° anhydrous aluminium chloride has an exclusively disintegrating action on ethane, propane, and *n*- and *iso*-butane, the percentage decomposition increasing with the mol. wt. of the hydrocarbon. In the case of *isobutane*, an unidentified higher hydrocarbon was obtained at 245° in the presence of this catalyst.

R. TRUSZKOWSKI.

Action of carbonyl chloride on ethylenic linkings. I. Hydrocarbons and alcohols. E. PACE (Gazzetta, 1929, 59, 578—590).—Carbonyl chloride reacts in presence of aluminium chloride with ethylenic hydrocarbons or alcohols in toluene solution to give, respectively, β -chloro-acid chlorides, and

β -chlorolactones. The reaction is carried out by passing carbonyl chloride into the solution, kept generally at 35—40°, for 2—20 hrs. until the mixture is dark brown and no more gas is absorbed, and the product is isolated by fractional distillation or evaporation of the toluene after brief treatment with water. Ethylene yields β -chloropropionyl chloride, b. p. 144.5°, hydrolysed to the acid by boiling dilute hydrochloric acid. *iso*Amylene yields β -chloro- γ -methylvaleryl chloride, b. p. 168° (acid, m. p. 72—73°, yielding γ -methyl- Δ^5 -pentenoic acid, b. p. 212° in boiling alkaline solution, and β -hydroxy- γ -methylvaleric acid, m. p. 127°, with silver oxide). Styrene yields β -chloro- β -phenylpropionyl chloride, m. p. 139° (decomp.). Allyl alcohol yields β -chloro- γ -butyrolactone, m. p. 45°, which yields the β -hydroxy- γ -butyrolactone, m. p. 68°, converted into β - γ -dihydroxybutyric acid, a syrup. Cinnamyl alcohol yields β -chloro- α -phenyl- γ -butyrolactone, m. p. 105°, whence β -hydroxy- α -phenyl- γ -butyrolactone, m. p. 86°, and β - γ -dihydroxy- α -phenylbutyric acid (+ H_2O), m. p. 125°, are obtained. α -Terpineol yields a chlorolactone, m. p. 51°, which yields a hydroxylactone, m. p. 112°, converted into an unstable dihydroxy-acid which readily loses carbon dioxide and water to give α -terpineol.

R. K. CALLOW.

Isomerides of Δ^5 -pentene. I. Δ^5 -Pentene from γ -bromopentane and γ -pentanol. M. L. SHERRILL, B. OTTO, and L. W. PICKETT. II. Δ^5 -Pentene from β -bromopentane and β -pentanol. M. L. SHERRILL, C. BALDWIN, and D. HAAS (J. Amer. Chem. Soc., 1929, 51, 3023—3033, 3034—3041).—I. Diethylcarbinol is saturated with hydrogen bromide at -10° and then heated at 60° until reaction is complete. Repetition of this process until absorption is complete gives γ -bromopentane (I), b. p. 118.2—118.5°/760 mm., d_4^{20} 1.2170, n_D^{20} 1.44431. If phosphorus tribromide or hydrogen bromide under pressure is used during the preparation of I some β -bromopentane is also formed. Δ^5 -Pentene (II), b. p. 36.40 \pm 0.05°/760 mm., d_4^{20} 0.6503, n_D^{20} 1.37965, is

obtained from I by the action of methyl-alcoholic potassium hydroxide at 110—115°, and purified by distillation of its azeotropic mixture, b. p. $31.4 \pm 0.05^\circ/760$ mm., with methyl alcohol (corresponding mixture with ethyl alcohol, b. p. $34.7 \pm 0.05^\circ$), and subsequent removal of the alcohol by washing. Dehydration of diethylcarbinol with 60% sulphuric acid gives II and polymerised (?) material. Addition of hydrogen bromide to II in carbon tetrachloride solution affords 98% of I, but in acetic acid solution 22% of β -bromopentane (III) is formed in addition to 78% of I (cf. Lucas and Moyse, A., 1925, i, 770; Kharasch, Chem. Rev., 1928, 5, 571). Addition of bromine to II gives $\beta\gamma$ -dibromopentane. Exposure of II to sunlight or ultra-violet light causes transformation into an isomeric pentene, which differed slightly from II in physical properties; a specimen with n_D^{20} 1.37934 when treated with hydrogen bromide yielded a mixture of 15% of I and 85% of III (cf. Kharasch, *loc. cit.*). With bromine, $\beta\gamma$ -dibromopentane is formed.

II. β -Bromopentane is converted as above into a mixture of Δ^a - and Δ^b -pentenes, separable by fractional distillation of the azeotropic mixtures with methyl alcohol. The purest Δ^b -pentene (IV) obtained had b. p. $35.85 \pm 0.05^\circ/760$ mm., d_4^{20} 0.6481, n_D^{20} 1.37849 (azeotropic mixtures with methyl and ethyl alcohols, b. p. $30.85 \pm 0.05^\circ$ and $33.7 \pm 0.2^\circ/760$ mm.; bromine additive product, $\beta\gamma$ -dibromopentane). Addition of hydrogen bromide to IV in absence of solvent gives 93—95% of β -bromopentane, but in acetic acid only 85% is formed. Exposure of IV to ultra-violet light causes a slight increase in the value of n , but the hydrogen bromide addition is the same as with IV. The results indicate that II and IV are electronic and not geometrical isomerides (cf. Kharasch, *loc. cit.*), IV being the more stable. H. BURTON.

Isomerides of Δ^b -pentene. III. Ultra-violet absorption spectra of isomeric Δ^b -pentenes. E. P. CARR (J. Amer. Chem. Soc., 1929, 51, 3041—3053).—Absorption spectra measurements have been made of the isomeric Δ^b -pentenes described by Sherrill and others (preceding abstract), and it is found that they show marked differences, particularly in the region of the shallow absorption band in the near ultra-violet. The curve for the stable Δ^b -pentene (from β -bromopentane) is similar in form to that of trimethylethylene (Lüthy, A., 1924, ii, 80), but differs widely from that of the Δ^b -pentene obtained from γ -bromopentane. This difference indicates that the pentenes are not *cis-trans* isomerides (cf. Errera and Henri, A., 1925, ii, 1137). The effect of a polar solvent (acetic acid) on the spectra of the isomerides is to cause a shift in the absorption of one towards the other; hexane (non-polar) has no effect. After prolonged exposure of the unstable Δ^b -pentene to diffused light there is a shift in the absorption towards that of the stable isomeride; a more absorptive polymeride is also produced (cf. *loc. cit.*). After exposure to ultra-violet light the absorption spectrum of the unstable pentene shows a decided shift to the visible, whilst under identical conditions the stable form shows only a slight shift towards the curve of its isomeride. The more absorptive isomeride is the

stable form. The results agree with the interpretation of electronic isomerism as proposed by Kharasch (Chem. Rev., 1928, 5, 571). H. BURTON.

n-Hentriacontene. R. PUMMERER and H. KRANZ (Ber., 1929, 62, [B], 2620—2628).—In relationship to the constitution of caoutchouc and guttapercha, the examination has been made of a long-chain hydrocarbon with an isolated terminal ethylenic linking.

Myricyl alcohol, m. p. 88° , is prepared by hydrolysis of carnauba wax by alcoholic potassium hydroxide in presence of benzene. It appears to have the composition $C_{31}H_{63}\cdot OH$ and to be identical with melissyl alcohol from beeswax. The compound is converted by palmityl chloride at 130—180° into myricyl palmitate, m. p. 75° , which, when boiled under 13 mm. pressure and then distilled, yields palmitic acid and hentriacontene, b. p. $295^\circ/15$ mm., m. p. 64° (yield 70—80%). Analyses and determinations of mol. wt. in camphor and naphthalene indicate the composition $C_{31}H_{62}$, the somewhat high values in naphthalene giving no certain criterion of association. One % solutions in warm benzene after long preservation solidify to jellies which contain no macroscopic crystals, but show bright and dark zones between crossed Nicols. Gel formation, such as is observed with azo-dyes and soap solutions, can therefore take place in the absence of charged particles (ions) which have a directive action. The relative viscosity of hentriacontene is very small. The sudden increase in solubility in benzene and chloroform for a rise of 10° is comparable with that observed for guttapercha in ether. Catalytic hydrogenation of the unsaturated hydrocarbon in presence of cyclohexane and spongy platinum affords hentriacontane, m. p. 68° , also obtained from palmitone by Clemmensen's method. When titrated with bromine in chloroform or treated with iodine chloride, hentriacontene gives the expected analytical results. The dibromide, m. p. 62° , prepared in carbon disulphide, loses part of its bromine (as hydrogen bromide) when treated with alcohol under mild conditions, yielding a product which is stable towards boiling alcohol and does not contain ethoxyl, and hence probably has a different arrangement of the carbon skeleton. Alkaline permanganate is slowly decolorised by hentriacontene in benzene; ozone converts the hydrocarbon into formic acid and an acid, m. p. 88° . H. WREN.

Homogeneous oxidation of acetylene. G. B. KISTIAKOWSKY and S. LENHER.—See this vol., 1395.

Induced chlorination of ethylene dichloride. Effect of oxygen on the reaction between ethylene and chlorine. T. D. STEWART and D. M. SMITH (J. Amer. Chem. Soc., 1929, 51, 3082—3095).—When ethylene and chlorine are allowed to react in a darkened glass vessel (previously heated at 500° and evacuated at 1×10^{-6} mm.) there is a short inhibition period followed by an autocatalytic reaction. The rate of reaction becomes relatively high as soon as the liquid reaction products begin to separate on the walls of the vessel. The following reactions occur: (a) $C_2H_4 + Cl_2 = C_2H_4Cl_2$; (b) $C_2H_4Cl_2 + Cl_2 = C_2H_3Cl_3 + HCl$; reaction b is not independent of reaction a. In presence of oxygen the total reaction rate decreases and reaction b tends to be eliminated; a small amount of oxygen is

almost as effective as a large amount. Nitrogen and water have no apparent effect on the induced substitution reaction. On an evacuated surface trichloroethane vapour is a more powerful catalyst than ethylene dichloride vapour for the reaction between ethylene and chlorine. On an unevacuated surface neither of the vapours is an effective catalyst. In presence of oxygen, liquid ethylene dichloride is a better catalyst than liquid trichloroethane; both liquids are more effective in absence of oxygen. The evacuated surface is not a catalyst, but as evacuation of the walls progresses more hydrogen chloride appears in the reaction mixture. Oxygen and excess of chlorine reduce the specific reaction rate to the same minimum value. It is suggested that there is an induced additive reaction as well as an induced substitution reaction; the latter is induced by the former, the heat of reaction of ethylene dichloride being utilised to promote the formation of trichloroethane.

H. BURTON.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. IV. Decomposition and synthesis of methyl alcohol by catalysts composed of zinc and chromium oxides. D. S. CRYDER and P. K. FROLICH.—See B., 1929, 934.

Tests for methyl alcohol. H. LEFFMANN and C. C. PINES.—See B., 1929, 886.

Synthesis of phytol. F. G. FISCHER and K. LOWENBERG (Annalen, 1929, 475, 183—204; cf. A., 1928, 989).—Condensation of $\beta\zeta$ -dimethylundecan- κ -one (obtained by reduction of ψ -ionone with hydrogen and palladised calcium carbonate in alcohol under pressure) with sodamide and acetylene gives $\gamma\eta\lambda$ -trimethyl- Δ^a -dodecinen- γ -ol (I), b. p. 135.5—136.5°/10 mm., d_4^{25} 0.8464, n_D^{25} 1.4488 (acetate, b. p. 152—152.5°/11 mm.; silver salt). Reduction of this with either sodium and moist ether or a zinc-copper couple in aqueous alcohol does not give satisfactory results, but with hydrogen and palladised calcium carbonate it is smoothly converted into $\gamma\eta\lambda$ -trimethyl- Δ^a -dodecen- γ -ol, b. p. 140.5°/10 mm. This is converted by heating with acetic anhydride for 90 hrs. at 100° into the acetate, b. p. 146—153°/11 mm. (at higher temperatures loss of water occurs with the formation of a hydrocarbon, b. p. 120—121°/10 mm., which is probably tetrahydrofarnesene), which undergoes a monotropic change and is separated by fractionation after hydrolysis into tetrahydrofarnesene, the original carbinol, and $\gamma\eta\lambda$ -trimethyl- Δ^a -dodecen- α -ol (tetrahydrofarnesol), b. p. 152—156°/10 mm. (acetate, b. p. 164—167°/11 mm.). The last is converted by the action of phosphorus tribromide in light petroleum at -10° into its bromide, b. p. 153—159°/10 mm. (slight decomp.), which is condensed in the crude state with ethyl acetoacetate in the presence of alcoholic sodium ethoxide at -10°. Ketonic hydrolysis of the condensation product yields methyl $\delta\mu$ -trimethyl- Δ^a -tridecenyl ketone, b. p. 173.5—175°/10 mm. This is reduced by hydrogen and palladised calcium carbonate to methyl $\delta\mu$ -trimethyltridecyl ketone, b. p. 173.5—174°/10 mm., d_4^{25} 0.8337, n_D^{25} 1.4434, identical with the ketone $C_{18}H_{36}O$ obtained by chromic acid oxidation of phytol (*loc. cit.*; cf. Heilbron and Thompson, this

vol., 790). Further condensation of this ketone with acetylene gives $\gamma\eta\lambda\pi$ -tetramethyl- Δ^a -hexadecen- γ -ol, b. p. 183—185°/11 mm., which undergoes similar rearrangement with acetic anhydride to yield tetramethyl- Δ^a -hexadecen- α -ol (silver salt of hydrogen phthalate, m. p. 117—119°; semicarbazone of the pyruvate, m. p. 72—75°), identical in all respects with natural phytol, together with phytadiene, identical with a specimen obtained by the action of phthalic anhydride on natural phytol. Investigation of the action of 98% formic acid on the various acetylenic tertiary carbinols prepared above shows that with the reagent, contrary to Rupe and his collaborators (cf. A., 1926, 821), $\alpha\beta$ -unsaturated methyl ketones are the main products of this rearrangement. Thus I gives mainly (90% of product, 55—60% yield) methyl $\alpha\epsilon$ -trimethyl- Δ^a -decenyl ketone, b. p. 148—149°/10 mm., isolated as its semicarbazone, m. p. 133—134°, and reduced by hydrogen and palladised calcium carbonate to methyl $\alpha\epsilon$ -trimethyldecyl ketone, b. p. 139—140°/10 mm. (semicarbazone, m. p. 45.5—46.5°), which is further reduced by sodium and alcohol to $\gamma\eta\lambda$ -trimethyl- Δ^a -dodecan- β -ol, b. p. 146.8—147.2°/11 mm. By means of its hydrogen sulphite derivative a small yield of $\beta\zeta\kappa$ -trimethyl- Δ^a -dodecenaldehyde, b. p. 156—157°/11 mm., is isolated from the products of the rearrangement. Similarly, the main product of the rearrangement of α -cyclohexylethin- α -ol with formic acid is not cyclohexylideneacetaldehyde (Rupe, Messner, and Kambli, A., 1928, 640), but Δ^1 -cyclohexenyl methyl ketone (reduced to cyclohexyl methyl ketone). *iso*Phytane, $C_{20}H_{42}$, b. p. 171.8—172.6°/11 mm., d_4^{25} 0.7853, n_D^{25} 1.4382, obtained by heating tetrahydrogeranyl bromide with potassium in benzene, is identical with phytan ($\beta\zeta\lambda$ -tetramethylhexadecane). Acid hydrolysis of ethyl tetrahydrogeranylacetate yields $\delta\epsilon$ -dimethyldecoic acid, b. p. 159.5—160.5°/10 mm., d_4^{25} 0.8862, which may be identical with the acid, $C_{18}H_{36}O_2$, obtained by oxidation of the ketone obtained by degradation of phytol (Willstatter, Mayer, and Huni, A., 1911, i, 144). J. W. BAKER.

Reactions relating to carbohydrates and polysaccharides. XXIII. Synthesis and properties of hydroxyalkylidene-glycols and -glycerols. H. HIBBERT and M. S. WHELEN (J. Amer. Chem. Soc., 1929, 51, 3115—3123).—Condensation of acraldehyde with ethylene glycol containing one third of its weight of hydrogen chloride gives ethylene γ -chloropropylidene ether, b. p. 70—72°/18 mm., which when heated with powdered potassium hydroxide affords ethylene acrylidene ether, b. p. 115—116°. Oxidation of this with dilute potassium permanganate yields 41% of ethylene $\beta\gamma$ -dihydroxypropylidene ether (I), b. p. 136—138°/5 mm., n_D^{25} 1.4695. Acraldehyde and glycerol condense after several weeks at 50—60°, forming $\alpha\beta$ -acrylidene-glycerol, b. p. 204—215°, n_D^{25} 1.4638 (cf. Nef, A., 1905, i, 3), methylated to the corresponding γ -methyl ether, b. p. 70°/13 mm., n_D^{25} 1.4408. This methyl ether is hydrolysed by 75% alcohol containing 0.5% hydrochloric acid to glycerol α -methyl ether, and is oxidised by dilute permanganate, yielding $\alpha\beta$ -($\beta'\gamma'$ -dihydroxypropylidene)glycerol γ -methyl ether, b. p. 146°/1—2 mm., n_D^{25} 1.4680. Similar oxidation of $\alpha\beta$ -acrylidene-glycerol gives only a small amount of

$\alpha\beta$ -($\beta'\gamma'$ -dihydroxypropylidene)glycerol (II), b. p. 146°/0.15 mm., 1.4888. When I or II is heated at 110° in absence or presence of potassium hydroxide, sodium or aluminium ethoxide, or exposed to sunlight, polymerisation does not occur. H. BURTON.

Action of the oxides of nitrogen on ethers. I. O. I. EGOROVA (Ukraine Chem. J., 1929, 4, 193—198).—The action of nitrogen oxides on isoamyl ether yielded a mixture of isoamyl nitrite, isoamyl nitrate, and a small quantity of nitroisopentane. With diphenyl ether a mixture of *o*- and *p*-nitrodiphenyl ethers was obtained, identified by reduction to the amino-compounds (m. p. 42.7°—44.7° and 83°, respectively) with tin and hydrochloric acid.

M. ZVEGINTZOV.

"Ring contraction" during the formation of internal ethers (oxides) from glycols. A. FRANKÉ (Monatsh., 1929, 53 and 54, 577—587).—Hückel's criticism of the author's previous results (A., 1923, i, 530) on the formation of $\alpha\epsilon$ -oxides from $\omega\omega'$ -diols has led to an examination of the oxide obtained from decane- $\alpha\alpha$ -diol (I).

[With H. GOMOLKA.]—Reduction of ethyl sebacate with sodium and alcohol gives a 66.5% yield of I, b. p. 179°/11 mm., m. p. 71°, which on treatment with 50% sulphuric acid and distillation with superheated steam yields $\alpha\epsilon$ -oxidodecane (II), b. p. 198—202°, 84°/14 mm. Oxidation of II with dilute potassium permanganate gives mainly succinic and hexoic acids, together with small amounts of glutaric and valeric acids. When II is heated with fuming hydrobromic acid at 100° in a sealed tube $\alpha\epsilon$ -dibromodecane, b. p. 155°/13 mm., is formed. This is converted by way of the diacetate, b. p. 153°/9 mm. (37—42% yield), into decane- $\alpha\epsilon$ -diol, b. p. 157°/9 mm., readily convertible into II.

H. BURTON.

Reactions of the α -oxides with amino-acid esters. III. Aromatic amino-acids. IV. Aliphatic and homologous aromatic acids. A. I. KIPRIANOV (Ukraine Chem. J., 1929, 4, 215—229).—III. Trimethylethylene oxide and isobutylethylene oxide react with aromatic amino-acids much less readily than ethylene oxide; in the case of trimethylethylene oxide no reaction takes place, whilst isobutylethylene oxide gave the normal additive products of the oxide molecule to the amino-group. With methyl anthranilate, isobutylethylene oxide gave methyl alcohol as a by-product, thus indicating the probable formation and decomposition of the ϵ -lactone, which, however, could not be isolated.

IV. Two mols. of isobutylene oxide reacted with glycine ester to give the compound

$\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{N}\langle\begin{smallmatrix}\text{CH}_2-\text{CO} \\ \text{CH}_2-\text{CMe}_2\end{smallmatrix}\rangle\text{O}$, b. p. 162—167°/5 mm. If molar proportions of the reacting substances were used, ethyl *N*-hydroxyisobutylaminoacetate, b. p. 155—160°/4 mm., was obtained.

With excess of ethylene oxide ethyl phenylaminoacetate also gave the corresponding lactone,

$\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}\langle\begin{smallmatrix}\text{CHPh}\cdot\text{CO} \\ \text{CH}_2-\text{CH}\end{smallmatrix}\rangle\text{O}$, b. p. 239—240°/7 mm. With equimolecular amounts, no product could be isolated. isobutylene oxide and methyl phenylaminoacetate in equimolecular proportions yielded

methyl phenyl- β -hydroxyisobutylaminoacetate, b. p. 170—173°/7 mm. Under the same conditions, ethyl phenylaminoacetate did not react.

M. ZVEGINTZOV.

Synthesis and properties of phenyl- β -hydroxyethylaminoacetic acid. A. I. KIPRIANOV (Ukraine Chem. J., 1929, 4, 231—240; cf. preceding abstract).—The action of α -oxides on the esters of amino-acids decreases with increase of mol. wt., so that amino-carbinol acids cannot be obtained by this method from secondary amines.

Phenyl- β -hydroxyethylaminoacetolactone,

$\text{NPh}\langle\begin{smallmatrix}\text{CH}_2-\text{CH} \\ \text{CH}_2-\text{CO}_2\end{smallmatrix}\rangle\text{O}$ m. p. 75°, was obtained by the action of ethylene chlorohydrin on sodium phenylaminoacetate when boiled under reflux condenser for 9 hrs. or by the action of phenyl- β -hydroxyethylamine on sodium chloroacetate; a third method was to act on phenyl- β -hydroxyethylamine with ethyl chloroacetate. If bromoacetic acid was used, some hydroxyethyliminodiacetic acid, m. p. 167—169°, was obtained. The lactone on keeping in air for 2 months became transformed into a violet substance very similar in appearance and properties to dyes of the triphenylmethane series, such as crystal-violet.

M. ZVEGINTZOV.

Partial esterification of polyhydric alcohols. IX. True β -ether of glycerol. A. FAIRBOURNE (J.C.S., 1929, 2232—2235).—The author questions the structure of the " α "-monomethyl and " $\alpha\beta$ "-dimethyl ethers of glycerol, given by Gilchrist and Purves (A., 1926, 153), and shows that migration of the methoxyl radical does not take place as assumed by these workers. $\beta\gamma$ -Dichloro- α -methoxypropane, b. p. 158°, *d* 1.162, *n* 1.443, was prepared by the chlorination of methyl allyl ether in ethereal solution, and found to differ from $\alpha\gamma$ -dichloro- β -methoxypropane, which was assumed by Gilchrist and Purves to be identical with the ether described. Glycerol β -monomethyl ether was prepared by hydrolysis of $\alpha\gamma$ -dichloro- β -methoxypropane and its structure confirmed by converting it into its di-*p*-nitrobenzoate, m. p. 155°, as compared with m. p. 108° for the corresponding α -ether derivative.

J. W. PORTER.

Alkyl peroxides. IV. Ultra-violet absorption of hydrogen peroxide and of the simple mono- and di-alkyl peroxides in solution. E. LEDERLE and A. RIECHE (Ber., 1929, 62, [B], 2573—2585; cf. Rieche and Hitz, this vol., 1268).—Very marked analogy in refraction and absorption is found between ketones and peroxides. Replacement of hydrogen by methyl in the chromophore itself causes a stabilisation, whereas loosening of the electron sheath of the chromophore is induced by the stabilisation of directly vicinal octets. The "deformation energy" caused by the replacement of hydrogen by methyl amounts to about 2 kg.-cal. per mol. for the CO group. The following absorption graphs are recorded: hydrogen peroxide, methyl and ethyl hydrogen peroxides in water; dimethyl, methyl ethyl, and diethyl peroxides in hexane; hydrogen peroxide and methyl hydrogen peroxide in 1% sodium or potassium hydroxide; methyl hydrogen peroxide in heptane. The graphs are closely similar to one another and disclose the

existence of the ions O_2^- , MeO_2^- , and EtO_2^- . The polarity of peroxides is discussed and a constitutional formula is proposed in which the two oxygen nuclei are placed in a common electron sheath and the valency directions to the hydrogen atoms or alkyl groups deviate by about 70° from the O—O axis.

H. WREN.

Influence of poles and polar linkings on the course pursued by elimination reactions. IV. Olefinic degradation of sulphones. G. W. FENTON and C. K. INGOLD (J.C.S., 1929, 2338—2341; cf. A., 1927, 650; 1928, 1126).—The decomposition of a series of complex sulphones by means of potassium hydroxide has been studied, and the ease with which the different alkyl groups are eliminated as olefines compared with a corresponding series of quaternary ammonium hydroxides, in which the order of ease of elimination is as follows: β -phenylethyl > ethyl, isopropyl, *sec.*-butyl > *n*-propyl > *n*-amyl > *n*-hexyl, *n*-heptyl, *n*-octyl > *iso*amyl > *isobutyl*. In the case of phenyl- β -phenylethyl-, diethyl-, diisopropyl-, and di-*n*-propyl-sulphones the decomposition proceeds smoothly, the last-named compound decomposing with less ease than the first two. With di-*n*-butylsulphone the reaction is exceedingly slow, whilst no decomposition takes place with di-*n*-octyl-, diisomyl-, and diisobutyl-sulphones. Ethylisomyl- and ethyl-*n*-octyl-sulphone decompose normally. It is concluded that there is some point between diethyl- and di-*n*-octyl-sulphones such that all sulphones $\text{R}'_2\text{SO}_2$ containing radicals, R' , occurring to the left of this point undergo the degradation whilst all sulphones $\text{R}''_2\text{SO}_2$, containing radicals, R'' , occurring to the right of it do so only slightly or not at all. The same is assumed to be true also for unsymmetrical sulphones containing a group such as phenyl, incapable of elimination as an olefine. The reactions are also discussed in terms of the electronic theory of valency. Ethyl-*n*-propyl-sulphone, m. p. 25° , b. p. $142\text{--}143^\circ/23\text{ mm.}$, and silver propane- α -sulphinic are described. J. W. PORTER.

New petroleum by-product: octanesultone [lactone of γ -hydroxy-*n*-octanesulphonic acid]. E. L. BALDESCHWIELDER and H. A. CASSAR (J. Amer. Chem. Soc., 1929, 51, 2969—2978).—During the manufacture of higher secondary and tertiary alcohols, the permanent gases from the stills are scrubbed with sulphuric acid. Dilution of the acid extract affords a liquid of high sulphur content which on cooling and storing deposits a dark-coloured solid, from which, by extraction with benzene and precipitation with petroleum, is isolated γ -hydroxy-*n*-octanesulphono-

lactone (I) $\text{C}_8\text{H}_{11}\text{CH}(\text{O})\text{CH}_2\text{CH}_2\text{SO}_2$, m. p. 129° . This is readily volatile in steam, does not react with bromine, acetyl chloride, or phosphorus pentachloride, and when heated with dilute sulphuric acid under pressure or distilled over potassium hydroxide yields isomeric octenes and octenes. Treatment of I with hot barium or potassium hydroxide solution affords the barium, $\text{C}_{16}\text{H}_{32}\text{O}_7\text{S}_2\text{Ba}$ (II), or potassium (III) salts (corresponding silver salt) [designated type A]. Acidification of II regenerates I, whilst bromination of II or III in aqueous solution gives a bromo-octanesultone (type A) (IV), $\text{C}_8\text{H}_{15}\text{O}_3\text{BrS}$, m. p.

112° (corresponding chloro-derivative, m. p. 122.5°) also formed by bromination of the solutions of salts obtained from I and 20% solutions of sodium hydroxide, or sodium and potassium carbonates. Hydrolysis of IV with barium or potassium hydroxide solution and purification through the lead salt affords a bromohydroxyoctanesulphonic acid, m. p. 90° (barium and potassium salts). The bromine atom in IV is not removed by fusion with sodium hydroxide. When I is hydrolysed with an aqueous suspension of barium carbonate a mixture of barium salts (type B, syrupy, and type C, crystalline) is obtained. Bromination of type B in aqueous solution yields a bromo-octanesultone (type B), $\text{C}_8\text{H}_{15}\text{O}_3\text{BrS}$, m. p. 139° [corresponding chloro-derivative (V), m. p. 118.5°]. Hydrolysis of V first with barium hydroxide solution and then with dilute sulphuric acid gives an octenesultone, $\text{C}_8\text{H}_{14}\text{O}_3\text{S}$, m. p. 92.5° , brominated in aqueous alkaline solution to a bromo-octenesultone, $\text{C}_8\text{H}_{13}\text{O}_3\text{BrS}$, m. p. 117° . Bromination of the calcium salt of type C (isomeric with type A) gives bromo- and dibromo-octanes, whilst steam distillation of the acidified salt yields a mixture of octenes, b. p. mainly $113\text{--}115^\circ$.

H. BURTON.

Helicoidal configuration in long-chain compounds. W. B. LEE and P. J. VAN RYSELBERGE (J. Physical Chem., 1929, 33, 1543—1557; cf. A., 1928, 107).—On the assumption of Baeyer's strain theory, in so far as the $\alpha\epsilon$ and $\alpha\zeta$ positions favour ring formation, a new helicoidal configuration for long-chain compounds is derived and briefly discussed. The carbon atoms of a straight chain are assumed to lie on a helix drawn on a cylinder which has the dimensions calculated by Langmuir from Adam's measurements on unimolecular films and are regularly spaced round a helix the pitch of which brings the odd and even carbon atoms in two perpendicular planes. This model is shown to account for many physical and chemical properties, which are discussed in relation to it, especially the C_5 , C_{10} , C_{15} periodicity exhibited by many organic acids.

L. S. THEOBALD.

Racemisation. I. Racemisation of halogen-substituted esters. T. WAGNER-JAUREGG (Monatsh., 1929, 53 and 54, 791—812).—A more detailed account of work previously reviewed (this vol., 425).

H. BURTON.

Crotonic acid. F. KAUFLE. I. By-products in the preparation [with P. HALBIG]. II. Addition of water to crotonic acid [with G. BASEL] (Monatsh., 1929, 53 and 54, 119—126).—I. Oxidation of crotonaldehyde with oxygen (cf. Duchesne and Delépine, A., 1924, i, 1281), subsequent conversion of the product into sodium salts, and extraction with alcohol gives about 6% of sodium isocrotonate. When oxidation is carried out in presence of sodium carbonate at 25° , and the reaction mixture is acidified with hydrochloric acid, acetic and 8% of β -chloro- α -hydroxybutyric acid, m. p. $85\text{--}86^\circ$ [sodium salt, $\text{C}_8\text{H}_{13}\text{O}_6\text{Cl}_2\text{Na}$, m. p. 172° (decomp.)] (separated through the insoluble zinc salt), are formed as by-products. The last-named acid is formed by the action of hydrochloric acid on $\alpha\beta$ -oxido-butyric acid.

II. When crotonic acid is heated with 20% hydrochloric acid about 80% is converted into a mixture of

β -hydroxy- and -chloro-butyric acids. With boiling 5, 10, or 20% sulphuric acid hydration to β -hydroxy-butyric acid occurs to the extent of 53–70% after 4–5 days.

H. BURTON.

Conductivity titration of solutions of the sodium salts of the lower fatty acids. M. GEHRKE and H. H. WILLRATH (Z. angew. Chem., 1929, 42, 988–990).—Excess of 0.1*N*-hydrochloric acid is added to the solution and the acidified mixture titrated with 0.1*N*-sodium hydroxide. Two discontinuities are shown by the conductivity curves corresponding with the beginning and end of the neutralisation of the fatty acid. Formic acid is exceptional in that one angle is flattened and the position is obtained by extrapolation. The method is general for acids having dissociation constants for 0.1*N*-solution greater than 5×10^{-4} and also to phenols.

C. IRWIN.

Tetramethylmargaric acid and tetramethylstearic acid. R. KUHN and H. SUGINOMÉ (Helv. Chim. Acta, 1929, 12, 915–921).—*Phytol iodide* [α -iodo- γ - λ -tetramethylhexadecane], b. p. 152–154°/0.12–0.22 mm., d_4^{20} 1.0791, n_D^{20} 1.4799, is prepared by saturating dihydrophytol (Willstätter and Mayer, A., 1908, i, 383) at –20° with hydrogen iodide and heating at 70–80° in a sealed tube. The bromide, b. p. 147°/13 mm., 161°/0.8 mm. (cf. Karrer, Helfenstein, and Widmer, this vol., 49), is obtained by heating dihydrophytol with hydrobromic acid at 210–220°. Condensation of the bromide, or, preferably, the iodide, with ethyl potassiomalonate yields *ethyl phytymalonate*, b. p. 191–192°/0.34 mm., converted into *evp-tetramethylstearic acid*, b. p. 182°/0.22 mm. (*tribromoanilide*, m. p. 63.5–64.5°). Treatment of the Grignard compound of phytol bromide with carbon dioxide yields *80 μ -tetramethylmargaric acid*, b. p. 169°/0.21 mm. (*tribromoanilide*, m. p. 62–63°).

R. K. CALLOW.

Sulphonated oils. V. Preparation of ricinoleic acid sulphuric ester from ricinoleic and sulphuric acids. K. NISHIZAWA and M. SINOZAKI (J. Soc. Chem. Ind. Japan, 1929, 32, 779–783; cf. Grün and Woldenberg, A., 1909, i, 284).—Sulphuric acid (100 g.) is gradually added during 3 hrs. to a mixture of 100 g. of ricinoleic acid (prepared from castor oil) and 100 g. of ether with vigorous agitation at 25°, the mixture is preserved for 2 hrs.; when 150 g. of ether are used, the mixture is preserved for 2–17 hrs. The product is colourless and almost pure and is isolated by acidification or as potassium hydrogen salt.

K. KASHIMA.

Photochemical decomposition of lactic acid. G. R. BURNS (J. Amer. Chem. Soc., 1929, 51, 3165–3171).—Aqueous solutions of lactic acid are decomposed by radiations of wave-lengths shorter than 2500 Å. in absence of oxygen. The main products of the decomposition are carbon dioxide and alcohol; the alcohol formed is, however, 19% in excess of the amount required by the change $\text{CHMe}(\text{OH})\cdot\text{CO}_2\text{H} \rightarrow \text{EtOH} + \text{CO}_2$. Other products of the decomposition are carbon monoxide (3.82%; the percentages are of the total gaseous products), methane (2.18%), ethane (2.18%), and unsaturated hydrocarbons (probably ethylene, 0.89%). Acetaldehyde or hydrogen

peroxide could not be detected. The ratio between the energy absorbed and the carbon dioxide produced corresponds with a quantum yield of approximately 0.65. The results agree in the main with those of von Euler (A., 1911, ii, 452; 1912, ii, 407; 1913, ii, 544; cf. Scharz, Arch. ges. Physiol., 1918, 170, 650) but not with those of Neuberg (A., 1912, i, 314) and Baudisch (A., 1920, ii, 461).

H. BURTON.

Acetoacetic ester condensation. S. M. McELVAIN (J. Amer. Chem. Soc., 1929, 51, 3124–3130).—An excess of ethyl acetate, propionate, butyrate, or isobutyrate is treated with dry sodium ethoxide (0.5 mol.) and the reaction mixture distilled periodically to remove excess of ester and the alcohol formed during the reaction (the distillate is replaced with ester until no more alcohol distils). Refractometric determinations of the alcohol in the distillate, formed according to the reaction $2\text{CH}_3\text{R}\cdot\text{CO}_2\text{Et} + \text{NaOEt} \rightarrow \text{CH}_3\text{R}\cdot\text{C}(\text{ONa})\cdot\text{CR}\cdot\text{CO}_2\text{Et} + 2\text{EtOH}$, give values of 0.83, 0.97, 1.03, and 0.03 mol., respectively. The yields of isolated keto-esters are 0.34, 0.405, 0.38, and 0 mol., respectively. The results support Claisen's mechanism (A., 1887, 583), which is reversible (cf. Higley, A., 1907, i, 461). Scheibler and Marhenkel's postulate of an intermediate enolate as an essential step in the reaction (A., 1927, 1167) is not upheld by the results with ethyl isobutyrate. It is suggested that the ethyl acetate-sodium ethoxide additive product may undergo decomposition either into the original components or sodium hydroxide and keten acetal (cf. Scheibler and Marhenkel, *loc. cit.*).

H. BURTON.

Determination of configuration in the terpene series. IV. Optically active isopropylsuccinic acids. J. VON BRAUN and W. REINHARDT (Ber., 1929, 62, [B], 2585–2587; cf. this vol., 679).—*dl*-isopropylsuccinic acid, b. p. 130°/15 mm. with considerable conversion into the anhydride, readily obtained from ethyl α -bromoisovalerate and ethyl sodiomalonate, is resolved with some difficulty into its optical antipodes by treatment with strychnine in aqueous solution. The more sparingly soluble alkaloidal salt affords (+)-isopropylsuccinic acid, m. p. 87–88°, $[\alpha]_D^{20} +24.01^\circ$ in water (*anilide*, m. p. 200°, $[\alpha]_D^{20} -36.5^\circ$ in alcohol). The mother-liquors from the salt of the (+)-acid yield (–)-isopropylsuccinic acid, which, after purification through the ethyl ester, b. p. 119–120°, d_4^{20} 0.9896, $[\alpha]_D^{20} -15.05^\circ$, had m. p. 85–90°, $[\alpha]_D^{20} >21^\circ$ in water.

H. WREN.

Reduction of methyl esters of polymethylene-dicarboxylic acids with fifteen to twenty-one carbon atoms by sodium and alcohol. P. CHUIT and J. HAUSER (Helv. Chim. Acta, 1929, 12, 850–859).—Glycols, $\text{OH}\cdot(\text{CH}_2)_n\cdot\text{OH}$ ($n=15-21$), have been prepared by reduction of the methyl esters of the corresponding acids (A., 1926, 499) by sodium and alcohol. Certain of the related compounds (cf. this vol., 677) have been prepared in a greater state of purity by improved methods. α -Dicyanotridecane, m. p. 31–31.5°, b. p. 215–216° (from α -dibromotridecane), yields tridecane- α -dicarboxylic acid, the methyl ester of which is reduced to pentadecane α -diol, m. p. 87°, which yields with hydrobromic acid α -dibromopentadecane, m. p. 27.2–27.5°, b. p.

197°/2 mm. Hexadecane- $\alpha\pi$ -diol yields $\alpha\pi$ -dibromohexadecane, m. p. 56.2—56.7°. α -Bromohexadecan- π -ol, m. p. 53—54° (acetate, m. p. 31°, b. p. 192—194°/1 mm.), is obtained in poor yield from hexadecane- $\alpha\pi$ -diol monoacetate and hydrogen bromide. Heptadecane- $\alpha\pi$ -diol, m. p. 96—96.5°, yields $\alpha\pi$ -dibromohexadecane, m. p. 38—38.4°, b. p. 208—210°/3 mm. Octadecane- $\alpha\pi$ -diol, m. p. 98.6—99° (lit. 92°), b. p. 210—211°/2 mm., yields $\alpha\pi$ -dibromohexadecane, m. p. 63.5—64°, b. p. 205—207°, from which heptadecane- $\alpha\alpha\pi$ -tetracarboxylic acid, m. p. 89—90°, may be obtained by condensation with malonic acid. Nonadecane- $\alpha\pi$ -diol, m. p. 101°, b. p. 212—214°/1.5 mm., yields $\alpha\pi$ -dibromononadecane, m. p. 46.2—46.5°, b. p. 210—211°/1.5 mm. Octadecane- $\alpha\pi$ -dicarboxylic acid, m. p. 123° (lit. 124—125°) (methyl ester, m. p. 65.5—66°, b. p. 223—224°/2 mm.; ethyl ester, m. p. 54.5—55°, b. p. 230—232°/2 mm.), is obtained by the malonic ester method. Eicosane- $\alpha\pi$ -diol, m. p. 103°, b. p. 215—217°/1.5 mm., yields $\alpha\pi$ -dibromoeicosane, m. p. 67.4—68°, b. p. 220—222°/2 mm. Nonadecane- $\alpha\pi$ -dicarboxylic acid, m. p. 123° (lit. 111°, 117°) [methyl ester, m. p. 65.3—65.8° (lit. 56—57°), b. p. 225—228°/3 mm.; ethyl ester, m. p. 57°, b. p. 238—239°/3 mm.], is obtained by the malonic ester method. Heneicosane- $\alpha\pi$ -diol, m. p. 105—105.5°, b. p. 223—224°/1.5 mm. (acetate, m. p. 60°, b. p. 240°/3 mm.), yields $\alpha\pi$ -dibromoheneicosane, m. p. 52.5—53°, b. p. 226—228°/2.5 mm. The ascending curves of the m. p. of the series of odd- and even-numbered glycols cross after the fifteen-atom member and then rejoin at the eighteen-atom member to give a single curve. The ascending curves of the m. p. of the dibromo-compounds, at first roughly parallel, afterwards converge slightly. The even-numbered compounds in each case have the higher m.-p. curve. R. K. CALLOW.

Constitution of anhydrotricarballic acid. R. MALACHOWSKI (Bull. Acad. Polonaise, 1929, A, 265—273).—The structure $\begin{array}{c} \text{O}=\text{C} \\ \text{CO}-\text{CH}_2 \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ for

anhydrotricarballic acid, prepared in 87—91% yield by the action of acetic anhydride below 45° on tricarballic acid, is supported by the following experiments. α -Methyl *trans*-aconitate is reduced by platinum-black and hydrogen to α -methyl tricarballic acid, m. p. 111—112°, and is identical with the ester obtained by the alcoholysis of anhydrotricarballic acid with methyl alcohol or by the treatment of the anhydro-acid with diazomethane in ether with the formation of the α -methyl ester of the anhydro-acid, m. p. 59—60°, followed by ring fission of the latter by water. Tricarballic acid, m. p. 160—161°, is produced in 87% yield from *trans*-aconitic acid, platinum-black, and hydrogen, and, in a less pure form, by the reduction of *cis*-aconitic acid. Attempts to reduce the anhydrides of *cis*- and *trans*-aconitic acid dissolved in glacial acetic acid with platinum-black and hydrogen were unsuccessful. A. I. VOGEL.

Tests for acetone and aldehyde. H. LEFFMANN and C. C. PINES (Bull. Wagner Free Inst., 1929, 4, 39—41).—For the detection of formaldehyde in the presence of acetaldehyde the most satisfactory results are obtained with a solution of 1 g. of potassium guaiacolsulphonate in 10 c.c. of concentrated sulphuric

acid. Acetone can be readily detected in the presence of formaldehyde by adding a concentrated aqueous or preferably glycerol solution of sodium nitroprusside containing ethylamine to a dilute aqueous solution of the mixture; a red ring is formed at the contact zone.

A. I. VOGEL.

Manufacture of chloroacetaldehyde. I. G. FARBENIND. A.-G.—See B., 1929, 887.

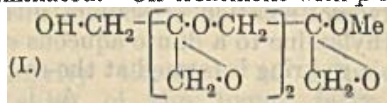
Bromination products of isobutaldehyde. R. DWORZAK and W. PRODINGER (Monatsh., 1929, 53 and 54, 588—595).—Bromination of isobutaldehyde (I) at about -10° and treatment of the product with alcohol affords α -bromoisobutaldehyde (II), its ethyl acetal (III), and bromopara-isobutaldehyde (IV) $\text{C}_{12}\text{H}_{23}\text{O}_3\text{Br}$, b. p. 128.5°/10 mm. Attempted depolymerisation of IV at 160° gives I, but II could not be isolated. Bromination of I at about 30° and treatment with alcohol gives small amounts of II, III, and IV; the main product is the compound (V), m. p. 82.5°, previously described (this vol., 1166). The stability of V towards various acidic reagents is noted, but hydrolysis with sodium hydrogen carbonate or alcoholic potassium hydroxide solution gives α -hydroxyisobutaldehyde. The substance is now considered to be $\alpha\alpha$ -tetrabromodiisobutyl ether (cf. Stepanov, A., 1927, 42; Hibbert, Perry, and Taylor, this vol., 791).

H. BURTON.

Thermal decomposition of acetone in the gaseous state. F. O. RICE and R. E. VOLLRATH (Proc. Nat. Acad. Sci., 1929, 15, 702—705; cf. Hinshelwood and Hutchison, A., 1926, 691).—When vaporised acetone was passed with nitrogen at a known rate through a quartz tube heated in an electric furnace, for every 100 mols. of acetone decomposed approximately 60 mols. of keten were recovered. Hence the primary reaction in the unimolecular decomposition of acetone is probably the separation of a molecule of methane and the formation of keten, which, at the high temperature, undergoes a bimolecular decomposition into ethylene and carbon monoxide. If this is the correct explanation, 100 mols. of decomposed acetone should give 100 mols. of methane, 30 mols. of ethylene, and 60 mols. of carbon monoxide. This result agrees fairly closely with that of Hinshelwood and Hutchison (*loc. cit.*) as far as the gases are concerned. A. J. MEE.

Polymerisation and condensation. V. Condensation products of methyleyclo-dihydroxyacetone. P. A. LEVENE and A. WALTY (J. Biol. Chem., 1929, 84, 39—47).—The action of methyl alcohol containing 0.5% of hydrogen chloride on commercial dihydroxyacetone led principally to the methyleycloacetal of dihydroxyacetone (cf. Fischer and Taube, A., 1927, 857). The mother-liquor was treated with ethyl acetate and the precipitated oil, after removal of solvents, was acetylated with acetic anhydride and pyridine, the product consisting of diacetoxyacetone and the acetate of the methyleycloacetal of dihydroxyacetone, m. p. 135°. The residue from the ethyl acetate mother-liquor was similarly acetylated, yielding acetyldihydroxyacetonylmethyleyclo-dihydroxyacetone, m. p. 184°. When heated at or slightly above its m. p., methyleyclo-dihydroxyacetone formed $[\text{di}(\text{dihydroxyacetonyl})]\text{methyleyclo-dihydroxyacetone}$.

oxyacetone (I), m. p. 300° (decomp.), methyl alcohol being eliminated. On treatment with *p*-nitrophenyl-



hydrazine acetate, the methylcycloacetal of dihydroxyacetone gave the *p*-nitrophenylosazone of dihydroxyacetone. The glucosidic linking in the acetal is thus so unstable as scarcely to modify the reactions of the compound in comparison with those of dihydroxyacetone itself.

C. R. HARRINGTON.

Detection and isolation of biochemically formed methylglyoxal as its dioxime. C. NEUBERG and M. SCHEUER (Monatsh., 1929, 53 and 54, 1031—1035).—A preparation of *B. lactis aerogenes* is washed successively with physiological saline and water, then dried, the dry material triturated with acetone, filtered, and washed with acetone and ether. The residual product produces methylglyoxal from magnesium hexosediphosphate solution (cf. this vol., 354, 722), which is isolated as the dioxime or the dioxime nickel salt.

H. BURTON.

Bial's reagent and various colour reactions of carbohydrates. H. SZANCER (Pharm. Zentr., 1929, 70, 663—665).—When 1 c.c. of a pentose solution is mixed with a few drops of alcoholic thymol solution, and an equal volume of concentrated sulphuric acid is poured down the side of the tube, a red ring is formed which gives its colour to the whole liquid on mixing; with dextrose or lactose a less intense red ring is obtained, but the colour disappears on mixing. With α -naphthol in place of thymol, pentoses, dextrose, and lactose give a dark blue ring with a lower brown ring, which is due to the α -naphthol alone; mixing yields a dark blue, turbid liquid, which deposits blue flocks on dilution with water. With β -naphthol, pentoses yield a deep violet ring, and, on mixing, a dirty grey, turbid liquid; dextrose or lactose gives an indistinct violet ring, disappearing on mixing. With vanillin, pentoses give a bright red ring and a deep red solution on mixing; dextrose yields a yellow ring and a red solution, gradually deepening, on mixing; lactose gives a bright yellow ring and a yellow mixed solution; eugenol gives a multicoloured ring due, not to furfuraldehyde, but to the eugenol itself.

T. H. POPE.

Bial's pentose reaction. H. SZANCER (Pharm. Zentr., 1929, 70, 645—646).—In its original form Bial's reaction for pentoses is characteristic of these sugars, hexo-aldehydes and the corresponding polysaccharides requiring a more protracted action of the hydrochloric acid present before giving the reaction. The lævulic acid formed in the latter case retards the reaction of orcinol with furfuraldehyde, but not that with hydroxymethylfurfuraldehyde. Mixtures of pentoses with other sugars sometimes fail to give the characteristic coloration. Thus, the presence of lævulose determines the production of a brown coloration, but aldoses cause no interference.

T. H. POPE.

Trinitrophenol as a sugar reagent. H. SZANCER (Pharm. Zentr., 1929, 70, 665—666).—Addition of ammonium sulphide to aqueous picric acid

solution results in the change, gradual in the cold but rapidly on heating, of the yellow colour to deep red, the picric acid being reduced to ammonium picramate. A similar reduction is effected by sugars with a free aldehydic or ketonic group when 2 c.c. of 0.5% aqueous picric acid solution is treated with 20—25 drops of 5% sodium or potassium hydroxide and 2 c.c. of the sugar solution of at least 0.20% concentration. The reaction is not applicable to the detection of sugar in urine, since normal urine is coloured deep red by neutral or faintly alkaline picric acid solutions owing to the presence of creatinine.

T. H. POPE.

Determination of reducing sugars with potassium mercuric iodide. P. FLEURY and J. MARQUE (J. Pharm. Chim., 1929, [viii], 10, 292—301).—The process of Baudouin and Lewin (A., 1927, 476) for the microdetermination of dextrose has been improved by the addition of barium sulphate, which greatly facilitates dissolution of the mercury, and the conditions under which it is specific have been determined. Under these conditions the presence of 2—3 parts of mannitol or 10 parts of sucrose with each part of dextrose does not appreciably affect the results. The method has been extended for the approximate determination of dextrose and mannitol in their mixtures.

A. A. GOLDBERG.

Oxidative decomposition of sugars. VI. Degradation of dextrose into C₃ chains by alkaline-earth carbonates. K. BERNHAUER and H. WOLF. VII. Transformation of methylglyoxal. K. BERNHAUER and B. GORLICH (Biochem. Z., 1929, 212, 443—451, 452—465).—VI. When dextrose is boiled with alkaline-earth carbonates, 12—13% is obtained as triose (methylglyoxal and glycerol) and the rest is present chiefly as a mixture of saccharic acids. Lactic acid is not formed.

VII. Methylglyoxal when treated with magnesium or calcium carbonates in aqueous suspension at the ordinary temperature is converted into a triose (probably glyceraldehyde) and is then partly condensed into hexose. The formation of lactic acid from methylglyoxal is discussed (cf. this vol., 297, 543).

P. W. CLUTTERBUCK.

Formation of glucosazone. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1929, 51, 3161—3165).—When dextrose is treated with an equimolecular quantity of phenylhydrazine in presence of alcohol and 75% acetic acid, and the mixture kept for some days, a 63% yield (on phenylhydrazine used) of glucosazone is obtained instead of the phenylhydrazone described by Behrend and Lohr (A., 1908, i, 765). In dilute acetic acid solution a 62.5% yield of the osazone results. Similar results are given by lævulose. The phenylhydrazones of dextrose (Fischer, A., 1887, 567; Skraup, A., 1889, 1130) and lævulose (Landrieu, A., 1906, ii, 270) undergo conversion into glucosazone when solutions in dilute acetic acid are kept for some days. The change probably involves intramolecular oxidation and reduction. Mannosephenylhydrazone is stable under the same conditions.

H. BURTON.

Glucosazone reaction. N. TAKETOMI and K. MIURA (J. Soc. Chem. Ind. Japan, 1929, 32, 776—779).

—For obtaining a maximum yield of glucosazone by Fischer's method, the ratio of phenylhydrazine hydrochloride and crystallised sodium acetate should be 1:2.7—2.8. The yield of osazone increases with increasing amount of the reagents up to about 3.2 g. of the hydrochloride in 20 c.c. of water. The duration of heating influences greatly the yield of osazone. The reaction is not completed within less than 3 hrs., but beyond this decomposition takes place.

K. KASHIMA.

Fluorine derivatives of carbohydrates. B. HELFERICH and R. GOOTZ (Ber., 1929, 62, [B], 2505—2507).— α -Acetobromoglucose is converted by technical silver fluoride in acetonitrile at the atmospheric temperature into β -acetofluoroglucose, m. p. up to 98° after very frequent crystallisations, $[\alpha]_D^{25} +21.9^\circ$ in chloroform. The product is considerably more stable than the corresponding chloro-compound, but de-acetylation by ammonia or sodium methoxide does not yield uniform products. Hepta-acetylfluorolactose is hydrolysed by sodium methoxide to the very stable α -fluorolactose, decomp. 180—195°, $[\alpha]_D^{25} +83.2^\circ$ in water.

H. WREN.

Modifications of galactose. C. N. RIBBER, J. MINSAAS, and R. T. LECHE (J.C.S., 1929, 2173—2185; cf. A., 1926, 1228).—A study of the change of volume of an aqueous solution of ordinary galactose (α -galactose) leads to the conclusion that more than two modifications of the sugar must be present. The presence of a third modification *B* together with α -galactose *A* and β -galactose *C* is postulated. A repetition of earlier work using β -galactose prepared by a new method, and also a study of the alteration in optical rotation, leads to the conclusion that each of the modifications is convertible into both the others (cf. Smith and Lowry, A., 1928, 510). This result does not preclude the existence of a fourth modification, the existence of which is suspected from a theoretical study of the optical rotations of the four penta-acetates of galactose and the three methylgalactosides.

The following constants are given for pure β -galactose, prepared by evaporation of an aqueous solution of ordinary galactose at the ordinary temperature under aseptic conditions over calcium chloride in a vacuum: monoclinic prisms, β 106° 25'; $a:b:c = 0.827:1:0.775$; $[\alpha]_D^{25} +54.2^\circ$ in water, $[R_D]_D^{25} 62.62^\circ$; V_m 108.94 c.c.

J. W. PORTER.

Melezitose in honey-dew honey from the lime. F. E. NOTTBOHM and F. LUCIUS.—See B., 1929, 955.

Synthesis of glucosides. III. Glucosides of hydroxyxanthones. A. ROBERTSON and R. B. WATERS (J.C.S., 1929, 2239—2243).—2-O-Tetra-acetyl- β -glucosidoxyxanthone, m. p. 173°, $[\alpha]_D^{25} -36.4^\circ$ in acetone, was prepared by the action of *O*-tetra-acetyl- α -glucosidyl bromide on 2-hydroxyxanthone, and gave 2- β -glucosidoxyxanthone, m. p. 237°, on hydrolysis. The latter is hydrolysed by warm 15% hydrochloric acid and by emulsin to 2-hydroxyxanthone and dextrose. 4-O-Tetra-acetyl- β -glucosidoxyxanthone, m. p. 199—200°, $[\alpha]_D^{25} -31.8^\circ$ in acetone, was prepared similarly to the 2-isomeride, and gave 4- β -glucosidoxyxanthone, m. p. 274° (decomp.), with similar properties to the 2-isomeride. 7-O-Tetra-

acetyl- β -glucosidoxy-1-hydroxyxanthone, m. p. 176—177°, $[\alpha]_D^{25} -33.4^\circ$ in acetone, was prepared in a similar manner from euxanthone, and gave on acetylation 7-O-tetra-acetyl- β -glucosidoxy-1-acetoxanthone, m. p. 211°, $[\alpha]_D^{25} -34.2^\circ$ in acetone. On de-acetylation 7- β -glucosidoxy-1-hydroxyxanthone (I), m. p. 218—219°, was formed. 1-Hydroxy-7-acetoxanthone diaceto-borate is produced when euxanthone and boroacetic anhydride are refluxed and is decomposed by water to give 1-hydroxy-7-acetoxanthone, m. p. 160°, which on methylation yields 7-acetoxy-1-methoxyxanthone, m. p. 176°. Hydrolysis of the latter furnishes 7-hydroxy-1-methoxyxanthone, m. p. 235°. 7-O-Tetra-acetyl- β -glucosidoxy-1-methoxyxanthone, m. p. 166—168°, was prepared by methylation of the corresponding hydroxy-compound, and hydrolyses readily to 7-hydroxy-1-methoxyxanthone. These reactions show conclusively that natural glycuronate euxanthic acid corresponds in structure with I. J. W. PORTER.

Plant colouring matters. XV. The sugar of α -crocin. P. KARRER and K. MIKI (Helv. Chim. Acta, 1929, 12, 985—986).— α -Crocin (A., 1928, 644) is hydrolysed by alcoholic ammonia at the ordinary temperature. The sugar formed in solution is acetylated and isolated as the acetate, which is identical with gentiobiose octa-acetate.

R. K. CALLOW.

Sulphurylation of starch. M. SAMEC (Monatsh., 1929, 53 and 54, 852—854).—A suspension of potato-starch in water is made into a paste with an equal volume of 0.8*N*-sodium hydroxide solution, and then treated with a chloroform solution of sulphuryl chloride at 5—7°. Dialysis and subsequent electro-dialysis of the reaction mixture affords mobile and viscous phases. These show widely differing physical properties; the mobile phase contains nearly four times as much SO_3 as the viscous.

H. BURTON.

Inulin phosphate. M. LUDTKE (Biochem. Z., 1929, 212, 475—476).—The preparation of inulin monophosphate by the action of phosphoryl chloride on inulin in pyridine and pouring into water is described. The ester reacts acid to litmus and liberates carbon dioxide from sodium carbonate, but is insoluble in water, aniline, ammonia, or sodium hydroxide.

P. W. CLUTTERBUCK.

Fractional precipitation of cellulose acetate and properties of the fractions. J. G. McNALLY and A. P. GODBOUT (J. Amer. Chem. Soc., 1929, 51, 3095—3101).—A sample of a commercial acetone-soluble cellulose acetate when fractionally precipitated by the addition of varying amounts of water or aqueous acetone (3:1) to a 10% solution in acetone, gives various fractions (removed by centrifuging) which have almost identical acetyl values and specific rotations, but differ widely in m. p., viscosity, and solubility in various organic solvents. The results indicate that the original acetate contains a series of micelles; these differ either in the number of glucose anhydride units they contain or in the manner in which they are joined together to form the micelle.

H. BURTON.

Cellulose methylene ether. F. C. WOOD (Nature, 1929, 124, 762).—*s*-Dichlorodimethyl sulphate reacts with soda-cellulose giving monomethylenecellulose,

$C_6H_7O_2(OH)(CH_2O_2)$. Other methylene inorganic and organic esters give somewhat similar results. Monochlorodimethyl sulphate forms a mixed methyl methylenecellulose ether. A. A. ELDRIDGE.

Pine lignin. IX. P. KLASON (Ber., 1929, 62, [B], 2523—2526).—An alternative method of calculation leads to the formula $C_{120}H_{132}O_{42}$ for lignin, identical with that deduced by Freudenberg and others (this vol., 1046). Freudenberg's conception is founded on the presence in lignin of an aliphatic hydroxyl group which can be methylated, but no phenolic hydroxyl group. Vanillin cannot be methylated by methyl sulphate. Irregular results in the methylation of α -lignosulphonic acid are thus explained, since the process affects only aliphatic hydroxyl groups, if present, whereas the *para*-phenolic hydroxyl is not affected. Freudenberg's assumption of the absence of a free phenolic hydroxyl group in lignin appears premature. Since Tiemann has shown that vanillin can be methylated by methyl bromide and alkali, this process has been extended to lignin. Dry lignin, containing 14% OMe, had 15.5% OMe after treatment with methyl sulphate, showing that the bulk of the water of the aliphatic part had been removed by desiccation. After treatment with alkali and methyl bromide the methoxyl content was 20.5%, or 20% after successive treatment with methyl sulphate and methyl bromide. The increase corresponds with the presence of one third of the phenolic hydroxyls in lignin in the free form; this assumption is confirmed by the behaviour of lignin towards *N*-potassium hydroxide. In lignin and in the α -sulphonic acid a trimeric form of lignin is present. The formula $(3C_{10}H_{10}O_3 + 2H_2O) + H_2SO_3 + C_{10}H_9N - H_2O$ is now advanced for naphthylamine α -lignosulphonate. The constitution of lignin is discussed. H. WREN.

Lignin. XII. Acetylated hydrochloric acid lignin. W. FUCHS and O. HORN (Ber., 1929, 62, [B], 2647—2653; cf. this vol., 1282).—Treatment of Willstätter lignin with acetic anhydride containing sulphuric acid yields almost quantitatively an acetyl-lignin with 19.2% of acetyl. Elementary analysis, coupled with determinations of methoxyl and acetyl, indicate in a compound, $C_{50}H_{55}O_{20}$, the presence of four methoxyl, four acetoxy-, and very probably an ethylene oxide group in a mixed aromatic-heterocyclic system. Lignin in wood can be so acetylated that the product appears to contain three acetyl groups in excess of those present in acetylated Willstätter lignin. It appears, therefore, that the mixed aromatic-heterocyclic nucleus which must be considered present in wood and isolated lignin must be so altered by hydrochloric acid that its activity towards acetylation is diminished. The action of bromine on acetyl-lignin is so greatly influenced by small amounts of water that little information is afforded by a study of the products of the change. Ozone converts acetyl-lignin suspended in acetic acid into about 10% of products resembling those derived from other complex natural materials. Hydrogen peroxide in pyridine does not greatly affect lignin in 48 hrs. at the ordinary temperature, but, under more drastic conditions the acetyl groups are largely removed; after re-acetyl-

ation a product with a very slightly increased oxygen content is obtained. Treatment of lignin, acetyl-lignin, and oxidised acetyl-lignin with hydrochloric acid gives very varying amounts of formaldehyde. It is considered doubtful if formaldehyde is a product of the fission of lignin, and the assumed presence of a piperonyl component in lignin is regarded as unjustified (cf. Freudenberg and Harder, A., 1927, 342). The possibility of characterising lignin in its various forms by quantitative study of its swelling in pyridine is indicated. H. WREN.

Lignin. I. Acetylation and preparation of degradation products soluble in water. H. FRIESE (Ber., 1929, 62, [B], 2538—2550).—Treatment of spruce wood with a mixture of acetic acid, acetic anhydride, and zinc chloride leaves a residue (yield about 150%) retaining the original structure and containing 54.67% of acetic acid and 3.88% OMe. Extraction of the residue with acetone removes about 8% of the material, which does not differ appreciably in constitution from the remainder, which is insoluble in all media. The precipitate obtained by pouring the acid liquor (see above) into water contains considerable amounts of lignin; a separation of the components is not effected by fractionation. If zinc chloride is replaced by sulphuric acid, about half the wood can be brought into solution, but the residue still contains carbohydrates even after the treatment has been repeated until nothing further is dissolved. Treatment of spruce and pine meal with sulphuric acid and acetic anhydride in differing concentrations at a relatively very low temperature leads to the isolation of a methoxyl-free fraction (*A*), soluble in chloroform but insoluble in water, and an unsaccharifiable component (*B*) rich in methoxyl and soluble in water. The portion *B*, provisionally regarded as lignin acetates (about 17% of the wood), is not homogeneous and is divided by hydrolysis into a portion very freely soluble in methyl alcohol and water and a part soluble in water only. The methoxyl content for different preparations varies between wide limits. A slight reducing power towards Fehling's solution is probably due to the presence of traces of sugars. The preparations are soluble in ammonia, alkali hydroxide, and sodium carbonate. Concentrated hydrochloric acid causes resinification. With pyridine and acetic anhydride an acetic acid content of 26—36% is reached, according to the richness in methoxyl. The portion insoluble in methyl alcohol is a brown powder which does not absorb moisture from the air, whereas the soluble portion is extraordinarily hygroscopic (also as acetate). The mol. wts. in freezing water are about 600 and 172, respectively. The first-named product has 51% C and the last-named only 38%. Products containing 62% C, as usually assumed for lignin, have not been isolated. Since oxidation during the course of the reaction is improbable, it is likely that the original lignin is in ether- or ester-like union with a portion of the polysaccharides of the wood. The union is easily disrupted by hydrolysis, but, if drastic conditions are employed, condensation and elimination of water occur simultaneously, thereby explaining the high carbon content of lignin.

H. WREN.

Lignin. V. Relation of lignin and resin. A. FRIEDRICH and A. SALZBERGER (Monatsh., 1929, 53 and 54, 989—1001).—The resin extracted from pine wood by an alcohol-benzene (1:1) mixture differs from the sap resin. The former resin (5.21% OMe) is separated into (a) benzene-soluble and (b) benzene-insoluble fractions; extraction of (a) with light petroleum gives a soluble part (60% of a) containing only 1.45% OMe. Dissolution of b in alcohol and precipitation with acidulated water affords a lignin-like substance, m. p. 129—134° with darkening (12.85% OMe); treatment of the alcoholic solution with light petroleum yields a product, decomp. above 300° (13.7% OMe), similar to pinewood lignin. Chloroform-ether extraction and precipitation affords a product (about 14.5% OMe) which can be methylated or benzoyleated. Its reactions with bromine, ferric chloride, and phenylhydrazine are similar to those of soluble pinewood lignin (B., 1926, 151; A., 1927, 861). Zinc dust distillation yields a product similar to that obtained by Karrer and Bodding-Wiger (A., 1923, i, 1183) from lignin.

A similar lignin-like substance is also isolated from beechwood resin. A relationship between the lignin found in the resin and that in the cellulose appears probable. H. BURTON.

Acetylated wood, the combination of the incrustation, and a method of separation of the constituents of wood. H. SUIDA and H. TITSCH (Monatsh., 1929, 53 and 54, 687—706).—Acetylation of resin-free, degummed, powdered beech and pine woods and of cotton with acetic anhydride in presence of pyridine and/or dimethylaniline for 15—35 days at 100°, gives products containing 30.1—35.2% OAc (cf. A., 1928, 1227). Using Fuchs' method (A., 1928, 743) and not degummed beech and pine woods the acetyl content is of the order 36—38% and not 41% (cf. Fuchs, *loc. cit.*; Horn, this vol., 175).

The separation of the resin-free, degummed beech wood into lignin and cellulose is carried out as follows. The acetylated wood (acetic anhydride, acetic acid, and sulphuric acid at 32—35°) is separated into (a) chloroform-soluble (86—91% of acetylated wood) and (b) chloroform-insoluble parts. Extraction of a with acetone gives soluble (22—26%) and insoluble fractions (69—74%), which on hydrolysis with sodium hydroxide solution afford lignin and cellulose, respectively. The above chloroform-soluble material is soluble in warm phenol and can be precipitated unchanged by the addition of alcohol.

Native cellulose (the wood skeleton) is regarded as a heteromicellar structure, whilst "purified" cellulose fibres are homomicellar (cf. Meyer and Mark, A., 1928, 621). H. BURTON.

Three compounds extracted from Steyrian lignite. A. SOLTYS (Monatsh., 1929, 53 and 54, 185—186).—The concentrated light petroleum extract of the lignite deposit a sterol-like substance, probably $C_{30}H_{50}O$, m. p. 265°, $[\alpha]_D^{25} - 19.1^\circ$ in benzene. Distillation of the residue yields 0.5—1% of a hydrocarbon $C_{14}H_{22}$ (probably a fully hydrogenated sesquiterpene), b. p. 265°, $d_4^{20} 0.8994$, $[\alpha]_D^{25} + 5.62^\circ$, and about 1% of iosene (cf. following abstract). H. BURTON.

Iosene, a new hydrocarbon from Steyrian lignite. A. SOLTYS (Monatsh., 1929, 53 and 54, 175—184).—The lignite crust is extracted with light petroleum and the residue from the extract distilled in a vacuum. The fraction, b. p. 195—220°/12 mm., contains the hydrocarbon iosene, $C_{20}H_{34}$, m. p. 74°, $[\alpha]_D^{25} + 23.81^\circ$ in alcohol. This is identical with hartite, bombicite, and hofmannite (cf. Ciusa and others, A., 1921, ii, 343; 1922, ii, 385), and probably with the hydrocarbon isolated from Piberstein-Lankovitz lignite by Dolch and Strebing (Mikrochem., 1924, 94). Individual substances could not be isolated when iosene is oxidised with nitric acid or potassium permanganate; iosene is saturated (to bromine; hydrogenation; ozone). Attempted dehydrogenation of iosene with sulphur at 260° affords a compound, $C_{20}H_{28}S_3$, m. p. 198°, $[\alpha]_D^{25} - 436.6^\circ$ in benzene. Prolonged treatment with selenium at 360—380° yields retene (quinone, m. p. 198°); iosene is, therefore, related to abietic acid. It is presumed that it contains four rings and alternative structures are indicated. H. BURTON.

Preparation of dihalogenated mixed secondary aliphatic amines. I. M. DE MONTMOLLIN and P. MATILE. II. M. DE MONTMOLLIN and F. ACHERMANN (Helv. Chim. Acta, 1929, 12, 870—873, 873—881).—I. An investigation of possible methods of preparing amines of the type of β -bromoethyl- β -bromobutylamine has been made. 2-Naphthyl β -p-toluenesulphonamidoethyl ether, m. p. 116°, is obtained in 45% yield by the condensation of p-toluenesulphonamide with 2-naphthyl β -bromoethyl ether in boiling alcoholic potassium hydroxide, and is then condensed with α -chloro- β -ethoxybutane by heating with the theoretical amount of alcoholic potassium hydroxide under pressure at 110°, whereby p-toluenesulphon- β -naphthoxyethyl- β -ethoxybutylamide (I), m. p. 137°, is obtained in 45% yield. The condensation of β -aminoethyl alcohol with α -chloro- β -ethoxybutane in alcoholic solution at 200° yields a mixture from which the secondary amine may be partly separated by distillation and converted into β -hydroxyethyl- β' -ethoxybutylnitrosoamine, b. p. 168—171°/15 mm., which yielded on hydrolysis a mixture (II) of the dihydroxy- and hydroxyethoxy-amines, b. p. 170—210°/15 mm. Finally, β -hydroxyethyl- β -hydroxybutylamine (III) (see below) was prepared by condensation of α -amino- β -hydroxybutane with ethylene oxide. Treatment of I, II, or III with hydrobromic acid (cf. this vol., 916) yielded the hydrobromide, m. p. 190° (decomp.), of β -bromoethyl- β -bromobutylamine (picrate, m. p. 139°).

II. A detailed investigation has been made of the best methods of preparing β -bromoethyl- β -bromobutylamine in quantity by the last of the methods outlined in the previous paper. α -Nitro- β -hydroxybutane (picrolonate, m. p. 154°), is prepared by condensation of propaldehyde with nitromethane, and is best reduced (yield 50%) to α -amino- β -hydroxybutane by aluminium amalgam (cf. Tordoir, A., 1902, i, 265). The interaction of α -butylene oxide (A., 1924, i, 360) and concentrated ammonia gives α -amino- β -hydroxybutane in 33% yield. α -Amino- β -ethoxybutane (picrate, m. p. 152—154°; picrolonate,

m. p. 169—170°), has been prepared by a modification of Bookman's method (A., 1896, i, 199) by the interaction of α -chloro- β -ethoxybutane and alcoholic ammonia at 140°. The condensation of α -amino- β -hydroxybutane with ethylene oxide (cf. Knorr, A., 1899, i, 461) is effected in the cold, and yields a mixture of the syrupy primary, secondary, and tertiary amines, which are separated only with difficulty by fractional distillation. No crystalline product is obtained by treatment with nitrous acid, but when the mixture is ethylated by treatment with potassium and ethyl bromide, β -ethoxyethyl- β -ethoxybutylamine, b. p. 105—107°/9 mm., 210—212°/720 mm. (nitroso-derivative, b. p. 150—152°), and di-(β -ethoxyethyl)- β -ethoxybutylamine, b. p. 140—142°/12 mm., are readily separated by fractional distillation. The condensation of α -amino- β -ethoxybutane with ethylene oxide yields similarly β -hydroxyethyl- β -ethoxybutylamine, b. p. 115—117°/10 mm. (nitroso-derivative, b. p. 165—166°; picrolonate, m. p. 125—126°), which is readily ethylated. Di-(β -hydroxyethyl)- β -ethoxybutylamine, b. p. 162°/11 mm., is obtained with excess of ethylene oxide. By heating the non-ethylated, partly ethylated, or completely ethylated bases with hydrobromic acid in sealed tubes there are obtained β -bromoethyl- β -bromobutylamine hydrobromide, m. p. above 300° (free base, an unstable oil; picrolonate, m. p. 148—150°), and di-(β -bromoethyl)- β -bromobutylamine hydrobromide, m. p. above 300° (base, an oil; picrate, decomp. 260°). R. K. CALLOW.

Hydrochlorides of α -amino-alcohols. K. A. KRASUSKI and K. G. KOSENKO (Ukraine Chem. J., 1929, 4, 199—209).—By passing dry hydrogen chloride through a cooled ethereal solution of α -amino-alcohols, the hydrochlorides were obtained as crystalline non-hygroscopic precipitates. With excess of hydrogen chloride the salts first became highly hygroscopic, and finally liquefied, forming liquid additive compounds with several molecules of hydrogen chloride which on keeping at the ordinary temperature, gave off hydrogen chloride and were reprecipitated the solid salts.

If dry solid hydrochlorides were further treated with hydrogen chloride, they liquefied with evolution of heat, but the resulting compounds were very unstable, and decomposed into the original salts with evolution of hydrogen chloride. Tertiary amines were found to add hydrogen chloride most readily to form additive compounds with two extra molecules; the secondary were less reactive and added only one extra molecule, whilst the primary reacted only to a very slight extent. In general, it was found that the less basic are the properties of the amino-alcohol, the more readily it absorbs excess of hydrogen chloride, and the more actively the hydrochloride reacts with the gas to form the unstable additive compounds. M. ZVEGINTZOV.

Action of isoamylamine on isopropylethylene oxide. K. A. KRASUSKI and F. F. KRIVONOS (Ukraine Chem. J., 1929, 4, 211—213).—isoPropylethylene oxide in 33% aqueous or benzene solution reacts with isoamylamine less readily than with ammonia (which reacts at the ordinary temperature), heating for 10 hrs. on the water-bath being necessary. A 50% yield of isoamylaminomethylisopropylcarbinol,

CHPr²(OH)·CH₂·NH·[CH₂]₂·Pr², b. p. 125—127°/25 mm. (hydrochloride, m. p. 263°; picrate, m. p. 130—132°), is obtained. M. ZVEGINTZOV.

Polysaccharides. XL. Enzymic degradation of chitin. II. P. KARRER and G. VON FRANÇOIS (Helv. Chim. Acta, 1929, 12, 986—988; cf. this vol., 915).—Chitin from mushrooms is decomposed by snail chitinase in the same way as chitin from lobster shells (*loc. cit.*) with the formation of *N*-acetylglucosamine in 80% yield, suggesting that plant and animal chitins are identical. When chitosan is acetylated by boiling with acetic anhydride and sodium acetate the product is decomposed by chitinase to yield *N*-acetylglucosamine, indicating that an acetyl group is necessary for this degradation and supporting the assumption that chitosan is simply de-acetylated chitin. R. K. CALLOW.

Preparation and properties of xanthhydrol as a reagent for carbamide. F. G. KNY-JONES and A. M. WARD (Analyst, 1929, 54, 574—575).—Xanthhydrol is very unstable; it has m. p. about 120—123° according to mode of heating, and decomposes above this temperature. For use in the determination of carbamide it should be freshly prepared by reducing xanthone by means of alcoholic sodium amalgam. The alkaline alcoholic solution is poured into excess of water, and the product collected and redissolved in methyl or ethyl alcohol, as the alcoholic solution is much more stable than the solid. D. G. HEWER.

Complex metallic cyanides. III. Compounds of iron and cobaltcyanic acids with bivalent heavy metals. H. REIHLEN and W. ZIMMERMANN (Annalen, 1929, 475, 101—119).—A systematic investigation of the complex salts formed by the action of cadmium sulphate on potassium ferro- and ferri-cyanide. When a hot solution of potassium ferricyanide is treated with an excess of cadmium sulphate solution the *potassium salt*

$[(\text{H}_2\text{O})_2\text{Fe}^{\text{III}}(\text{CN})_6\text{Cd}]_3[\text{K}(\text{H}_2\text{O})]_{12}\cdot 12\text{H}_2\text{O}$ (I) is formed. If the precipitate obtained with cold solutions is treated at 100° with cadmium sulphate solution it is converted into the *cadmium salt*, $[(\text{H}_2\text{O})_2\text{Fe}^{\text{III}}(\text{CN})_6\text{Cd}]_3\text{Fe}^{\text{III}}(\text{CN})_6\cdot 22\text{H}_2\text{O}$. In the presence of 3.5*N*-ammonia solution I is not stable, the precipitate then consisting of the basic salt $[(\text{HO})_2\text{Fe}^{\text{III}}(\text{CN})_6\text{Cd}]_3[\text{Cd}(\text{NH}_3)_4]_3\cdot 3\text{NH}_3$ (II), providing the ratio Cd : Fe in the solution is > 2 : 1. If this ratio is less than this value initial crystallisation of II is followed by separation of the compound

$[\text{Cd}(\text{CN})_6\text{Fe}^{\text{III}}(\text{OH})_2]_3[\text{Cd}(\text{NH}_3)_4]_2(\text{NH}_4)_3\cdot 3\text{H}_2\text{O}$. With potassium cobaltcyanide a *basic cobalt salt* similar to II is obtained. When I is dissolved in 2*N*-ammonia and the solution is saturated with ammonia at -15° the complex *ammonium salt*

$[(\text{HO})_2\text{Fe}^{\text{III}}(\text{CN})_6\text{Cd}]_3[\text{Cd}(\text{NH}_3)_4]_7$ crystallises, contaminated with the compound

$[\text{Fe}(\text{CN})_6\text{Cd}(\text{OH})_2]_3[\text{Cd}(\text{NH}_3)_4]_{10.3}(\text{NH}_4)_{6.35}\cdot 14\text{H}_2\text{O}$. By similar methods the corresponding complex zinc and nickel salts,

$[(\text{OH})_2\text{FeZn}(\text{CN})_6]_3[\text{Zn}(\text{NH}_3)_4]\cdot \text{K}\cdot 8\text{H}_2\text{O}$ and $[(\text{OH})_2\text{Fe}(\text{CN})_6\text{Ni}]_3[\text{Ni}(\text{NH}_3)_4]_4(\text{NH}_4)_{4.5}\cdot 27\text{H}_2\text{O}$, are obtained. Degradation of the complex heptabasic anion $[\text{Fe}_3\text{Cd}_4(\text{CN})_{18}(\text{OH})_6]^-$ to derivatives of the simple anion $[\text{FeCd}(\text{CN})_6]^-$ may be effected in

two ways. First by dissolving any salt of type I in ammonia, adding ammonium sulphate to depress the hydroxyl-ion concentration, and removing the excess of ammonia over sulphuric acid in a vacuum, and thus is obtained the *hexammine cadmium* salt, $[\text{Fe}(\text{CN})_6\text{Cd}]_2[\text{Cd}(\text{NH}_3)_6]_2 \cdot 2\text{H}_2\text{O}$. Fission of the co-ordination complex to yield the corresponding ferricyanide, $[\text{Fe}(\text{CN})_6][\text{Cd}(\text{NH}_3)_6]_2$, is not possible in solution. The second method consists in the addition of cadmium sulphate solution to a hot solution of potassium chloride and ferricyanide, no precipitation occurring, but on cooling the *potassium* salt, $[\text{Fe}(\text{CN})\text{Cd}]\text{K}$, slowly crystallises. The chief differences between the complex cadmicyanides of bi- and ter-valent iron is that the polymerised (polynuclear) co-ordination complex which the former are also presumed to form is much more readily broken down to the simple anion $[\text{Fe}''\text{Cd}(\text{CN})_6]'$ (which is stable to 6*N*-ammonia), and the salts contain no water molecules combined in the co-ordination complex. The *sodium* salt, $[\text{Fe}''(\text{CN})_6\text{Cd}][\text{NaH}_2\text{O}]_2 \cdot \text{H}_2\text{O}$, is obtained either by heating cadmium sulphate solution with an excess of sodium ferrocyanide solution ($\text{Fe} : \text{Cd} = 2.5 : 1$), or by shaking the precipitate obtained when an excess of cadmium sulphate is used for a long period with concentrated sodium chloride solution. The corresponding *potassium* (+4H₂O) and *ammonium* (+6H₂O) salts are similarly prepared. In the presence of a high concentration of ammonia the *hexammine cadmium* salt $[\text{Fe}''(\text{CN})_6\text{Cd}][\text{Cd}(\text{NH}_3)_6] \cdot \text{H}_2\text{O}$, and with lower concentrations the *tetrammine cadmium* salt $[\text{Fe}''(\text{CN})_6\text{Cd}][\text{Cd}(\text{NH}_3)_4] \cdot \text{H}_2\text{O}$ and +6H₂O, are obtained. That the precipitate obtained by heating together solutions of sodium ferrocyanide and cadmium sulphate is a mixture of the compounds $[\text{FeCd}(\text{CN})_6]\text{Na}_2$ and $[\text{FeCd}(\text{CN})_6]\text{Cd} \cdot \text{H}_2\text{O}$ and not the complex $\{[\text{Fe}''\text{Cd}(\text{CN})_6]_3\text{Cd}\}\text{Na}_4$ is proved by the fact that the ratio Cd : Fe in the precipitate remains the same as that in the mother-liquor when its value in the latter is altered. The structure of these complex salts and their bearing on the constitution of insoluble Prussian blue are discussed. J. W. BAKER.

Alkylation of hexacyanocobaltic acid. F. HOLZL, T. MEIER-MOHAR, and F. VIDITZ (Monatsh., 1929, 53 and 54, 237—255).—When hexacyanocobaltic acid or its alkoxonium derivatives (this vol., 898) are heated with alcohols in a sealed tube at 100°, alkylation occurs. Thus the acid and alcohol give the compound $[(\text{CN})_5\text{Co} \cdot \text{CNEt}]\text{H}_2$, isolated as its *dipyridine* salt. Treatment of the reaction product from methyl alcohol and the methoxonium derivative of the acid with pyridine affords a substance, $[(\text{CN})_5\text{Co} \cdot \text{CNMe}]\text{H}_2(\text{C}_5\text{H}_5\text{N})_3$ or $[(\text{CN})_4\text{Co} \cdot (\text{CNMe})_2]\text{H}(\text{C}_5\text{H}_5\text{N})_3$. Propylation is similar to ethylation, but proceeds more slowly. Carbylamine is formed during the reactions. The relation between time of reaction and corrected amount of 0.1*N*-alkali hydroxide necessary for neutralisation of the reaction mixture is studied. The mechanism of the formation of the alkylated products is discussed; the production of an intermediate imino-compound is postulated. H. BURTON.

Photosensitiveness of nitroprussides. H. LEFFMANN and C. C. PINES (Bull. Wagner Free Inst.,

1929, 4, 41—42).—When a concentrated aqueous solution of sodium nitroprusside is mixed with aqueous solutions of uranium acetate, silver nitrate, mercuric nitrate, ferrous sulphate, or ferric chloride, precipitates, presumably of the corresponding nitroprussides, are formed in all cases except with ferric chloride. All the precipitates, except that of uranium, were notably changed after exposure to sunlight for 10 min.

A. I. VOGEL.

Possibility of formation of tetrazomethane, CN₄. H. HOLTER and H. BRETSCHNEIDER (Monatsh., 1929, 53 and 54, 963—984).—Treatment of methylene-bisurethane (I) with nitrous fumes in ethereal suspension affords impure *dinitrosomethylenebisurethane* (II), a yellow oil, which decomposes readily when heated; II does not give Liebermann's reaction. Decomposition of II with dilute alkali hydroxide (whereby tetrazomethane might be produced) causes evolution of nitrogen; with concentrated aqueous or methyl-alcoholic alkali hydroxide in the cold, a sodium salt is first formed and decomposes on warming or diluting with water. Decomposition of an ethereal solution of II with water gives a trace of formaldehyde (isolated as the "dimedon" compound); the amount of formaldehyde is increased when aqueous sodium hydroxide is used. With sodium propoxide in ethereal propyl-alcoholic solution, II gives a small amount of a substance, probably formaldehyde dipropylacetal, b. p. 134—142°, hydrolysed by 50% sulphuric acid to formaldehyde.

Treatment of pyrocatechol with an ethereal solution of II in presence of 25% methyl-alcoholic potassium hydroxide solution affords a small amount of methylenedioxybenzene. Similarly, 3:4-dihydroxyaniline, methyl protocatechuate, and the phenolic base from *dl*-tetrahydroberberine (Späth and Mosettig, A., 1926, 965) all furnish varying amounts of the corresponding methylenedioxy-derivatives. The above reactions are to be expected with tetrazomethane. It is suggested that the tetrazomethane reacts only with free phenols and not with phenoxides; it is shown that an ethereal solution of diazomethane does not react with sodium β-naphthoxide until methyl alcohol is added.

The by-reactions occurring during the decomposition of II by alkali hydroxide have been studied. With methyl-alcoholic potassium hydroxide, I and *ethylmethoxymethylurethane* (III), b. p. 103—104°/9 mm. [obtained from methoxyacetamide by Blaise's method (A., 1926, 943)], were isolated. Hydrolysis of III with 10% sulphuric acid gives methyl alcohol and formaldehyde; benzylamine and III at 200° yield dibenzylcarbamide. When II is decomposed with sodium benzyloxide in benzyl alcohol-ether solution, *ethylbenzyloxymethylurethane*, b. p. 185—190°/10 mm., is produced. The formation of these alkyl-oxy-derivatives probably occurs thus: $[\text{CO}_2\text{Et} \cdot \text{N}(\text{NO})]_2 \cdot \text{CH}_2 \xrightarrow{+\text{H}_2\text{O}} \text{CO}_2\text{Et} \cdot \text{N}(\text{NO}) \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et} \xrightarrow{\text{KOH}}$

$\text{N}_2\text{CH} \cdot \text{NH} \cdot \text{CO}_2\text{Et} \xrightarrow{\text{H-OH}} \text{OR} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$. An ethereal solution of II gradually decomposes to I and nitrogen oxides. H. BURTON.

Influence of poles and polar linkings on the course pursued by elimination reactions. V. Thermal decomposition of quaternary phosphon-

ium hydroxides. G. W. FENTON and C. K. INGOLD (J.C.S., 1929, 2342—2357).—The decomposition of quaternary ammonium hydroxides results in the production of olefines, whilst the simpler phosphonium hydroxides yield paraffins. It is suggested that in the latter case, paraffinic degradation takes place at a lower temperature than that required for olefinic degradation. The facility of olefinic degradation depends largely on the extent to which the β -hydrogen atom eliminated from the cation is activated or de-activated by the β -substituents of the group forming the olefine. Electron-repelling alkyl groups de-activate, and consequently phosphonium hydroxides which should be capable of forming simple aliphatic olefines are not favourable cases for observation of olefinic degradation. For this reason the decomposition of the following complex phosphonium hydroxides was studied. The β -phenylethyl-triethyl compound gave some styrene and triethylphosphine at the temperature of paraffinic decomposition, which was still the main reaction, whilst $\beta\beta$ -diphenylethyl-tri-*n*-butylphosphonium hydroxide yielded *as*-diphenylethylene and tri-*n*-butylphosphine as the main products. The presence of paraffinic degradation products was just discernible. Olefinic degradation of phosphonium hydroxides is thus possible and the conditions for its facilitation are similar to those established for the ammonium series. A table is given showing quantitatively the hydrocarbon products of the decomposition of a number of phosphonium hydroxides.

The phosphonium hydroxides were prepared by interaction of the corresponding phosphines and alkyl halides followed by treatment with moist silver oxide under suitable conditions. The following compounds are described: *tetramethylphosphonium picrate*, m. p. $>290^\circ$. The residue after decomposition of the hydroxide was trimethylphosphine oxide, b. p. $210-212^\circ$, m. p. $140-141^\circ$ (*hydroxytrimethylphosphonium trichloroacetate*, m. p. 64°); *trimethyl-ethylphosphonium picrate*, m. p. 290° ; *dimethylethylphosphine oxide*, b. p. $223-225^\circ$, m. p. $73-75^\circ$; *methyl-triethylphosphonium picrate*, m. p. 239° , triethylphosphine oxide, b. p. $238-240^\circ$, m. p. about 46° (chromate, $99-100^\circ$); *triethyl-*n*-propylphosphonium picrate*, m. p. 91° ; *ethyltri-*n*-propylphosphonium iodide* and *picrate*, m. p. 64° ; *tri-*n*-propyl-*n*-butylphosphonium iodide*, m. p. $239-240^\circ$, and *picrate*, m. p. 67° ; *tri-*n*-propyl-*n*-octylphosphonium chloroaurate*, m. p. 38° ; *phenyltrimethylphosphonium iodide*, m. p. 236° ; *benzyltrimethylphosphonium bromide*, m. p. 222° ; *triphenylbenzylphosphonium bromide*, m. p. 288° ; β -phenylethyltriethylphosphonium *picrate*, m. p. 70° . $\beta\beta$ -Diphenylethyltri-*n*-butylphosphonium *hydroxide*, no salts described. *n*-Propyltri-*n*-butylphosphonium *hydroxide*, no salts described. ω -Carboethoxytetramethylphosphonium *chloride*, m. p. 160° (decomp.), and *picrate*, m. p. $124-125^\circ$. Full details are given of the thermal decomposition products of the above phosphonium hydroxides. J. W. PORTER.

Constitution and dissociation of the Grignard reagent. H. GILMAN and R. E. FOTHERGILL (J. Amer. Chem. Soc., 1929, 51, 3149—3157).—Magnesium alkyl, aralkyl, and aryl halides have been treated

with an equivalent of magnesium and benzophenone in ether-benzene solution, and the amounts of benzpinacol formed determined. With magnesium ethyl and benzyl chlorides and phenyl bromide no pinacol results. Amounts varying from 0.057 to 17.3% (on benzophenone used) are formed with magnesium methyl and *n*-butyl iodides and benzyl bromide. With magnesium *n*-butyl iodide, *tert*.-butyl chloride, and benzyl bromide and no added magnesium no pinacol is formed, but magnesium triphenylmethyl chloride and bromide give, under the same conditions, 22.0 and 31.6% of the pinacol respectively; at the same time triphenylmethyl peroxide (55.3 and 57.9%) is also formed. This is explained by a dissociation of the Grignard reagent, $\text{CPh}_3\cdot\text{MgX} \longrightarrow \text{CPh}_3\cdot + \text{MgX}\cdot$; the pinacol formation is a function of the $\cdot\text{MgX}\cdot$. A mixture of magnesium diethyl, magnesium iodide, magnesium, and benzophenone in ether-benzene solution and an atmosphere of hydrogen yields after prolonged stirring benzpinacol (12.83%) and diphenylethylcarbinol. When the reaction is carried out in an atmosphere of nitrogen for a short time, only diphenylethylcarbinol (18%) is isolated. The following change occurs: $\text{MgEt}_2 + \text{MgI}_2 \longrightarrow 2\text{Et}\cdot\text{MgI}\cdot$. It is concluded that the equilibrium $2\text{R}\cdot\text{MgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$ and the dissociation $\text{R}\cdot\text{MgX} \longrightarrow \text{R}\cdot + \text{MgX}\cdot$ probably occur to some extent with all Grignard reagents. H. BURTON.

Sterol group. V. Constitution of cholesterolene. A. C. BOSE and W. DORAN (J.C.S., 1929, 2244—2248).—The action of heat on methyl cholesteryl xanthate, m. p. 127° , $[\alpha]_D^{25} -51.1^\circ$ in toluene (best prepared by the action of carbon disulphide and methyl iodide on potassium cholesteryl oxide obtained by the action of emulsified potassium on a dry benzene solution of cholesterol) (Tschugaev and Fomin, A., 1910, i, 734), forms only one hydrocarbon, cholesterolene, m. p. 79° , identical with the product obtained by the dehydration of cholesterol with anhydrous copper sulphate (Mauthner and Suida, A., 1896, i, 425; a cleaner product being obtained by heating the reactants at $200^\circ/5$ mm.), since either product is reduced by hydrogen and palladium-black to the same mixture of cholestane and ψ -cholestane. The supposed isomeride " β -cholesterylene" described by Tschugaev and Fomin (*loc. cit.*) is an impure form of cholesterolene containing sulphur which is removed only by repeated treatment with concentrated alcoholic potassium hydroxide or by liquid sodium-potassium amalgam.

J. W. BAKER.

Quantitative evidence of the structure of the benzene ring and the orientation of its six hydrogen atoms. R. REINICKE (Z. Elektrochem., 1929, 35, 780—789).—A theory of the structure of benzene, based on the tetrahedral quadrivalency of carbon and the value of the space-lattice of the diamond obtained by Ehrenberg (Z. Krist., 1926, 63, 320), is advanced, in support of which various physical data, e.g., dielectric constants, of some benzene derivatives are quoted. H. T. S. BRITTON.

Catalytic hydrogenation of halogenated organic compounds. M. BUSCH and W. SCHMIDT (Ber., 1929, 62, [B], 2612—2620; cf. A., 1925, ii, 823).—

During the quantitative removal of bromine from bromobenzene, by means of hydrogen, diphenyl is produced in considerable amount in addition to benzene. Hydrogen derived from hydrazine does not act more advantageously, although more rapidly, than that derived from other sources. Apparently the proportion of diphenyl produced is connected with the dielectric constant of the solvent. In methyl alcohol the yield is 60%, whilst in ethyl alcohol it is 30% (depressed by addition of water) and reaches a minimum in isopropyl alcohol. Hydrogenation of the nucleus is not observed. Partial poisoning of the catalyst by benzene, phenol, or dimethylaniline depresses the yield of diphenyl, which attains its maximum when the halogen is removed from the nucleus as rapidly as possible. Other reducing agents (zinc dust and potassium hydroxide or ammonia) do not affect bromobenzene, which, however, affords about 10% of diphenyl when treated with methyl-alcoholic potassium hydroxide and palladised calcium carbonate at 140°. The presence of substituents in halogenobenzenes influences the production of diaryls in proportion as it affects the mobility of the halogen atoms, but, in general, the yield of diaryl is somewhat lower than with the unsubstituted compounds. 1-Bromonaphthalene does not yield dinaphthyl. *o*-Dibromobenzene behaves as a normal disubstituted product, either remaining intact or being reduced to benzene. *p*-Dibromobenzene gives diphenyl, *p*-diphenylbenzene, and *p*-diphenyldiphenyl containing halogen. *p*-Di-iodobenzene behaves similarly. Bromo- and iodo-diphenyl yield homogeneous *p*-diphenyldiphenyl. The tendency towards the production of long ring chains finds its limitation in the physical properties of the complex compounds which cause their immediate separation from the alcoholic solution, thus preventing further action. Benzyl halides afford dibenzyls in appreciable amount. If palladium as catalyst is replaced by platinum or nickel, diaryls are not produced or are formed only in minor amount; this may be connected with their much slower rate of reaction. H. WREN.

Polymethylbenzenes. I. Jacobsen reaction with pentamethylbenzene, and preparation of prehnitene [1:2:3:4-tetramethylbenzene]. L. I. SMITH and A. R. LUX (J. Amer. Chem. Soc., 1929, 51, 2994—3000).—The formation of hexamethylbenzene (I) and prehnitenesulphonic acid (II) from pentamethylbenzene, by treatment with sulphuric acid at the ordinary temperature (cf. Jacobsen, A., 1887, 660), has been studied in detail. Reaction occurs essentially in the manner described by Jacobsen (*loc. cit.*). The initial reaction mixture is decomposed by a specific amount of ice; this precipitates I and II. These are separated by extraction with water. Prehnitene is obtained conveniently from sodium prehnitenesulphonate by slow addition of a saturated solution of the sodium salt to sulphuric acid at 140—155°, and removing the hydrocarbon formed in a current of steam. The yield is 80—90%. When pentamethylbenzenesulphonic acid is kept in a desiccator over sulphuric acid for 8 weeks small amounts of I and II appear to be formed. This indicates that the first stage of the Jacobsen reaction is sulphonation with

subsequent rearrangement of the sulphonic acid produced. H. BURTON.

Polymethylbenzenes. II. M. p. of tetra-, penta-, and hexa-methylbenzenes, and f.-p. diagram of mixtures of durene [1:2:4:5-tetramethylbenzene] and isodurene [1:2:3:5-tetramethylbenzene]. L. I. SMITH and F. H. MACDOUGALL (J. Amer. Chem. Soc., 1929, 51, 3001—3008).—Bromination of mesitylene in carbon tetrachloride solution and treatment of the product formed with alcoholic sodium ethoxide (to remove bromomethyl derivatives) affords bromomesitylene, b. p. 102.5—103.5°/14 mm., m. p. —1 to 1°. Conversion of this into the Grignard reagent and treatment with methyl sulphate gives a 60% yield of isodurene, b. p. 86.5°/18 mm. When bromoprehnitene, m. p. 26.2—26.4° (lit. 30°), is converted into the Grignard reagent and this is decomposed by dilute acid, a 61% yield of prehnitene is obtained. The f. p. of this is identical with that prepared by the Jacobsen method (preceding abstract). The f. p. (corr.) of the hydrocarbons prepared are: durene, 79.28±0.05°; isodurene, —24.0±0.1°; prehnitene, —6.40±0.05°; penta-methylbenzene, 54.0±0.1°; hexamethylbenzene, 164.8±0.1°. The f.-p. diagram for the system durene-isodurene is given, and the molar latent heats of fusion of durene and isodurene are calculated to be 5022 and 2550 g.-cal., respectively. H. BURTON.

Synthesis of propyl- and propenylbenzene and their homologues. L. BERT and M. ANGLADE (Compt. rend., 1929, 189, 645—646).—Reduction of cinnamyl *n*-butyl ether (prepared by the action of alcoholic potassium hydroxide on α -chloro- γ -phenyl- Δ^a -propene; cf. A., 1925, i, 803) with sodium and alcohol gives a mixture of *n*-propyl- and propenylbenzene. Similarly, from 2:4-dimethylcinnamyl *n*-butyl ether are obtained 2:4-dimethyl-*n*-propylbenzene, b. p. 92°/18 mm., 206—207° (corr.)/735 mm., d_4^{20} 0.8786, n_D^{20} 1.501, and 2:4-dimethyl- Δ^a -propenylbenzene, b. p. 100°/20 mm., 213—215° (corr.)/735 mm., d_4^{20} 0.9096, n_D^{20} 1.540, which is separated from the saturated hydrocarbon as its dibromide, b. p. 178°/22 mm., d_4^{20} 1.5435, n_D^{20} 1.586, or its hydrobromide, b. p. 138°/19 mm., d_4^{20} 1.233, n_D^{20} 1.545. J. W. BAKER.

Action of iodine on the alkali derivatives of acinitro-compounds. C. D. NENITZESCU (Ber., 1929, 62, [B], 2669—2672).—A solution of the potassium salt of 9-isonitrofluorene is converted by iodine in potassium iodide or by electrolysis at a platinum anode and copper cathode into $\alpha\beta$ -dinitro- $\alpha\beta$ -ditriphenylene-ethane, m. p. 184°. $\alpha\beta$ -Dinitro- $\alpha\beta$ -diphenylethane, m. p. 150—151°, is obtained from iodine and the sodium derivative of phenylisonitromethane at 0°, whereas if cooling is not adopted or if the solution is electrolysed a dark brown oil is obtained which is converted by hot, 50% potassium hydroxide into 3:4:5-triphenylisooxazole, m. p. 212°. When phenylisonitromethane is dissolved in a large excess of alkali hydroxide and treated with iodine in boiling solution, stilbene is formed in 80% yield.

H. WREN.

Chloronitrotoluenes. L. GINDRAUX (Helv. Chim. Acta, 1929, 12, 921—934).—A comparative study of the chlorination of benzene, toluene, and

o-nitrotoluene in presence of various catalysts shows that a mixture of iron and iodine is exceptionally active. A 90% yield of monochlorotoluenes (60% *o*-, 40% *p*-) is obtained from toluene at 50°. *o*-Chlorotoluene has d_{25}^{21} 1.077, n_D^{19} 1.5275, and *p*-chlorotoluene has d_{25}^{21} 1.031, n_D^{19} 1.5223. The proportions of the isomerides in a mixture are readily determined from the refractive index, the variation of which with composition is practically linear. Chlorination of *o*-nitrotoluene at 50–60° yields 6-chloro-*o*-nitrotoluene, m. p. 37° (65.9%), and 4-chloro-*o*-nitrotoluene, m. p. 37° (34.1%) (crystallographic data) (cf. G.P. 107,505; Fierz, "Operationen der Farbenchemie," p. 100; G.P. 434,402). Separation is achieved by a combination of fractional distillation, when the 6-chloro-compound, b. p. 114.6°/11 mm., distils first, and freezing out, the eutectic being at 3.5°, 45% of 6-chloro-*o*-nitrotoluene. 6-Chloro-*o*-nitrotoluene is best converted into 6-chloro-*o*-nitrobenzaldehyde, m. p. 70.5°, by Janson's method (G.P. 107,501) of bromination to the benzyl bromide, m. p. 58°, and oxidation of the latter. 4:4'-Dichloroindigotin (crystallographic data) and 4:4'-dichloro-5:5'-dibromoindigotin (G.P. 193,438) have absorption maxima in xylene at $\lambda = 599.5$ and 614.3, respectively. 6-Chloro-*o*-toluidine is converted by the method of G.P. 241,910 into 3-chloro-2-methylphenylthiolacetic acid, m. p. 104°; this yields 6:6'-dichloro-7:7'-dimethylthioindigotin, which dyes cotton in bright red and wool in brownish-red shades and has an absorption maximum in xylene at $\lambda = 544.8$. 5-Chloro-2-methylphenylthiolacetic acid, m. p. 101°, and 4:4'-dichloro-7:7'-dimethylthioindigo (brownish shades, absorption maximum in xylene at $\lambda = 553.6$) are obtained similarly. Nitration of *p*-chlorotoluene in sulphuric acid under different conditions yields slightly varying proportions of the 2- and 3-nitro-compounds (53–62.5% and 37.5–47%, respectively). 4-Chloro-*m*-nitrotoluene reacts with ammonia at 175° under pressure to give 3-nitro-*p*-toluidine, m. p. 114°, in 82% yield. 3-Nitro-*p*-cresol cannot be prepared from the chloro-compound, but is obtained in 90% yield by the action of 10% sodium hydroxide solution on 3-nitro-*p*-toluidine. The preparation of 4-methoxy-*m*-toluidine, m. p. 50°, from 3-nitro-*p*-chlorotoluene by heating with potassium hydroxide and methyl alcohol and reduction of the product is described. The "eriochromazurole" dyes obtained by condensing *o*-cresotic acid with 2:4- and 2:6-dichlorobenzaldehyde and oxidation of the products have absorption maxima at $\lambda = 593.0$ and 597.8, respectively, in sodium hydroxide, and at $\lambda = 521.5$ and 536.3, respectively, in sulphuric acid solution.

R. K. CALLOW.

Organo-alkali compounds containing sulphur. K. FUCHS (Monatsh., 1929, 53 and 54, 438–444).—Various sulfoxides have been treated with sodium phenyl or benzyl in the hope of obtaining sulphonium compounds. The products isolated are highly coloured, air-sensitive organo-alkali compounds (formed from equimolecular amounts of the reactants in benzene or toluene solution at the ordinary temperature). Thus diphenyl sulfoxide (I) and sodium benzyl (II) in benzene afford a red product, decomposed by hydrogen chloride to I and a small amount of

phenyl benzyl sulfoxide (III). When the reaction is carried out in toluene, the hydrogen chloride decomposition products are III (35%) and a small amount of I. *pp'*-Ditolyl sulfoxide and II react similarly in toluene and after treatment with hydrogen chloride, 30–35% of *p*-tolyl benzyl sulfoxide and some unchanged material are obtained. Similar decomposition of the product from III and II gives only III. Decomposition of the reaction product from I and II with carbon dioxide gives a small amount (benzene) or 35–40% (toluene) of the acid $\text{Ph}\cdot\text{SO}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ (IV), decomp. 142–143°, according to the solvent. This acid is synthesised from sodium α -chlorophenylacetate and sodium phenyl sulphide in methyl alcohol, whereby α -phenylthiophenylacetic acid, $\text{SPh}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, m. p. 102–103°, results. Oxidation of this with hydrogen peroxide in acetone or acetic acid solution gives IV. Thermal decomposition of IV yields thiophenol and benzoylformic acid whilst oxidation of IV with an excess of hydrogen peroxide gives benzenesulphonylphenylacetic acid, decomp. 142–143° into carbon dioxide and phenyl benzyl sulphone.

When I is treated with sodium phenyl at 80–90° in benzene and an atmosphere of nitrogen, a 50% yield of diphenylene sulphide is obtained; *pp'*-ditolyl sulfoxide gives dimethyldiphenylene sulphide. Similarly, I and II yield a small amount of diphenylene sulphide. Diphenyl sulphide does not react with sodium aryls at the ordinary temperature; at 70–80° some fission occurs. Diphenyl sulphone and II react in toluene solution forming a red solution; decomposition of this with hydrogen chloride at –60° gives the original sulphone, oily products, and a compound, m. p. 178.5°, of composition corresponding with $\text{Ph}\cdot\text{SO}_2\cdot\text{CHPh}_2$.

H. BURTON.

Reactions of vinyl chloride and benzene in presence of aluminium chloride. J. M. DAVIDSON [with A. LOWY] (J. Amer. Chem. Soc., 1929, 51, 2978–2982).—When benzene is treated with vinyl chloride in presence of aluminium chloride at 0–5°, the main products are *as*-diphenylethane and an anthracene-type resin; small amounts of ethylbenzene and 9:10-dimethyl-9:10-dihydroanthracene are also formed (cf. Boeseken and Bastet, A., 1914, i, 156). Very small amounts of aluminium chloride give small yields of the products, whilst relatively large amounts cause a diminution in the amount of *as*-diphenylethane formed. When the reaction is carried out at 60–70° an increased amount of the anthracene derivative is produced; this is not the case when the initial reaction mixture (0–5°) is heated. The presence of a trace of iodine accelerates the reaction at 0–5°, and relatively large amounts of the anthracene are formed; the amounts of *as*-diphenylethane and resin are diminished. In presence of a small amount of mercury increased production of ethylbenzene occurs, probably owing to reduction of α -chloro- α -phenylethane, which is considered to be the intermediate product. Styrene or metastyrene is not produced during the reaction (cf. Boeseken and Bastet, *loc. cit.*). The resin formed during the reaction melts at 50–65°, decomposes when heated to 300°, affords small amounts of 9:10-dimethyl-9:10-dihydroanthracene

at 220°/0.5 mm., and on oxidation with chromic oxide in acetic acid-benzene solution gives anthraquinone.
H. BURTON.

Mechanism of formation of compounds of the dibenzyl series from the nitrotoluenes and their derivatives by the action of alcoholic alkali hydroxides. A. K. PLISOV (Ukraine Chem. J., 1929, 4, 241—279).—A *résumé* of former work on the formation of stilbene derivatives from chlorinated aromatic nitro-compounds, and the investigation of the action of alcoholic alkali hydroxides on toluene derivatives. Sodium or potassium alkoxides were allowed to react with benzyl chloride, benzyl bromide, benzylidene chloride, *o*- and *p*-nitrotoluene, *p*-nitrotoluene-*o*-sulphonic acid, *o*- and *p*-dinitrotoluene, *p*-nitrobenzyl bromide, *o*- and *p*-nitrobenzylidene chloride, the following conclusions being reached. The *o*- and *p*-nitrotoluenes and most of their derivatives form products of the dibenzyl series, the reaction taking place even below 0°, whilst the *m*-compounds do not react in this way. With halogen derivatives of the nitrotoluenes which have the halogen in the side-chain ethers are obtained in the case of the *m*-compounds, and dibenzyl derivatives (with ethers as by-products) in the case of the *o*- and *p*-compounds. Coloured intermediate compounds are also formed; these, however, cannot be isolated. The dibenzyl derivatives can be produced only from the *o*- and *p*-compounds if in the alcoholic radical a hydroxyl can take up a position adjacent to the "tautomeric" hydrogen atom (i.e., from the side-chain); this does not take place in the case of *m*-compounds. All the nitrotoluenes, and most of their derivatives, react in the tautomeric form, giving first unstable quinonoid salts, which are rapidly decomposed. The formation of stilbene derivatives is effected by the nitroso-compounds, but at high temperatures the formation of stilbenes may not take place at all, whilst azo-compounds can be formed. The rates of the various reactions depend on the presence of other groups. A series of mechanisms for the various reactions is discussed.

M. ZVEGINTZOV.

Stereochemistry of aromatic compounds. IX. Tetraphenylene and the mobility of benzene rings. R. KUHN (Annalen, 1929, 475, 131—136).—The hydrocarbon, m. p. 318° (corr.), obtained by heating dry 4 : 4'-di-iododiphenyl with copper at 300° is not a cyclic tetraphenylene as stated by Sircar and Majumdar (A., 1928, 1235), but is *pp'*-diphenyl-diphenyl identical with a specimen prepared by Gerngross and Dunkel's method (A., 1924, i, 720). The other products of the reaction are fractions containing iodide, that subliming at 450—500°/15 mm. being reduced by zinc and acetic acid to a hydrocarbon, m. p. 465°, probably hexaphenyl. The stereochemistry of compounds containing aromatic ring systems is discussed.
J. W. BAKER.

Highly polymerised compounds. XXII. Constitution of polyindene. H. STAUDINGER, A. A. ASHDOWN, M. BRUNNER, H. A. BRUSON, and S. WEHRLI. **XXIII. Behaviour of polyindenes when heated.** H. STAUDINGER, H. JOHNER, and V. WIEDERSHEIM. **XXIV. Hydropolyindenes.** H. STAUDINGER, H. JOHNER, G. SCHIFMANN, and V.

WIEDERSHEIM (Helv. Chim. Acta, 1929, 12, 934—957, 958—961, 962—972).—XXII. The polymerisation of indene takes place rapidly under the influence of catalysts, the best of which are, in order of efficacy, stannic chloride, titanous chloride, boron trichloride, antimony pentachloride, and antimony trichloride. The reaction is carried out in benzene or chloroform solution, and the product is isolated by pouring the coloured solution into alcohol. The product is a white powder, mean mol. wt. 2000—5000. Polyindenes are hemicolloidal; no eucolloidal products can be obtained (cf. this vol., 305). The product is a mixture of polymeric homologues which are partly separable by extraction and precipitation with solvents into a series of fractions of successively higher temperatures of liquefaction (180—185° to 230—240°), increasing mol. wts. (1600—6000), and increasing viscosities in solution, corresponding with a variation in mean degree of polymerisation from 14 to 52. The viscosities of solutions of indene and of styrene, on the one hand, and of polyindenes and of polystyrenes, on the other, are similar in magnitude, and this indicates a similar molecular structure in the two polymeric homologous series. Polyindenes, unlike polystyrenes, however, do not undergo ozonolysis. The product of the action of ozone is a white powder, charring at 200°, the composition of which corresponds with a mixture of polymerised monoxide and dioxide. Polystyrenes and polyindenes are probably, like polymerised α -methylstyrenes, formed from long chains, the terminal valencies of which become saturated by forming rings. The fact that the mol. wt. is the greater the lower is the temperature and the higher the concentration at which polymerisation is carried out is probably due to the easier formation of rings in the one case, and the tendency to form longer chains in the other. No polyindenes showing evidence of crystalline structure with X-rays can be isolated.

XXIII. The behaviour of polyindenes when heated shows that they are true polymerides, in which the original indene molecules are bound by covalencies, and not merely associated. Polyindene mixtures of mean mol. wt. 1500, 3000, and 6000, and correspondingly different viscosities in solution, show no change in the viscosities when heated dry or in solution at 200° in nitrogen. In air or oxygen the products of highest mol. wt. show signs of breaking down and darken. At 270—280° there is evidence of partial cracking.

XXIV. Polyindenes are reduced by hydrogen in presence of nickel at 270° under the same conditions as polystyrenes (this vol., 306) to yield hydropolyindenes; these are white powders of lower m. p. (100—200°) which are unattacked by concentrated sulphuric acid and give no coloration with tetranitromethane. When heated above 300° cracking takes place and products of paraffin-like odour are formed. It is not possible to prove strictly that complete hydrogenation takes place in all cases without change in molecular size on account of the partial cracking of polyindenes which takes place at the elevated temperatures necessary for reduction, but incomplete hydrogenation yields products of only slightly lower viscosity, whilst the Florida earth on which the catalyst is deposited can alone cause degradation. In solution in methylcyclohexane or decahydronaphthal-

ene at 299° it is possible to hydrogenate polyindenes of low mol. wt. without decomposition. The results with polystyrene (this vol., 1287) show, however, that cryoscopic measurements indicate the size of the molecules, which can react without disruption.

R. K. CALLOW.

meso-Derivatives of anthracene and of 9:9'-dianthranyl. M. MINAEV and B. FEDOROV (Ber., 1929, 62, [B], 2489—2494).—9-Nitroanthracene is converted by sodium sulphite in boiling aqueous solution into sodium nitrite and a mixture of unchanged 9-nitroanthracene, sodium 9:9'-dianthranyl-

10-sulphonate, $\text{CH} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C}-\text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C}-\text{SO}_3\text{Na}$, and

sodium anthracene-9-sulphonate. The last-named compound is readily decomposed by boiling, dilute mineral acids into anthranol and sodium hydrogen sulphite, which react further to yield anthracene and sodium hydrogen sulphate. When oxidised by alkaline permanganate it gives anthraquinone almost quantitatively. With aqueous ammonia at 200° it affords 9-aminoanthracene, m. p. 115—116° (decomp.) (cf. Meisenheimer and Connerade, A., 1904, i, 391). Sodium 9:9'-dianthranyl-10-sulphonate (also *monohydrate*) may be prepared in poor yield by the action of warm, very dilute sodium hydroxide on sodium anthracene-9-sulphonate; it is oxidised in alkaline solution to anthraquinone and transformed by dilute acids into 9:9'-dianthranyl. 10-Hydroxy-9:9'-dianthranyl appears to be produced in poor yield by the action of sodium hydroxide, whereas aqueous ammonia at 190—200° yields 10-amino-9:9'-dianthranyl, m. p. above 305° (decomp.). Unlike 9-aminoanthracene, 10-amino-9:9'-dianthranyl suffers normal diazotisation and the products couple with β -naphthol and other hydroxynaphthalenes and their sulphonio acids.

H. WREN.

Synthesis of anthracene homologues. I. 2:6- and 2:7-Dimethylantracenes. G. T. MORGAN and E. A. COULSON (J.C.S., 1929, 2203—2214).—The presence of the above homologues of anthracene in the distillate from low-temperature tar has been confirmed by comparison with the synthetic products, and doubts concerning the constitution of other homologues have been cleared up. Three methods are given for the preparation of 2:4:4'-trimethylbenzophenone, and the structure of the ketone is made clear by one of them, viz., the interaction of the Grignard compound of 4-bromo-*m*-xylene with *p*-toluonitrile. The ketimine thus formed is hydrolysed to the ketone, which when maintained at its b. p. for some time slowly passes into 2:7-dimethylantracene, identical with the 1:6- or 1:7-compound described by Lavaux (A., 1910, i, 548). In a similar manner 2:5:4'-trimethylbenzophenone can be prepared from 2-iodo-*p*-xylene and *p*-toluonitrile, and converted into 2:6-dimethylantracene, which corresponds with the homologue described by Lavaux as the 2:7-derivative (cf. Flumiani, A., 1924, i, 1327).

2:7-Dimethylantracene, m. p. 241° (corr.), yields on oxidation 2:7-dimethylantraquinone, m. p. 170° (corr.), which is further oxidised to 2-methylantraquinone-7-carboxylic acid, m. p. 283° (corr.) (described

by Lavaux as 6-methylantraquinone-1-carboxylic acid). Anthraquinone-2:7-dicarboxylic acid, m. p. above 360°, is produced when 2-methylantraquinone-7-carboxylic acid is boiled with an excess of chromic anhydride in acetic acid.

J. W. PORTER.

Phenanthrene derivatives. R. K. CALLOW and J. M. GULLAND (J.C.S., 1929, 2424—2425).—Details are given of an improved method for the preparation of 9-bromo-10-nitrophenanthrene based on that of Austin (*ibid.*, 1908, 93, 1760). The preparation of a dinitrophenanthrene, m. p. 255—260°, is also described. 9-Phenanthrylaminoacetonitrile, m. p. 231—235°, was prepared by the action of potassium cyanide in formaldehyde solution on 9-aminophenanthrene, and on alkaline hydrolysis furnished 9-phenanthrylglycine, m. p. 199—201°. This when boiled with acetic acid yielded a substance, m. p. 203—206° (decomp.), probably 2:5-diketo-1:4-di-(9'-phenanthryl)piperazine. Diphenanthracidine or a complex acridine derivative, m. p. above 320°, is stated to be formed by the action of formaldehyde on 9-aminophenanthrene in acetic acid solution.

J. W. PORTER.

Linear pentacene series. XIII. Nomenclature. Questions of structure. E. PHILIPPI (Monatsh., 1929, 53 and 54, 638—642).—Dinaphthanthracene (Philippi, A., 1914, i, 826) is renamed *lin.*-pentacene; the numbering is as before. Re-investigation of the hydrocarbon (*loc. cit.*) confirms its instability. Energetic reduction of a dinitropentacenequinone has given tetradecahydropentacene, m. p. 227°. The author considers that the dihydroxypentacenediquinone of Hernler and Sommer (this vol., 1453) has each of the hydroxyl hydrogen atoms related to three oxygen atoms.

H. BURTON.

Formation of tertiary amines in the reduction of nitriles and carbonyl compounds in basic solution. A. SKITA and F. KEIL (Monatsh., 1929, 53 and 54, 753—763).—The formation of tertiary (and in some cases secondary) amines has been observed during the reduction of nitriles, alone or in presence of other compounds. Tertiary amines are also produced during the reduction of ketones in presence of amines (cf. A., 1928, 1120, 1228).

[In part with H. HAVEMANN and W. FAUST.]—Hydrogenation of acetonitrile in aqueous solution and in presence of colloidal platinum at the ordinary temperature affords 85% of triethylamine. When a mixture of the nitrile and cyclohexanone is used, 5% of *N*-ethylcyclohexylamine is isolated in addition to 45% of triethylamine. Tripropylamine is obtained similarly from propionitrile; in presence of cyclohexanone, 10% of *N*-propylcyclohexylamine, b. p. 185° (hydrochloride, m. p. 248—250°); phenylthiocarbimide derivative, m. p. 122—123°, and 25% of dipropylamine result. Butyronitrile furnishes a mixture of di- [hydrochloride, m. p. 283—284°; picrate, m. p. 60—61° (lit. 59.5°)] and tri-butylamines [picrate, m. p. 104—105° (lit. 100.5°)]; in presence of cyclohexanone, 10% of *N*-butylcyclohexylamine, b. p. 207° (hydrochloride, m. p. 290°), 20% of di-, and 16% of tri-butylamines result. Valeronitrile yields mainly di-*n*-amylamine [hydrogen oxalate, m. p. 212.5—213° (lit. 210—211°)]; a small amount of the tertiary

amino is also formed. Reduction of *p*-methoxybenzonitrile in presence of cyclohexanone affords di-*p*-methoxybenzylamine, m. p. 34—35° (*hydrochloride*, m. p. 243—244°; *picrolonate*, m. p. 208°), and *p*-methoxybenzylcyclohexylamine (*hydrochloride*, m. p. 202°). *p*-Hydroxybenzylcyclohexylamine (*loc. cit.*) is obtained similarly from *p*-hydroxybenzonitrile.

Dimethylisopropylamine, b. p. 67—67.5° (*hydrochloride*, m. p. 205—206°), is formed from acetone and dimethylamine. *dl*-*N*-Methylephedrine [β -dimethylamino- α -hydroxy- α -phenylpropane][*O*-benzoate, b. p. 212—214°/20 mm., m. p. 65° (*hydrochloride*, m. p. 185—187°)], is prepared by reduction of a mixture of phenyl methyl diketone and dimethylamine, or the diketone, formaldehyde, and methylamine.

H. BURTON.

Triphenyltriaminoethylene. I. Synthesis of triphenyltriaminoethylene and some of its derivatives. II. Action of sulphur on triphenyltriaminoethylene. R. SHIBATA (Tech. Rep. Tohoku, 1929, 8, 21—25, 27—39).—Triphenyltriaminoethylene, m. p. 147° (decomp.), is obtained in 29% yield by heating trichloroethylene (1 mol.) with aniline (3 mols.) in the presence of excess of 16% aqueous sodium hydroxide at 90—95° for 48 hrs. The following derivatives are described: *mono*-, and *tetra-sulphonic acids* (the latter with 8H₂O), by heating with three times its weight of sulphuric acid for 4 hrs.; *acetyl derivative*, m. p. 123°; *dihydrochloride*, m. p. 167° (decomp.). *Tri-p-tolyltriaminoethylene*, m. p. 143° (decomp.), is produced by heating *p*-toluidine, trichloroethylene, and 20% aqueous sodium hydroxide at 100° for 48 hrs.

II. The following substances were isolated by heating together sulphur (1 part) and triphenyltriaminoethylene (5 parts) at 150° for 40 min.: diphenyldiaminoethylene, m. p. 132.5°; a *compound*, C₂₀H₁₅N₃S, m. p. 102—104°, probably triphenyltriaminothioethylene, C(NHPh)₂C(NHPh)SH; dithio-oxanilide, m. p. 134.5—135°, and a *compound*, m. p. 149.5°, of unknown constitution. Similar treatment of tritolyltriaminoethylene yielded two *compounds*, m. p. 200° and 136—137°, respectively, the constitution of which was not elucidated. Oxidation of dithio-oxanilide in acetone with potassium permanganate afforded oxanilide and thio-oxanilide, whilst a *substance*, C₁₄H₁₀N₂S₂, m. p. 137°, and probably dehydrothio-oxanilide together with phenyl thiocarbimide were obtained by oxidation of a benzene solution with lead peroxide and glacial acetic acid.

A. I. VOGEL.

Bromination of *p*-anisidine and *p*-acetanisidide, and nitration of 3:5-dibromo-*p*-acetanisidide and some of its derivatives. E. BUREŠ and M. NEDELKOVÁ (Časopis Českoslov. Lek., 1929, 9, 23—28; Chem. Zentr., 1929, i, 2639).—The violet product of interaction of bromine and *p*-anisidine obtained by Wieland and by Fries is considered to be an additive compound. The action of dry bromine on *p*-acetanisidide or *p*-anisidine yields the 3:5-dibromo-compound.

A. A. ELDRIDGE.

† Compounds of the nature of "germanin" (Bayer 205). H. BAUER and J. BECKER (Arb. Staatsinst. exp. Ther., Frankfurt a. M., 1928, 16 pp.;

Chem. Zentr., 1929, i, 2970).—Variations in the composition of "germanin" weaken its therapeutic activity. Nitrobenzoyl chloride was allowed to react with an aminonaphthalenesulphonic acid, the product was reduced, and the resulting substance again treated with nitrobenzoyl chloride, the product being again reduced and the amino-compound condensed with carbonyl chloride. Variations consisted in the substitution of benzenesulphonic or aminobenzene-arsinic for naphthalenesulphonic acids, and of thiocarbamide, oxalyl, malonyl, diethylmalonyl, phthalyl, isophthalyl, and terephthalyl for the carbamide grouping. Further, methyl groups were replaced by propyl or isopropyl, were removed, or were increased in number. The following acid chlorides were employed: 3-nitro-4-methylbenzoyl chloride, b. p. 139—140°/2 mm., f. p. 11°, from *p*-toluonitrile by nitration, hydrolysis of the product, and treatment of the acid, m. p. 187°, with phosphorus pentachloride; 5-nitro-2:4-dimethylbenzoyl chloride, m. p. 58° (approx.), from *m*-xylydine by conversion through the diazo-compound into 2:4-dimethylbenzonitrile, hydrolysis, nitration of the acid to the 5-nitro-compound, and treatment with phosphorus pentachloride; 3-nitro-4-methoxybenzoyl chloride, m. p. 43—46° (indef.); 3-nitro-4-dimethylaminobenzoyl chloride.

A. A. ELDRIDGE.

Reduction of nitro-compounds in pyridine solution. O. L. BRADY, J. N. E. DAY, and C. V. REYNOLDS (J.C.S., 1929, 2264—2266).—Reduction of nitro-compounds which are only sparingly soluble in alcohol with hydrogen or ammonium sulphide may be effected by passing hydrogen sulphide into a solution or suspension of the nitro-compound in pyridine containing a little water with or without the addition of ammonia or piperidine, the conditions depending on the particular nitro-compound. Thus 2:4-dinitromethylaniline, 2:5-dinitroaniline, 2:5- and 3:5-dinitro-*p*-toluidine give, respectively, 4-nitro-2-aminomethylaniline (60% yield), 4-nitro-*m*-phenylenediamine, 5-nitro-2:4-tolylenediamine, and 5-nitro-3:4-tolylenediamine. 4:6-Dinitromethyl-*m*-toluidine gives 6-nitro-4-aminomethyl-*m*-toluidine, m. p. 180°, converted by nitrous acid into 5-nitro-1:6-dimethyl-1:2:3-benzotriazole, m. p. 203°, whilst *m*-dinitrobenzene and 1-nitronaphthalene give *m*-nitroaniline (67% yield) and α -naphthylamine (76% yield). Reduction of 2:4:6-trinitrotoluene with hydrogen sulphide in hot pyridine solution in the presence of piperidine gives 6-nitro-2:4-tolylenediamine, whilst at 0° the product is 2:6-dinitro-*p*-toluidine.

J. W. BAKER.

Derivatives of 4:4'-diaminodiphenylmethane. H. RIVIER and A. FARINE (Helv. Chim. Acta, 1929, 12, 865—869).—4:4'-Diaminodiphenylmethane is prepared more conveniently by condensing aniline hydrochloride with methylal, instead of formaldehyde. Oxidation of the acetyl derivative with chromic acid in acetic acid gives a 70% yield of 4:4'-diaminobenzophenone, m. p. 244—245° (phenylhydrazone, m. p. 240—241°), by way of the acetyl derivative, m. p. 235° (cf. Fierz and Koechlin, A., 1918, i, 549). Partial bromination of 4:4'-diaminodiphenylmethane gives a poor yield of the 3:3'-dibromo-compound, m. p.

111—112°, which is best prepared by hydrolysis of the *acetyl* derivative, m. p. 230—231°, obtained by bromination of 4:4'-diacetamidophenylmethane in acetic acid. The 3:5:3':5'-*tetrabromo*-compound, decomp. 250°, or m. p. 270° (decomp.) when rapidly heated, is prepared by bromination in acid solution. The bromo-compounds are formed in poor yield from the corresponding anilines and methylal. 3:3'-*Di-bromo*-4:4'-*diaminobenzophenone*, m. p. 243—244°, is obtained by direct bromination, and the *acetyl* derivative, m. p. 237—238°, by bromination, *acetyl*-ation, or oxidation from the appropriate compound.

R. K. CALLOW.

Fluorene series. Action of benzaldehyde on 2:7-diaminofluorene and the relation of fluorene to diphenyl. Action of phthalic anhydride on 2:7-diaminofluorene. A. NOVELLI (Anal. Asoc. Quím. Argentina, 1929, 17, 25—30, 31—41, and Anal. Fis. Quím., 1929, 27, 740—749, 750—754).—2:7-Diaminofluorene condenses with benzaldehyde when heated, preferably in alcoholic solution. The product is not a "Kaufler compound," analogous to that supposed to have been obtained from benzidine (Barzilowski, A., 1892, 854; cf. Dennett and Turner, A., 1926, 391), but 2:9-dibenzylidene-2:7-diaminofluorene, m. p. 247—250° (decomp.), which may be diazotised in concentrated sulphuric acid and the diazonium sulphate coupled with β -naphthol to yield a blue *azo-dye*.

2:7-Diaminofluorene condenses with phthalic anhydride in boiling water to yield *N-monophthalyl*-2:7-diaminofluorene, m. p. above 300°, for which a phthalide structure is suggested. The reaction is thus analogous to that of benzidine (Le Fevre and Turner, A., 1926, 1131). The compound may be diazotised in concentrated sulphuric acid and the diazonium compound coupled with β -naphthol. When boiled with benzaldehyde or salicylaldehyde it yields the 2:9-dibenzylidene derivative, m. p. above 300°, and the 2:9-disalicylidene derivative, m. p. about 300°.

R. K. CALLOW.

Oxidation of 2:7-diaminofluorene. C. RUIZ (Anal. Asoc. Quím. Argentina, 1929, 17, 42—48).—The formation of 4:4'-di-(*p*-aminophenyl)azobenzene by the transformation of 4:4'-diphenylquinonediimine, obtained by the oxidation of benzidine, is regarded as an argument in favour of the Kaufler formula for benzidine. 2:7-Diaminofluorene, similarly, is oxidised by lead dioxide in boiling chloroform to give 7:7'-diamino-2:2'-azofluorene, m. p. 273—275° (*dihydrochloride*, m. p. above 300°), in 14% yield. This compound may be diazotised in suspension in concentrated hydrochloric acid and the solution coupled with naphthionic acid. It is reduced by stannous chloride to give 2:7-diaminofluorene.

R. K. CALLOW.

***p*-Cymene.** XII. 2-*p*-Cymyl-4-semicarbazide and derivatives. A. S. WHEELER and J. G. PARK (J. Amer. Chem. Soc., 1929, 51, 3079—3082).—2-*p*-Cymylcarbamide (I), m. p. 168—169° (cf. Demonbreun and Kremers, A., 1924, i, 1002), is conveniently prepared from 2-amino-*p*-cymene and potassium cyanate in acetic acid solution. When 2-amino-*p*-cymene is heated with carbamide at 150—170°, the chief product formed is *s-di*-2-*p*-cymylcarbamide, m. p.

240° with darkening. Prolonged treatment of I with hydrazine hydrate in alcoholic solution affords 2-*p*-cymyl-4-semicarbazide, m. p. 112° [*hydrochloride*, m. p. 166—168° (decomp.)]. This condenses readily with ketones and 2-*p*-cymyl-4-semicarbazones of the following are described: acetone, m. p. 182° (this and the following m. p. are corr.); methyl ethyl ketone, m. p. 182—183°; α -dichloroacetone, m. p. 173° (decomp.); mesityl oxide, m. p. 163°; ethyl acetoacetate, m. p. 133.5°; cyclohexanone, m. p. 192.5°; camphor, m. p. 217°; carvone, m. p. 97°; benzophenone, m. p. 150°; acetophenone, m. p. 212°, and benzoin, m. p. 172°.

H. BURTON.

***p*-Cymene.** XIII. 2-*p*-Cymylhydrazine and derivatives. A. S. WHEELER and C. L. THOMAS (J. Amer. Chem. Soc., 1929, 51, 3135—3139).—Diazotisation of 2-amino-*p*-cymene and subsequent reduction with sodium sulphite affords 2-*p*-cymylhydrazine (I), b. p. 129—132°/5 mm., m. p. 26.5°, d_{25}^{25} 0.9863, n_D^{25} 1.5551 (cf. Demonbreun and Kremers, A., 1924, i, 1002) [*hydrochloride*, m. p. 198° (lit. 186—187°); *hydrobromide*, m. p. 174°; *sulphate*, m. p. 130°; *picrate*, decomp. suddenly at 124°; *p-nitrobenzoyl* derivative, m. p. 177°]. *Cinnamaldehyde*, m. p. 90°; *salicylaldehyde*, m. p. 87°, and *benzophenone*-2-*p*-cymylhydrazones, m. p. 88°, are described. Unstable derivatives were obtained by using methyl ethyl ketone, acetophenone, and benzaldehyde (cf. Demonbreun and Kremers, *loc. cit.*), whilst no condensation occurred with methyl nonyl ketone, *pp'*-tetramethyldiaminobenzophenone, or benzoylacetone. When I is treated with carbamide, 2-*p*-cymyl-1-semicarbazide, m. p. 171°, is formed; with potassium thiocyanate in acetic acid solution 2-*p*-cymyl-1-thiosemicarbazide, m. p. 184°, results. Carbon disulphide and I yield an unidentified compound, m. p. 177°.

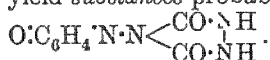
H. BURTON.

Relation between quinonehydrazones and *p*-hydroxyazo-compounds. VII. Aliphatic-aromatic *pp'*-dihydroxy- and -diamino-bisazo-compounds. W. BORSCHKE, W. MULLER, and C. A. BODENSTEIN (Annalen, 1929, 475, 120—131).—Condensation of benzoquinone with the dihydrazides of various dibasic acids in alcoholic solution in the presence of hydrochloric acid does not yield cyclic benzoquinonehydrazones of the type

$$\text{C}_6\text{H}_4 \begin{array}{c} \text{N-NH-CO} \\ \text{N-NH-CO} \end{array} [\text{CH}_2]_n$$
 but 2 mols. of benzoquinone condense with 1 mol. of the dihydrazide to yield *p*-hydroxyazo-compounds of the type

$\text{R}(\text{N}(\text{N}(\text{C}_6\text{H}_4\text{OH})_2)_2$. Thus with carbohydrazide is obtained *di-p-hydroxyphenylcarbodiazone* ($\text{R}=\text{CO}$) decomp. 228°, whilst by addition of sodium acetate and anisaldehyde to the filtrate the *anisylidene* derivative, m. p. 187°, of *p*-hydroxybenzeneazoformhydrazide (which cannot itself be isolated) is obtained, the same substance being obtained, together with the dianisylidene derivative, by condensation of anisaldehyde-carbohydrazide with benzoquinone. Similarly, by addition of acetophenone instead of anisaldehyde is obtained *acetophenone-p-hydroxybenzeneazoformhydrazide*, m. p. 168—169°. Similar condensation of benzoquinone with carboxyamido-carbohydrazide (Pellizzari and Roncagliolo, A., 1907, i, 833) yields ω -carboxyamido-*p*-hydroxybenzeneazoformhydrazide,

$\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 215—216° (decomp.). Toluquinone and carbonylhydrazide condense to give *di-4-hydroxy-3-methylphenylcarbodiazone*, m. p. 207° (decomp.). With the dihydrazides of the following dibasic acids, oxalic, m. p. 244—245° (lit. 241°); malonic; succinic; glutaric; adipic, m. p. 178° (lit. 171°); sebacic, m. p. 187—188° (lit. 184—185°), and *diphenic acid*, m. p. 216—217° (*dibenzylidene*, m. p. 186—187°; *dianisylidene*, m. p. 224—225° derivatives; acetophenone condensation product, m. p. 214°), benzoquinone condenses to yield *oxalyl-* + $2\text{H}_2\text{O}$ and anhydrous, m. p. 242—243°; *malonyl-*, m. p. 242—243°; *succinyl-* [*dibenzoyl* derivative, m. p. 200° (decomp.)]; *glutaryl-*, decomp. 193—194°; *adipyl-* (*dibenzoyl* derivative, m. p. 258—259°); *sebacyl* + MeOH , m. p. 195°, and *diphenyl-2:2'-dicarboxyl-*, m. p. 170—171°, *-bis-4-azophenols*, whilst by the action of benzaldehyde on the appropriate mother-liquors are obtained *p-hydroxybenzeneazomalonyl-*, m. p. 238—239°, and *p-hydroxybenzeneazosebacyl-*, m. p. 135—137°, *-benzylidenehydrazone*. *Succinylbis-5-azo-o-cresol*, m. p. 204—205°, is prepared similarly from toluquinone. Condensation products of a similar type, $\text{R}(\text{NH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{OH})_2$, are obtained with benzoquinone monoxime and thus are obtained *bisbenzoquinone-1:1'-oxime-4:4'-carbohydrazone* + H_2O , decomp. 205°, *-oxalhydrazone*, decomp. above 320°; *-malonhydrazone*, decomp. 235°; and *sebacylhydrazone*, decomp. 205°. These are reduced by hydrogen and colloidal palladium in *N*-sodium hydroxide solution to the *p*-aminobenzenehydrazo-derivatives $\text{R}(\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, and thus are obtained *carbodi-p-aminophenylhydrazide* and *succindi-(p-aminophenylhydrazide)*. These are oxidised by atmospheric oxygen to *di-p-aminophenylcarbodiazone*, m. p. 205—210° (decomp.), and *succinylbis-4-azoaniline*, decomp. 320°, respectively. Aminourazole (obtained by heating carboxyamidocarbohydrazide) condenses with benzoquinone and toluquinone to yield substances probably of the type



J. W. BAKER.

Cleavage of azo-dyes by sulphites. K. H. ENGEL (J. Amer. Chem. Soc., 1929, 51, 2986—2994).—Prolonged treatment of an azobenzene derivative with an aqueous solution of a normal sulphite (2 mols.) at 90—95° in closed vessels causes fission, usually with the formation of an aniline, salts of a sulphamic acid, $\text{R}\cdot\text{NH}\cdot\text{SO}_3\text{H}$, and compounds of the type $\text{R}\cdot\text{N}(\text{O}\cdot\text{SO}_3\text{H})_2$. Thus, 4-hydroxyazobenzene is decomposed by ammonium sulphite to aniline (0.78 mol.), phenylsulphamic, (0.22 mol.), *p*-hydroxyphenylsulphamic (0.22 mol.), and *p*-aminophenol-*NN*-disulphonic acids (0.78 mol.). No free ammonia or *p*-aminophenol and only a small amount of sulphate are formed during the reaction; 98.8% of the sulphite used is in combination with the fission products. Treatment of the mixed sulphonic acids formed with boiling hydrochloric acid gives aniline, *p*-aminophenol-2-sulphonic acid, and the very soluble *p*-aminophenol-*O*-sulphonic acid (α -naphthaleneazo-derivative). The last-named compound is hydrolysed only slowly by 5*N*-hydrochloric acid at 90—93°. With sodium or potassium sulphite, reaction is carried out at 140—

150°; with ammonium sulphite at 130—135°, reaction is more rapid than at 90—93°, but the products formed are essentially the same. 4-Hydroxyazobenzene-4'-sulphonic acid undergoes similar fission with ammonium sulphite; free sulphanilic acid is produced. Rearrangement of the *N*-sulphonic acids obtained gives *p*-aminophenol-2- and *O*-sulphonic acids. It is suggested that the primary product of the change is an additive compound formed from the azobenzene and sulphite. The two nitrogen atoms of the azo-group are assumed to differ functionally from one another.

H. BURTON.

Direct dibromination of *m*-bromophenol. H. H. HODGSON and J. NIXON (J.C.S., 1929, 2424).—Bromination of 3-bromo-2-nitrophenol in acetic acid yields 3:4:6-tribromo-2-nitrophenol, m. p. 109°. This is converted by methyl sulphate into 3:4:6-tribromo-2-nitroanisole, identical with a specimen obtained by methylation and nitration of the product of the bromination of *m*-bromophenol (Kohn and Strassmann, A., 1925, i, 1264). The product of the last-named reaction is therefore 3:4:6-tribromo-phenol.

J. W. BAKER.

Bromophenols. XXXIV. Debromination of bromocresols with zinc dust and acetic acid. M. KOHN and A. ARON (Monatsh., 1929, 53 and 54, 48—61; cf. A., 1927, 966).—Treatment of tetrabromo-*o*-cresol with zinc dust and acetic acid affords 3:5:6-tribromo-*o*-cresol [*methyl ether* (I), b. p. 308—311°/745 mm., m. p. 71°; *benzoate*, m. p. 133°; *acetate*, m. p. 77—78° (corr.)], purified by conversion into I and subsequent demethylation with 66% hydrobromic acid in acetic acid solution. Nitration of I gives the 4-nitro-derivative, m. p. 111°. 3:5-Dichloro-4:6-dibromo-*o*-cresol, m. p. 199° (lit. 196—197°), is debrominated similarly to 3:5-dichloro-6-bromo-*o*-cresol, m. p. 68° (*methyl ether*, b. p. 283—286°/745 mm., m. p. 59°; *benzoate*, m. p. 102°), whilst 2:3:5-tribromo- or tetrabromo-*p*-cresol furnishes 2:5-dibromo-*p*-cresol, m. p. 60° (*methyl ether*, b. p. 274—278°/748 mm., m. p. 78°; *benzoate*, m. p. 89°). Nitration of this in acetic acid solution yields 2:5-dibromo-3-nitro-*p*-cresol, m. p. 118°.

H. BURTON.

Substitution products of 4-nitro- and 4-acetamido-diphenyl ether. H. A. SCARBOROUGH (J.C.S., 1929, 2361—2367).—Iodine monochloride in acetic acid converts 4-nitrodiphenyl ether (I) into 4-iodo-4'-nitro-, m. p. 71° (*iodochloride*), reduced and acetylated to give 4-iodo-4'-acetamido- (II), m. p. 174° [also obtained by iodination of the 4-acetamidocompound, (III), m. p. 127°], which is hydrolysed to 4-iodo-4'-amino-diphenyl ether, m. p. 91°. This is converted into 4-bromo-4'-iodo-, m. p. 72°, which is also obtained by bromination of 4-iodo-, m. p. 48°, prepared from 4-amino-diphenyl ether (*hydrochloride*, m. p. 238°). Chlorination and bromination of I also occurs in the 4'-position. Dry bromine converts I or 4-bromo-4'-nitro- into 2:4-dibromo-4'-nitro-diphenyl ether (IV), m. p. 81° (also prepared from potassium 2:4-dibromophenoxide and *p*-chloronitrobenzene). Reduction and acetylation of 4-chloro-4'-nitro- gives 4-chloro-4'-acetamido-, m. p. 146°, converted by nitric (*d* 1.5) and acetic acids at 80° into 4'-chloro-3-nitro-4-acetamido-, m. p. 98° [also obtained in small yield by

chlorination of V (below)], hydrolysed to 4'-chloro-3-nitro-4-amino-, m. p. 114°, which is deaminated to 4'-chloro-3-nitro-diphenyl ether, m. p. 60°. Bromination of III in acetic acid in the presence of fused sodium acetate yields 4-bromo-4'-acetamido-, m. p. 161° (also obtained by reduction and acetylation of the 4-bromo-4'-nitro-derivative), which is converted by nitric and acetic acids at 80° into 4'-bromo-3-nitro-4-acetamido-diphenyl ether, m. p. 107° [also obtained by bromination of V (below)]. The last is hydrolysed to 4'-bromo-3-nitro-4-amino-, m. p. 144°, which is deaminated to 4'-bromo-3-nitro-diphenyl ether, m. p. 64°. Nitration of II gives 4'-iodo-3-nitro-4-acetamido-, m. p. 123° [also, in small yield, by iodination of V (below)], hydrolysed to 4'-iodo-3-nitro-4-amino-diphenyl ether, m. p. 155°. Nitration of III gives 3-nitro-4-acetamido-(V), m. p. 100°, hydrolysed to 3-nitro-4-amino-, m. p. 82°, which is converted by deamination, reduction, and acetylation into 3-acetamido-diphenyl ether (Ullmann and Sponagel, A., 1907, i, 38). Reduction and acetylation of IV gives 2:4-dibromo-4'-acetamido-, m. p. 158°, nitrated to the 3'-nitro-derivative, m. p. 141°, hydrolysed to 2:4-dibromo-3'-nitro-4'-amino-diphenyl ether, m. p. 107°. This is deaminated to 2:4-dibromo-3'-nitrodiphenyl ether, m. p. 72°. 4:4'-Di-iododiphenyl ether, m. p. 139°, is obtained by the action of excess of iodine monochloride in acetic acid on diphenyl ether, or by the Sandmeyer reaction from the 4-iodo-4'-amino-derivative. J. W. BAKER.

Products of condensation of aminophenols with aldehydes. T. G. LEVI (Gazzetta, 1929, 59, 544—548).—A number of compounds, some of which are applied in rubber manufacture, have been prepared by the condensation of aldehydes with aminophenols. The latter react in aqueous solution or suspension, or as the hydrochloride in presence of sodium acetate, when the hydrochloride of the product separates. With aldehydes insoluble in water the reaction is carried out in acetic acid. The following are described: derivatives of *p*-aminophenol: methylene- (G.P. 68,708) and ethylidene-, brown, insoluble, infusible powders, probably polymerides; *furfurylidene*-, m. p. 176.5° (hydrochloride); *o*-nitrobenzylidene-, m. p. 154°; *terephthalylidene*-, m. p. 256°; derivatives of *o*-aminophenol: methylene- and ethylidene- (polymerides?); *furfurylidene*-, amorphous; *o*-nitrobenzylidene-, m. p. 104°; *terephthalylidene*-, m. p. 213°; derivatives of 2:4-diaminophenol: dimethylene- and diethylidene- (polymerides?); diisovalerylidene- (hydrochloride, m. p. 126°); difurfurylidene-, tarry; dibenzylidene-, m. p. 106°; disalicylidene-, m. p. 170°; dicannamylidene- (hydrochloride); divanillylidene- (hydrochloride); *terephthalylidene*-, infusible and insoluble.

R. K. CALLOW.

Mixed aromatic hydroxysulphonates. I. Hydroxyphenyl-*p*-hydroxytolylsulphone. J. ZEHENTER and F. GOSCH (J. pr. Chem., 1929, [ii], 123, 276—283).—When a mixture of phenol and *p*-cresol is heated with concentrated or fuming sulphuric acid at 160—180° there are obtained 4:4'-dihydroxydiphenylsulphone, di-*p*-hydroxyditolylsulphone, and hydroxyphenyl-*p*-hydroxytolylsulphone + H₂O (I), m. p. 175° (diacetate, m. p. 161°; dibenzoate, m. p. 165°; sodium salt + 2EtOH, by the action of sodium carbonate;

disodium salt + EtOH, by the action of sodium on an alcoholic solution of I). Treatment of I with nitric acid (*d* 1.1—1.26) at 100° gives a nitro-derivative, m. p. 181—182° (decomp.), whilst bromination in ethereal solution affords a tribromo-derivative, m. p. 215°. Treatment of I with sulphuric acid at the ordinary temperature furnishes a disulphonic acid (barium salt + 7H₂O), together with phenol-4- and *p*-cresol-3-sulphonic acids; at higher temperature complete fission of I into the phenol- and cresol-sulphonic acids occurs. H. BURTON.

Highly polymerised compounds. XXV. Polyanethole. H. STAUDINGER and M. BRUNNER (Helv. Chim. Acta, 1929, 12, 972—984).—The polymerisation of anethole to polyanethole is readily effected in solution by Florida earth (cf. Lebedev and Filonenko, A., 1925, i, 225) or by metallic chlorides, such as stannic chloride, which forms a deeply-coloured solution. 1 Molecule of stannic chloride can cause quantitative polymerisation of 274 molecules of anethole, i.e., a much larger amount than that with which it could form a complex compound. Polyanethole is a white, amorphous powder of hemi-colloidal properties. The degree of polymerisation increases with fall of temperature or increase of concentration of the reaction mixture. The product may be separated into more and less soluble fractions having mean mol. wts. rising from 950 to 9500, temperatures of liquefaction rising from 110—140° to 280—330°, and increasing viscosities in solution, corresponding with a variation in the mean degree of polymerisation from 7 to 65. The variation of the viscosity of solutions with temperature indicates that no dissociation occurs. Treatment of polyanethole with hydriodic acid yields polypropenylphenol, which, instead of showing the expected phenolic properties, is a brown powder, swelling, but not dissolving, in alcoholic potassium hydroxide, phenol, or alcohol, and may be a "three-dimensional" condensation product.

R. K. CALLOW.

α -Naphtholsulphonic acids. E. GEBAUER-FULNEGG and A. GLUCKMANN (Monatsh., 1929, 53 and 54, 100—110).—Treatment of a potassium α -naphtholsulphonate with ethyl chloroformate gives the corresponding potassium *O*-carbethoxy- α -naphtholsulphonate, converted by phosphorus pentachloride into the *O*-carbethoxy- α -naphtholsulphonyl chloride. The following are described: *O*-carbethoxy- α -naphthol-2-, m. p. 130°; -3-, m. p. 140°; -5-, m. p. 174°; -6-, m. p. 112°, and -7-sulphonyl chlorides, m. p. 105°. Instead of the -8-sulphonyl chloride the compound SO₂Cl·C₁₀H₆·O·POCl₂(1:8), m. p. 78°, is formed. *O*-Carbethoxy- α -naphthol-2:7-disulphonyl chloride, m. p. 156°, is obtained similarly from the disulphonic acid formed by hydrolysis of α -naphthol-2:4:7-trisulphonyl chloride (A., 1928, 751). *O*-Carbethoxy- α -naphthol-5- and -6-sulphonanilides, m. p. 127° and 140°, respectively, are hydrolysed by alcoholic potassium hydroxide to α -naphthol-5- and -6-sulphonanilides, m. p. 201° and 181°, respectively (the -7-sulphonanilide, m. p. 155°, is also described). When *O*-carbethoxy- α -naphthol-3-sulphonyl chloride is treated with aniline an oxygen-free substance, m. p. 153°, results. Hydrolysis of this with potassium

hydroxide solution gives a compound, m. p. 236° with charring, which is sulphur- and nitrogen-free.

Treatment of α -naphthol-2-, -4-, or -7-sulphonic acids with an excess of chlorosulphonic acid at the ordinary temperature affords α -naphthol-2 : 4 : 7-trisulphonyl chloride, m. p. 174° (cf. *loc. cit.*). α -Naphthol-5-, -6-, and -8-sulphonic acids yield similarly α -naphtholtrisulphonyl chlorides with m. p. 140°, 203°, and 217°, respectively [the corresponding trianilides have m. p. 227°, 203°, and 240° (all with charring)]. The probable alternative orientations of these tri-derivatives are discussed. The product obtained from α -naphthol-3-sulphonic acid and chlorosulphonic acid could not be obtained crystalline; when it is treated with aniline a *chloronaphtholdisulphondianilide*, m. p. 250° with charring, results.

H. BURTON.

β -Naphtholdisulphonyl chlorides. J. POLLAK, E. GEBAUER-FULNEGG, and E. BLUMENSTOCK-HALWARD [with A. SCHLESINGER and H. STEHNO] (*Monatsh.*, 1929, 53 and 54, 83—89).—The β -naphtholdisulphonyl chloride (I), m. p. 177°, previously described (A., 1928, 751, 752) is formulated as the 1 : 5-derivative, since it is obtained by the action of chlorosulphonic acid on β -naphthol-5-sulphonic acid at the ordinary temperature. The potassium salt of *O*-carbethoxy- β -naphthol-5-sulphonic acid [sulphonyl chloride (II), m. p. 101°; *anilide*, m. p. 188°] is converted similarly into I. Hydrolysis of I with slightly diluted hydrochloric acid and treatment of the residue first with ethyl chloroformate and then with phosphorus pentachloride yields II (not affected by similar hydrolysis and treatment). β -Naphthol-1 : 7-disulphonyl chloride, m. p. 169° (*dianilide*, m. p. 233°), is obtained by the action of chlorosulphonic acid on β -naphthol-7-sulphonic acid. β -Naphthol-4-sulphonic acid gives an uncrystallisable product; when this is treated with aniline a β -naphtholdisulphondianilide, m. p. 290°, results. *Tribarium* and *tripotassium* salts of β -naphthol-1 : 5-, -1 : 6-, and -1 : 7-disulphonic acids are described.

H. BURTON.

***N*-Hydroxyethyl derivatives of *o*-aminophenol.** I. G. FARBERIND. A. G.—See B., 1929, 935.

Nitration of β -naphthol-6-sulphonic acid. N. N. VOROSHTZOV and N. M. KASATKIN.—See B., 1929, 934.

Halogen derivatives of cyclohexane-1 : 4-diol. L. PALFRAY and B. ROTHSTEIN (*Compt. rend.*, 1929, 189, 701—703).—Treatment of cyclohexane-1 : 4-diol with hydrochloric acid (3 mols.; *d* 1.19) at 100° for 6 hrs. gives 1 : 4-dichlorocyclohexane (principal product), 4-chlorocyclohexanol, and smaller amounts of $\Delta^{1:4}$ -cyclohexadiene and Δ^1 -cyclohexen-4-ol. When the dichloro-compound is cooled, crystals of trans-1 : 4-dichlorocyclohexane, m. p. 102°, b. p. 79—80°/13 mm., are precipitated, the residual liquid, b. p. 79—80°/13 mm., *d*₄²⁰ 1.1831, *n*_D²⁰ 1.4950, consisting mainly of *cis*-isomeride. Diminution of the amount of hydrochloric acid increases the yield of 4-chlorocyclohexanol, b. p. 105°/12 mm., *d*₄²⁰ 1.1435, *n*_D²⁰ 1.4930, but it was impossible to separate this substance into two isomerides. The *phenylurethane*, m. p. 99°, is described. Treatment of cyclohexane-1 : 4-diol with hydrobromic acid gave the corresponding dibromo-

compound, which on freezing deposited crystals of trans-1 : 4-dibromocyclohexane, m. p. 112°, the residual liquid, b. p. 114—115°/15 mm., *d*₄²⁰ 1.7834, *n*_D²⁰ 1.5531, being the impure *cis*-isomeride. The use of a smaller excess of hydrobromic acid gave 4-bromocyclohexanol, which could not be separated from the dibromo-compound by distillation. The action of benzoyl chloride on the mixture gave 4-bromocyclohexyl benzoate, b. p. 203—204°/18 mm., *d*₄²⁰ 1.3456, *n*_D²⁰ 1.5520. Treatment of cyclohexane-1 : 4-diol with acetyl chloride at 100° in a closed vessel yielded 4-chlorocyclohexyl acetate, b. p. 111—112°/18 mm., *d*₄²⁰ 1.1282, *n*_D²⁰ 1.4659. 4-Bromocyclohexyl acetate, b. p. 124°/17 mm., *d* 1.3381, *n*_D²⁰ 1.4873, is also described. The action of the requisite hydracid on these compounds gave small amounts of mixed 1 : 4-dihalogenocyclohexanes. A. A. GOLDBERG.

Physical properties of guaiacol. T. S. CARSWELL (*J. Amer. Pharm. Assoc.*, 1929, 18, 995—997).—Guaiacol, purified by crystallisation of the sodium salt, precipitation as the magnesium salt, repeated fractional crystallisation, and fractionation in vacuum, had m. p. 28.2°, b. p. 204.65°/746.4 mm. A needle-shaped form, m. p. —3.2°, has been prepared by crystallisation of molten guaiacol supercooled to —10°.

E. H. SHARPLES.

Bromoguaiacol carbonate. Determination of guaiacol carbonate. L. H. CHERNOFF (*J. Amer. Chem. Soc.*, 1929, 51, 3072—3074).—Bromination of guaiacol carbonate (I) in warm methyl-alcoholic solution gives bromoguaiacol carbonate, m. p. 178°. Using 0.1—0.5 g. of I and diluting the reaction mixture with an equal volume of water gives almost quantitative yields. For the determination of guaiacol carbonate admixed with substances such as starch, it is extracted with chloroform. The chloroform is evaporated and the residue brominated as above.

H. BURTON.

Alkylation of aromatic compounds. H. MEYER and K. BERNHAUER (*Monatsh.*, 1929, 53 and 54, 721—752).—When a solution of an aromatic compound in an alcohol is added gradually to well-stirred 70—80% sulphuric acid at 70—80° (bath temperature), alkylation occurs. When benzyl alcohol is used, reaction is best carried out at 40°. If the compound used is insoluble in the alcohol, the latter is added drop by drop and the former either gradually or altogether. With *n*-butyl alcohol, *sec*-butyl derivatives are formed; *n*-propyl alcohol affords isopropyl derivatives, and isobutyl alcohol furnishes *tert*-butyl compounds. Methyl alcohol does not react and ethyl alcohol ethylates only at 170° under pressure. Benzene, benzyl alcohol, and 70% sulphuric acid at 40° give diphenylmethane and 1 : 4-dibenzylbenzene (*dinitro*-derivative, m. p. 146°) (oxidised by chromic and acetic acids to 1 : 4-dibenzoylbenzene). Benzene, isopropyl alcohol, and 80% sulphuric acid at 65° yield isopropyl- (I), 1 : 4-diisopropyl- (II), and 1 : 3 : 4-trisopropyl-benzenes (III). Sulphonation of I affords a disulphonic acid (*barium* salt), converted by fusion with potassium hydroxide at 330—340° into a dihydroxyisopropylbenzene, m. p. 108—109° (*dibenzoate*, m. p. 114—115°). Oxidation of II with chromic, acetic, and sulphuric acids furnishes terephthalic acid,

whilst oxidation of III with nitric acid (*d* 1.16) gives an *isopropylbenzenedicarboxylic acid*, m. p. above 300°. Benzene and *isobutyl* alcohol afford a mixture of *tert*.-butyl- and 1:4-*di-tert*.-butyl-benzenes; *n*- or *sec*.-butyl alcohol yields *sec*.-butyl- and 1:4-*di-sec*.-butyl-benzenes (a small amount of the 1:2-derivative is also formed); *cyclohexanol* furnishes mainly *cyclohexylbenzene*. Benzylolation of toluene gives *phenyl-p*-tolylmethane and anthracene; *o*-xylene yields 4-benzyl-*o*-xylene (oxidised to trimellitic acid) and 1-methylantracene, m. p. 199° (oxidised to *anthraquinone-1-carboxylic acid*, m. p. 292°); *m*-xylene affords 4-benzyl-*m*-xylene (*nitro*-derivative, m. p. 115°) and 2-methylantracene (IV) [oxidised to *anthraquinone-2-carboxylic acid*, m. p. 284° (*chloride*, m. p. 147°; *ethyl ester*, m. p. 147°)]; *p*-xylene furnishes IV and the corresponding benzylxylene. The above anthracenes are formed by oxidation of the intermediate 9:10-dihydro-derivatives. *iso*Propylation of toluene yields *p*-cymene, oxidised by potassium dichromate and sulphuric acid at 60° to a mixture of *p*-methylacetophenone (*phenylhydrazone*, m. p. 97°) and *p*-acetobenzaldehyde, b. p. 135—138°/vac. (*bisphenylhydrazone*, m. p. 121°; *dioxime*, m. p. 177°). *p-tert*.-Butyl- and *p-sec*.-butyl-toluenes are obtained from toluene and *iso*- and *sec*.-butyl alcohols, respectively.

Benzylation of phenol gives a small amount of 2-, in addition to 4-hydroxydiphenylmethane; with *cyclohexanol*, 4-*cyclohexylphenol* (*benzoate*, m. p. 118.5°; *methyl ether*, m. p. 59°) is formed. Phenol and methylcyclohexanol furnish 4-methylcyclohexylphenol, m. p. 110—111° (*benzoate*, m. p. 87°; *methyl ether*, m. p. 41°), decomposed by treatment with silver sulphate (attempted dehydrogenation) to phenol and tetrahydrotoluene, b. p. 104°. Benzylation of *o*-cresol yields *phenyl-4-hydroxy-m-tolylmethane*, m. p. 35° (*oxalate*, m. p. 109°; *benzoate*, m. p. 115°); *isobutyl* alcohol and *o*-cresol give *o-tert*.-butyl-*o*-cresol (*nitro*-derivative, m. p. 85—86°). *iso*Propylation of *m*-cresol affords 6-*isopropyl-m*-cresol [*nitroso*-derivative, m. p. 165—167° (decomp.); *methyl ether*, b. p. 215—220°]. *p*-Cresol could not be alkylated.

Resorcinol and *isopropyl* alcohol form 4-*isopropyl*-, m. p. 105°, and 4:6-*diisopropyl-resorcinol*, m. p. 162° (*monomethyl ether*, m. p. 123°, by alkylation of resorcinol monomethyl ether); resorcinol dimethyl ether furnishes *mono*-, b. p. 245—250°, and *diisopropylresorcinol dimethyl ethers*, m. p. 41° (main product). Similarly, salicylic acid gives 5-*isopropyl-salicylic acid* (*acetyl* derivative, m. p. 63.5°; *phenyl ester*, m. p. 43°). 5-*tert*.-Butylacetylsalicylic acid has m. p. 128°. 2-*Nitro-5-isopropyltoluene*, b. p. 230—240°, and 4-chloro-*isopropylbenzene*, b. p. 190—195°, are obtained by *isopropylation* of *o*-nitrotoluene and chlorobenzene, respectively.

*iso*Propylation of naphthalene in presence of 80% sulphuric acid at 80° gives alkylated naphthalene-sulphonic acids. Dilution of the reaction mixture and distillation with superheated steam yields the *iso*-propylnaphthalenes. The following derivatives are described: 1-*isopropyl*naphthalene, purified through the 4-sulphonic acid [*potassium* and *aniline*, m. p. 190° (decomp.), salts]; 2-*isopropyl*naphthalene, sulphonated to the 1-sulphonic acid, m. p. 137° (decomp.)

[*potassium* and *aniline*, m. p. 209—210° (decomp.), salts; *sulphonyl chloride*, m. p. 61°; *sulphonamide*, m. p. 140°]; 1:6-*diisopropyl*naphthalene, m. p. 52°, oxidised by 5% nitric acid to naphthalene-1:6-dicarboxylic acid (*methyl ester*, m. p. 98—98.5°) and 1(or 6)-*isopropyl-6(or 1)-naphthoic acid* (*methyl ester*, b. p. 323—327°); *triisopropyl*naphthalene (oxidation and subsequent esterification furnishes a *methyl diisopropyl*naphthoate, b. p. 206°/vac., and *methyl isopropyl*naphthalenedicarboxylates, m. p. 192° and 132—134°, respectively); *tetraisopropyl*naphthalene, m. p. 127° (*nitro*-derivative, m. p. 201°), oxidised by nitric acid (*d* 1.3) to a *diisopropyl*naphthalenedicarboxylic acid, m. p. above 300°. A mixture of 2:6- and 2:7-*diisopropyl*naphthalenes is also obtained (from the oxidation products a *methyl isopropyl*naphthoate, m. p. 73—74°, is isolated after esterification). 4- and 2-*iso*Propyl- α -naphthol (*benzoate*, m. p. 121°; *methyl ether*, b. p. 217—222°/50—55 mm.) have m. p. 72° and 65—66°, respectively. Distillation of a mixture of potassium cyanide and 2-*isopropyl*naphthalene-1-sulphonate in a current of carbon dioxide, and hydrolysis of the resulting nitrile with 40% alcoholic alkali hydroxide, furnishes 2-*isopropyl- α -naphthoic acid*, m. p. 146°.

*iso*Propylation of naphthalene-2-sulphonic acid in presence of concentrated sulphuric acid at 120° gives 1:6-*diisopropyl*naphthalene-3(or 7)-sulphonic acid (V) [*potassium* + H₂O, and *o*-toluidine, m. p. 215—216°, salts; *sulphonyl chloride*, m. p. 71°; *sulphonamide*, m. p. 179—180°; *hydrazide*, m. p. 130—132° (decomp.); *methyl ester*, m. p. 77°], converted by the usual methods into 1:6-*diisopropyl- β -naphthol*, m. p. 90° (*methyl ether*, m. p. 59°; *benzoate*, m. p. 99°), and 1:6-*diisopropyl*naphthalene. The residue after removal of V is desulphonated, oxidised, and esterified, whereby methyl naphthalene-2:6-dicarboxylate and a methyl *isopropyl*naphthoate, m. p. 73°, are formed. *iso*Propylation of naphthalene-1-sulphonic acid at 40—45° yields a *diisopropyl*naphthalenesulphonic acid (*o*-toluidine, m. p. 214°, and *potassium* salts; *sulphonyl chloride*, m. p. 119°; *sulphonamide*, m. p. 151°), converted into a *diisopropyl*naphthalene, b. p. 317—319°, m. p. 38°. Tetra-*isopropyl*naphthalene is obtained by steam-distillation of the reaction mixture. Naphthalene and *isobutyl* alcohol afford mainly a *di-tert*.-butyl-naphthalene, m. p. 142°. H. BURTON.

Sequoite [pentahydroxymethoxycyclohexane], a cyclose from redwood (*Sequoia sempervirens*). E. C. SHERRARD and E. F. KURTH (J. Amer. Chem. Soc., 1929, 51, 3139—3141).—The cycloses extracted from the dry heartwood of *Sequoia sempervirens* (B., 1928, 636) are pinite and sequoite (trace <0.06%), m. p. 234—235° (*penta-acetate*, m. p. 198°), separable by fractional crystallisation from aqueous alcohol. The new cyclose is decomposed by hydriodic acid, yielding methyl iodide and *i*-inositol, thus showing it to be a monomethyl ether of *i*-inositol (cf. *loc. cit.*).

H. BURTON.

Sterol group. VI. Dihydroergosterol and the formation of isomerides. I. M. HEILBRON, F. JOHNSTONE, and F. S. SPRING (J.C.S., 1929, 2248—2255).—Reduction of ergosterol with sodium and boiling amyl alcohol gives mainly α -dihydroergosterol

I) (Heilbron, Sexton, and Spring; this vol., 809) together with a small quantity of the stereoisomeric γ -dihydroergosterol (II), m. p. 205—206° [α]_D²⁰ —10° in chloroform, saturation of the 1:2 (or 1:13) double linking having occurred, and in agreement with this neither I nor II gives a colour with antimony trichloride. Moreover, I is converted into II by heating with a solution of sodium amyloxide. Acetic anhydride converts I into an acetate, the m. p. and specific rotation of which depend on the duration of acetylation, which is converted by anhydrous hydrogen chloride in chloroform solution into the acetate, m. p. 108—109°, [α]_D²⁰ —25.2° in chloroform, of β -dihydroergosterol + xH₂O (III), m. p. 124°, [α]_D¹⁸ —7.0° in chloroform (no colour with antimony chloride), the free dihydrosterol being liberated by the action of alcoholic potassium hydroxide. It is suggested that the conversion of the α - into the β -dihydro-isomeride involves the prior addition of hydrogen chloride to the 6:7-double linking and subsequent elimination from the 2:7-positions giving rise to a new double linking at 2:3. Both isomerides absorb 1 mol. of hydrogen in the presence of palladium in ether to give α -ergosterol. Boiling alcoholic mercuric acetate converts I with elimination of 2 atoms of hydrogen into ergosterol-D (ergostatrienol-D), m. p. 167°, +17.8° (acetate, m. p. 172°, [α]_D²⁰ +15.9° in chloroform) (cf. Windaus and Auhagen, this vol., 1065), which is characterised by three bands in its absorption spectrum at 235, 243, and 252. A similar banded structure is shown by ergosterol-A and, contrary to Windaus and Linert (A., 1928, 1372), by dehydroergosterol, which has bands at 312, 327, and 345 μ . Similarly, III is converted by alcoholic mercuric acetate into ergosterol-E + xH₂O, m. p. 124—125°, [α]_D¹⁸ —22.9° in chloroform (yellow colour with antimony trichloride) (acetate, m. p. 119—120°, [α]_D¹⁸ —38.0° in chloroform). Oxidation of I with chromic oxide and acetic acid, or catalytically by heating with copper bronze at 250—270°/2 mm., converts it into α -ergostadienone (IV), m. p. 182—183° [semicarbazone, m. p. 254° (decomp.)], identical with the ketone obtained by Windaus and Auhagen (*loc. cit.*) by the action of nickel on ergosterol. The action of anhydrous hydrogen chloride on a chloroform solution of IV isomerises it to β -ergostadienone, m. p. 125° (semicarbazone, m. p. 266°), which is also obtained by chromium oxide oxidation of III. Both the α - and β -ketones are reduced by hydrogen (2 mols.) and palladium-black to α -ergosterol. J. W. BAKER.

Yeast ergosterol. IV. F. REINDEL and A. DETZEL (Annalen, 1929, 475, 78—86).—*epi*Ergostanol, m. p. 207°, [α]_D +13.5°, obtained together with *allo*- α -ergostanol (I) by the catalytic reduction of *allo*- α -ergostanone, and differentiated from I by its non-precipitation by digitonin, is oxidised by chromic anhydride in glacial acetic acid at 70° to *allo*- α -ergostanone, m. p. 160—164° (ketazine, m. p. 272°), identical with the ketone obtained from I, and thus proving that it is a configurational isomeride, and a dicarboxylic acid, C₂₇H₄₆O₄, m. p. 219°. By the addition of warm alcohol to a warm ethereal solution of α -ergostanyl acetate (Reindel and Walter, A., 1928, 295), and repeated crystallisation from methyl alcohol

followed by hydrolysis of the resulting pure acetate, m. p. 184°, [α]_D —20°, with sodium ethoxide, dihydroergosterol, m. p. 174—179°, [α]_D —19.4°, was isolated: this indicates that the previously described α -ergostanol is a mixture containing dihydroergosterol. When ergosterol, m. p. 150°, [α]_D —130°, is distilled under low pressure, it passes over at 248—250°/0.8 mm.; the method is therefore unsuitable for the separation of the sterols. The pale yellow distillate had m. p. 140—145°, [α]_D —104.5°, was almost completely precipitated by digitonin, and absorbed 1 mol. of oxygen when kept in a vacuum over calcium chloride for 14 days, the rotation increasing simultaneously. A labile moloxide together with a small quantity of a peroxide is formed; acetylation gave ergosteryl acetate, m. p. 163°. If the distilled ergosterol is recrystallised five times from alcohol, a white product, [α]_D —104°, is obtained which is unchanged on long keeping. A. I. VOGEL.

Sterol group. VII. Isolation of zymosterol.

I. M. HEILBRON and W. A. SEXTON (J.C.S., 1929, 2255—2257).—By the action of bromine in acetic acid on the crude mixture of yeast sterols left after removal of most of the ergosterol a mixture of bromides is obtained which is separated by fractional crystallisation from chloroform and alcohol. The least soluble bromide, m. p. 168°, is converted by debromination with zinc dust into a sterol, m. p. 108—110°, [α]_D²⁰ +38.6° in chloroform, apparently identical with zymosterol isolated by Wieland and Asano (this vol., 1200) and, in agreement with these authors but contrary to Smedley-Maclean (A., 1928, 329), having the composition C₂₇H₄₄O (acetate, m. p. 106—107°; Wieland and Asano, *loc. cit.*, give m. p. 104—106°). This sterol is reduced by hydrogen and palladium to dihydrozymosterol + H₂O, m. p. 115—116°, [α]_D²⁰ +28.9° in chloroform (acetate, m. p. 83—84°).

J. W. BAKER.

Zymosterol. F. REINDEL and A. WEICKMANN (Annalen, 1929, 475, 86—100).—Crude zymosterol, purified by fractional crystallisation from light petroleum followed by methyl alcohol, had [α]_D +30° to +35°; subsequent repeated boiling with animal charcoal gave a product with m. p. 107—110°, [α]_D +49.5° (acetyl derivative, m. p. 102—104°, [α]_D +32.4°), in which the presence of ergosterol could not be detected by the very sensitive Tortelli-Jaffé colour reaction or by the ultra-violet absorption spectrum. Analysis led to the formula C₂₇H₄₄O (cf. Maclean, A., 1928, 329, C₂₇H₄₂O; Penau and Tanret, this vol., 809, C₂₇H₄₂O₂). Zymosterol gives the Salkowski colour reaction, the sulphuric acid becoming yellowish-red and the chloroform remaining colourless; with acetic anhydride and sulphuric acid there is a blue coloration becoming green; with arsenic trichloride, a steel-blue coloration becoming violet with a green fluorescence, and with antimony chloride, a pale red coloration becoming yellow and finally bluish-green. Titration with perbenzoic acid in chloroform solution indicated the presence of two double linkings. Reduction in glacial acetic acid or in glacial acetic acid-ether solution with platinum-black and hydrogen resulted in the absorption of 1 mol. of hydrogen and the formation of dihydrozymosterol (I), m. p. 120—

122°, $[\alpha]_D +20.7^\circ$, precipitated by digitonin (acetate, m. p. 81—84°, also obtained by direct hydrogenation of zymosteryl acetate; cf. preceding abstract); perbenzoic acid revealed the presence of one double linking in I. The presence of three double linkings indicated by iodine titration (Maclean, *loc. cit.*; Penau and Tanret, *loc. cit.*) is attributed to substitution by, as well as addition of, iodine. The presence of only two double linkings is supported by the small values of the absorption coefficients in the ultra-violet (cf. cholesterol).

When a vigorous stream of hydrogen chloride is passed into a dry chloroform solution of zymosterol acetate at 0° for 1 hr., two isomeric *zymosterol hydrochlorides*, m. p. 87—88° and 120—122°, respectively, are obtained. Dihydrozymosterol under similar conditions yielded an *isomeride*, m. p. 75°. Zymosteryl acetate in ether-glacial acetic acid solution containing ammonium acetate reacts with 1 mol. of bromine in glacial acetic acid to form an impure *zymosteryl acetate dibromide*, m. p. 156—157°.

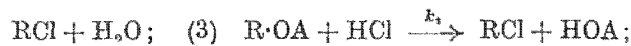
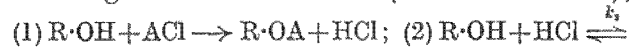
A. I. VOGEL.

Determination of double linkings in sterols. F. REINDEL and K. NIEDERLANDER (*Annalen*, 1929, **475**, 147—157).—Examination of the results obtained with a large number of sterol derivatives shows that the Hübl method for the determination of the number of double linkings in the molecule is untrustworthy, the values being high if no allowance is made for the amount of hydrogen iodide evolved and very low if this is determined by addition of potassium iodate and titration of the liberated iodine, and this value deducted from the total amount of iodine absorbed. With Marshall's method (iodine chloride in carbon tetrachloride solution; A., 1900, ii, 376) trustworthy results are obtained with cholesterol derivatives but not with those of ergosterol. The large amount of hydrogen iodide liberated is probably formed in accordance with the reactions: $\cdot\text{CH}_2 + \text{HI} = \cdot\text{CHCl} + \text{HI}$ and $\cdot\text{CHCl} \cdot \text{CHI} \cdot \text{CH}_2 \cdot \rightleftharpoons \cdot\text{CHCl} \cdot \text{CH} \cdot \text{CH} \cdot$ (or $\cdot\text{CCl} \cdot \text{CH} \cdot \text{CH}_2 \cdot$) + HI. Much more trustworthy results are obtained by Kaufmann's method (0.1N-solution of bromine in carbon tetrachloride) if allowance is made for the large quantity of hydrogen bromide formed, although even with this reagent somewhat low results are obtained with ergosterol derivatives.

J. W. BAKER.

Substitution and addition. II. Esterification with *p*-nitrobenzoyl chloride. J. MEISENHEIMER and W. SCHMIDT (*Annalen*, 1929, **475**, 157—182; cf. A., 1925, i, 527).—Esterification of phenylethylcarbinol (1 mol.) with *p*-nitrobenzoyl chloride (2 mols.) in ethereal solution under reflux reaches its maximum value (20—30%) only after several days. If the reaction is carried out in a sealed tube at 100° with benzyl alcohol, 95% esterification occurs after 3 days, whilst with phenylethylcarbinol only 2% of the ester is obtained. In carbon tetrachloride (in which hydrogen chloride is much less soluble) under reflux, however, 80% esterification of phenylethylcarbinol has occurred after 20 hrs. In the sealed tube experiments the ester is first formed, but suffers fission into α -chloro- α -phenylpropane and *p*-nitrobenzoic acid during the prolonged heating at 100°, and it is shown

that such fission of the pure ester is almost complete after heating with 2*N*-ethereal hydrogen chloride at 100° for 3 days. Of the six possible reactions the following must be considered: (ACl=acid chloride);



(4) $\text{ACl} + \text{H}_2\text{O} \xrightarrow{k_4} \text{HCl} + \text{HOA}$, and by a kinetic analysis the reaction velocity curve for each of these reactions is plotted. Initially (1) is predominant, but its velocity rapidly decreases, whilst (2) and (4) increase rapidly to a maximum and then decrease rapidly: (3) persists throughout but is important relative to (1), (2), and (4) only after a long period, when these last reaction velocities have become very

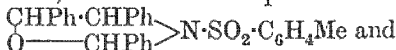
small. The reaction $\text{R} \cdot \text{OH} + \text{HOS} \rightleftharpoons \text{R} \cdot \text{OS} + \text{H}_2\text{O}$

is unimportant. For phenylethylcarbinol the values of the various velocity coefficients are, respectively, k_1 8×10^{-4} ; k_2 1×10^{-2} ; k_2' 5×10^{-3} ; k_3 3×10^{-3} ; k_4 3×10^{-2} ; $k_5 = k_5' = 1 \times 10^{-4}$. The experimentally determined curve showing the percentage of ester formed at various times is in good agreement with the compound curve based on these reactions. Similar agreement between the theoretical and experimental curves is obtained for the esterification of ethylvinylcarbinol, for which the values of the velocity coefficients are k_1 1.0×10^{-3} ; k_2 3.5×10^{-3} ; k_2' 1.0×10^{-3} , and k_3 0.17×10^{-3} . Thus the velocity of esterification is about 1.25 times that of phenylethylcarbinol, whilst fission of the esters occurs more slowly, and hence under similar conditions a large percentage of ester is formed with ethylvinylcarbinol. The detection of 1.4% of benzyl alcohol in the presence of 98.6% of phenylethylcarbinol depends on the very small velocity of fission of benzyl *p*-nitrobenzoate into *p*-nitrobenzoic acid and benzyl chloride. Similar esterification (in a sealed tube) of other alcohols has been investigated, and under approximately comparable conditions benzyl and allyl alcohols are esterified to the extent of 90%, methylethylcarbinol 99%, diphenylcarbinol (*p*-nitrobenzoate, m. p. 131—132°) and phenylvinylcarbinol yield very little ester, the chlorohydrocarbon being the main product, and in the last case, in confirmation of Burton (A., 1928, 880), it is the chloride or ester of cinnamyl alcohol which is formed by rearrangement. Styrylethylcarbinol (*p*-nitrobenzoate, m. p. 53°) yields mainly α -phenyl- Δ^6 -pentadiene by loss of water, so that the results are not comparable, whilst very little esterification occurs with trimethylcarbinol. The results of Norris and Ashdown (A., 1925, i, 626) on the velocity of esterification of alcohols with *p*-nitrobenzoyl chloride in ether are criticised on the basis of this investigation, since a large quantity of hydrogen chloride is formed as a result of the reactions (2) and (4), thus making some of the values too high. The correctness of the structures of styrylethylcarbinol, its chloride, and of phenylvinylcarbinol is proved by ozonolysis.

J. W. BAKER.

Optically active diphenylhydroxyethylamines and isohydrobenzoin. II. J. READ, I. G. M. CAMPBELL, and T. V. BARKER (*J.C.S.*, 1929, 2305—2318).—Resolution of *dl*-isodiphenylhydroxyethyl-

amine (I) (Read and Steele, A., 1927, 557) is effected by successive treatment with *d*-tartaric acid and *d*-camphor-10-sulphonic acid. The hydrogen tartrate, m. p. 177°, $[\alpha]_D -42.6^\circ$, of the *l*-base, m. p. 115°, $[\alpha]_D -133^\circ$ in alcohol (Erlenmeyer, A., 1897, i, 480, gives -109.7°) [*d*- α -bromocamphor- π -sulphonate, m. p. 210° (decomp.), $[\alpha]_D +15.9^\circ$ in water], separates first, whilst from the base obtained from the mother-liquor the *d*-camphor-10-sulphonate, $[\alpha]_D +60.4^\circ$, of the *d*-base, m. p. 115°, $[\alpha]_D +134^\circ$ in alcohol [*d*- α -bromocamphor- π -sulphonate, m. p. 220° (decomp.), $[\alpha]_D +94.0^\circ$ in water], is prepared. Attempts to resolve the *dl*-base with *d*- α -bromocamphor- π -sulphonic acid give only *dl*-isodiphenylhydroxyethylamine *d*- α -bromocamphor- π -sulphonate, $[\alpha]_D +51.7^\circ$. *O*-Acetyl-*dl*-isodiphenylhydroxyethylamine (II), m. p. 152°, best prepared by the action of acetic anhydride in benzene on I, could not be made to react with benzaldehyde, but *acetylbenzylidene-dl-isodiphenylhydroxyethylamine*, m. p. 114°, is obtained by the action of boiling acetic anhydride on benzylidene-*dl*-isodiphenylhydroxyethylamine (III), and is converted into II by bromine and alcohol. *O*-Acetyl-*l*-isodiphenylhydroxyethylamine (IV) has m. p. 158°, $[\alpha]_D -6.3^\circ$ in alcohol (hydrochloride, m. p. 190°, $[\alpha]_D -32.8^\circ$ in water). Boiling acetic anhydride converts the original bases into the diacetyl-*dl*-, m. p. 118°, and diacetyl-*l*-, m. p. 127°, $[\alpha]_D +27.7^\circ$ in alcohol (hydrolysed to IV), derivatives. Contrary to Erlenmeyer and Arnold (A., 1905, i, 193), no racemisation of the monoacetyl derivatives occurs in boiling alcohol. *p*-Toluenesulphonyl chloride and pyridine convert I into its *O*-*p*-toluenesulphonyl derivative, m. p. 142—145° (*N*-acetyl derivative, m. p. 161—162°), whilst with III it gives two isomeric *O*-*p*-toluenesulphonylbenzylidene-*dl*-isodiphenylhydroxyethylamines, m. p. 179° (less soluble in acetone), and m. p. 173—174°, for which the respective structures



are suggested, since only the latter is hydrolysed by bromine and alcohol. *d*-isodiphenylhydroxyethylamino-*d*-methylene-camphor, m. p. 168°, $[\alpha]_D +144^\circ$ to 179° in alcohol, is prepared by the usual method. The following derivatives of *l*-isodiphenylhydroxyethylamine are described: *O*-benzoyl, m. p. 215°, $[\alpha]_D -38.5^\circ$ in methyl alcohol (lit. -29.0°); *O*-*p*-nitrobenzoyl, m. p. 132°, $[\alpha]_D -48.3^\circ$ in alcohol; salicylidene, m. p. 132—134°, $[\alpha]_D -91.5^\circ$ in alcohol; anisylidene, m. p. 152°, $[\alpha]_D -72.4^\circ$ in alcohol; piperonylidene, m. p. 144°, $[\alpha]_D -83.3^\circ$ in alcohol; 4-hydroxy-3-methoxybenzylidene, m. p. 155°, $[\alpha]_D -84.4^\circ$ in alcohol. By the action of nitrous acid on *l*-isodiphenylhydroxyethylamine is obtained *l*-isohydrobenzoin, m. p. 146°, $[\alpha]_D -92^\circ$ (diacetyl, m. p. 109—110°, $[\alpha]_D 26.9^\circ$ in alcohol, and benzylidene, m. p. 70.5°, $[\alpha]_D -27.6^\circ$ in alcohol, derivatives), and from the *d*-base is obtained *d*-isohydrobenzoin, m. p. 146°, $[\alpha]_D +92^\circ$ in alcohol (acetone derivative, m. p. 48°, $[\alpha]_D +65.2^\circ$ in alcohol). Benzylidene-*dl*-isohydrobenzoin has m. p. 84°.

A detailed crystallographic study of *d*-, *l*-, and *dl*-isohydrobenzoin is described. When deposited from ethyl acetate the *d*- and *l*-forms exhibit characteristic hemihedral facets which are not developed when chloroform is the solvent. In agreement with this

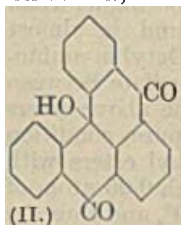
the *dl*-compound separates from ethyl acetate as a conglomerate of enantiomorphously related crystals composed of *d*- and *l*-components. A similar resolution into *d*- and *l*-forms occurs from chloroform, though in this case the characteristic hemihedral facets are absent; segregation is here rendered possible through the circumstance that either the right or left side of each crystal displays a marked tendency to degenerate into curved boundaries. The relationship between molecular enantiomorphism and crystalline form is discussed.

J. W. BAKER.

Triphenylmethyl chloride and pyridine. [Goldschmiedt's condensation products of 2-hydroxy-3-naphthoic acid with aromatic aldehydes and their relationships to the triphenylmethane group.] M. REBEK [with G. MANDRINO] (Ber., 1929, 62, [B], 2508—2509; cf. this vol., 556).—Agreement is expressed with Helferich (A., 1925, i, 790, 1269; 1926, 517) in ascribing the formula $\text{C}_{19}\text{H}_{15}\text{O}_3\text{Cl}_2\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$ to the compound obtained from triphenylmethyl chloride, pyridine, and water, since it yields triphenylcarbinol after prolonged desiccation at 100°/vac. The existence of a compound, $\text{C}_{19}\text{H}_{15}\text{Cl}_2\text{C}_5\text{H}_5\text{N}$, from triphenylmethyl chloride and anhydrous pyridine is, however, probable. Methyl 2-hydroxy-1- α -chlorobenzyl-3-naphthoate, pyridine, and water afford the compound $\text{C}_{19}\text{H}_{15}\text{O}_3\text{Cl}_2\text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}$, m. p. 162—164°, whilst anhydrous pyridine appears to give a salt free from water.

H. WREN.

Triphenylmethane derivatives with linked benzene nuclei. V. Diketodimethylenetriphenylcarbinol. R. WEISS and J. REICHEL (Monatsh., 1929, 53 and 54, 187—198).—Magnesium *o*-tolyl bromide and *o*-benzoylbenzoic acid give phenyl-*o*-tolylphthalide, m. p. 120°, reduced by sodium amalgam and alcohol to 2-methyltriphenylmethane-2'-carboxylic acid, m. p. 197° (methyl ester, m. p. 94°). Oxidation of this phthalin with alkaline potassium permanganate yields triphenylmethane-2 : 2'-dicarboxylic acid (I), m. p. 214—215° (dimethyl ester), which when treated with sulphuric acid at 70—90° in acetic acid solution undergoes ring closure and oxidation, forming the acetate, m. p. 230°, of diketodimethylenetriphenylcarbinol (II), m. p. 232°.



Formation of II occurs also when I is treated with sulphuric acid and when the chloride of I is treated with aluminium chloride in carbon disulphide solution. When I is treated with sulphuric acid in presence of aluminium filings at 50—60°, II is again formed. Reduction of II does not occur with sodium amalgam and alcohol, whilst with hydriodic acid (*d* 1.7) a compound, $\text{C}_{21}\text{H}_{14}\text{O}_2$ (probably dimethylenetriphenylmethaneketonol), m. p. 241—242°, is formed. This last-named compound is soluble in dilute ammonia or sodium hydroxide solution.

Magnesium *o*-tolyl bromide and ethyl benzoate give phenyldi-*o*-tolylcarbinol (III), b. p. 210—213°/16 mm., which, contrary to the statement of Cook (A., 1928, 293), could not be oxidised by potassium permanganate solution to triphenylcarbinol-2 : 2'-dicarboxylic

acid. Treatment of III with dry hydrogen bromide at 130—140° gives unexpectedly *phenyldi-o-tolylmethane*, b. p. 180—185°/12 mm., m. p. 104°; a small amount of the hydrocarbon is obtained also by reducing III with zinc and hydrochloric acid in acetic acid solution. Chlorination of *phenyldi-o-tolylmethane* at 125—130° in sunlight gives a *dichloro-*, m. p. 57°, or a *tetrachloro-*derivative, m. p. 63—65°, according to the time of reaction. H. BURTON.

Optical activity and polarity of substituent groups. XI. *sec.-β-Octyl esters of benzoic acids containing basic and acidic substituents*. H. G. RULE, J. B. MILES, and (in part) W. E. MACGILLIVRAY (J.C.S., 1929, 2274—2281; cf. this vol., 570).—The rotatory powers, for light of various wave-lengths, of amino-, dimethylamino-, hydroxy-, and carboxy-substituted benzoates of *d-* and *l-sec.-β-octyl* alcohols have been determined both in the ionised and non-ionised states. In the *o*-substituted derivatives the presence of a substituent of *op*-directive type leads to a fall in rotatory power which is greatest with the amino- and dimethylamino-groups, these two basic esters exhibiting anomalous dispersion. Conversion into their hydrochlorides (formation of a positive pole) results in increased rotatory power and much less complex dispersion. The increase in rotation due to the presence of the *m*-directive carboxyl group is changed into a depression in the sodium salt, the sign of the rotation of the salt in aqueous solution becoming inverted at concentrations above $c=13$. In the presence of 1 equivalent of potassium ethoxide the rotatory power of the salicylate is depressed to such an extent that the sign is inverted. The relative changes in rotatory power due to different *o*-substituents are $\text{NO}_2 > \text{CO}_2\text{H} > \text{H}, \text{OH} > \text{Me} > \text{Br} > \text{Cl} > \text{I} > \text{OMe} > \text{NMe}_2 > \text{NH}_2$, the very small effect of the hydroxyl group probably being due to chelation. The *p*-dimethylamino- and *p*-amino-substituted esters possess abnormally high rotatory powers which fall to normal values in their hydrochlorides. The values for various *p*-substituents are in the order $\text{NMe}_2 > \text{NO}_2 > \text{CO}_2\text{H} > \text{Br} > \text{OMe} > \text{Cl}, \text{Me} > \text{H}$, which closely approximates to that of the general polar type. Contrary to this suggestion, however, the value for sodium octyl terephthalate tends to be higher than that of the hydrogen octyl ester, and is almost independent of concentration. *sec.-β-Octyl m*-aminobenzoate has optical properties intermediate between those of the *o*- and *p*-derivatives. The above esters are best prepared in an optically pure condition (20—40% yield) by heating the methyl esters with *d-* or *l-β-octyl* alcohol (1 mol.), in which 0.05 atom of sodium has been dissolved, at 130—140°, and thus are prepared *l-sec.-β-octyl anthranilate*, b. p. 183°/10 mm., *p*-aminobenzoate, b. p. 200°/10 mm., m. p. 69—70° (hydrochloride, m. p. 131—133°); *d-β-octyl p*-dimethylaminobenzoate, b. p. 180°/1.8 mm., *salicylate*, b. p. 170°/10 mm. *l-Octyl m*-aminobenzoate, b. p. 195—198°/18 mm. (slight decomp.), is prepared by reduction of the corresponding nitro-derivative with aluminium amalgam. J. W. BAKER.

Chemical effects of penetrating radium radiation. XVIII. Action on acetyl and benzoyl chlorides. A. KAILAN.—See this vol., 1406.

Benzylthiobenzamide. T. G. LEVI (Gazzetta, 1929, 59, 548—549).—*Benzylthiobenzamide*, m. p. 86°, is prepared by heating benzylamine (1 mol.) and sulphur (1 atom) at 130—140°, rising to 200°, or in a sealed tube at 180° for several hours. Thiobenzamide is not found in the product under these conditions (cf. Wallach, A., 1891, 189). The same compound is formed from benzylbenzamide and phosphorus pentasulphide. It is decomposed by fusion with solid potassium hydroxide to give benzylamine. It is insoluble in 10% sodium hydroxide solution.

R. K. CALLOW.

Dioximes. LV. G. PONZIO (Gazzetta, 1929, 59, 552—555).—The statement by Gastaldi (A., 1926, 1247) that the action of hydroxylamine on benzoylurethane yields benzamidoformhydroxamic acid is erroneous, and the criticism of the author's formulation of the transformation of phenylhydroxyglyoxime into 3-hydroxy-5-phenyl-1:2:4-oxadiazole (A., 1926, 850, 1159) is fallacious. In fact, the product is benzhydroxamic acid, and the transformation of acylurethanes, $\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, when treated with hydroxylamine in methyl alcohol at 40—50° for several days, into hydroxamic acids, $\text{R}\cdot\text{C}(\text{NOH})\cdot\text{OH}$, is a general reaction. In this way acetylurethane yields acethydroxamic acid, *propionylurethane*, m. p. 83°, yields propionhydroxamic acid, m. p. 98—99°, and benzoylurethane, m. p. 112° (prepared by an improved method), yields benzhydroxamic acid, m. p. 128—129°. The reaction is analogous to that of β -ketonic esters, and further analogy is found in the reaction of benzoylurethane with phenylhydrazine to give the *phenylhydrazone*, m. p. 217°, which decomposes when melted to give 3-hydroxy-2:5-diphenyl-1:2:4-triazole, m. p. 231—232°. This compound is also formed in small amount by dehydration of the substance, $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3$, m. p. 133—134°, obtained by the interaction of phenylhydrazine and benzoylformhydroxamic acid, or of the product obtained by the action of hydroxylamine on ethyl phenylglyoxylate.

R. K. CALLOW.

Isomerism of the oximes. XXXV. Amid-oximes. O. L. BRADY and F. H. PEAKIN (J.C.S., 1929, 2267—2271).—The action of alcoholic dimethylamine on *m*-nitrobenzhydroxamyl chloride at 0° affords *m*-nitrobenzodimethylamidoxime (I), m. p. 160° (together with *mm'*-dinitrodiphenylfuroxan). Although in this compound the tautomeric system $\text{CR}(\text{NOH})\cdot\text{NH}_2 \rightleftharpoons \text{CR}(\text{NH})\cdot\text{NH}\cdot\text{OH}$ is blocked, all attempts to prepare stereoisomerides were unsuccessful. This may be due to a betaine structure, and in agreement with this view it cannot be converted into an *O*-methyl ether, treatment with dry silver oxide and methyl iodide in boiling benzene causing decomposition to *m*-nitrobenzodimethylamide, m. p. 81°, and *N*-methylhydroxylamine. Methylation of *m*-nitrobenzamidoxime with methyl sulphate in sodium hydroxide gives its *O*-methyl ether, m. p. 75°, converted by sodium nitrite and concentrated hydrochloric acid into *m*-nitrobenzmethoxamyl chloride, m. p. 51°, which with dimethylamine gives only *m*-nitrobenzoic acid. Ethyl chloroformate converts a dry chloroform suspension of I into the *carbethoxy-*derivative, m. p. 94°, which is different from and not convertible under the usual conditions of betaine change into the similarly

prepared carbomethoxy-derivative, m. p. 87° , of *m*-nitrobenzomethylethylamidoxime, m. p. 123° , the last-named being prepared by the action of alcoholic methylethylamine on *m*-nitrobenzhydroxamyl chloride at 0° . The failure of this interconversion and the fact that it does not undergo the Beckmann change makes it impossible to assign a configuration to *m*-nitrobenzodumethylamidoxime. Thus phosphorus pentachloride in ether or concentrated sulphuric acid at 130° is without action, whilst benzenesulphonyl chloride and anhydrous sodium carbonate in chloroform and benzoyl chloride in 2*N*-sodium hydroxide convert it, respectively, into its benzenesulphonyl, m. p. 138° , and benzoyl, m. p. 152° , derivatives. J. W. BAKER.

Nature of the alternating effect in carbon chains. XXXI. Directive influence of ψ -acid systems in aromatic substitution. Nitration of ψ -acidic phenylnitromethanes and their salts. J. W. BAKER (J.C.S., 1929, 2257—2264).—The proportion of the *m*-isomeride formed in the nitration of the lithium salt, +EtOH, and solvent-free, m. p. 200° , of ethyl α -nitrophenylacetate at -12° to 0° increases from 29% in nitric acid, d_4^{25} 1.497, to 82.5% in nitric acid, d_4^{25} 1.529, whilst over the same range of acid concentration the proportion of *m*-isomeride produced in the nitration of free ethyl α -nitrophenylacetate remains constant at 84—85%. Similarly, over the same range of acid concentration the potassium (or sodium) salt of phenylnitromethane yields 42—67% of *meta*, whilst for free phenylnitromethane the proportion of *meta* remains constant at 67%. Thus, whilst in agreement with Baker and Ingold (A., 1926, 1131), nitration of ψ -acidic phenylnitromethane derivatives of the type $\text{CHPhR}\cdot\text{NO}_2$ yields mainly *m*-nitro-products, nitration of the anions of

the *aci*-form, $\text{CPhR}\cdot\text{NO}\cdot\text{O}^-$, occurs largely in the *op*-positions (despite the contrary influence of the more distant dipole on the nitro-group) owing to the directive effect of the anionic charge which, by tautomeric displacements, has free access to the carbon atom adjacent to the benzene nucleus. The results suggest that the speed of conversion of the liberated anion of the molecular ψ -acid is greatly increased with increasing strength of the acid medium. In the preparation of ethyl α -nitrophenylacetate by condensation of ethyl phenylacetate and ethyl nitrate with sodium in ether small quantities of substances, m. p. 162 — 163° and 133 — 134° , are also obtained. J. W. BAKER.

Beckmann rearrangement in presence of free radicals. E. S. WALLIS (J. Amer. Chem. Soc., 1929, 51, 2982—2986).—When a solution of benzylmethylacetazide in benzene is mixed with triphenylmethyl in absence of oxygen and kept at 35° , rearrangement of the azide into α -benzylethylcarbimide occurs (cf. Jones and Wallis, A., 1926, 279). No other product, other than triphenylmethyl peroxide, is isolated during the analysis of the rearrangement products. The result appears to support the view that in the change $\text{R}\cdot\text{CON}_3 \rightarrow \text{R}\cdot\text{NCO}$, the radical R during its migration from carbon to nitrogen becomes a positive ion (cf. *loc. cit.*). H. BURTON.

Tyrosines methylated in the nucleus and the formation of melanin. H. SCHMALFUSS and W.

PESCHKE (Ber., 1929, 62, [B], 2591—2598).—Introduction of methyl groups into *p*-tyrosine, no matter what position they occupy in the benzene nucleus, impedes the production by tyrosinase of melanin or an intermediate product leading to melanin.

Hippuric acid is converted by 4-hydroxy-*o*-tolu-aldehyde, acetic anhydride, and sodium acetate into α -benzamido-4-acetoxy-2-methylcinnamylactimide, $\text{C}_{19}\text{H}_{15}\text{O}_5\text{N}$, m. p. 157° , hydrolysed by sodium hydroxide to α -benzamido-4-hydroxy-2-methylcinnamic acid, decomp. 254° , converted by phosphorus and hydriodic acid into dl- α -amino- β -4-hydroxy-*o*-tolylpropionic acid, decomp. 261° . α -Benzamido-4-acetoxy-2:5-dimethylcinnamylactimide, m. p. 166° , similarly yields successively α -benzamido-4-hydroxy-2:5-dimethylcinnamic acid, decomp. 239° , and dl- α -amino- β -4-hydroxy-2:5-dimethylphenylpropionic acid, decomp. 249° . α -Benzamido-4-acetoxy-3:5-dimethylcinnamylactimide, m. p. 190° , α -benzamido-4-hydroxy-3:5-dimethylcinnamic acid, decomp. 222° , and dl- α -amino- β -4-hydroxy-3:5-dimethylphenylpropionic acid, decomp. 253° , are described, as are also α -benzamido-4-acetoxy-2:3-dimethylcinnamylactimide, m. p. 183° , α -benzamido-4-hydroxy-2:3-dimethylcinnamic acid, m. p. 236° , and dl- α -amino- β -4-hydroxy-2:3-dimethylphenylpropionic acid, decomp. 284° . H. WREN.

Comparative stability of stereoisomeric ethylene derivatives and their synthesis by ultraviolet light. (MME.) RAMART-LUCAS and J. HOCH (Compt. rend., 1929, 189, 696—699).—The applicability of measurements of absorption spectra and of heats of combustion to the differentiation of the *cis*- and *trans*-isomerides in cases of geometrical isomerism is discussed. Measurements of the absorption curves of diethyl $\alpha\alpha'$ -diphenylfumarate, diethyl $\alpha\alpha'$ -diphenylmaleate: dimethyl $\alpha\alpha'$ -di-*m*-tolylfumarate, dimethyl $\alpha\alpha'$ -di-*m*-tolylmaleate; dimethyl $\alpha\alpha'$ -di-*p*-tolylfumarate and dimethyl $\alpha\alpha'$ -di-*p*-tolylmaleate show that, contrary to general rule, in all these three pairs the absorption curve of the *cis*-isomeride lies closer to the visible region than does that of the *trans*-isomeride. According to the work of Ramart-Lucas (A., 1928, 760, 1000) these facts show that, in these three pairs of isomerides, the *cis* is the more stable at low temperatures. In view of these facts, the method of differentiating *cis*- and *trans*-isomerides (Henri and Errera, A., 1925, ii, 1137) is criticised. The three fumarates were prepared from the corresponding maleates by the (irreversible) action of ultra-violet light; this reaction gave, in addition, carbalkoxyarylidones, also formed by the action of ultra-violet light on the dialkyl $\alpha\alpha'$ -diaryl fumarates. Irradiation of the sodium salts of the $\alpha\alpha'$ -diaryl maleic acids with ultra-violet light gave the sodium salt of the arylidone-carboxylic acid. A. A. GOLDBERG.

Action of alkali hypochlorite on hemipinimide. W. M. RODIONOV, S. J. KANEVSKAJA, and G. W. KUPINSKAJA (Ber., 1929, 62, [B], 2563—2567).—Hemipinic acid is prepared by oxidation of opianic acid by alkaline permanganate or by treatment of it with hot, very concentrated sodium hydroxide and separation of meconine from the product by cold, 10% sodium carbonate. Hemipinimide is treated with potassium hydroxide and potassium hypochlorite at

a temperature not exceeding 60° and, after addition of sodium hydrogen sulphite, the solution is neutralised to litmus with hydrochloric acid and then acidified with acetic acid, whereby 2-aminoveratric acid, m. p. 181—182°, is precipitated (yield 31%). Extraction of the filtrate with chloroform leads to the isolation of 2-amino-5:6-dimethoxybenzoic acid, m. p. 98—99° (yield about 64%), converted by deamination into 2:3-dimethoxybenzoic acid. 2-Hydrazino-5:6-dimethoxybenzoic acid hydrochloride, m. p. 195—196° after darkening at about 140—145°, is described.

H. WREN.

Derivatives of hemipinic acid. F. FALTIS and F. KLOIBER (Monatsh., 1929, 53 and 54, 620—637).—Various derivatives of hemipinic acid have been synthesised in connexion with the constitution of an oxidative degradation product of isochondrodendrine (cf. this vol., 698).

[With L. GUTLOHN and A. B. G. ATTIA.]—Opianic acid is nitrated in acetic acid solution to nitro-opianic acid (I) and its anhydride, m. p. 240—245° (decomp.) (cf. Wegscheider, A., 1897, i, 348). Reduction of I with stannous chloride and hydrochloric acid in boiling aqueous suspension gives 3:4-dimethoxyanthranil-2-carboxylic acid, which on dissolution in 20% sodium hydroxide and subsequent treatment with the theoretical amount of sulphuric acid affords 6-aminohemipinic acid + H₂O (II), which loses water of crystallisation at 100°, and at 110—130° is transformed into the anhydride. When heated rapidly, II decomposes at 190—210°. Elimination of carbon dioxide occurs during the esterification of II with methyl-alcoholic hydrogen chloride, and methyl 3-amino-5:6-dimethoxybenzoate (hydrochloride) is probably formed. Diazotisation of II and subsequent treatment with potassium iodide gives 6-iodohemipinic anhydride, m. p. 190—191°, converted by treatment with concentrated potassium hydroxide solution and methyl sulphate into methyl 6-iodohemipinate (III), m. p. 62° (formed also by the action of diazomethane on the methyl hydrogen ester). 6-Chlorohemipinic anhydride has m. p. 165—166°. 6-Diazohemipinic acid decomposes in aqueous suspension at 85—90° to 6-hydroxyhemipinic acid, m. p. 167° (decomp.) or 194—196° after softening at 175°, according to the rate of heating (the isolation of this acid is carried out with peroxide-free ether). Treatment of this with diazomethane and subsequent hydrolysis with alcoholic potassium hydroxide furnishes 3:4:6-trimethoxyphthalic acid (+H₂O), m. p. 216—217°. When diazohemipinic acid is treated with cuprous cyanide in acid solution and the product formed hydrolysed with hydrochloric acid, about 20% of 3-hydroxy-5:6-dimethoxybenzoic acid, m. p. 186—188°, is obtained (cf. Faltis and Kloiber, this vol., 699). 3:5:6-Trimethoxybenzoic acid has m. p. 101—102°.

Condensation of III with the sodium derivative of methyl *p*-hydroxybenzoate in presence of copper powder and copper acetate gives methyl anisate instead of the expected condensation product (Faltis and Zwerina, this vol., 698). Methyl anisate is formed by the decomposition of III to a sodium salt with simultaneous methylation of the methyl *p*-hydroxybenzoate. When the sodium derivative of methyl *p*-hydroxybenzoate is treated with copper powder and

copper acetate, about 27% of methyl anisate is formed thus: $2\text{NaO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me} \longrightarrow \text{NaO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na} + \text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$.
H. BURTON.

Action of nitric acid on abiestic acid and certain derivatives. P. LEVY [with T. PESCH, A. CLAUBERG, and H. RAALF] (Ber., 1929, 62, [B], 2497—2504).—Under the conditions adopted, trimellitic acid (cf. Ruzicka and Pfeiffer, A., 1925, i, 1419) or nitroabiestic acid is never obtained by the action of nitric acid on abiestic acid. It depends entirely on experimental conditions whether oxidation or nitration is observed.

Abiestic acid, m. p. 170—171°, [α]_D −98.45°, the homogeneity of which is established by its oxidation by permanganate to tetrahydroxyabiestic acid as sole non-volatile product, is converted by prolonged boiling with nitric acid (*d* 1.18), which is occasionally renewed during the process, into $\beta\beta$ -dinitropropane, m. p. 53°, minute amounts of fatty acids volatile with steam, and an acid, C₁₁H₁₆O₆, m. p. 224° (decomp.), identical with that obtained by Steele (A., 1922, i, 739); occasionally it is possible to isolate an acid, C₁₂H₁₈O₆, m. p. 214° (decomp.), identical with that to which the author has previously assigned the composition C₈H₁₂O₄ (A., 1913, i, 620). Treatment of abiestic acid with a mixture of 1 vol. of nitric acid (*d* 1.52) and 5 vols. of acid (*d* 1.40) at a temperature raised slowly from the atmospheric to 130° affords a mixture of the acids C₁₂H₁₈O₆ and C₁₁H₁₆O₆. Dibromodihydroabiestic acid, m. p. 171°, [α]_D −102.8°, when heated with nitric acid of gradually increased concentration affords $\alpha\alpha$ -dibromo- α -nitropropane, b. p. 76°/15 mm., and the acid, C₁₁H₁₆O₆, m. p. 222°; this acid is also obtained when a concentrated acid is used initially, but volatile compounds do not appear to be produced. Oxidation of tetrahydroxyabiestic acid with nitric acid by the "gradual process" yields the acids C₁₁H₁₆O₆ and (?)C₁₂H₁₈O₆. Abiestic acid therefore contains a retene skeleton with a terminal substituted hexahydrobenzene ring.
H. WREN.

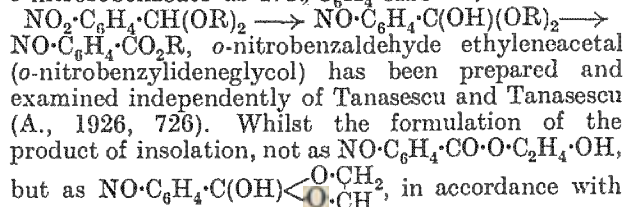
Polysulphides of aromatic carboxylic acids and esters. R. EDER.—See B., 1929, 889.

Isomerisation of hydroxyaldehydes. II. Transformation of bromodicyclohexylacetaldehyde and dicyclohexylglycollaldehyde. S. DANILOV and E. VENUS-DANILOVA (Ber., 1929, 62, [B], 2653—2668; cf. A., 1928, 64).—Dicyclohexylacetaldehyde, b. p. 153—153.5°/10 mm., *d*₄²⁰ 0.9621, *n*_D 1.49025, is converted by bromine in dry carbon disulphide at 0° into bromodicyclohexylacetaldehyde, m. p. 59.5° (yield about 77%). It is transformed by aqueous-alcoholic hydroxylamine or semicarbazide into the oxime, m. p. 143° (decomp.) after becoming yellow at 126° and softening at 138°, and semicarbazone, m. p. 215—218° (decomp.) after becoming yellow at 185° and brown at 210°, of hydroxydicyclohexylacetaldehyde. When heated with silver oxide and water at 100° it yields dicyclohexylacetic acid, m. p. 134.5—135°. Treatment of the bromoaldehyde with silver acetate in aqueous alcohol affords hydroxydicyclohexylacetaldehyde, m. p. 74.5°, and a non-crystalline product, (?) $\frac{\text{C}(\text{C}_6\text{H}_{11})_2}{\text{CH}(\text{OH})} > \text{O}$. Both products give the oxime and semicarbazone described above and are oxidised to dicyclohexyl ketone, b. p. 160°/

24 mm. [*oxime*, m. p. 154—155°; *semicarbazone*, m. p. 195° (decomp.)], and *dicyclohexylglycollic acid*, m. p. 162—163° (further identified by reduction to *dicyclohexylacetic acid*, m. p. 134·5°). Both forms of the aldehyde are isomerised when heated with aqueous alcohol containing a little sulphuric acid at 135° to *dodecahydrobenzoin*, b. p. 140—141·5°/3 mm., d_4^{20} 1·0100, n_D 1·49170, with slight decomposition and formation of a diketone [*oxime*, m. p. 117—118°; α -*semicarbazone*, m. p. 175—176°; β -*semicarbazone*, m. p. 188° (decomp.)]. The benzoin is oxidised by Fehling's solution to *dodecahydrobenzil*, b. p. 168—169°/16 mm., d_4^{20} 1·0134, n_D 1·48453 [*dioxime*, m. p. about 213° (decomp.)]; *disemicarbazone*, m. p. about 116° (decomp.)]. The diketone, in contrast to benzil, is not converted into the corresponding hydroxy-acid by aqueous-alcoholic potassium hydroxide, but yields hexahydrobenzaldehyde and *cyclohexanecarboxylic acid* with resinous products. The action of sodium on ethyl *cyclohexanecarboxylate* in ether yields a mixture of *dodecahydrobenzoin* (84%) and *dodecahydrobenzil* (16%), from which the hydroxyketone is obtained by reduction with zinc and sulphuric or, preferably, acetic acid. It is transformed by magnesium phenyl bromide into α -*phenyl- $\alpha\beta$ -dicyclohexylethane- $\alpha\beta$ -diol*, m. p. 163—163·5°, oxidised by chromic acid in acetic acid to phenyl *cyclohexyl ketone*, m. p. 53·5° (*semicarbazone*, m. p. 167·5—168°), and *cyclohexanecarboxylic acid*.
H. WREN.

Photochemistry of nitrated benzaldehydes. II.

E. BAMBERGER and F. ELGER (Annalen, 1929, 475, 288—308).—In continuation of previous work (A., 1910, i, 267) which led to the formulation of the transformation of *o*-nitrobenzaldehyde into alkyl *o*-nitrosobenzoate as $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO} \rightarrow$



the second of the above series of reactions, has some support, the evidence as a whole is ambiguous. Glycol monobenzoate, m. p. 37—38° (lit. 45°), like the product, does not react with phthalic anhydride, and the proof of the absence of a primary alcoholic group in the latter is, therefore, invalid. Again, the condensation of silver *o*-nitrosobenzoate with β -iodoethyl alcohol yields an identical product, although the isomerisation of glycol mono-*o*-nitrosobenzoate to the cyclic compound is not excluded.

The insolation of *p*-nitrobenzaldehyde in methyl alcohol yields as chief product *p*-nitrobenzaldehyde dimethylacetal, m. p. 28.2–29° (lit. 24.5–25.5°), accompanied by small amounts of an *acid*, m. p. 235–235.5°, traces of *p*-aminobenzoic acid, and a small quantity of *methyl p*-(*p*'-nitrobenzylidencamino)benzoate, m. p. 216–216.5°. This Schiff's base is hydrolysed by hot dilute sulphuric acid to give *p*-aminobenzoic acid and *p*-nitrobenzaldehyde, or by sodium hydroxide in aqueous acetone to give the methyl ester and the aldehyde, and it may be prepared by condensation of

the two last-named compounds in acetic acid. Insol-
 ation of *m*-nitrobenzaldehyde in ethylalcohol yields the
 diethylacetal, some *m*-nitrobenzoic acid, amorphous
 acids, traces of an amino-acid, and a *substance*,
 (?) $\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_2$, m. p. $242-242.5^\circ$, which is not
 identical with the Schiff's base, *ethyl m*-(*m'*-nitro-
benzylideneamino)benzoate, m. p. $124-125.5^\circ$. In
 preliminary investigations on the insolation of
 heptaldehyde and benzaldehyde in alcohol the acetals
 have been separated, but these are also formed in
 control experiments in the dark. Insolation of
p-nitrobenzaldehyde yields in ether 2:2'-azoxy-
 benzaldehyde and an acid, m. p. $225-235^\circ$, in toluene,
 polymerised *p*-aminobenzaldehyde and an acid, m. p.
 $234-235^\circ$, and in benzene a similar acid.

R. K. CALLOW.

Tautomerism of *o*-nitrobenzaldehyde. I. J. POSTOVSKI (J. Russ. Phys. Chem. Soc., 1929, **61**, 719—722).—The tautomerism of *o*-nitrobenzaldehyde:

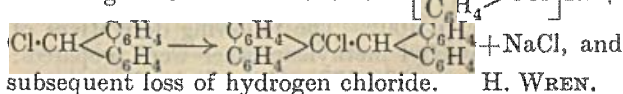
(I)

(II) alleged by

Tanasescu (A., 1926, 1247; 1928, 178), was investigated by Sugden's method of parachor determination. The calculated parachor values for formulæ I and II are 312.2 and 294.0, respectively, whilst the average experimental value for molten *o*-nitrobenzaldehyde (m. p. 93–93.5°) is 308.5, thus indicating that isomeride I greatly predominates, although the existence of II, especially in solution, is not excluded.

M. ZVEGINTZOV.

[Occurrence of free, substituted methylenes in chemical reactions.] E. KLEUCKER (Ber., 1929, 62, [B], 2587—2588).—The high m. p. 187—189° of the product obtained by Bergmann and Hervey (this vol., 695) from benzyl chloride and *o*-nitrobenzaldehyde excludes the possibility that it is a *p*-nitrostilbene oxide, the two forms of which have been described (m. p. 74—76° and about 122°, respectively) by Chrzescinski (Diss., Strassburg, 1911). The production of ditriphenylene-ethylene from 9-chlorofluorene does not necessarily involve the primary formation of a free methylene radical, but can be explained according to the scheme $\left[\text{C}_6\text{H}_4 \right]_2 \text{C} \cdot \text{CCl} \text{Na} +$



subsequent loss of hydrogen chloride. H. WREN.

Catalytic effect of platinum-black and platinum oxide in hydrogenation. F. SIGMUND (Monatsh., 1929, 53 and 54, 607—619).—When phenylacetaldehyde di-*n*-propylacetal (I) is treated with hydrogen in presence of platinum oxide (6% of wt. of I) and alcohol, absorption of hydrogen ceases after a short time. Addition of acetic acid (half volume of alcohol) causes reduction to proceed and *hexahydrophenylacetaldehyde di-n-propylacetal*, b. p. 122—126°/10 mm., is obtained. Cinnamaldehyde diethylacetal is reduced readily in presence of platinum-black and alcohol to *β-phenylpropaldehyde diethylacetal*, b. p. 121—124°/9 mm. Further reduction in presence of the oxide and alcohol ceases after a time, but addition of acetic acid catalyses the reduction. With 30% of platinum-black in acetic acid or 10—12% of platinum oxide in alcohol and acetic acid (2 : 1) reduction proceeds with the same

velocity. β -Hexahydrophenylpropaldehyde diethyl-acetal has b. p. 130—132°/12 mm.

Reduction of benzaldehyde diethylacetal in presence of platinum-black gives a mixture of hexahydro-tolucene, hexahydrobenzyl ethyl ether, and hexahydrobenzyl alcohol (cf. Skita, A., 1916, i, 41).

H. BURTON.

α -Hydroxydiphenylacetaldehyde. E. ZERNER and H. GOLDHAMMER (Monatsh., 1929, 53 and 54, 485—492).—Reduction of α -acetoxydiphenylacetyl chloride, m. p. 91°, by Rosenmund and Zetzsche's method (A., 1918, i, 300; 1921, ii, 320) and hydrolysis of the product with 1% hydrochloric acid gives α -hydroxydiphenylacetaldehyde, m. p. 154—155° [the phenylhydrazone (I), m. p. 132°, is identical with the product obtained by the action of magnesium phenyl bromide on ethyl diazoacetate (Zerner, A., 1913, i, 1312, 1387); oxime, m. p. 127°; semicarbazone, m. p. 144°]. When the phenylhydrazone (I) is boiled with dilute sulphuric acid a red substance (II) is produced by loss of 1 mol. of water. Oxidation of II with potassium permanganate gives benzophenone, whilst reduction with zinc dust, acetic acid, and a small amount of hydrochloric acid affords phenylhydrazine and a substance (III) $C_{28}H_{20}O_2$ (probably a dimeric diphenylketene), m. p. 113—114°. Hydrolysis of III with alcoholic potassium hydroxide gives diphenyl-acetic acid. Reduction of II with hydrogen in presence of palladised charcoal and benzene gives diphenylacetaldehydephenylhydrazone, indicating that II is diphenylketenphenylhydrazone. When II is heated with acetic acid, alone or in presence of hydrochloric acid, a nitrogen-free substance, m. p. 136°, is formed in small amount. Treatment of this with zinc dust and acetic acid gives III. α -Methoxy-diphenylacetyl chloride has m. p. 89—90°.

H. BURTON.

Displacement of the aldehyde group in piperonal and its derivatives. A. H. PARIJS (Diss., Leiden, 1928, 194 pp.).—Nitration of piperonal (25 g.) afforded 6-nitro-3:4-methylenedioxybenzaldehyde (I), m. p. 147° (5 g.) and 4-nitropyrocatechyl methylene ether, m. p. 95.5° (26.4 g.); on further nitration the former yielded 4:5-dinitropyrocatechyl methylene ether (II), m. p. 100°. The following derivatives of 4-nitropyrocatechyl methylene ether were prepared: 5-amino-, m. p. 193—197°; 5-methylamino-, m. p. 171°; 5-ethylamino-, m. p. 133°; 5-propylamino-, m. p. 115°; 5-butylamino-, m. p. 137°; 5-amylamino-, m. p. 95°; 5-heptylamino-, m. p. 79°; 5-dimethylamino-, m. p. 98°. Derivatives of I were prepared as follows: diacetate, m. p. 142°; 6:6'-dinitro-3:4:3':4'-bismethylenedioxybenzylideneazine, m. p. 257° (decomp.); phenylhydrazone, m. p. 218.5° (decomp.); *p*-nitrophenylhydrazone, m. p. 245° (decomp.); semicarbazone, m. p. 272.5—278° (decomp.). With methyl-alcoholic sodium sulphide, II afforded 6:6'-dinitro-3:4:3':4'-bismethylenedioxydiphenyl sulphide, m. p. 234° (transition at 215—220° to orange form); sodium disulphide gave a disulphide, m. p. 266°. On chlorination, piperonal (25 g.) gave 6-chloropiperonal (III), m. p. 115° (19 g.), and 4:5-dichloropyrocatechyl methylene ether, m. p. 82° (2.5 g.). Nitration of III [diacetate, m. p. 133°; benzylideneazine, m. p. 303° (decomp.); phenyl-

hydrazone, m. p. 117—118°; *p*-nitrophenylhydrazone, m. p. 281—282° (decomp.); semicarbazone, m. p. 280° (decomp.); semioxamazone, m. p. 299° (decomp.)] gave 5-chloro-4-nitropyrocatechyl methylene ether, m. p. 70° [corresponding amino-compound, m. p. 254—255° (decomp.)]. Bromination of piperonal (50 g.) afforded 6-bromopiperonal, m. p. 129° (28.5 g.) [diacetate, m. p. 128°, benzylideneazine, m. p. 249—252° (decomp.); *p*-nitrophenylhydrazone, m. p. 253° (decomp.); semicarbazone, m. p. 230° (decomp.); semioxamazone, m. p. 278—279° (decomp.)], and 4:5-dibromopyrocatechyl methylene ether, m. p. 85°. Nitration of the former compound gave the 4-nitro- and 3:4-dinitro-derivatives; 5-bromo-3-nitro-4-methylaminopyrocatechyl methylene ether has m. p. 67° (decomp.). With nitric acid the diacetate of I affords 6-nitro-3:4-dihydroxybenzaldehyde, m. p. 203° (decomp.) [benzylideneazine, m. p. 278° (decomp.); semicarbazone, m. p. 254° (decomp.); phenylhydrazone, m. p. 203° (decomp.); *p*-nitrophenylhydrazone, m. p. 290° (decomp.)]; 6-bromo-3:4-dihydroxybenzaldehyde, m. p. 220° (from 6-bromopiperonal and nitric acid), gave a benzylideneazine, m. p. 251° (decomp.); semicarbazone, m. p. 239°; *p*-nitrophenylhydrazone, m. p. 243° (decomp.). 4-Nitro-5-amino-1:2-dimethoxybenzene, m. p. 175°, was obtained from 4:5-dinitroveratrole; the following homologues were prepared: 5-ethylamino-, m. p. 174—175°; 5-propylamino-, m. p. 141—142°; 5-butylamino-, m. p. 114°; 5-amylamino-, m. p. 90.5°; 5-heptylamino-, m. p. 84°; 5-dimethylamino-, m. p. 130—131°. 4:5-Dinitroveratrole and sodium sulphide afford 6:6'-dinitro-3:4:3':4'-tetramethoxydiphenyl sulphide, m. p. 220—220.5° (corresponding disulphide, m. p. 212° (decomp.)).

CHEMICAL ABSTRACTS.

Preparation of 2:4:6-trihydroxybenzaldehyde 4-methyl ether and its tetra-acetylglucoside. P. KARRER, N. LICHTENSTEIN, and A. HELFENSTEIN (Helv. Chim. Acta, 1929, 12, 991—993; cf. A., 1927, 564; 1928, 65).—Phloroglucinolaldehyde (2:4:6-trihydroxybenzaldehyde) in acetone is boiled with methyl sulphate and sodium hydroxide. The oil left on evaporation is dissolved in dilute sulphuric acid, and the ethereal extract of this is evaporated and extracted with hot water. The aqueous solution deposits 2:4-dihydroxy-6-methoxybenzaldehyde, and when the filtrate is evaporated and extracted with carbon tetrachloride, 2:6-dihydroxy-4-methoxybenzaldehyde is obtained. Use of excess of methyl sulphate leads to formation of the 2:4-dimethyl ether. 2-Tetra-acetylglucosidophloroglucinolaldehyde 4-methyl ether, m. p. 177° after sintering at 175°, is obtained by interaction of the 4-methyl ether with acetobromoglucose in cold, aqueous acetone in presence of potassium hydroxide, and 4-tetra-acetylglucosidophloroglucinolaldehyde 2-methyl ether, m. p. 151°, is prepared by a similar method from the 2-methyl ether.

R. K. CALLOW.

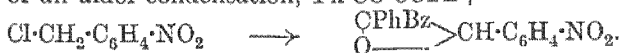
Isomerism of oximes. XXXVI. Methylation of aldoximes and ketoximes. O. L. BRADY and N. M. CHOKSHI (J.C.S., 1929, 2271—2274).—In agreement with previous results (Brady and Goldstein, A., 1926, 1142) methylation of various pairs of isomeric ketoximes which differ only slightly in their dissoci-

ation constants gives approximately the same proportion of *N*- to *O*-ethers with both α - and β -isomerides. Thus the ratio *N*-ether/*O*-ether for α - and β -furfuraldoximes, *p*-nitrobenzophenoneoximes, and phenyl *p*-tolyl ketoximes, determined by the method previously described (*loc. cit.*), is, respectively, 1:0.95 and 1:0.85, 1:1.15 and 1:2.55, 1:2.97 and 1:2.16, the corresponding values of $k_a \times 10^{11}$ for the first four named being 1.5, 1.4, 1.4, and 3.4, respectively. With α -2-methoxy-1-naphthaldoxime, acetophenoneoxime (k_a 0.33×10^{-11}), and benzophenoneoxime (k_a 0.50×10^{-11}) the ratio *N*-/*O*-ether is 1:0.96 (cf. Brady and Goldstein, A., 1927, 973), 1:1.43, and 1:1.16, respectively, the values for the amount of *N*-ether formed from ketoximes being minimum ones. When α -*p*-nitrobenzophenoneoxime is exposed in benzene to ultra-violet light some *p*-nitrobenzophenone is formed, but most of the oxime is recovered unchanged. J. W. BAKER.

Polymorphism of organic compounds. II. Prognosis of polymorphism and systems of polymorphs. C. WEYGAND (Ber., 1929, 62, [B], 2603—2612; cf. this vol., 815, 1072).—Systematic examination of the relationships in the chalkone series permits the prediction of a further modification of phenyl styryl ketone, m. p. 48°, and indicates its actual method of isolation by seeding supercooled phenyl styryl ketone with 3:5-diphenylisooxazole. The second missing form of phenyl styryl ketone is produced initially when undercooled phenyl styryl ketone is inoculated with the stable "59" variety.

A reply is made to von Auwers and Schaum (this vol., 1082). H. WREN.

[Occurrence of free substituted methylenes in chemical reactions.] G. HAHN (Ber., 1929, 62, [B], 2485—2489).—The action of phenylhydrazine on the condensation product from *p*-nitrobenzyl chloride and benzil (cf. Bergmann and Hervey, this vol., 695) gives the corresponding phenylhydrazone, $C_{27}H_{21}O_3N_3$, m. p. 169—170°. Bergmann's "*p*-nitrobenzylidene ether of stilbenediol" is α -benzoyl- α -phenyl- β -*p*-nitrophenylethylene oxide, reaction occurring in the manner of an aldol condensation, $Ph \cdot CO \cdot COPh +$



Similarly, the formation of a phenylhydrazone, $C_{27}H_{19}O_3N_3$, m. p. 134—135°, from the "*p*-nitrobenzylidene derivative of phenanthraquinol" (*loc. cit.*) shows the compound to be the oxide of 9-keto-10-*p*-nitrobenzylidene-9:10-dihydrophenanthrene. The synthesis of α -benzoyl- α -phenyl- β -*p*-nitrophenylethylene oxide is effected by the action of hydrogen peroxide in alkaline solution on *p*-nitrobenzylidenedeoxybenzoin, m. p. 163—164°, prepared by the condensation of *p*-nitrobenzaldehyde with deoxybenzoin under the influence of alcoholic hydrogen chloride.

The experiments of Bergmann and Hervey do not appear capable of placing the transitory existence of methylene radicals beyond doubt. H. WREN.

Organic compounds of sulphur. XV. Thermolabile thio-ethers. A. SCHÖNBERG, O. SCHÜTZ, V. BRÜCKNER, and J. PETER (Ber., 1929, 62, [B], 2550—2562; cf. this vol., 1300).—*s*-Tetraaryldimethyl sulphides undergo thermal decom-

position according to the scheme $(Ar_2CH)_2S_2 \longrightarrow Ar_2C:S + Ar_2CH_2$, and very labile thio-ethers can be obtained by suitable choice of the aryl group. Purely aromatic dithiols are very unstable thermally, giving disulphides, thioketones, and non-uniform products; change appears to occur according to the scheme: $2Ar_2C(SAr') \longrightarrow Ar'S \cdot SAr' + Ar_2C:S$ (and other heterogeneous stabilisation products). Aryl triarylmethyl sulphides decompose thus: $2Ar_3C \cdot SAr' = 2Ar_3C + Ar'S \cdot SAr'$. Highly arylated sulphur compounds derived from methyl sulphide, ethylene sulphide, or dithiolmethane are thermally more labile than the corresponding oxygen compounds, but more stable than the corresponding disulphides. Replacement of the substituent CPh_2R by $O < \begin{array}{c} C \\ \text{H} \end{array} > CR$ (*R* is a univalent residue) increases lability as observed in the hexa-arylothane group.

Diphenylmethane is obtained from dibenzhydryl sulphide at 290°, whereas dibenzhydryl disulphide undergoes decomposition at 185°. Di-9-xanthyl sulphide at 205° yields xanthene, xanthione, and dixanthyl; the last-named substance can be prepared by heating xanthene with xanthione in an atmosphere of dry carbon dioxide at 200—210°. Diphenylthiol-diphenylmethane at 200—225°/0.03 mm. affords thiobenzophenone (identified as tetraphenylethylene sulphide) and diphenyl disulphide. Di-*p*-tolylthiol-diphenylmethane, m. p. 73°, from benzophenone chloride and *p*-tolyl mercaptan, at 210° yields thiobenzophenone and di-*p*-tolyl disulphide. Di- β -naphthylthiol-diphenylmethane, m. p. 133°, decomposes at 210°. Xanthone is converted by boiling oxalyl chloride into the corresponding dichloride, which, with *p*-thiocresol, yields di-*p*-tolylthiolxanthene, m. p. 107°, transformed at 205° into xanthione and di-*p*-tolyl disulphide. Diphenylthiolxanthene, m. p. 117°, affords xanthione and diphenyl disulphide; diphenyl does not appear to be produced. Diphenyl-*p*-tolylmethyl chloride is converted by *p*-tolylmercaptan into diphenyl-*p*-tolyl-*p*-tolylthiolmethane, m. p. 87—88°, which yields di-*p*-tolyl disulphide, m. p. 45—46°, at 200°. Triphenylphenylthiolmethane affords a small amount of diphenyl disulphide at 220°/0.05 mm.

Since mild reduction of the "dibiphenylenethiol-pinacol" of Manchot and Krische (A., 1905, i, 142) yields fluorene and hydrogen sulphide, the compound is regarded as di-9-fluorenyl disulphide (cf. Bergmann and Hervey, this vol., 695). H. WREN.

Nuclear condensation of phenols and phenolic ethers with nitriles to ketimines and ketones of phenols and phenolic ethers. IV. Syntheses with phenol, *o*-, *m*-, and *p*-cresols, and *p*-tolyl methyl ether. J. Houben and W. Fischer (J. pr. Chem., 1929, [ii], 123, 262—275).—Trichloroacetonitrile reacts with phenol in presence of chlorobenzene and aluminium chloride at 50—60° affording a 95% yield of $\omega\omega\omega$ -trichloro-4-hydroxyacetophenone, b. p. 170°/0.5 mm., m. p. 99—99.5°, readily decomposed by alkali hydroxide or carbonate to chloroform and *p*-hydroxybenzoic acid. Similar condensation of *o*-cresol gives 90% of $\omega\omega\omega$ -trichloro-4-hydroxy-3-methylacetophenone, m. p. 90—91°; when condensation is effected in presence of benzene the yield of

ketone is 40% and some *o*-tolyl trichloroacetate is formed. *m*-Cresol yields a mixture of equal parts of $\omega\omega\omega$ -trichloro-4-hydroxy-2-methyl-, m. p. 84–87° [ketimine, m. p. 122–124° (slight decomp.)], and $\omega\omega\omega$ -trichloro-2-hydroxy-4-methyl-acetophenone, b. p. 162–163°/17 mm. *p*-Tolyl methyl ether furnishes $\omega\omega\omega$ -trichloro-2-methoxy-5-methylacetophenone, b. p. 168–169°/15 mm., m. p. 46–49° (cf. A., 1927, 1078); in absence of chlorobenzene the yield is improved. *p*-Cresol yields 80% of *p*-tolyl trichloroacetate and 11% of the corresponding acetophenone, hydrolysed by alkali to 6-hydroxy-*m*-toluic acid, m. p. 148–151°; when condensation is carried out in benzene some $\omega\omega\omega$ -trichloroacetophenone is produced.

H. BURTON.

Constitution of phloridzin. F. WESSELY and K. STURM (Monatsh., 1929, 53 and 54, 554–561).—Methylation of phloridzin (I) with diazomethane in ethereal methyl-alcoholic solution gives an amorphous trimethyl derivative, $[\alpha]_D^{25}$ –58.69° in methyl alcohol, hydrolysed by 4% sulphuric acid to dextrose and trimethylphloretin (II), m. p. 110.5° (acetate, m. p. 58–60°). Methylation of phloretin also gives II. Treatment of II with acetic anhydride and sodium acetate at 160–170° affords 5:7-dimethoxy-4- β -*p*-methoxyphenylethylcoumarin, m. p. 168° after sintering at 166.5° (obtained also by methylation of the known 5:7-dihydroxy-derivative), showing that II is 2-hydroxy-4:6-dimethoxyphenyl β -*p*-methoxyphenylethyl ketone. This is proved by reducing 2-hydroxy-4:6-dimethoxyphenyl *p*-methoxystyryl ketone with hydrogen in presence of platinum and alcohol, whereby II is formed. Phloridzin is, therefore, 4:6-dihydroxy-2-glucosidoxyphenyl β -*p*-hydroxyphenylethyl ketone.

H. BURTON.

Manufacture of naphthalene derivatives [synthesis of naphthazarin from quinol]. BRIT. CELANESE, LTD., G. H. ELLIS, H. C. OLPIN, and E. W. KIRK.—See B., 1929, 935.

Synthesis of alizarin. V. I. MINAEV and B. P. FEDEROV.—See B., 1929, 936.

Hystazarin ethylene ether. H. RAUDNITZ [with W. BOHM] (J. pr. Chem., 1929, [ii], 123, 284–288).—Condensation of phthalic anhydride with dihydrobenzdioxin (Ghosh, J.C.S., 1915, 107, 1588) in presence of a mixture of aluminium and sodium chlorides at 130–140°, and subsequent vacuum sublimation of the neutral product formed, gives hystazarin ethylene ether (I), m. p. 299–300°, and a small amount of alizarin ethylene ether. These are separated by treatment with hydrobromic acid (*d* 1.49) at 170–180°, whereby I is unaffected. Hydrolysis of I with sulphuric acid at 200° causes migration of a hydroxyl group and alizarin is the main product obtained. Hystazarin, not melted at 330° [diacetate, m. p. 213° (lit. 205–207°)], is purified by vacuum sublimation.

H. BURTON.

Reduction potentials of various phenanthrene-quinones. L. F. FIESER (J. Amer. Chem. Soc., 1929, 51, 3101–3111).—The normal reduction potentials of 43 phenanthrenequinones have been determined at 25° by titration with potassium ferricyanide, titanous chloride, tetrabromo-*o*-benzoquinone, or benzoquinone (?) in presence of (a) 0.1*N*-hydrochloric acid,

(b) 50% alcohol, 0.1*N* in hydrochloric acid and 0.2*N* in lithium chloride, (c) 37% alcohol, 0.047*M* in potassium dihydrogen phosphate and 0.047*M* in disodium hydrogen phosphate, or (d) 95% alcohol, 0.2*N* in hydrochloric acid and 0.2*N* in lithium chloride. Comparison of the results for phenanthrene-1:2-, -1:4-, and -3:4-quinones (and derivatives) with the values for the corresponding naphthaquinones (and derivatives) shows that the former compounds have the higher potentials; this is attributed to the more reactive naphthalene (as compared with benzene) ring which is joined to the benzoquinone residue. The values for phenanthrene-9:10-quinone are abnormally high, probably because of a strain resulting from the spatial configuration of the molecule. Introduction of groups into either the 1- or 3-position of the 9:10-quinone causes the same change in potential, which is greater than when the substituent is in the 2- or 4-position. An increased potential occurs with introduced nitro- (most effective), cyano-, keto-, carboxy-, or sulphy- (least effective) groups, and a decreased value with methoxy-, hydroxy-, methyl-, or amino-groups. Introduction of a second like substituent causes a further increase or decrease.

Oxidation of methyl phenanthrene-3-carboxylate, m. p. 97°, with chromic oxide in acetic acid gives methyl phenanthrene-9:10-quinone-3-carboxylate, m. p. 212°. Similar oxidation of 3-benzoylphenanthrene (from magnesium phenyl bromide and phenanthrene-3-carboxyl chloride) yields 3-benzoylphenanthrene-9:10-quinone, m. p. 205–206°.

H. BURTON.

1:2-Benzo-3:4-anthraquinone [2:3-benzo-phenanthraquinone]. L. F. FIESER and E. M. DIETZ (J. Amer. Chem. Soc., 1929, 51, 3141–3148).—*o*-4-Methoxy-1-naphthoylbenzoic acid, m. p. 196–197° (improved method of preparation given) (cf. Scholl, Seer, and Zincke, A., 1921, i, 677), is reduced with zinc dust and sodium hydroxide solution to phenyl-4-methoxy-1-naphthylmethane-2'-carboxylic acid, m. p. 221–223° (corr.). This readily undergoes ring closure on dissolution in cold sulphuric acid, yielding 3-methoxy-1:2-benz-10-anthrone [acetyl derivative, m. p. 197° (corr.)], which is reduced by aluminium amalgam and ammonia in alcoholic suspension to 3-methoxy-1:2-benzanthracene, m. p. 167–168° (9:10-quinone, m. p. 188.5°). Demethylation of this with 40% hydrobromic acid in acetic acid affords 3-hydroxy-1:2-benzanthracene, m. p. 196–205° (decomp.) [acetate, m. p. 129° (9:10-quinone, m. p. 232°)], which with *p*-nitrobenzenediazonium sulphate in acetic acid gives the 4-*p*-nitrobenzeneazo-derivative, dark red. The moist azo-compound is reduced by stannous chloride and hydrochloric acid in boiling butyl alcohol to 4-amino-3-hydroxy-1:2-benzanthracene [triacyl derivative, m. p. 203–205° (corr.)]; corresponding methyloxazole, m. p. 175.5°. Oxidation of this amine with chromic oxide in acetic acid yields 1:2-benzo-3:4-anthraquinone (I), m. p. 262–263° (corr.; some decomp.), which with zinc dust, acetic anhydride, and sodium acetate gives 3:4-diacetoxy-1:2-benzanthracene, m. p. 201° (corr.) (9:10-quinone, m. p. 198–199°). 3:4-Dihydroxy-1:2-benzanthraquinone gives an intense green coloration with boracetic anhydride, indicating that one hydroxyl group

is adjacent to a quinone carbonyl group. Oxidation of I with hydrogen peroxide in acetic acid solution affords 2-phenylnaphthalene-3:2'-dicarboxylic acid, m. p. 252° (corr.), converted by treatment with sulphuric acid into 1:2(or 2:3)-benzofluorenone-4(or 5)-carboxylic acid, m. p. 268° (corr.).

H. BURTON.

Perylene and its derivatives. XXVI. A. ZINKE and H. KOLMAYR (Monatsh., 1929, 53 and 54, 361—366).—Condensation of dibromo- (I) or dichloro- perylene-3:10-quinone (II) (Zinke and others, A., 1924, i, 1080) with *o*-thiolbenzoic acid in presence of amyl alcohol, potassium carbonate, and copper powder gives a *di*-(*o*-carboxyphenylthiol)perylene-3:10-quinone (red aqueous solution). Attempts to obtain the corresponding thioxanthone from this afforded only amorphous products. Bromination or chlorination in nitrobenzene solution at 100° regenerates I or II. Similar condensation of I or II with anthranilic acid affords an *o*-carboxyanilinoperylene-3:10-quinone, violet-black; one halogen atom is replaced by hydrogen during the reaction. Treatment of this acid with sulphuric acid at 100° affords the corresponding *acridone*, reddish-brown. Orientation of the halogen atoms in I and II is not possible from these results.

H. BURTON.

Linear pentacene series. XIV. Pentacene-6:13-quinone. F. HERNLER and K. SCHNURCH (Monatsh., 1929, 53 and 54, 643—645; see this vol., 1436).—Oxidation of pentacene, tetrahydropentacene, or the compound obtained by reduction of pentacenediquinone with zinc dust and ammonia (Seka and Sekora, A., 1927, 363) with ferric chloride in acetic acid solution affords varying amounts of pentacene-6:13-quinone, m. p. 393° (corr.; cf. Mills and Mills, J.C.S., 1912, 101, 2194).

H. BURTON.

Linear pentacene series. XV. 6:13-Dihydropentacene-5:7:12:14-diquinone. F. HERNLER and O. SOMMER (Monatsh., 1929, 53 and 54, 646—650).—1:4-Dihydroxy- β -naphthoic acid is converted by prolonged treatment with sulphuric acid at the ordinary temperature into 6:13-dihydropentacene-5:7:12:14-diquinone (I), m. p. 424° (corr.) (*diacetate*, m. p. 358°) (cf. Hartenstein, Diss., Jena, 1892, 6; Russig, A., 1900, i, 601). Attempted reduction of I with zinc dust, acetic anhydride, and sodium acetate gives the above diacetate; treatment with red phosphorus and hydriodic acid has no effect. Distillation of I over copper in a current of hydrogen gives mainly unchanged material, and it is considered that Russig's tetrahydropentacenequinone cannot be prepared. Oxidation of I with chromic acid affords unchanged material and water-soluble products. Pentacene-5:6:7:12:13:14-triquinone (cf. Russig, *loc. cit.*) is unknown.

H. BURTON.

Linear pentacene series. XVI. Pentacene-5:7:12:14-diquinonedisulphonic acid and tetrahydropentacene-5:7:12:14-diquinone. F. HERNLER and T. BRUNS (Monatsh., 1929, 53 and 54, 651—658).—Sulphonation of pentacene-5:7:12:14-diquinone (cf. Philippi and Seka, A., 1925, i, 556) with fuming sulphuric acid (45—50% SO₃) at 130° in presence of a small amount of mercury affords a disulphonic acid (probably 1:8 or 1:11), darkens at

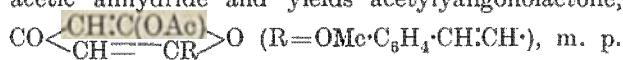
280°, sinters about 300°, softens about 390°, and is not melted at 500° (potassium and silver salts). Fusion of this acid with potassium hydroxide at 180—200° in presence or absence of potassium nitrate yields a mixture of *tetrahydroxypentacenediquinones*, not melted at 500°, partly separable by extraction with ether or alcohol. The products give a characteristic red colour in concentrated sulphuric acid, blue in alkaline solution, reduced by hyposulphite to a brown vat.

H. BURTON.

Linear pentacene series. XVII. Dinitro-, diamino-, and dihydroxy-pentacene-5:7:12:14-quinones. G. MACHEK (Monatsh., 1929, 53 and 54, 659—667).—Nitration of pentacene-5:7:12:14-diquinone with nitric (*d* 1.51) and sulphuric acids at 65° affords a mixture of isomeric dinitro-derivatives (I), decomp. above 400° (43.1%), and (II), decomp. 346—350° (45.8%) (cf. Seka and Schmidt, A., 1927, 363). Reduction of I with alkaline sodium hyposulphite or sodium hydrogen sulphide solution yields a *diaminopentacenediquinone* (III), dark violet, decomp. above 450°; II yields similarly a *diamino*-derivative (IV), reddish-violet, decomp. 389—390°. Decomposition of the diazonium salts from III and IV at 100° gives the corresponding *dihydroxypentacene*-5:7:12:14-*diquinones*, m. p. 375—380° after darkening and partial decomp. at 320°, and 304—305° after darkening and partial decomp. at 270°, respectively. All the above derivatives can be sublimed at 270—310°/0.02—0.05 mm. The positions of the substituents in these derivatives are probably 1:8 and 1:11.

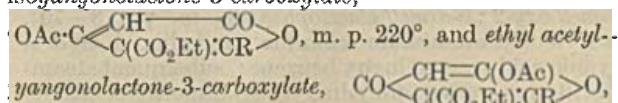
H. BURTON.

Constituents of kawa root. IX. Synthesis of yangonin. W. BORSCHKE and C. K. BODENSTEIN (Ber., 1929, 62, [B], 2515—2523; cf. this vol., 442).—Yangonic acid, m. p. 123—124° (decomp.), obtained according to Winzheimer (A., 1908, i, 805), is converted by diazomethane into its *methyl ester*, C₁₅H₁₆O₅, m. p. 78.5°, which loses methyl alcohol when boiled with acetic anhydride and yields acetylyangonolactone,



obtained but not investigated by Winzheimer; the compound is prepared also from yangonic acid and boiling acetic anhydride. It is converted by methyl alcohol at 100° or by methyl-alcoholic potassium hydroxide at the atmospheric temperature into yangonolactone, m. p. 238°, from which yangonin is derived by the action of ethereal diazomethane or of methyl sulphate and sodium hydroxide.

Ethyl acetonedicarboxylate, sodium, and *p*-methoxycinnamyl chloride in ether afford *ethyl α -p-methoxycinnamylacetone-xx'-dicarboxylate*, CO₂Et·CH₂·CO·CHR·CO₂Et, m. p. 51—52° (copper compound, m. p. 138—140°), which, when heated with acetic anhydride, gives a mixture of *ethyl acetylyangonolactone-3-carboxylate*,



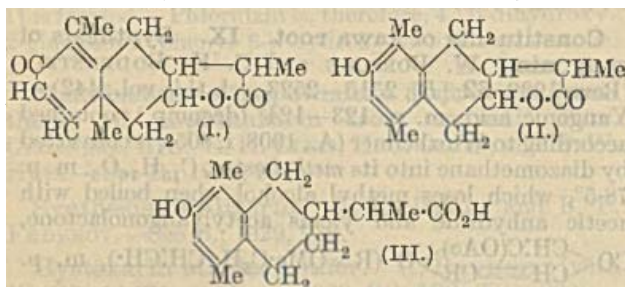
m. p. 104—105°. Treatment of the mixture of acetylated esters with methyl-alcoholic sodium hydroxide affords *ethyl yangonolactone-3-carboxylate*, orange

prisms or golden-brown rhombs, m. p. 149—150°, hydrolysed to the corresponding acid, $C_{15}H_{12}O_6$, m. p. 212—215° (decomp.). Decarboxylation of the acid in boiling nitrobenzene gives yangonolactone, m. p. 238—239°.

On an isolated occasion, treatment of yangonic acid with boiling acetic anhydride gave *acetyl-yangonolactone*, $C_{16}H_{14}O_5$, m. p. 185—186°, which is stable towards cold alkali hydroxide solution, but converted by boiling 10% sodium hydroxide into yangonolactone. In alkaline solution it is hydrogenated in presence of colloidal palladium to *acetyl-dihydroisoyangonolactone*, (?) $OAc \cdot C \begin{smallmatrix} \text{CH} \cdot \text{CO} \\ \text{CH} \cdot \text{CHR}' \end{smallmatrix} > O$ ($R' = OMe \cdot C_6H_4 \cdot CH_2 \cdot CH_2$), m. p. 107—108°. Hydrogenation of acetylyangonolactone suspended in methyl alcohol in presence of colloidal palladium affords *dihydroyangonolactone*, $CO \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH} \cdot \text{CHR}' \end{smallmatrix} > O$, m. p. 181—182°, converted by methyl sulphate and sodium hydroxide into dihydroyangonin, m. p. 101—103°.

H. WREN.

Constitution of santonin. I. Synthesis of *dl*-santonous acid. G. R. CLEMO, R. D. HAWORTH, and E. WALTON (J.C.S., 1929, 2368—2387).—Earlier formulæ for santonin are critically discussed and a new formula (I) is advanced which conforms better with its chemical properties and with modern views of structural units (isoprene units forming a farnesene skeleton). Santonin thus falls in the selinene group of sesquiterpenes. Its conversions into *desmotropo*-santonin (II) and *dl*-santonous acid (III) are



considered to involve the migration of the methyl group attached to the quaternary carbon atom together with the wandering of a nuclear hydrogen atom. The following investigations have led to the synthesis of III: *m*-xylene, β -cyanoethyl *p*-toluenesulphonate, and powdered aluminium chloride when boiled together yielded β -2:4-dimethylphenylpropionitrile, b. p. 264—267°/760°, which by hydrolysis with methyl-alcoholic potassium hydroxide gave β -2:4-dimethylphenylpropionic acid, m. p. 106°. Similar experiments with *p*-xylene gave identical compounds owing to migration of a methyl group. Slow addition of aluminium chloride to *p*-xylyl methyl ether and acetyl chloride in light petroleum solution formed 4-methoxy-2:5-dimethylacetophenone, m. p. 78—79°. *p*-Xylenol, aluminium chloride, and liquid hydrocyanic acid reacted in dry benzene; subsequent steam-distillation gave 6-hydroxy-2:5-dimethylbenzaldehyde, m. p. 62°, 4-hydroxy-2:5-dimethylbenzaldehyde, m. p. 132—133°, and *di*-(4-hydroxy-2:5-dimethylphenyl)acetonitrile, m. p. 250° (methyl ether,

m. p. 190°). 4-Hydroxy-2:5-dimethylbenzaldehyde condensed with malonic acid in hot pyridine solution containing a little piperidine to form 4-hydroxy-2:5-dimethylcinnamic acid, m. p. 223—225° (acetyl derivative, m. p. 168—169°). Methyl sulphate and methyl-alcoholic potassium hydroxide converted it into 4-methoxy-2:5-dimethylbenzaldehyde, b. p. 147—149°/12 mm., m. p. 34° (corresponding acid, m. p. 163—165°), which with malonic acid, pyridine, and piperidine at 100° gave 4-methoxy-2:5-dimethylcinnamic acid, m. p. 200—202°. This was reduced by sodium amalgam in 5% sodium hydroxide solution to β -4-methoxy-2:5-dimethylphenylpropionic acid, m. p. 120—121°, from which the corresponding chloride, b. p. 171°/12 mm., m. p. 34°, was obtained, using thionyl chloride. Heating the chloride with aluminium chloride and light petroleum gave 6-methoxy-4:7-dimethyl- α -hydrindone, m. p. 162—164°, whilst β -4-methoxy-2:5-dimethylphenylpropion-anilide and -amide (3-bromo-derivative, m. p. 152°), m. p. 134—135° and 127—128°, respectively, were formed normally. Treatment of the amide with sodium hypochlorite solution etc. led to β -4-methoxy-2:5-dimethylphenylethylamine, b. p. 120—122°/0.25 mm. [hydrochloride, m. p. 212—215° (decomp.)]; acetyl derivative, m. p. 147—148°, accompanied by a little methyl β -4-methoxy-2:5-dimethylphenylethylcarbamate, b. p. 175—185°/12 mm., m. p. 57.5°. β -4-Methoxy-2:5-dimethylphenylethyl alcohol, b. p. 125—126°/0.25 mm. (corresponding phenylcarbamate, m. p. 110°), isolated from the foregoing ethylamine by interaction with sodium nitrite in dilute acetic acid solution, gave with 45% aqueous hydrobromic acid β -4-methoxy-2:5-dimethylphenylethyl bromide, b. p. 128—130°/1 mm., which with ethyl sodiomalonate formed ethyl β -4-methoxy-2:5-dimethylphenylethylmalonate, b. p. 185°/0.25 mm., whence by hydrolysis with methyl-alcoholic potassium hydroxide the corresponding ethylmalonic acid, m. p. 145° (decomp.), and γ -4-methoxy-2:5-dimethylphenylbutyric acid, m. p. 101—102° (also formed by Clemmensen reduction of β -4-methoxy-2:5-dimethylbenzoylpropionic acid, m. p. 131°, obtained by the interaction of *p*-xylyl methyl ether, aluminium chloride, succinic anhydride, and benzene), were prepared successively. Brief heating of the foregoing butyric acid with concentrated sulphuric acid afforded 1-keto-7-methoxy-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene, m. p. 63—64° (dibromo-derivative, by bromination in chloroform, m. p. 93°), which condensed with amyl nitrite in ether containing potassium ethoxide to give 2-isonitroso-1-keto-7-methoxy-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene, m. p. 170—180° (decomp.).

β -4-Methoxy-2:5-dimethylbenzoylacrylic acid, m. p. 156—157°, from aluminium chloride, *p*-xylyl methyl ether, maleic anhydride, and light petroleum, at 70°, gave with hydrogen bromide in acetic acid α -bromo- β -4-methoxy-2:5-dimethylbenzoylpropionic acid, m. p. 144—147° (ethyl ester, m. p. 90—91°). The corresponding ethyl α -chloro-ester, m. p. 89—90°, was prepared analogously; amalgamated zinc and hydrochloric acid converted it into γ -4-methoxy-2:5-dimethylphenylbutyric acid, whilst condensation with ethyl sodiomalonate led to ethyl γ -4-methoxy-2:5-dimethylbenzoylpropane- $\alpha\alpha\beta$ -tricarboxylate, an oil, hydro-

lysed by methyl-alcoholic potassium hydroxide to the related acid. The last compound, when (a) heated at 160°, gave γ -4-methoxy-2:5-dimethylbenzoylpropane- $\alpha\beta$ -dicarboxylic anhydride, m. p. 152—153°, by elimination of carbon dioxide (corresponding acid, m. p. 148—150°), (b) reduced by amalgamated zinc and hydrochloric acid, formed β -4-methoxy-2:5-dimethylphenylethylsuccinic acid, m. p. 140—142°, which with sulphuric acid gave 7-methoxy-1-keto-5:8-dimethyl-1:2:3:4-tetrahydronaphthyl-2-acetic acid, m. p. 143—145°, from which, by Clemmensen reduction, 7-methoxy-5:8-dimethyl-1:2:3:4-tetrahydronaphthyl-2-acetic acid, m. p. 130—131°, was obtained. Brief heating of this methoxy-acid with hydriodic acid gave the related 7-hydroxy-acid (norsantonous acid), m. p. 163—164°.

Ethyl α -chloro- β -4-methoxy-2:5-dimethylbenzoylpropionate and ethyl sodiomethylmalonate interacted to give ethyl δ -4-methoxy-2:5-dimethylbenzoylbutane- $\beta\beta$ -tricarboxylate, m. p. 99°, b. p. (with slight decomp.) 220°/0.1 mm., hydrolysis of which with methyl-alcoholic potassium hydroxide gave 4-methoxy-2:5-dimethylacetophenone and the two racemic forms of δ -4-methoxy-2:5-dimethylbenzoylbutane- $\beta\gamma$ -dicarboxylic acid, m. p. 155—162°, resolved by crystallisation from alcohol into mainly one form of the acid, m. p. 163—168°. Clemmensen reduction of the acid mixture of m. p. 155—162° gave small yields of an unknown acid, m. p. 181—182°, along with α (β -4-methoxy-2:5-dimethylphenylethyl)- α -methylsuccinic acid (two forms: m. p. 169—171° and 130—132°, respectively). Either of the two preceding acids when warmed with sulphuric acid gave a lactone, m. p. 160—162°, alkaline hydrolysis of which produced a mixture of the two racemic forms of α -7-methoxy-1-keto-5:8-dimethyl-1:2:3:4-tetrahydronaphthyl-2-propionic acid, m. p. 105—115°. Clemmensen reductions of this mixture afforded the two possible racemic forms of *dl*-santonous acid methyl ether, m. p. 97—110°; these by boiling with hydriodic acid gave *dl*-santonous acid, m. p. 150—152° (ethyl ester, m. p. 125°), identical with santonous acid and its ester from santonin.

Attempts to condense β -methoxy-2:5-dimethylphenylethyl bromide with ethyl sodiopropene- $\alpha\beta$ -tricarboxylate yielded two products, b. p. 135—150°/12 mm. and b. p. 235—250°/12 mm. Treatment of the former with methyl-alcoholic potassium hydroxide gave 4-methoxy-2:5-dimethylstyrene(?), b. p. 120°/12 mm.

An improved preparation of *p*-xylene and *p*-xyleneol from *p*-xylidine is described incidentally.

R. J. W. LE FEVRE.

Cryoscopic measurements with caoutchouc solutions and the separation of mixed phases from solutions of caoutchouc in benzene. IX. R. PUMMERER, A. ANDRIESEN, and W. GUNDEL (Ber., 1929, 62, [B], 2628—2636; cf. A., 1928, 793).—Re-examination of the mol. wt. of caoutchouc in camphor shows that the hydrocarbon is not cracked at the high temperature (or cracking is complete within 5 min.), that melting camphor is not "catalytically" decomposed by caoutchouc and guttapercha, and that the depressions of the f. p. cannot be attributed to products of decomposition of oxygenated impurities in the caoutchouc, since camphor can be almost

quantitatively sublimed from the mixture and is found practically unchanged in m. p. Re-determination of the mol. wt. of caoutchouc in menthol in an apparatus designed to examine the effect of delay in crystallisation gives values higher than those observed previously, which indicate the presence of 16—24 isoprene residues. Examination of sol caoutchouc in freezing benzene gives very varying results (mol. wt. 1500—8000) due to the separation of caoutchouc with the solid phase. No value can therefore be placed on determinations in benzene. In menthol, the variations are less marked, but more considerable than is usual, whereas in camphor the depressions proceed strictly stoichiometrically and give almost the same values (about 1200) as the experiments in menthol.

H. WREN.

Iodine and oxygen values of sol and gel caoutchouc. X. R. PUMMERER and F. J. MANN (Ber., 1929, 62, [B], 2636—2647).—The iodine value is determined by means of iodine chloride in anhydrous chloroform, excess of the reagent being converted into iodine by addition of finely-divided potassium iodide. The acid liberated during the Wijs reaction is determined by a "dry" method, which consists in removing excess of iodine chloride in a parallel experiment by silver powder, distilling about half of the chloroform at about 20°/70 mm. into an excess of 0.1*N*-sodium hydroxide, and titrating the excess of the latter, and by a "wet" method in which the mixture remaining after use of thiosulphate is titrated directly with 0.1*N*-sodium hydroxide in presence of phenolphthalein. It is immaterial whether the experiment be performed at 0° or the ordinary temperature; the mixture is preserved for 6 or 72 hrs., and the solution contains 0.7 or 0.2% of caoutchouc. Addition of pyridine to sol caoutchouc (as offset against the nitrogenous impurities of gel caoutchouc) is without influence. The oxygen value is determined by means of perbenzoic acid in chloroform, the operation being complete within 48 hrs. Sol and gel caoutchoucs from latex, "revertex," crêpe, and smoked sheet are employed (cf. A., 1927, 1193; B., 1928, 793). Sol caoutchouc from latex and revertex gives almost the theoretical iodine values calculated for the absorption of 1 mol. of iodine per C_5H_8 group (denominated 100%). For sol caoutchouc from crêpe or smoked sheet the values 97.6% and 98.3% are observed. Halogen acid is not found in the chloroform. The oxygen values are 5—6% below the iodine values. For gel caoutchouc from latex, revertex, and crêpe the iodine values 108.6—110.3% and oxygen values 98.25—100.5% are observed. Gel caoutchoucs differ fundamentally from the sol products in that they evolve halogen acid in indifferent media. If it is assumed that the acid is formed by substitution, and 1 mol. of iodine is deducted for each mol. of hydrogen halide, the iodine value is almost exactly 100%, and the actual number of double linkings is identical in sol and gel caoutchouc. The "dry acid value" of gel caoutchouc is about 5% of the added halogen. If a correction based on the "wet acid value" (deduction of 1 mol. of iodine for 2 mols. of hydrogen halide) is applied to the iodine values, the corrected figure for all four pairs

of sol and gel caoutchouc is almost identical with the oxygen value.

If the sol caoutchouc-iodine solution is treated with water, 6—7% of the added halogen is eliminated as hydrogen halide which must be due to hydrolysis or ring formation [cf. the behaviour of hentriacontene dibromide towards alcohol (this vol., 1420)].

The original communication should be consulted for the detailed consideration of the theoretical aspects of the experiments.

H. WREN.

Modified Curtius reaction. IV. Degradation of perhydronorbixin. C. NAEGELI and P. LENDORFF (Helv. Chim. Acta, 1929, **12**, 894—899).—Perhydronorbixin is converted by thionyl chloride into the acid chloride; this is treated with sodium azide, and the product is decomposed with hydrochloric acid (cf. this vol., 540). The main product is *bixamine hydrochloride*, an amorphous powder, sintering at 147° (chloroplatinate, sintering at 208°; chloroaurate, decomp. 65—70°; dicarbamido-derivative, pasty), accompanied by a mixture of ω -aminocarboxylic acids, from which a chloroplatinate is obtainable.

R. K. CALLOW.

Conjugated unsaturated compounds. X. The ethylene group as chromophore. R. KUHN and A. WINTERSTEIN (Helv. Chim. Acta, 1929, **12**, 899—903).—A reply to Faltis and Viebock (this vol., 575). The intense colour of bixin is sufficiently accounted for by the cumulative effect of the nine conjugated unsaturated linkings and the two carboxyl groups in the formula proposed (A., 1928, 869). The colours of α -crocetin, norbixin, and bixin are comparable, respectively, with those of $\alpha\omega$ -diphenyltetradecaheptaene, $\alpha\omega$ -diphenylhexadecaheptaene (A., 1928, 281), and with that to be expected in the next member of the series. Evidence is brought forward in support of the chromophoric equivalence of the phenyl and carboxyl groups. The formula of Faltis and Viebock would correspond with a blue-black substance.

R. K. CALLOW.

Conjugated unsaturated compounds. XI. Bixin and its degradation to bixane. R. KUHN and L. EHLMANN (Helv. Chim. Acta, 1929, **12**, 904—915).—A further reply to Faltis and Viebock (this vol., 575). In support of the formula $C_{25}H_{30}O_4$ for bixin new analytical data and molecular refractivities are given. The formula is also supported by the number of methyl groups determined (this vol., 425), and by the isomerisation phenomena (Karrer and others, this vol., 1075).

Details are given of an improved method of extraction of bixin from the seeds of *Bixa Orellana*. Perhydrobixin, b. p. 224°/0.30 mm., d_4^{20} 0.9368, n_D^{20} 1.4615, is obtained by hydrogenation of bixin in presence of platinum oxide-platinum-black, and is hydrolysed to perhydronorbixin, b. p. 227°/0.03 mm., 245.5°/0.24 mm., d_4^{20} 0.9528—0.9561, 1.4685—1.4678, which is esterified to perhydromethylbixin, b. p. 219°/0.55 mm., d_4^{20} 0.9234, n_D^{20} 1.4658. Reduction of perhydromethylbixin with sodium in amyl alcohol yields the glycol, $\alpha\omega$ -dihydroxybixane, b. p. 198°/0.12 mm., and an acid substance, b. p. 281—285°/0.32 mm., n_D^{20} 1.4675. The glycol is converted by heating in a sealed tube with hydrobromic acid

into the oily dibromo-compound, which is reduced by a zinc-copper couple in 60% acetic acid to the hydrocarbon *bixane* (tetramethyleicosane), b. p. 162°/0.52 mm., d_4^{20} 0.8054, n_D^{20} 1.4502. The b. p. of this hydrocarbon is concordant with its formulation as a homologue of farnesane and phytane. Reduction of perhydrobixin yields an oil, b. p. 254°/0.53 mm., from which a cyclic hydrocarbon, $C_{11}H_{20}$, m. p. 66°, is obtained in 1% yield by boiling with acetic anhydride. R. K. CALLOW.

Strophanthin. XVII. Dehydration and lactone cleavage in isostrophanthic acid derivatives. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1929, **84**, 183—190).— β -isostrophanthic lactone acid (A., 1927, 1194) when heated with acetic anhydride and acetyl chloride, gave an *anhydro-anhydride acetate*, $C_{25}H_{30}O_7$, m. p. 280—281°, which, when hydrolysed with sodium hydroxide, neutralised 3 equivalents of alkali and yielded an *acid*, $C_{23}H_{30}O_7$, m. p. 230—232° (*dimethyl ester*, m. p. 199—200°, $[\alpha]_D^{20}$ —28.0° in methyl alcohol); treatment of the anhydride with methyl-alcoholic hydrogen chloride gave the *acetate* of the above ester, m. p. 170—171°. The ester was hydrogenated to give a saturated *ester*, $C_{25}H_{36}O_7$, m. p. 229—231°. The reaction is explained by cleavage of the unstable lactone ring, the liberated carboxyl forming a succinic anhydride with the carboxyl already free; the liberated hydroxyl is removed with introduction of a double linking and the second hydroxyl is acetylated (compare formulæ, A., 1928, 1376). The explanation is confirmed by the fact that the action of acetic anhydride and acetyl chloride on the methyl ester of β -isostrophanthic lactone acid leads only to the *acetate*, $C_{26}H_{34}O_8$, m. p. 235—237°. Also the prolonged action of methyl-alcoholic hydrogen chloride on β -isostrophanthic lactone acid leads to an unsaturated *dimethyl ester*, $C_{25}H_{34}O_7$, m. p. 154—155°, $[\alpha]_D^{20}$ +90° in methyl alcohol, the isomerism of which with the ester described above is explained by the fact that it belongs to the δ -isostrophanthic acid series (A., 1927, 1194). The *l*-ester was unchanged by heating with methyl-alcoholic hydrogen chloride, as was the *d*-ester after alkaline hydrolysis and re-esterification; the isomerisation must therefore involve carbon atom 6 (formulæ, *loc. cit.*) and have occurred prior to the opening of the lactone ring. C. R. HARRINGTON.

Fungi resins. N. FROSCHL and J. ZELLNER (Monatsh., 1929, **53** and **54**, 146—152).—Hydrolysis of *Lentinus squamosus*, Schroet., with alcoholic potassium hydroxide and separation of the reaction mixture into (a) ether-soluble, (b) water-soluble, and (c) ether- and water-insoluble gelatinous products gives (a) a sterol-like substance, m. p. 152—154°, (b) amorphous acidic substances, and (c) resin acids and a neutral substance (termed *lentinol*), $C_{27}H_{44}O_3$, m. p. 265° after darkening at 250° (*triacyl derivative*, m. p. 227—228°). This gives an olive-brown coloration with Liebermann's reagent and belongs to the resinol group. The alcoholic extract of the fungus contains the major part of the resin; this is separated into lentinol and resin acids. The resin from *Hypholoma fasciculare*, Huds., is separated as above into (a) a small amount of a substance, m. p. 173°, (b) acid products, and (c) a substance, m. p. 148—150° (cf.

A., 1912, ii, 195). The resin acid fraction from *Polyporus pinicola*, Fr. (Hartmann and Zellner, this vol., 108), contains two isomeric acids, m. p. 208.5° after slight coloration at 198°, $[\alpha]_D^{20} +35.7^\circ$ in alcohol, and m. p. 271° after darkening at 265°, $[\alpha]_D^{20} +23.4^\circ$ in alcohol, termed α - and β -pinicolic acids, respectively.

H. BURTON.

Breins from Manila elemi resin. A. ROLLETT (Monatsh., 1929, 53 and 54, 231—236).—The commercial resin is freed from essential oil by steam-distillation and then extracted with alcohol. The residue from this extract deposits the brein B, m. p. 180—190°, of Vesterberg (A., 1906, i, 686). The residue from this contains brein (I), $C_{30}H_{50}O_2$ (+EtOH), m. p. 218—219° [cf. *loc. cit.*; dibenzoyl derivative (+EtOH), m. p. (alcohol-free) 209—210°], obtained crystalline from an acetic acid solution, or as the acetyl derivative, m. p. 195°, by acetylation with acetic anhydride. Oxidation of I with chromic and acetic acids gives a small amount of a substance, $C_{30}H_{48}O_2$, m. p. 161—163° [*oxime*, m. p. 246—248° (decomp.)], probably a keto-alcohol. H. BURTON.

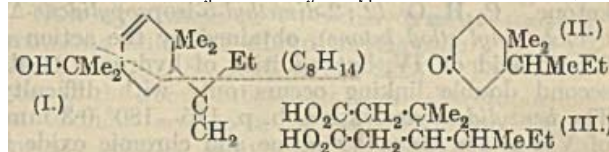
Constitution of resins. I. Boswellic acid from olibanum (frankincense). K. BEAUCOURT (Monatsh., 1929, 53 and 54, 897—913).—Boswellic acid (I), $C_{32}H_{52}O_4$, m. p. 150—151° after sintering at 142° (Tschirch and Halbey, A., 1899, i, 69), on distillation at 245—260° (bath)/0.2 mm. gives acetic acid, an acid, m. p. 95—98° after sintering at 80°, isomeric with I, and a hydrocarbon (II), $C_{30}H_{48}$, m. p. 126—127°, $[\alpha]_D^{18} +183^\circ$ in benzene (crystallographic data given). The presence of one double linking in II is shown by bromine and perbenzoic acid titrations, and by catalytic reduction in presence of platinum-black or platinum oxide and amyl ether. The reduction product has m. p. 112—120°, and is probably a mixture. H. BURTON.

Behaviour of saturated di- and tri-cyclic terpene hydrocarbons towards catalytic reduction and dehydrogenation. N. D. ZELINSKI and R. J. LEVINA (Annalen, 1929, 476, 60—70).—Reduction of di- and tri-cyclic terpenes containing a trimethylene ring with hydrogen and platinised charcoal at 160° readily causes fission of this ring (cf. Zelinski, A., 1913, i, 254). Thus carane gives *p*-menthane, cyclofenchene gives isobornylane identical with the product obtained by reduction of α -fenchene, whilst tricyclene yields camphane. Catalytic dehydrogenation with platinised charcoal at 300° in a current of carbon dioxide causes similar ring fission with the formation of an unsaturated hydrocarbon which, if hydroaromatic, is further dehydrogenated to the corresponding benzene derivative. Thus carane yields *p*-cymene, but thujane gives only a hydrocarbon, $C_{10}H_{18}$, b. p. 163.5—164.5°, $n_D^{21} 1.4452$, which may be 1:2-dimethyl-3-isopropylidenecyclopentane, 1:2-dimethyl-3-isopropyl- Δ^2 - or 1:3-dimethyl-3-isopropyl- Δ^1 -cyclopentene. Similar fission of a tetramethylene ring occurs, but less readily, pinane giving mainly *p*-cymene (oxidised to terephthalic acid), but the pentamethylene ring in fenchane or isobornylane is unattacked. Similar dehydrogenation of cyclofenchene causes partial

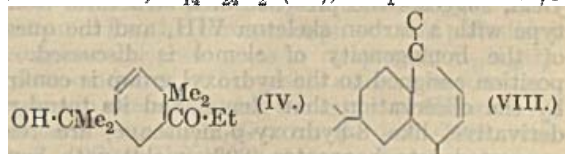
fission of the trimethylene ring, giving a mixture of α - and β -fenchenes.

J. W. BAKER.

Higher terpene compounds. XL. Constitution of elemol. L. RUZICKA, A. G. VAN VEEN [and, in part, D. KORVER, J. VAN DER KAMP, and H. J. WIGMAN] (Annalen, 1929, 476, 70—112).—Further details concerning the structure of elemol and its degradation products (cf. A., 1926, 1148) have been elucidated, and on the basis of the results, which are briefly summarised below, the structure I is suggested for elemol. Catalytic dehydrogenation of elemene



with sulphur at 140—160° and removal of the thionaphthen derivative obtained by fractionation of the picrates and treatment with mercuric acetate in alcohol yields eudalene, which, together with an azulene, is obtained in 25% yield by two successive dehydrogenations with selenium at 280°, cyclisation of the side-chains occurring to form a second ring. Attempts to effect dehydrogenation of tetrahydroelemene to the corresponding benzene hydrocarbon were unsuccessful with a palladised-charcoal catalyst which was effective with hexahydrozingiberene. The formation of two isomeric tetrahydroelemenes (*loc. cit.*) by elimination of water (or hydrogen chloride) from tetrahydroelemol (or its chloride) receives support from the observation that elimination of hydrogen chloride from 8-chloro-*p*-menthane occurs in both possible directions, ozonolysis of the product giving formaldehyde, acetone, and ketones which are further oxidised by hypobromite to hexahydro-*p*-toluic and β -methyladipic acids. The mixed tetrahydroelemenes obtained either by the action of (1) 95% formic acid or magnesium phenyl bromide on tetrahydroelemol or (2) methyl-alcoholic potassium hydroxide or aniline on the corresponding chloride, give the same products on the corresponding chloride, give the same products on ozonolysis at 0° (cf. *loc. cit.*). Of these the ketone $C_{12}H_{22}O$, now identified as 4:4-dimethyl-3-sec-butylcyclohexanone (II) (picrate of aminoguanidine compound, m. p. 210°), forms a benzylidene derivative, b. p. 175—180°/0.5 mm., which ozonisation converts into the same dibasic acid, $C_{12}H_{22}O_4$ (III), as is obtained by hypobromite oxidation of the keto-acid, $[C_{10}H_{15}](CO_2H)(COPr^B)$ (*loc. cit.*), obtained from the keto-aldehyde also formed in the original ozonolysis of tetrahydroelemene. The dimethyl ester of III is converted by cyclisation with sodium in boiling benzene and hydrolysis of the resulting keto-ester into 4:4-dimethyl-3-sec-butylcyclopentanone, b. p. 90—95°/0.5 mm. (semicarbazone, m. p. 208°). The ketonic alcohol, $C_{14}H_{24}O_2$ (IV), b. p. 125—135°/0.3



mm., obtained together with formaldehyde, by ozonolysis of elemol, is reduced by hydrogen and platinum-

black in ethyl acetate to 2:2-dimethyl-5-(α -hydroxy-isopropyl)cyclohexyl ethyl ketone (V), b. p. 132°/0.3 mm. (amorphous semicarbazone), which is converted by formic acid into 2:2-dimethyl-5-isopropylidene-cyclohexyl ethyl ketone (VI), b. p. 125—135°/12 mm. (semicarbazone, m. p. 172°). This is reduced catalytically to 2:2-dimethyl-5-isopropylcyclohexyl ethyl ketone (VII), b. p. 131—133°/18 mm., d_4^{25} 0.9120, n_D^{25} 1.4702 (semicarbazone, m. p. 172°; picrate of aminoguanidine compound, m. p. 145°). The latter is also obtained by catalytic reduction of the doubly unsaturated ketone, $C_{14}H_{22}O$ (2:2-dimethyl-5-isopropylidene- Δ^3 -cyclohexenyl ethyl ketone), obtained by the action of formic acid on IV, but addition of hydrogen to the second double linking occurs only with difficulty. The benzylidene derivative, b. p. 175—180°/0.3 mm., of VII is converted by ozone and chromic oxide in acetic acid into 2:2-dimethyl-5-isopropylcyclohexane-1-carboxylic acid (chloride, b. p. 135°/12 mm.; amorphous amide), isolated as its methyl ester, b. p. 128—135°/12 mm. Catalytic reduction of elemol to its tetrahydro-derivative proceeds smoothly only with specimens purified through the benzoate or phenylurethane, specimens obtained merely by fractionation yielding dihydroelemol, b. p. 138°/12 mm., m. p. 47°, d_4^{25} 0.934, n_D^{25} 1.4925 (erroneously described by Jansch and Fantl, A., 1923, i, 814, as a dicyclic alcohol), which is actually a mixture of isomerides, an exocyclic double linking still being present. Thus ozonolysis of dihydroelemol gives acetaldehyde and formaldehyde, whilst by treatment of the main fraction of the neutral product in various ways the same (impure) semicarbazone, m. p. 171°, of V is obtained, although the pure ketone did not form a crystalline semicarbazone. This is converted by successive treatment with oxalic and 95% formic acids into VI, which is also obtained from the neutral fraction, b. p. 125—160°/3 mm., of the ozonolysis after oxidation with permanganate and successive treatment with alkali and 95% formic acid. The acid fraction of the products of ozonolysis of dihydroelemol is an acid, $C_{13}H_{24}O_3$, m. p. 145°, which is probably a γ - or δ -hydroxy-acid, since it lactonises by distillation in a high vacuum, and is converted by heating with either 85% formic acid or methyl-alcoholic potassium hydroxide into a lactone, $C_{13}H_{22}O_2$, m. p. 37°, b. p. 109—111°/high vacuum. When the ethereal extract of the acidified solution of this lactone in dilute alkali is evaporated on a water-bath, the original lactone is regenerated, but evaporation at the ordinary temperature in a vacuum yields a substance, m. p. 118°, which, however, is still contaminated with the lactone. The formation of the acid $C_{13}H_{24}O_3$ and acetaldehyde, together with the fact that from the products of oxidation of elemol with manganese dioxide and sulphuric acid trimellitic acid is isolated in small yield, suggests the presence of a structural isomeric type with a carbon skeleton VIII, and the question of the homogeneity of elemol is discussed. The position assigned to the hydroxyl group is confirmed by the observation that elemol and its tetrahydro-derivative, like 8-hydroxy-*p*-menthane, are readily converted into benzoates (80% yield) with benzoyl chloride and pyridine, whilst with 4-hydroxy-*p*-menthane only a 10% yield of the ester is obtained. No

dimethylmalonic acid could be isolated by the successive action of formic acid and potassium permanganate on elemene, oxalic acid being the only product. Elemene is not reduced by sodium and amyl alcohol at 120—200°, and gives only a trace of condensation product with ethyl diazoacetate.

J. W. BAKER.

Constitution of ψ -baptisin. E. SPATH and O. SCHMIDT (Monatsh., 1929, 53 and 54, 454—470).—When anhydrous ψ -baptisin (I), $C_{28}H_{30}O_{13}$, $[\alpha]_D^{25}$ —98.1° in methyl alcohol (crystallises also $+3H_2O$, which are lost at 120°) (cf. Gorter, A., 1897, i, 627; 1898, i, 39; 1906, i, 973; 1908, i, 97), is heated in a vacuum it sinters at 140°, melts at 140—150°, re-solidifies at 180—210°, and re-melts at 249—251° with partial decomp. Hydrolysis of I with 10% sulphuric acid gives dextrose, rhamnose, and ψ -baptigenin (II), $C_{16}H_{10}O_5$ (cf. loc. cit.), m. p. 296—298° [acetyl derivative, m. p. 173°; the ethyl ether (III), m. p. 172°, and not ψ -baptigin (Gorter, loc. cit.), is obtained by the action of ethyl iodide on the sodium derivative of II]. Boiling 5% potassium hydroxide decomposes II, forming formic acid and ψ -baptigenetin (IV), $C_{15}H_{12}O_5$, m. p. 151° [methyl ether, m. p. 145°; dimethyl ether; ethyl ether, m. p. 129°, obtained also by decomposition of III with potassium hydroxide solution; oxime, m. p. 206° (slight decomp.)]. Treatment of IV with nitric acid (d 1.5) gives styphnic acid, whilst oxidation with 1% potassium permanganate at the ordinary temperature affords piperonylic acid. It is shown that IV is 2:4-dihydroxyphenyl 3:4-methylenedioxybenzyl ketone by the Hoesch condensation of resorcinol and 3:4-methylenedioxyphenylacetonitrile. Resorcinol and β :3:4-methylenedioxyphenylpropionitrile afford similarly 2:4-dihydroxyphenyl β :3:4-methylenedioxyphenylethyl ketone, m. p. 130° (oxime, m. p. 192—194°, not sharp). ψ -Baptigenin is, therefore, 7-hydroxy-3':4'-methylenedioxyisoflavone, and ψ -baptisin is the corresponding sugar derivative.

H. BURTON.

α -Furfuryl chloride and derivatives. II. W. R. KIRNER and G. H. RICHTER (J. Amer. Chem. Soc., 1929, 51, 3131—3135).—The following compounds are prepared from α -furfuryl chloride (2-chloromethylfuran) (A., 1928, 1019) by the usual methods: ethyl α -furfurylmalonate, b. p. 125.5—127°/4 mm., d_4^{20} 1.10999, n_D^{20} 1.4591, ethylated to ethyl α -furfuryl-ethylmalonate, b. p. 135.5—136.5°/5 mm.; 5- α -furfuryl-, m. p. 186—187.5° (lit. 193°), and 5- α -furfuryl-5-ethyl-barbituric acids, m. p. 144.5—145° [prepared from the above esters by the method of Dox and Yoder (A., 1922, i, 681)]; ethyl α -furfurylacetacetate, b. p. 111—111.5°/4 mm., d_4^{20} 1.10366, n_D^{20} 1.4718 (hydrolysed to β -2-furylpropionic acid and α -furfuryl-acetone); α -furylacetonitrile, b. p. 74—75°/27 mm., d_4^{20} 1.04627, n_D^{20} 1.4833 (hydrolysed to 2-furylacetic acid, m. p. 108.5—109.5°), and α -furfuryl thiocyanate, b. p. 111.5—112.5°/27 mm., d_4^{20} 1.18709, n_D^{20} 1.5614. Condensation of α -furfuryl chloride with thiocarbamide and hydrolysis of the resulting product gives α -furfuryl mercaptan, b. p. 84°/65 mm., d_4^{20} 1.13186, n_D^{20} 1.5329, ethylated to α -furfuryl ethyl sulphide, b. p. 90.5—91°, d_4^{20} 1.04958, 1.5140.

H. BURTON.

1:6-Addition of hydrogen to unsaturated 1:4-diketones. R. E. LUTZ (J. Amer. Chem. Soc., 1929, 51, 3008—3023).—Reduction of a series of unsaturated 1:4-diketones under various conditions gives chiefly the corresponding furan (in some cases exclusively). The corresponding saturated diketones afford little or no furan under the same conditions, indicating that 1:6-addition of hydrogen occurs thus: $O:C:C:C:C:O + H_2 \rightarrow HO:C:C:C:C:OH$.

When a mixture of saturated ketone and furan is obtained, these compounds are, presumably, independent end-products of the reaction.

Bromine and *trans*- $\alpha\beta$ -di-*p*-chlorobenzoyl-ethylene in chloroform solution at 60° yield approximately equal amounts of *meso*- (Conant and Lutz, A., 1925, i, 681) and *dl*- $\alpha\beta$ -dibromo- $\alpha\beta$ -di-*p*-chlorobenzoyl-ethane, m. p. 124.5°; in acetic acid solution the main product is the *meso*-derivative (cf. Lutz, A., 1927, 59). Treatment of the dibromoethane with sodium methoxide affords α -methoxy- $\alpha\beta$ -di-*p*-chlorobenzoyl-ethylene (I), m. p. 130°. When an alcoholic suspension of dibromodibenzoyl-ethane is treated with an excess of phenol dissolved in 2.5% alcoholic sodium ethoxide a 63% yield of α -phenoxy- $\alpha\beta$ -dibenzoyl-ethylene (II) is obtained. Similarly, α -*p*-tolyl- (III) and α -*m*-methoxyphenoxy- $\alpha\beta$ -dibenzoyl-ethylene, m. p. 110° (10% yield), are prepared, using *p*-cresol and resorcinol monomethyl ether, respectively. A new α -*m*-tolyl- $\alpha\beta$ -dibenzoyl-ethylene, m. p. 95°, is obtained in addition to the form of m. p. 103° (Conant and Lutz, *loc. cit.*), when *m*-cresol is used in the above reaction; reduction of both forms by various reagents gives the same α -*m*-tolyl- $\alpha\beta$ -dibenzoyl-ethane (*loc. cit.*).

Reduction of α -methoxy- $\alpha\beta$ -dibenzoyl-ethylene with aqueous-alcoholic sodium hyposulphite (method *a*) gives mainly α -methoxy- $\alpha\beta$ -dibenzoyl-ethane (IV), which when heated at 210—215° decomposes into methyl alcohol and $\alpha\beta$ -dibenzoyl-ethylene. Reduction with zinc dust and acetic acid (sometimes with added acetic anhydride) (method *b*) affords 3-methoxy-2:5-diphenylfuran (V), whilst with alcoholic chromous chloride (method *c*) IV and V are obtained in varying amounts, depending on the conditions. $\alpha\beta$ -Dibenzoyl- α -phenylethylene gives (*a*) mainly $\alpha\beta$ -dibenzoyl- α -phenylethane, (*b*) a mixture of the ethane and 2:3:5-triphenylfuran. α -Methoxy- $\alpha\beta$ -di-*p*-bromobenzoyl-ethylene furnishes (*b*) mainly 3-methoxy-2:5-di-*p*-bromophenylfuran, m. p. 113°, (*a*) and (*c*) mixtures of the furan and α -methoxy- $\alpha\beta$ -di-*p*-bromobenzoyl-ethane, m. p. 72° (decomposes at 210—220° into methyl alcohol and $\alpha\beta$ -di-*p*-bromobenzoyl-ethylene). Reduction of I yields (*a*) α -methoxy- $\alpha\beta$ -di-*p*-chlorobenzoyl-ethane (VI), m. p. 58—59° (decomposes at 200°, forming methyl alcohol and $\alpha\beta$ -di-*p*-chlorobenzoyl-ethylene), or 3-methoxy-2:5-di-*p*-chlorophenylfuran (VII), m. p. 113°, according to the conditions, (*b*) a mixture of VI and VII. Reduction of II by method *b* gives a mixture of α -phenoxy- $\alpha\beta$ -dibenzoyl-ethylene, m. p. 120° (decomposes at 270° yielding phenol and dibenzoyl-ethylene), and 3-phenoxy-2:5-diphenylfuran, m. p. 91°; similarly III furnishes a mixture of α -*p*-tolyl- $\alpha\beta$ -dibenzoyl-ethane, m. p. 108.5°, and 3-*p*-tolyl-2:5-diphenylfuran, m. p. 113°. In the above reductions variations in the conditions cause vari-

ations in the products formed. Treatment of the substituted ethanes under identical conditions gives either unchanged material or small amounts of furan; with the α -methoxy- and α -aryloxy- $\alpha\beta$ -diarylethanes elimination of the methoxy- or aryloxy-group occurs to varying extents.

α -Benzoyl- β -trimethylacetylstyrene is reduced by zinc dust and acetic acid and anhydride to desylpinacolin (Boon, J.C.S., 1910, 97, 1258) which is unstable towards hot hydriodic acid. H. BURTON.

Synthetical experiments in chromone group.

I. New syntheses of 7:8-dihydroxy-2-methyl-chromone and 7:8-dihydroxyflavone. K. VENKATARAMAN (J.C.S., 1929, 2219—2223).—The preparations of the above substances from gallacetophenone and sodium acetate-acetic anhydride or sodium benzoate-benzoic anhydride mixtures respectively are described. The m. p. of the two hydroxyl compounds are given as 241—242°, 246°, and of their corresponding diacetyl derivatives as 189° (after shrinking at 110° and losing water of crystallisation) and 194° (lit. 243°, 239°, 120°, 193°, respectively). The reactions and tinctorial properties of these substances are described in detail. R. J. W. LE FEVRE.

Grape pigments. VI. Anthocyanins in Ives grapes. R. L. SHRINER and R. J. ANDERSON (N.Y. Agric. Exp. Sta. Tech. Bull., 1929, No. 152, 11 pp.).—See this vol., 192.

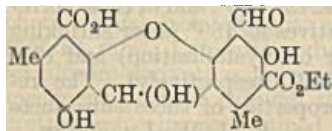
Constitution of cetraric acid. G. KOLLER and E. KRAKAUER (Monatsh., 1929, 53 and 54, 931—951).—When cetraric acid (I), $C_{20}H_{18}O_9$ (Zopf, A., 1898, i, 489; Hesse, A., 1898, i, 531; 1901, i, 85; 1905, i, 138; Simon, A., 1903, i, 98; 1906, i, 961), is heated with hydriodic acid and phenol at 140—150°, ethyl iodide is formed and 2 mols. of carbon dioxide are eliminated. The ethoxyl group is present in the ester form, since I is hydrolysed by 10% sodium carbonate solution (in a current of hydrogen) at 50°. Acetylation of I with acetic anhydride and pyridine gives a *diacetate*. Methylation of I with methyl sulphate at 65—70° affords *methyl monomethylcetrarate* (II), $C_{22}H_{22}O_9$, m. p. 191—192° after sintering at 189° (contains a phenolic hydroxyl), and *methyl dimethylcetrarate* (III), $C_{24}H_{24}O_9$, m. p. 151—152°; a *compound* (IV), $C_{25}H_{20}O_{10}$, m. p. 99° (*ferrichloride*), is formed as a by-product. Further methylation of II gives a mixture of III and IV; similarly, III yields IV. The production of IV from III indicates the presence of an oxide ring in III; this undergoes fission. A free hydroxyl group is shown to be present in III (Zerevitinov), but phenolic groups are absent. The *oximes* of III and IV have m. p. 189—190° (decomp.) and 174—175°, respectively, and since oxidation of III with potassium permanganate in acetone solution affords an *acid*, $C_{23}H_{24}O_{10}$, m. p. 212—213°, an aldehyde group must be present in I. Reduction of I with hydrogen in presence of palladised charcoal and alcohol gives a *compound*, $C_{20}H_{20}O_9$. Energetic oxidation of III yields acidic, resinous products, but in one case (using a mixture of III and IV), a *substance* (V), $C_{11}H_{12}O_6$, m. p. 167—168°, was isolated. When V is heated in a vacuum, carbon dioxide is eliminated and sparassol (methyl 6-hydroxy-4-methoxy- α -toluate) (Späth and Jeschki, A., 1924, i,

513) is formed. Methylation of V affords *methyl 3:5-dimethoxytoluene-1:4-dicarboxylate* (VI), m. p. 56—57°; V is probably *methyl (2) hydrogen 3-hydroxy-5-methoxytoluene-2:4-dicarboxylate*.

Ethyl acetonedicarboxylate condenses with ethyl acetoacetate in presence of sodium, affording *ethyl orcinol-2:4-dicarboxylate*, m. p. 52—53°. Similar condensation of the methyl esters yields a mixture of *methyl 2:4-dihydroxy-5-carbomethoxymethylbenzene-1:3-dicarboxylate* (Dootson, J.C.S., 1900, 77, 1196) and *methyl orcinol-2:4-dicarboxylate*, m. p. 107—108°. Methylation of the last-named compound with diazomethane in ethereal methyl-alcoholic solution affords a mixture of *methyl 3-hydroxy-5-methoxytoluene-2:4-dicarboxylate*, m. p. 124—125°, and VI.

Zinc dust distillation of I in a current of hydrogen gives unidentified hydrocarbons similar to those obtained similarly from resacetophenone.

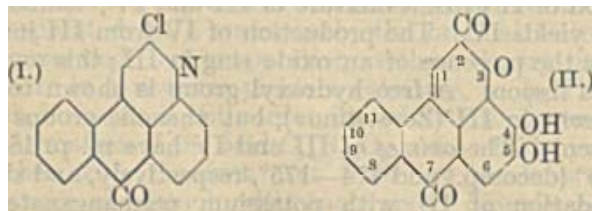
The annexed constitution is assigned provisionally to I. Methylation of the xanthhydrol hydroxyl group does not occur during the formation of II and III.



H. BURTON.

Pyridanthrone and anthracoumarin syntheses.

II. R. SEKA, G. SCHRECKENTAL, and P. S. HEILPERIN (Monatsh., 1929, 53 and 54, 471—484).—Treatment of 3-phenylpropionlamido-*p*-toluic acid, m. p. 260—261°, with sulphuric acid, first at the ordinary temperature and then at 60°, gives 13% of 4-methylpyridanthrone, decomp. 354—358° (for nomenclature see A., 1925, i, 1316), and a substance, $C_{17}H_{15}O_4N$, m. p. 215—216°, probably formed by addition of water to the triple linking of the original acid. Similarly, *m*-phenylpropionlamidobenzoic acid, m. p. 253—254°, affords pyridanthrone and the substance, $C_{16}H_{13}O_4N$, m. p. 207—208°. *m*-4'-Methylcinnamoylamidobenzoic acid, m. p. 264°, is converted by sulphuric acid at 90° into 9-methylpyridanthrone, m. p. 395—398°. Similarly, 3-4'-methyl- and 3-4'-methoxycinnamoylamido-*p*-toluic acids, m. p. 269° and 279° (decomp.), respectively, give 4:9-dimethyl-, m. p. 340° (decomp.), and 9-methoxy-4-methyl-pyridanthrones, m. p. (vac.) 312°, respectively. Treatment of pyridanthrone with phosphorus pentachloride in dichlorobenzene yields the compound (I), m. p. (vac.)



255°; methylation (methyl iodide) gives 3-methylpyridanthrone, m. p. 267—268°. Nitration of pyridanthrone with nitric acid (*d* 1.52) affords a nitropyridanthrone, m. p. 354—356°, which on boiling with aniline or *p*-toluidine furnishes anilino-, m. p. 385—390°, or *p*-toluidino-pyridanthrone, m. p. 388—392°, respectively. Reduction of the nitro-compound with alkaline sodium hyposulphite gives the unstable aminopyridanthrone, m. p. 364—368° (benzylidene

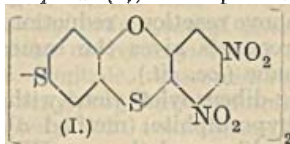
derivative, decomp. 232—237°); attempted reduction with sodium stannite causes a considerable loss of nitrogen from the compound.

Treatment of a mixture of cinnamic and gallic acids with sulphuric acid at 90° gives 4:5-dihydroxyanthracoumarin (II), m. p. 392—394° (diacetate, m. p. 263—265°), described previously by Jacobsen and Julius (A., 1888, 56) as styrogallol, $C_{16}H_{10}O_6$. Cinnamic and 3:5-dihydroxybenzoic acids yield similarly 5-hydroxyanthracoumarin, m. p. 332—334° (cf. Kostanecki, A., 1888, 292) (acetate, m. p. 248—250°); 2:5-dihydroxybenzoic acid gives 6-hydroxyanthracoumarin, m. p. 282—285° (acetate, m. p. 237—239°). *m*-Hydroxycinnamic and gallic acids afford 4:5:10(or 8)-trihydroxyanthracoumarin, m. p. 388° (triacetate, m. p. 280—282°). H. BURTON.

Sulphur dyes. III. Hydroxythiophenols.

II. J. POLLAK and E. RIESZ (Monatsh., 1929, 53 and 54, 90—99).—Di- and tri-thiol derivatives of phenol are prepared by reduction of the corresponding phenolsulphonyl chlorides (cf. A., 1926, 514, 832; this vol., 60).

[With A. NADEL and (in part) R. BRAUN and P. POLLAK].—Phenol-2:4-disulphonyl chloride is reduced by zinc and hydrochloric acid in ethereal solution yielding impure 2:4-dithiolphenol (tribenzoyl derivative, m. p. 96°). Treatment of the *dipicryl* derivative, m. p. 155°, with alcoholic potassium hydroxide gives 2:4:2':4'-tetranitrodibenzophenoxethene 6:6'-disulphide (I), decomp. when heated, which is reduced by



sodium sulphide to a dye (light reddish-brown on cotton). Methylation of 2:4-dithiolphenol with methyl sulphate gives a dimethoxydimethyldithioldiphenyl disulphide, m. p. about 200° after some change at 77—90°. 2:4-Dimethyldithiolanisol, m. p. 38—39°, is obtained by methylation of 2:4-dithiolanisol (Gebauer-Fülneegg and von Meissner, A., 1928, 997) [diacetyl, m. p. 62°, dicarbethoxy-, m. p. 30—32°, di(carboxymethyl), m. p. 142—144°, and *dipicryl*, m. p. 190—194°, derivatives]. Phenol-2:4:6-trisulphonyl chloride is reduced to impure 2:4:6-trithiolphenol (tetrabenzoyl derivative, m. p. 132°; *tripicryl* derivative, decomp. 150—160° without melting). When cotton is treated with an alkaline solution of 2:4-dithiolphenol, dithiol-*o*-cresol, or 2:4:6-trithiolphenol, and then dyed with a concentrated solution of brilliant-green, the dyed fibre is stable towards short heating with potash soap.

[With A. NADEL].—Chlorination of *p*-thioltoluene in hydrochloric acid suspension gives *p*-toluenesulphonyl chloride. Similarly, dithiol-*o*- and *m*-cresols afford the corresponding cresoldisulphonyl chlorides, whilst I and its 7:7'-dimethyl derivative (this vol., 60) undergo fission and oxidation to phenol- and *m*-cresol-disulphonyl chlorides. The sulphur dyes from *o*- or *m*-cresol, sulphur, and sodium sulphide (G.P. 102,897) are chlorinated to *o*- or *m*-cresoldisulphonyl chlorides, but the corresponding dye from phenol gives *diphenyl-4:4'-disulphonyl chloride*, m. p. 203°. The diphenyl structure is presumably formed by the action of the intermediate sodium oxide on the

intermediate diphenylsulphone 4 : 4'-disulphide derivative (cf. Otto, 1886, 1031).

H. BURTON.

Synthesis of 2-ethylpyrrolidine. A. MÜLLER and H. WACHS (Monatsh., 1929, 53 and 54, 420—426).—Reduction of ethyl γ -keto-*n*-hexoate with sodium and alcohol gives *n*-hexane- α -diol (27% of theory) converted into α -dibromo-*n*-hexane, b. p. 94—97°/10 mm. Treatment of a mixture of this dibromide and *p*-toluenesulphonamide in boiling alcohol with alcoholic potassium hydroxide affords a 36% yield of the 1-*p*-toluenesulphonyl derivative, m. p. 76.9° (corr.), of 2-ethylpyrrolidine (I), b. p. 122.4° (corr.)/744 mm., d_4^{25} 0.844, n_D^{25} 1.4442 [hydrochloride, m. p. below 100° (is very hygroscopic); chloroplatinate, decomp. 190—191°; chloroaurate, m. p. 96.2° (corr.); picrate, m. p. 85° (corr.); phenylthiocarbimide derivative, m. p. 89° (corr.)]. 1:1-Di-methyl-2-ethylpyrrolidinium iodide, m. p. about 220° (not sharp), is prepared from I and an excess of methyl iodide and methyl-alcoholic potassium hydroxide. The hexamethyleneimine described by Schmidt (A., 1922, i, 761) is probably I.

H. BURTON.

Action of diazomethane on aromatic ketones. E. MOSETTIG and L. JOVANOVIĆ (Monatsh., 1929, 53 and 54, 427—437; cf. this vol., 814).—Treatment of acetophenone with ethereal methyl-alcoholic diazomethane at about 20° gives phenylacetone and an oxide (probably α -phenyl- α -methyl-ethylene oxide); the oxide is separated from unchanged acetophenone by conversion into the corresponding piperidino-alcohol (cf. *loc. cit.*) (picrate, m. p. 138—140°). Similarly, acetoveratrone affords small amounts of veratryl-acetone [semicarbazone, m. p. 178—181° (lit. 175—176°)] and an oxide [the picrate (I) of the corresponding piperidino-alcohol has m. p. 150—152°]. Acetopiperone [obtained by the Friedel-Crafts reaction from methylenedioxybenzene, b. p. 55—56°/9 mm., n_D^{25} 1.5423 (picrate, m. p. 94—96°)], does not react with diazomethane. Piperonylacetone, b. p. 150—152°/11 mm. (picrate, m. p. 71—73°), yields with diazomethane about 60% of an oxide (probably α -3:4-methylenedioxybenzyl- α -methyl-ethylene oxide), b. p. 152—156°/10 mm., converted by aqueous piperidine into α -piperidino- β -3:4-methylenedioxybenzylpropan- β -ol [hydrochloride, m. p. 162—163°; picrate, m. p. 152—154°; chloroplatinate, m. p. 172—175° (decomp.)], and by aqueous dimethylamine into α -dimethylamino- β -3:4-methylenedioxybenzylpropan- β -ol [picrate, m. p. 86—88°; chloroplatinate, m. p. 169—171° (decomp.)]. Veratrylacetone and diazomethane yield an oxide (probably α -3:4-dimethoxybenzyl- α -methyl-ethylene oxide), b. p. 161—162°/10 mm., converted into α -piperidino- β -3:4-dimethoxybenzylpropan- β -ol (picrate, m. p. 152—153°, identical with I).

H. BURTON.

Natural rotation of polarised light by optically active bases. IV. Rotation of synthetic isoquinoline derivatives. W. LEITHE (Monatsh., 1929, 53 and 54, 956—962).—Reduction of 1-methyl-3:4-dihydroisoquinoline with sodium and alcohol gives dl-1-methyl-1:2:3:4-tetrahydroisoquinoline, b. p. 233°/745 mm., resolved by *d*-tartaric acid into the l-base (I), d^{20} 1.024, $[\alpha]_D^{20}$ -79.5° (hydrochloride, m. p. 213°; d-hydrogen tartrate, m. p. 92°). dl-1-

Phenyl-1:2:3:4-tetrahydroisoquinoline, m. p. 97°, furnishes similarly the corresponding l-base (II), m. p. 84°, $[\alpha]_D^{20}$ -43.4° in ether, +6.2° in alcohol (hydrochloride, m. p. 204°), and ethylation of l- α -phenylethylamine yields 1-N-ethyl- α -phenylethylamine (III), b. p. 100° (bath)/16 mm., 0.913, $[\alpha]_D^{20}$ -60.0°.

The effect of ring closure (comparison of III and I) is to cause an increase in the molecular rotatory power. Introduction of a second phenyl group into the ring system (as in II) lowers the rotatory power, probably because the molecule thereby acquires an increased symmetry. The rotatory powers of I in various solvents are analogous to those of phenylethylamine, whilst those of II are similar to pipercoline (cf. A., 1928, 1022; this vol., 647). The specific solution volume of II is highest in cyclohexane; the orders of the values in various solvents agree with the rotatory powers in the same solvents (cf. this vol., 1079). H. BURTON.

Catalytic hydrogenation of 1-methylpyrrole and dehydrogenation of 1-methylpyrrolidine. N. D. ZELINSKI and J. K. JURJEV (Ber., 1929, 62, [B], 2589—2590).—If pyrrole mixed with hydrogen is passed over palladised asbestos at 160°, smooth hydrogenation to pyrrolidine does not occur; the last-named compound is mainly decomposed with evolution of ammonia. Under these conditions, 1-methylpyrrole affords 1-methylpyrrolidine, b. p. 80°, d_4^{20} 0.8399, n_D^{20} 1.4480, in very good yield. Repeated passage of 1-methylpyrrolidine over palladised asbestos at 160° causes production of a certain amount of 1-methylpyrrole; the process becomes quantitative at 250°.

H. WREN.

Additive compounds of organic bases with salts of heavy metals. J. V. DUBSKÝ and A. RABAS (Coll. Czech. Chem. Comm., 1929, 1, 528—537).—Zinc chloride, either anhydrous or in aqueous solution, combines with pyridine to give the compound $\text{ZnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, m. p. 210—213°. Aniline and aqueous zinc chloride yield $\text{ZnCl}_2 \cdot 2\text{PhNH}_2$, m. p. 266° (decomp.). *o*- and *p*-Toluidines in alcoholic solution combine similarly with (aqueous) zinc chloride to form the compounds $\text{ZnCl}_2 \cdot 2(\text{o-Me-C}_6\text{H}_4\text{-NH}_2)$, m. p. 234°, and $\text{ZnCl}_2 \cdot 2(\text{p-Me-C}_6\text{H}_4\text{-NH}_2)$, m. p. 267°, respectively. The corresponding hydrated compounds described by Lachowicz and Bandrowski (A., 1888, 1281) are non-existent. Zinc chloride (1 mol.) in aqueous solution and quinoline (2 mols.) in alcohol give the compound $\text{ZnCl}_2 \cdot 2\text{C}_8\text{H}_7\text{N}$, m. p. 210°. Aqueous cupric sulphate and β -naphthylamine in benzene give the substance $\text{CuSO}_4 \cdot 2(\beta\text{-NH}_2\text{-C}_{10}\text{H}_7)$, m. p. 260° (decomp.), whilst with aniline the compound $\text{CuSO}_4 \cdot 2\text{PhNH}_2$, m. p. 260° (decomp.), is produced. Dimethylaniline (2 mols.) with aqueous zinc chloride or cupric sulphate (1 mol.) yielded basic salts. An attempt to prepare $\text{ZnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 2\text{AcOH}$ from zinc chloride in dilute acetic acid solution and pyridine afforded the compound $\text{ZnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, m. p. 196°. Contrary to the statement of Lachowicz and Bandrowski (*loc. cit.*), zinc chloride (1 mol.) combines with glycine (0.75 mol.) to give the substance $\text{ZnCl}_2 \cdot 3(\text{NH}_2\text{-CH}_2\text{-CO}_2\text{H})$, m. p. 235° (decomp.).

A. I. VOGEL.

4-Piperonyl-2:6-dimethylpyridine. A. STEIN and F. ULZER (Wiss. Mitt. Oesterr. Heilmittelstelle,

1928, 15—16, 1929, 1—5; Chem. Zentr., 1929, i, 2778—2779).—Interaction of ethyl acetoacetate (2 mols.), piperonal (1 mol.), and alcoholic ammonia (1 mol.) affords ethyl 4-piperonyl-2 : 6-dimethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate, which, by treatment in alcoholic suspension with nitrous acid affords ethyl 4-piperonyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate. Hydrolysis with alcoholic potassium hydroxide affords the acid ester (hydrochloride), which may be esterified with diazomethane. If the hydrolysis with alcoholic alkali is followed by long-continued hydrolysis with aqueous potassium hydroxide the dicarboxylic acid is produced. Distillation of the dicarboxylic acid with soda-lime affords the piperonyl-lutidine, which is formulated as 4-3' : 4'-methylenedioxyphenyl-2 : 6-dimethylpyridine.

A. A. ELDRIDGE.

Manufacture of pyridines. I. OSTROMISS-LENSKY etc.—See B., 1929, 958.

1 : 3-Dicarbonyl compounds. I. Mechanism of cyanoacetamide and cyanoacetic ester condensations. J. C. BARDHAN (J.C.S., 1929, 2223—2232).—Condensation of ethyl acetylpyruvate with cyanoacetamide in alcoholic solution containing diethylamine gave ethyl 3-cyano-6-methyl-2-pyridone-4-carboxylate, m. p. 219° (5-bromo-derivative, decomp. 232—233°), which by the action of methyl iodide, sodium methoxide, and methyl alcohol gave ethyl 3-cyano-1 : 6-dimethyl-2-pyridone-4-carboxylate, m. p. 177—179°. The last-named compound was converted by hydrochloric acid at 150—160° into 6-methyl-2-pyridone-4-carboxylic acid, m. p. 314° (methyl ester, m. p. 228°), from which 2-chloro-6-methylpyridine-4-carboxylic acid (identical with the product of oxidation of 2-chloro-4 : 6-dimethylpyridine) was obtained by treatment with phosphorus pentachloride and phosphorus pentachloride, followed by digestion with water.

Benzoylacetone and cyanoacetamide gave a mixed condensation product, m. p. 270—286°, resolved by fractional crystallisation into 3-cyano-6-phenyl-4-methyl-2-pyridone, m. p. 310° (decomp.) (methyl derivative, m. p. 267°), which when boiled with 80% sulphuric acid gave 6-phenyl-4-methyl-2-pyridone, m. p. 182—183°, and 3-cyano-4-phenyl-6-methyl-2-pyridone, m. p. 249° (lit. 266—267°), identified by heating with hydrochloric acid, when 4-phenyl-6-methyl-2-pyridone was obtained.

Propionylacetophenone and cyanoacetamide yielded chiefly 3-cyano-6-phenyl-4-ethyl-2-pyridone, m. p. 240° (decomp.).

Propionylacetone and cyanoacetamide condensed spontaneously, giving 3-cyano-4-methyl-6-ethyl-2-pyridone, m. p. 240—241°, which when heated with concentrated hydrochloric acid passed into 4-methyl-6-ethyl-2-pyridone, m. p. 144°; this in turn yielded 2-chloro-4-methyl-6-ethylpyridine, b. p. 224°/765 mm., 124°/35 mm., by treatment with phosphorus pentachloride and water etc. The last-named compound, when heated with hydriodic acid (*d* 1.94) and red phosphorus or when its vapours were passed in a current of hydrogen over zinc dust heated to redness, was transformed into 4-methyl-6-ethylpyridine (picrate, m. p. 122—123°; lit. 115—116°, 120—121°).

C-Ethylacetylacetone and cyanoacetamide con-

densed readily, giving 3-cyano-4 : 6-dimethyl-5-ethyl-2-pyridone, m. p. 272° (decomp. after previous darkening), and, by hydrolysis of this with hydrochloric acid, 4 : 6-dimethyl-5-ethyl-2-pyridone, m. p. 150°.

Condensation of acetylacetone and cyanoacetamide produced successively 3-cyano- ψ -lutidocarbostyryl, m. p. 289°, and ψ -lutidocarbostyryl, m. p. 180—181°.

α -Cyanopropionamide (from ethyl α -cyanopropionate by the action of concentrated aqueous ammonia), m. p. 100—101° (lit. 81°, 105°), would not react with acetylacetone.

Propionylphenylacetylene condensed with ethyl malonate in ethyl-alcoholic sodium ethoxide solution, giving ethyl 4-phenyl-6-ethyl- α -pyrone-3-carboxylate, m. p. 72—73°, and with the sodium derivative prepared by addition of sodium ethoxide in absolute-alcoholic solution to cyanoacetamide in boiling alcohol, to form 3-cyano-4-phenyl-6-ethyl-2-pyridone, m. p. 260°.

The results show that the β -diketones react with cyanoacetamide mainly in the keto-phase, producing in each case only one pyridine derivative, and also that the condensation is effected by the carbonyl group adjacent to the positive alkyl group in the diketone.

R. J. W. LE FEVRE.

Manufacture of 6-ethoxy-2 : 4-dimethylquinoline. H. T. CLARKE and others.—See B., 1929, 935.

Unilaterally acylated diamines of therapeutic activity [quinoline derivatives]. I. G. FARBENIND. A.-G.—See B., 1929, 958.

Pharmaceutical products [quinolines and piperidines]. I. G. FARBENIND. A.-G.—See B., 1929, 958.

Vat dyes of the α -naphthaquinone [carbazole] series. I. G. FARBENIND. A.-G.—See B., 1929, 890.

Formation of 1-phenyl-5-methyl-3-pyrazolone. K. BRUNNER and H. MOSER (Monatsh., 1929, 53 and 54, 682—686).—When a mixture of acetylphenylhydrazine, magnesium oxide, and fused potassium acetate is heated at 300—320° in a current of hydrogen, about 7.5% of 1-phenyl-5-methyl-3-pyrazolone (I), m. p. 166—167°, is obtained. The probable reaction is: $2\text{NHPh}\cdot\text{NHAc} \rightarrow \text{NHPh}\cdot\text{NH}_2 + \text{H}_2\text{O} + (\text{I})$.

H. BURTON.

Derivatives of creatinine and diketopiperazine. L. R. RICHARDSON and C. E. WELCH [with S. CALVERT] (J. Amer. Chem. Soc., 1929, 51, 3074—3079).—When creatinine is heated with aromatic aldehydes at 150° the corresponding 5-arylidene derivatives are formed. The benzylidene, m. p. 244° (formed similarly from creatinine and benzylidenedianiline), *m*-nitrobenzylidene, decomp. 288°, and 4-hydroxy-3-methoxybenzylidene, m. p. 267° (decomp.), derivatives are described. Diketopiperazine condenses with aromatic aldehydes only in presence of acetic anhydride and sodium acetate. The following are described: 2 : 5-diketo-3 : 6-di-4'-acetoxy-3'-methoxybenzylidene-, decomp. 310° after darkening at 290°; -dicinnamylidene-, decomp. 350° after darkening at 335°; -dipiperonylidene-, decomp. 320° after darkening at 290°; -di-*m*-acetoxybenzylidene-, m. p. 255°; -di-*m*-toluylidene-, decomp. 320° after darkening at 305°, and -di-*o*-chlorobenzylidene-piperazine, decomp. 340° after darkening at 330°. Aliphatic aldehydes do not give simple

3 : 6-dialkylidene derivatives, poor yields of condensation products are obtained with *o*-hydroxybenzaldehydes, and condensation does not occur with amidines. Diketopiperazine furnishes a *bis-α-naphthyl-carbimide* derivative, m. p. 232° (decomp.), which with *m*-nitrobenzaldehyde and *m*-tolualdehyde (as above) undergoes hydrolysis and subsequent condensation to the 3 : 6-diarylidene derivatives. The dienol form of diketopiperazine is therefore the 2 : 5-dihydroxy-compound.
H. BURTON.

Naphthoisoindigotins. A. WAHL and J. LOBECK (Ann. Chim., 1929, [x], 12, 156—202).—In part, a more detailed account of work already described (this vol., 938). The following facts appear to be new: α -benzisatin (α -naphthisatin) has m. p. above 200° with blackening, whilst β -benzisatin, m. p. 199°, may be obtained by condensation of α -benzisatin and oxindole with hydrochloric acid or potassium hydroxide. Whilst α -benzisatin by treatment with hydrogen sulphide yields $\alpha\alpha'$ -dibenzdisulphisatide, convertible into $\alpha\alpha'$ -dibenzisoindigotin (I) (*loc. cit.*), β -benzisatin by similar treatment yields a sulphur compound, probably $\beta\beta'$ -dibenzdisulphisatide, which could not be converted into the corresponding $\beta\beta'$ -dibenzisoindigotin. Sulphuric acid converts I into $\alpha\alpha'$ -dibenzisoindigotindisulphonic acid (sodium, potassium, barium, and silver salts).

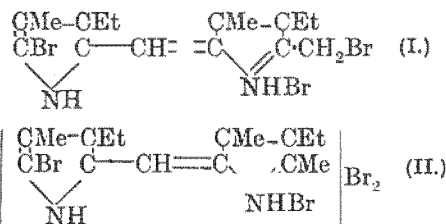
β -Naphthylamine and ethyl mesoxalate condense in 50% acetic acid to give *ethyl di-β-naphthylaminomalonate*, m. p. 150—152°, converted by hot glacial acetic acid into ethyl β -benzoxindole-3-carboxylate (ethyl β -naphthoxindole-3-carboxylate, cf. A., 1919, i, 457), also obtained directly from the reactants in glacial acetic acid. In the presence of dilute hydrochloric acid β -naphthylamine (1 mol.) and ethyl mesoxalate (2 mols.) undergo an oxidative reaction leading to β -benzisatin.

The action of cuprous chloride in acetic acid appears to be a general method for the conversion of disulphisatides into isoindigotins; in this way *pp'*-dimethyl-, *oo'*-dimethyl-, and *oo'*-dichloro-disulphisatide yield, respectively, *pp'*-dimethylisoindigotin (55%), *oo'*-dimethylisoindigotin (43%), and *oo'*-dichloroisoindigotin (55%), whilst disulphisatide (A., 1924, i, 322) affords isoindigotin (50%); $\beta\beta'$ -dibenzdisulphisatide furnishes an unstable, bluish-black, amorphous substance.

The method of Wahl and Bagard (Bull. Soc. chim., 1909, [iv], 5, 1039) has been applied to the synthesis of β -benzindirubin. β -Benzisatin and phosphorus pentachloride in chlorobenzene give β -benzisatin chloride, which reacts with oxindole in the same medium at 100—132° to furnish β -benzindirubin (II). α -Benzisatin by similar treatment gives an amorphous product. Condensation of α -benzisatin with

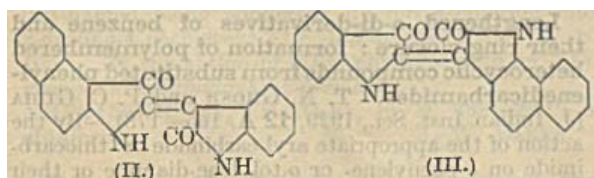
corresponding β -benzindirubin could not be obtained, condensation of β -benzisatin and indoxyllic acid under various conditions yielding only normal indirubin.
C. W. SHOFFEE.

Halogenated pyrroles. VII. Halogenated methenes of cryptopyrrole and their constitution. H. FISCHER, E. BAUMANN, and H. J. RIEDL (Annalen, 1929, 475, 205—241).—The two brominated methene hydrobromides obtained by bromination of cryptopyrrole (A., 1926, 1261) have been further investigated and their constitution has been elucidated. Methene I hydrobromide, m. p. above 350°, is assigned the constitution I. It is formed in good yield only when



the bromination takes place at higher temperatures, and it yields more aetio-porphyrin than methene II hydrobromide. Both facts support the assumption of bromination in the side-chain. When the preparation of the free base is attempted by treatment of the hydrobromide with alcohol and then with chloroform and sodium hydroxide, the product is a base, m. p. 73° [*picrate*, m. p. 145° (decomp.)], which is probably the compound containing an ethoxyl group in the side-chain mixed with a small amount of the hydroxy-compound. The analogous, partly methoxylated base, m. p. 84°, is obtained similarly. Treatment of the base, m. p. 73°, with bromine (1 mol.) in acetic acid yields methene I hydrobromide. Treatment with zinc dust in alcohol gives a zinc compound, $(\text{C}_{18}\text{H}_{23}\text{ON}_2\text{Br})_2\text{Zn}$, m. p. 140°. Bromination of methene I hydrobromide yields a perbromide, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{Br}_4$, m. p. 98°.

The second methene hydrobromide, m. p. 149°, is a perbromide, since it brominates acetone in the cold. It is assigned the constitution II. If this perbromide is warmed with alcohol containing a little sodium hydroxide it yields *methene II hydrobromide*, m. p. 215° (decomp.), which can be brominated in acetic acid at 50° to give the perbromide, or in boiling solution to give *methene I hydrobromide*, whilst treatment with sodium hydroxide solution and chloroform yields *methene II base*, m. p. 103° [*hydrochloride*, m. p. 212°; *hydriodide*, m. p. 213°; *picrate*, m. p. 188° (decomp.)]. Attempted debromination of this base by heating with aniline in toluene yields the *anilino-derivative*, m. p. 116° [*hydrochloride*, m. p. 234°; *hydrobromide*, m. p. 240°; *picrate*, m. p. 209°; complex salts with *copper*, $(\text{C}_{22}\text{H}_{26}\text{N}_2)_2\text{Cu}$, and with *iron*, *cobalt*, and *nickel*], from which the anilino-group cannot be eliminated. With zinc in alcohol the base yields a zinc compound, $(\text{C}_{16}\text{H}_{20}\text{N}_2\text{Br})_2\text{Zn}$, m. p. 180°. The relationship of the two products of bromination of cryptopyrrole is shown by the fact that each yields the *methene II hydriodide* when heated with hydriodic acid in acetic acid. Again, the *methene II base*, by bromination in the cold with 1 or 2 mols. of bromine,



indoxyllic acid in the presence of hydrochloric acid in 50% alcohol gives α -benzindirubin (III). The

yields the hydrobromide or the perbromide, but in boiling acetic acid the methene I hydrobromide is formed, whilst the methene II hydrobromide perbromide, when boiled in acetic acid, yields, by migration of a bromine atom, methene I hydrobromide. Consistently poor yields of *ætioporphyrin* are given by methene II derivatives with the usual reagents, and from methene II hydrobromide perbromide and sulphuric acid the methene II base is produced.

The synthesis of methene II hydrobromide has been carried out by condensing cryptopyrrole with 4-methyl-3-ethylpyrrole-2-aldehyde-5-carboxylic acid. Bromination of the resulting *methenecarboxylic acid*, m. p. 139° (decomp.), is accompanied by loss of carbon dioxide, and methene II hydrobromide perbromide is obtained. An analogous synthesis establishes the constitution of the product of bromination of *hæmopyrrole* (A., 1928, 77). *Opsopyrrolealdehyde* is prepared by a Gattermann reaction from *opso-pyrrole*. It is reduced by hydrazine to *hæmopyrrole*, and condensation of the aldehyde with *hæmopyrrole* yields a *methene*, m. p. 83° (*hydrobromide*, m. p. 188°), which gives on bromination (2-bromo-4-methyl-3-ethylpyrrol)-(2:3-dimethyl-4-ethylpyrrolenyl)methene hydrobromide perbromide, identical with the product from *hæmopyrrole*.

A method of synthesis of the corresponding methanes is described. The interaction of cryptopyrrole and magnesium ethyl bromide yields magnesium 5-cryptopyrrol bromide, which reacts with ethyl 4-methyl-2-bromomethyl-3-ethylpyrrole-5-carboxylate to yield (5-carbethoxy-4-methyl-3-ethyl)-(3':5'-dimethyl-4'-ethyl)-2:2'-dipyrrolmethane, m. p. 142°, which gives *phylopyrrole* when heated with hydriodic acid and phosphonium iodide. The *methenecarboxylic acid*, m. p. 145° (decomp.), obtained by hydrolysis of the ester, yields on bromination, with simultaneous loss of carbon dioxide, the above methene II hydrobromide perbromide. Interaction of the same Grignard compound with ethyl 4-methyl-3- β -dicarbethoxyethyl-2-bromomethylpyrrole-5-carboxylate (A., 1927, 1088) yields (5-carbethoxy-4-methyl-3- β -dicarbethoxyethyl)-(3':5'-dimethyl-4'-ethyl)-2:2'-dipyrrolmethane, m. p. 139°. (5-Carbethoxy-4-methyl-3- β -dicarbethoxyethyl)-(3':5'-dimethyl)-2:2'-dipyrrolmethane, m. p. 105°, and (5-carbethoxy-4-methyl-3-ethyl)-(3':5'-dimethyl)-2:2'-dipyrrolmethane, m. p. 129°, are obtained similarly.

Chlorinated methenes have not been isolated from the reaction between chlorine and cryptopyrrole, but the action of sulphuryl chloride on the cooled ethereal solution yields a *chlorinated methene hydrochloride*, m. p. 203° (decomp. from 170°), the constitution of which is analogous to that of the brominated methene II hydrobromide. Only traces of *ætioporphyrin* are formed with the usual reagents. The hydrochloride is converted into the *hydriodide*, m. p. 179° (decomp.), by the action of potassium iodide in acetic acid. Bromination yields in the cold a *perbromide*, m. p. 156°, and in hot solution a *product*, m. p. above 350°, is obtained which probably contains a 2-bromo-methyl group, since it readily yields *ætioporphyrin*. The action of pyridine or of sodium hydroxide and chloroform on the chlorinated methene hydrochloride

yields the *base*, m. p. 106° [*picrate*, m. p. 183° (decomp.)], which is converted into the same anilino-derivative as that obtained from the brominated methene II base.

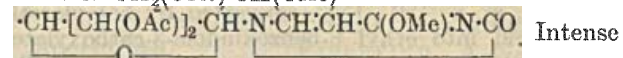
4-Methyl-3-ethylpyrrole-2:5-dialdehyde, m. p. 84°, is obtained in 1% yield by the interaction of sulphuryl chloride and cryptopyrrolealdehyde in ether.

R. K. CALLOW.

[Isomerism of diphenylmethylpyrazoles.] E. OTT (Ber., 1929, 62, [B], 2685; cf. von Auwers and Schaum, this vol., 1082).—The occurrence of isomerism which cannot be satisfactorily explained in certain classes of compounds has been noted previously by the author (A., 1912, i, 828).

H. WREN.

Synthesis of pyrimidine-nucleosides. T. B. JOHNSON and G. E. HILBERT (Science, 1929, 69, 579—580).—By heating the lactim ether, 2:4-dimethoxy-pyrimidine, slightly above the b. p., it is transformed into the lactam ether, whilst treatment with methyl iodide at the ordinary temperature converts it into the lactim lactam ether, 2-keto-6-methoxy-3-methyl-2:3-dihydropyrimidine. The corresponding ethoxy-compound can be formed in a similar manner. Hydrolysis of these two last-named compounds with acid yields 3-methyluracil. Bromotetra-acetylglucose gives with the 2:4-dimethoxypyrimidine at 50° a good yield of colourless needles of the pyrimidine-nucleoside, $C_{19}H_{24}O_{11}N_2$, m. p. 221°, having the formula $CH_2(OAc) \cdot CH(OAc) \cdot$



Intense but not mild, hydrolysis with hydrochloric acid gives rise to reducing substances.

L. S. THEOBALD.

Condensation products of the benzodiazine [quinazoline] series. I. G. FARBENIND. A.-G.—See B., 1929, 935.

Derivatives of 6:7-benzo-1:8-naphthyridine. G. KOLLER and E. STRANG (Monatsh., 1929, 53 and 54, 952—955).—The condensation product, $C_{14}H_{10}O_4N_2$, from methyl 2-aminoquinoline-3-carboxylate and ethyl sodiomalonate (this vol., 76), is methyl 2:4-dihydroxy-6:7-benzo-1:8-naphthyridine-3-carboxylate. This is hydrolysed by potassium hydroxide solution to 2:4-dihydroxy-6:7-benzo-1:8-naphthyridine, m. p. 343° (elimination of carbon dioxide occurs during hydrolysis), converted by phosphoryl chloride at 100° into the 2:4-dichloro-derivative (I), m. p. 195.5—196.5°. Reduction of I with sodium and alcohol gives octahydro-6:7-benzo-1:8-naphthyridine, m. p. 158—159°, whilst treatment with methyl-alcoholic sodium methoxide affords 2:4-dimethoxy-6:7-benzo-1:8-naphthyridine, m. p. 152—153° [*methiodide*, m. p. 158° (decomp.)]. H. BURTON.

Lengthened o-di-derivatives of benzene and their ring closure: formation of polymembered heterocyclic compounds from substituted phenylhenedicarbamides. T. N. GHOSH and P. C. GUHA (J. Indian Inst. Sci., 1929, 12 A, 165—178).—By the action of the appropriate aryl-carbimide or -thiocarbimide on o-phenylene- or o-tolylene-diamine or their monothiocarbamides are obtained: o-phenylene-di-o- (I), m. p. 161°, and -di-p- (II), m. p. 178°, -tolyl-, di-

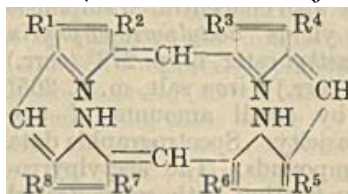
m-xylyl- (III), m. p. 145°, -dimethyl- (IV), m. p. 175°, -*s*-phenylallyl- (V), m. p. 245°, -*s*-phenyl-*o*-tolyl- (VI), m. p. 136°, -*s*-phenyl-*p*-tolyl- (VII), m. p. 165°, -dithiocarbamides, -*s*-diphenyldicarbamide (VIII), m. p. 220°; *o*-tolylenediphenyldithiocarbamide (IX), m. p. 142°; 1-phenylcarbamido-2-phenyl- (X), m. p. 220°, -2-*p*-tolyl- (XI), m. p. 165°, -2-methyl- (XII), m. p. 98°, and -2-allyl- (XIII), m. p. 160°, -thiocarbamidobenzene. By the action of boiling hydrochloric acid (*d* 1.19), I—VII and IX and similar known derivatives are converted into substituted aminoheptathiodiazines of the type $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \cdot \text{CS} \cdot \text{S} \\ \text{N} = \text{C} \cdot \text{NHR} \end{smallmatrix}$ aniline being eliminated in each case, and thus are obtained 4-anilino-, m. p. 290—291° (acetyl derivative, m. p. 160°, converted by the action of iodine into the disulphide, m. p. 210°), 4-*o*-toluidino-, m. p. 300° (acetyl derivative, m. p. 200°), 4-*p*-toluidino-, m. p. 300° (acetyl derivative, m. p. 200°; disulphide, m. p. 190°), 4-*m*-xylydino-, m. p. 295° (acetyl derivative, m. p. 296°; amorphous disulphide, m. p. 172°), 4-methylamino-, m. p. 168° (disulphide, m. p. 194°), 4-allylamino-, m. p. 293° (disulphide, m. p. above 300°), -2-thio keto-1 : 2-dihydrobenz-3 : 1 : 5-thioheptadiazine, and 4-anilino-2-thio keto-1 : 2-dihydrotolu-3 : 1 : 5-heptatriazine, but with *o*-phenylenediallyldithiocarbamide, hydrogen sulphide is eliminated with the formation of 2 : 4-di(allylamino)benz-3 : 1 : 5-thioheptadiazine, m. p. above 300° (diacetyl derivative, m. p. 185°). Boiling hydrochloric acid converts X, XI, XII, and XIII into, respectively, 3-phenyl-, m. p. 185° (disulphide, m. p. 128—130°), and 3-*p*-tolyl-, m. p. 175—176° (disulphide, m. p. 164°), -2-keto-4-thio ketobenz-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 5-heptatriazine, 2-anilino-4-methylaminobenz-3 : 1 : 5-thioheptadiazine, m. p. 195°, and 4-anilino-2-keto-1 : 2-dihydrobenz-3 : 1 : 5-thioheptadiazine, whilst *o*-phenylenedicarbamide gives 2 : 4-diketo-1 : 2 : 3 : 4-tetrahydrobenz-1 : 3 : 5-heptatriazine + 2H₂O, sublimes above 300° (acetyl derivative, m. p. 190°), and VIII is unattacked. *s*-*o*-Amino-phenylphenyl- (XIV) (disulphide, m. p. 230°; acetyl derivative, m. p. 200°), *o*-aminophenyl-*o*-tolyl-, m. p. 160°, and -*p*-tolyl- (XV), m. p. 146—147°, and *o*-aminophenylmethyl-, m. p. 117°, -thiocarbamides all give *o*-phenylenethiocarbamide, m. p. 301—302° (lit. 290°), by boiling with hydrochloric acid, but *s*-*o*-aminophenylallylthiocarbamide, m. p. 115°, is converted into 1-allylaminobenzthiazole, m. p. 180° (acetyl derivative, m. p. 198°). By the action of ferric chloride XIV and XV are converted into 3-anilino-, m. p. 155—156°, and 3-*p*-toluidino-, m. p. 93°, -benz-2 : 1 : 4-thio-diazine, respectively, whilst by condensation of XIV with the appropriate aldehyde are obtained the *o*-nitrobenzylidene, m. p. 215°; *m*-nitrobenzylidene, m. p. 153—154°; *o*-hydroxybenzylidene, m. p. 180°; and benzylidene, m. p. 265—267°, derivatives, the last-named being converted by ferric chloride into 2-anilino-4-phenylbenz-3 : 1 : 5-thioheptadiazine, m. p. 105°. By the action of ethyl chloroformate on XIV phenylthiocarbamidophenylurethane, NHPh·CS·NH·C₆H₄·NH·CO₂Et, m. p. 288—290°, is obtained.

J. W. BAKER.

Triazoles. X. Oxidation products of the three 1-tolyl-3 : 5-dimethyl-1 : 2 : 4-triazoles. F.

HERNLER (Monatsh., 1929, 53 and 54, 668—681).—Oxidation of 1-*o*-tolyl-3 : 5-dimethyl-1 : 2 : 4-triazole (I) with 25% nitric acid at 200° gives 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole-2'-carboxylic acid (II), m. p. 238—240° (hydrochloride, m. p. 243—245°); with 15% nitric acid at 150° or boiling 25% acid, the nitrate, m. p. 146—147° with previous sintering, of I is formed. Oxidation of I with alkaline potassium permanganate at 100° also gives II. Further oxidation of II with an excess of permanganate affords 1-phenyl-1 : 2 : 4-triazole-3(or 5) : 2'-dicarboxylic acid (anhydrous and +H₂O), m. p. 235—240°. Nitric acid oxidation of 1-*m*-tolyl-3 : 5-dimethyl-1 : 2 : 4-triazole (nitrate, m. p. 139—140°) furnishes 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole-3'-carboxylic acid, m. p. 198—199° (hydrochloride, m. p. 253—256° with evolution of gas), whilst permanganate oxidation affords as the primary product 1-phenyl-3(or 5)-methyltriazole-5(or 3) : 3'-dicarboxylic acid, m. p. 242° with previous sintering. Further oxidation of this yields 1-phenyltriazole-3(or 5) : 3'-dicarboxylic acid, m. p. 233—234°. 1-*p*-Tolyl-3 : 5-dimethyl-1 : 2 : 4-triazole (nitrate, m. p. 173—174° with gas evolution) is oxidised (nitric acid) to 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole-4'-carboxylic acid (III) (A., 1927, 1090) (hydrochloride +H₂O, m. p. 296—296.5° after sintering at 295°), whilst initial permanganate oxidation affords 1-phenyl-3(or 5)-methyltriazole-4'-carboxylic acid + H₂O (IV). Further oxidation (permanganate) of III or IV gives 1-phenyltriazole-3(or 5) : 4'-dicarboxylic acid (anhydrous and +H₂O, m. p. 302—303°). H. BURTON.

Porphyry syntheses. XXV. Chlorophyll. VIII. Syntheses of porphinmonopropionic acids VI, III, and I; conversion of pyrroporphyrin into porphinmonopropionic acid III. H. FISCHER, H. K. WEICHMANN, and K. ZEILE (Annalen, 1929, 475, 241—266).—The remaining three of the eight isomeric porphinmonopropionic acids (cf. A., 1928, 651) have now been synthesised. "Porphinmonopropionic acid VI" (1 : 3 : 5 : 8-tetramethyl-4 : 6 : 7-triethylporphin-2-



propionic acid; cf. annexed formula [methyl ester, m. p. 246° (corr.); copper salt, C₃₃H₃₆O₂N₄Cu, and iron salt (haemin), C₃₃H₃₈O₂N₄ClFe] is

obtained by the usual method by condensation of (2-bromo-3-methyl-4-ethylpyrryl)-(2'-bromo-3'-methyl-4'-ethylpyrrol-enyl)methene hydrobromide with (3-methyl-2-bromo-methyl-4-ethylpyrryl)-(4'-methyl-5'-bromomethyl-3'-β-carboxyethylpyrrol-enyl)methene hydrobromide by heating with hydrobromic acid. Modified methods are used for the synthesis of the other two acids on account of their unsymmetrical structure. (2 : 5-Dimethyl-4-ethylpyrryl)-(3'-methyl-4'-β-carboxyethylpyrrol-enyl)methene hydrobromide and (2-bromo-3-methyl-4-ethylpyrryl)-(3'-methyl-5'-bromomethyl-4'-ethylpyrrol-enyl)methene hydrobromide are condensed by fusion with succinic acid, and the porphinmonopropionic acid is separated by means of its insoluble sodium salt from the aetioporphyryrin derived from the second reactant. The "porphinmonopropionic acid

III" (1:3:5:8-tetramethyl-2:4:6-triethylporphin-7-propionic acid) thus obtained yields a methyl ester, m. p. 271° (corr.) [copper salt, m. p. 223°; iron salt (*hæmin*), m. p. 265°; *phyllin*]. A better yield is obtained by another synthesis. (3:5-Dimethyl-4- β -carboxyethylpyrrol)-(3'-methyl-4'-ethylpyrrolenyl)-methene hydrobromide, decomp. slowly at 235–240°, is obtained by condensing opopyrrole with 3:5-dimethyl-4- β -carboxyethylpyrrole-2-aldehyde, and condenses in turn with (3-methyl-2-bromomethyl-4-ethylpyrrol)-(2'-bromo-4'-methyl-3'-ethylpyrrolenyl)-methene hydrobromide (obtained by bromination of *hæmopyrrole*, cf. this vol., 1463), when fused with succinic acid to give the same "porphinmonopropionic acid *III*." (3-Methyl-4-ethyl-2-carboxypyrryl)-(3':5'-dimethyl-4'- β -carboxyethylpyrrolenyl)-methene hydrobromide (unpublished work with H. BERG) condenses with (2-bromo-3-methyl-4-ethylpyrryl)-(4'-methyl-2'-bromomethyl-3'-ethylpyrrolenyl)-methene hydrobromide (obtained by bromination of cryptopyrrole, cf. this vol., 1463) when fused with succinic acid to yield "porphinmonopropionic acid *I*" (1:3:5:7-tetramethyl-4:6:8-triethylporphin-2-propionic acid), which yields the methyl ester, m. p. 237° (corr.) [copper salt, m. p. 226°; iron salt (*hæmin*), m. p. above 270°].

A further step in the orientation of the substituents in the chlorophyll porphyrins has been made by converting chlorophyll pyrroporphyrin, already known to be a tetramethyldiethylporphinmonopropionic acid, into the above porphinmonopropionic acid *III* by the introduction of an ethyl group, and the possible structures for pyrroporphyrin are reduced to three, of which *XV* (Annalen, 1929, 473, 213) is most probable. The derivation of chlorophyll porphyrins from *ætioporphyrin III* is thus established, and *hæmin* and chlorophyll therefore have a similar arrangement of side-chains. The constitution of chlorophyll is discussed.

Pyrro*hæmin* in acetic anhydride is treated with stannic chloride; the reaction is not allowed to go to completion in order to avoid excessive decomposition. Treatment of the product with concentrated sulphuric acid to remove iron yields acetylpyrroporphyrin [copper and iron salts; methyl ester, m. p. 278° (corr.) (copper salt, m. p. 245° (corr.); iron salt, m. p. 265° (corr.))], accompanied by small amounts of two porphyrins of different basicity. Spectrographic data are given for these compounds. The acetylpyrroporphyrin is reduced by heating with concentrated alcoholic potassium hydroxide to the *carbinol*, which is accompanied by a spectroscopically similar porphyrin which is stable to concentrated sulphuric acid or heating in a vacuum. Reduction of the impure *carbinol* with hydriodic acid and phosphonium iodide yields porphinmonopropionic acid *III*, identical with the synthetic product and yielding the same derivatives.

R. K. CALLOW.

Porphyrin syntheses. XXVI. Syntheses of mesoporphyrins I, IV, XIII, and XIV. H. FISCHER and A. KIRRMANN (Annalen, 1929, 475, 266–287).—A detailed account is given of work already briefly summarised (this vol., 1316). An alternative synthesis of mesoporphyrin *I* (copper salt) is carried out by condensation of (4:5-dimethyl-3- β -

carboxyethylpyrryl)-(3'-methyl-4'- β -carboxyethylpyrrolenyl)methene and (4:5-dimethyl-3-ethylpyrryl)-(2'-bromo-5'-methyl-4'-ethylpyrrolenyl)-methene by fusion with succinic acid. The coproporphyrin, m. p. 244° (corr.), obtained as a by-product in the first synthesis has been identified as coproporphyrin *I*. Mesoporphyrin *XIII*, m. p. above 280° (copper and iron salts, both m. p. above 280°), is obtained by condensation of (2-bromo-3-methyl-4- β -carboxyethylpyrryl)-(2'-bromo-3'-methyl-4'- β -carboxyethylpyrrolenyl)-methene hydrobromide and (4-methyl-2-bromomethyl-3-ethylpyrryl)-(4'-methyl-2'-bromomethyl-3'-ethylpyrrolenyl)-methene hydrobromide by fusion with succinic acid and converted into the methyl ester, m. p. 217° [copper salt, m. p. 238°; iron salt (*hæmin*), m. p. 257°]. The absorption spectra of the mesoporphyrins are indistinguishable, as are those of their corresponding derivatives.

Since it has been found that mesoporphyrins *I* and *IX* are readily separable, the identification of isomeric *hæmins*, if they occur, should be possible by conversion into the mesoporphyrins. However, fractionation of mesoporphyrin from ox blood yields only mesoporphyrin *IX*, identified as the methyl ester, and dog-fish blood and blood from a case of porphyria yield the same mesoporphyrin.

R. K. CALLOW.

Natural porphyrins. XXIV. Hæmatoporphyrin. H. FISCHER, A. TREIBS, and G. HUMMEL (Z. physiol. Chem., 1929, 185, 33–73).—An attempt to reduce hæmatoporphyrin hydrochloride with boiling alcoholic potassium hydroxide was unsuccessful. The product was converted into the hydrochloride and then represented the dihydrochloride of hæmatoporphyrin with 1 mol. of water, although the carbon percentage was low. It was shown spectroscopically to contain 10% of protoporphyrin. The potassium salt with methyl-alcoholic hydrogen chloride gave the crystalline dimethyl ester, m. p. 212°, chief absorption bands, 624.8, 575.6, 569.5, 529.3, 495.7. This was converted into tetramethylhæmatoporphyrin, m. p. 120°. The dimethyl ester at 185–195° gave protoporphyrin ester. Tetramethylhæmatoporphyrin ester *C*, m. p. 145°, which lost methyl alcohol only at 185°, showed a higher m. p. after rubbing (185°). Tetraethylhæmatoporphyrin, m. p. 149°, was prepared by esterification of the potassium salt with alcoholic hydrogen chloride (chief absorption bands 495.9, 530.1, 569.5, 576.2, 624.7). When the temperature of the hæmatoporphyrin-alcoholate mixture rose to 180°, reduction occurred, giving the meso-ester, m. p. 194°. The Busch reduction to indicate the hydroxyvinyl radical met with no success. With hydrogen iodide and acetic acid, reduction to mesoporphyrin was effected. Bromination of the hæmatoporphyrin dimethyl ester yielded dibromodeuteroporphyrin. Acetic acid and hydrobromic acid gave hæmatoporphyrin. Hæmatoporphyrin is easily converted into mesoporphyrin by way of a hydrobromic acid additive product, which also points to the equivalence of the side-chains. The oxidation of tetramethylhæmatoporphyrin decided this point. Methoxymethylmaleimide, m. p. 59°, was obtained and hæmatinic acid in yield corresponding with two pyrrole nuclei. Oxidation of meso-

porphyrin likewise gave a yield of more than 1 mol. of methylethylmaleimide. Bromoporphyrin I gave more than 1 mol. of bromocitraconimide. The action of bromine on tetramethylhæmatoporphyrin in chloroform gave dibromodeuteroporphyrin ester. The brominated imide, m. p. 76°, of Küster and Grosse could not be obtained. In place of the dichlorodimethylhæmin of Küster and Schlayer a crystalline chlorohæmin of a *monochlorotetramethylhæmatoporphyrin* was obtained. Oxidation gave a small amount of chlorocitraconimide. It is doubtful if the imide, m. p. 76°, has the constitution assigned to it. Bromination of mesoporphyrin ester, its copper salt, and of ætiohæmin gave well-crystallised perbromides which were debrominated by acetone.

Oxidation of 2-methyl-4-ethylpyrrole gave ethylmaleimide, m. p. 80°, bromination gave the crystalline (3 : 5-dibromo-4-ethylpyrrol)- (5'-methyl-3'-ethyl-4'-bromopyrrolenyl)methene hydrobromide. By the action of sodium hydroxide, the free methene, m. p. 133°, was obtained; this on fusion with succinic acid gave *tetrabromotetraethylporphyrin* (?). Oxidation of the iron salt of tetramethylhæmatoporphyrin gave the *methoxylated imide*, m. p. 58°. J. H. BIRKINSHAW.

Molecular compounds of porphyrins. A. TREIBS (Annalen, 1929, 476, 1—60).—A comprehensive investigation of the salts and molecular additive compounds formed by a large number of porphyrins and their esters with styphnic, picric, picrolonic, and flavianic acids, and of their spectra both in powder form and in solution, is described. For details in individual cases the original must be consulted, the main general conclusions being briefly summarised below. Coloured compounds of 1 mol. of the porphyrin with 1—5 mols. of the acid are formed, exhibiting all variations of solubility, the m. p. of which are reproducible only with very rapid heating and are of no value for mixed m.-p. determinations. Like the spectra of the porphyrins themselves, the spectra of these compounds are not trustworthy as a guide to constitution, since they fall into three definite types, individual compounds within each type having closely similar spectra. Thus in ethereal solution the spectra of ætio-, meso-, deuto-, copro-, and pyrroporphyrins exhibit four chief bands of approximately equal intensity (neutral type). In hydrochloric acid an entirely different type of spectrum (type II) is obtained consisting of three bands of very unequal intensity in the green, two additional weak bands appearing with increasing concentration of hydrochloric acid, which also causes a general shift towards the red. With the molecular compounds, however, increase in the concentration of the acid component causes a shift towards the violet, and in these compounds an intermediate spectrum type (type I) due to the presence of mono-acid salts is obtained. A corresponding type [type (I)] is obtained with powder spectra (such spectra being indicated by the bracketed type number), these showing a shift of 6—10 μ towards the red compared with the corresponding solution spectra. Each spectrum type corresponds with a definite type of compound. Thus most compounds in which the ratio porphyrin : nitrophenolic acid is 1 : 1 give spectra of type (I) and are true mono-acid salts.

In this group, however, dibromodeuteroporphyrin picrate and ætioporphyrin 2 : 6-dinitrobenzoate give the neutral type spectra and are therefore true molecular additive compounds, similar results being obtained with the picryl chloride additive compounds of ætioporphyrin-I, m. p. 251°, and mesoporphyrin ester, m. p. 158°, and with the bromo-2 : 4-dinitrobenzene additive compound (1 : 2), m. p. 188°, of ætioporphyrin-I. Most compounds with the porphyrin : acid ratio 1 : 2 give spectra of type (II) and are true di-acid salts, but the picrolonates give type (I) spectra and are, therefore, additive compounds of the mono-acid salts. The spectra of these change to type II, however, in the presence of a large excess of picrolonic acid. Compounds with the ratio 1 : 3 give type II spectra and are additive compounds of the di-acid salts. Such compounds, with the exception of the styphnate of ætioporphyrin-II, are found only in the flavianic acid series. The 2 : 6-dinitrobenzoates of ætioporphyrin-I, m. p. 203°, and mesoporphyrin ester, m. p. 153°, are the only examples, respectively, of compounds with the ratio 1 : 4 and 1 : 5, and are additive compounds of the di-acid salts. Dissociation of these molecular compounds occurs in solution, its extent depending on the solvent and increasing with rise of temperature, so that different types of spectra may be obtained by varying the conditions in these respects. Thus by addition of equimolecular quantities of ætioporphyrin-I in chloroform and picric acid in methyl alcohol, the solution, after concentration, exhibits a type I spectrum in which the neutral type can still be observed. The latter disappears on addition of 10—15% excess of picric acid, but for this solution of homogeneous spectrum type the 1 : 2 picrate showing spectrum type (II) is obtained, whilst the mother-liquor still has the type I spectrum, proving the existence of an equilibrium in solution. Explanations of the detailed results are discussed, and it is concluded that the porphyrin molecule exhibits residual affinity and hence that the iron in hæmin and the magnesium in chlorophyll are not bound merely by substitution of 2 atoms of hydrogen, but by means of the residual affinity of the complex. In addition to spectrographic data the following m. p. data are recorded (all corr. and with decomp.), each set of values being those of the styphnate, picrate, picrolonate, and flavianate, respectively : ætioporphyrin-I, 223°, 232°, 262°, indef. 230°; ætioporphyrin-II, 217°, 223°, 228°, 250°; mesoporphyrin, 232°, 178°, 204°, indef. 215°; mesoporphyrin ester, 185°, 145°, 195°, 235°; protoporphyrin, 234°, indef. 180° (1 : 1) and 157° (1 : 2), indef. 160°, 211° (1 : 2) and 215° (1 : 3); protoporphyrin ester, 135°, 150°, 143° (1 : 1) and 115° (1 : 2), decomp. 260° (1 : 2) and decomp. 230° (1 : 3); deuteroporphyrin, 183°, indef. 240°, 118°, 275°; deuteroporphyrin ester, 127° (1 : 1) and 188° (1 : 2), 148°, 212° (1 : 1) and 141° (1 : 2), 204°; hæmatoporphyrin, —, —, decomp. 180°, decomp. 200°; tetramethylhæmatoporphyrin, 171°, 155°, 132° and 110° (two forms both 1 : 1), 183°; coproporphyrin-I, 295°, 251°, 256°, indef. 310°; coproporphyrin-I ester, 143° and 154° (both 1 : 2), 146°, 245°, 225°; uroporphyrin ester, —, —, —, 176°; iscoporphyrin ester, 232°, 240°, —, 215°; dibromodeuteroporphyrin ester, —, 177°, —, indef. 165°; phylloporphyrin, 163°, 156°.

212°, 235°; phylloporphyrin ester, 210°, indef. 135°, —, indef. 230°; pyrroporphyrin, 206°, 152°, 154°, indef. 220°; pyrroporphyrin ester, 177°, 169°, 175°, indef. 262°; rhodoporphyrin, 257°, —, —, meso-rhodin ester, 169°, 211°, 135°, decomp. 300°. *Ætio*-porphyrin-I forms additive compounds with chloranilic acid, m. p. 251°, 2:4:6-trinitro-, m. p. 304°, and 2:6-dinitro-, m. p. indef. 175° (1:1) and 203° (1:4), -benzoic acids, and bromo-2:4-dinitrobenzene, m. p. 188°.

J. W. BAKER.

Phylloerythrin. L. MARCHLEWSKI (Z. physiol. Chem., 1929, 185, 8).—Phylloerythrin forms a stable additive product with chloroform, but the latter can be eliminated by dissolving the complex in warm pyridine and pouring into a large volume of alcohol or acetic acid.

J. H. BIRKINSHAW.

Fulminic acids. VIII. Constitution of polymerised fulminic acids. Erythrocyanic acid and β -isocyanic acid. H. WIELAND, W. FRANK, and Z. KITASATO (Annalen, 1929, 475, 42–54).—The reaction between erythrocyanic acid and aniline incompletely studied by Will (Diss., Munchen, 1923) has been fully investigated. Erythrocyanic acid and aniline (2 mols.) react in warm ethyl acetate solution with the formation of 1-phenyl-4-triazolyl-isonitrosoacetanilide (I),



and hydroxylamine. The former slowly dissolves in boiling methyl-alcoholic potassium hydroxide and the solution on dilution yields the *potassium* salt, m. p. 212–213° (decomp.), from which the anilide is regenerated by acids. It is unaffected after boiling for 2 hrs. with concentrated hydrochloric acid, dissolves in concentrated sulphuric acid, and is precipitated unchanged on the addition of water, is unaffected by bromine or by chromic acid in acetic acid and also by nitrous acid. The *acetyl* derivative of I has m. p. 171–172°, and is converted into I by boiling with dilute alkali. Thionyl chloride and I give 4-cyano-1-phenyl-1:2:3-triazole, m. p. 121–122°, converted by prolonged hydrolysis with *N*-alcoholic potassium hydroxide into an insoluble *compound*, m. p. 232°, and 1-phenyl-1:2:3-triazole-4-carboxylic acid, m. p. 150°. The last-named affords 1-phenyltriazole, m. p. 55–56°, when heated above the m. p. for several minutes. The mechanism of the reaction between erythrocyanic acid and aniline and the subsequent transformations is given (cf. A., 1925, i, 1048). Erythrocyanic acid and phenylhydrazine react in alcohol to give a *compound*, (1 mol. acid, 3 mols. phenylhydrazine, loss of 1 mol. NH_3), m. p. 217–218° (decomp.), which reduces ammoniacal silver nitrate containing a little sodium hydroxide, is dehydrated by bromine in glacial acetic acid to an azo-compound, and gradually dissolves in boiling concentrated hydrochloric acid to a solution from which a *compound*, m. p. 261–262°, is precipitated by water.

*iso*Cyanilic acid (Steinkopf, A., 1910, i, 305) and benzoyl chloride (3 mols.) in pyridine yield a *dibenzoyl* derivative, m. p. 155°, whilst boiling with aniline hydrochloride in aqueous solution affords an anil-oxime, m. p. 121–122°, identical with the compound

obtained from the α -acid (cf. A., 1925, i, 1049). The open-chain structure originally assigned to this anil-oxime is withdrawn and the cyclic structure

$\text{NPh}\cdot\text{CH}\cdot\text{C}\cdot\text{N}\cdot\text{O}$ substituted. When β -isocyanic acid is warmed with thionyl chloride for a short time, *cyanofuroxanaldoxime*, m. p. 90–91°, is formed (also obtained by boiling the acid with water), which when treated with 1 equivalent of 0.1*N*-sodium hydroxide, followed by acidification, is converted into anhydro-*isocyanic* acid, m. p. 185–186° (lit. 180°), identical with the substance obtained from *isocyanic* acid and phosphorus pentachloride. With dilute hydrochloric acid alone no change takes place, thus indicating that the original oxime undergoes a preliminary Beckmann transformation in presence of alkali. β -*iso*-Cyanilic acid reacts slowly with ammonia to give *pericyanic* acid, m. p. 187°, and *metacyanic* acid, m. p. 70°. Dicyanofuroxan, m. p. 40–41°, is produced when β -isocyanic acid is vigorously boiled with thionyl chloride.

A. I. VOGEL.

Fulminic acids. IX. Constitution of polymerised fulminic acids. *peri*Cyanilic, *epi*-cyanilic, and *metacyanic* acids. H. WIELAND and Z. KITASATO [with F. FROMM] (Annalen, 1929, 475, 54–78).—*peri*Cyanilic acid, m. p. 187° (decomp.) (previously called *hydratoisocyanic* acid), prepared by the action of mild alkalis, e.g., ammonia, on *isocyanic* acid, is best purified by decomposing the characteristic sparingly soluble *ammonium* salt with dilute hydrochloric acid. It forms a sparingly soluble *pyridine* salt, m. p. 179° (decomp.), a *trimethyl* ester, m. p. 128°, when treated in methyl-alcoholic solution with diazomethane in ether at 0°, a *tribenzoyl* derivative, m. p. 189° (decomp.) (4 mols. of benzoyl chloride in pyridine solution), and a *tri-acetyl* derivative, m. p. 162° (decomp.), when boiled for a short time with acetic anhydride. When *peri*-cyanilic acid in chloroform solution is warmed with thionyl chloride at 70° for 3 hrs., *anhydroepicyanic* acid, m. p. 102°, is formed. This acid is unaffected by cold concentrated sulphuric acid or by hot concentrated hydrochloric acid at 100°, is decomposed by alkali giving ammonia and carbon dioxide, yields a *dibenzoyl* derivative, m. p. 158° (benzoyl chloride in pyridine), and is decomposed by boiling *N*-baryta solution into ammonia and 3-hydroxyfurazan-4-carboxylamide, m. p. 202–204°, identical with the previously known *isofulminuric* acid (*benzoyl* derivative, m. p. 212°), and separated by means of the sparingly soluble barium salt; prolonged boiling with baryta yields hydroxyfurazancarboxylic acid, m. p. 175°. 3-Hydroxy-4-furazanisonitrosoacetic acid, m. p. 165° (decomp.), was isolated from the filtrate of the barium salt separation.

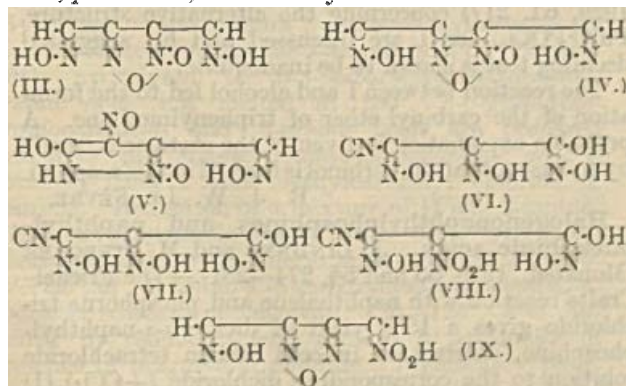
α -*epi*Cyanilic acid, m. p. 170° (decomp.), is formed by heating *pericyanic* acid with aqueous aniline hydrochloride at 100° or by dissolving *pericyanic* acid in concentrated sulphuric acid at 10° and later pouring the solution on to ice. The acid yields a *tetrabenzoyl* derivative, m. p. 179° (decomp.), which gives no coloration with ferric chloride; when boiled with thionyl chloride *anhydroepicyanic* acid, m. p. 102°, is produced. Cyanoglyoximecarboxylic acid

(I), m. p. 162° (decomp.), is obtained from the α -acid by heating with concentrated hydrochloric acid; it gives a brownish-red colour with ferric chloride, whilst the α -acid gives a carmine-red colour. I is also produced from the β -acid (Thiele, Diss., München, 1921) and undergoes decarboxylation when heated with 2*N*-methyl-alcoholic potassium hydroxide, giving cyanoglyoxime, m. p. 175° (also produced directly from the β -acid by boiling with 2*N*-methyl-alcoholic potassium hydroxide), identical with the compound obtained from *amphichloroglyoxime* and sodium cyanide in alcohol.

*meta*Cyanilic acid, m. p. 70°, is best prepared by the addition of excess of concentrated aqueous ammonia to a solution of *pericyanilic acid* in pyridine, keeping, removing the precipitated ammonium *pericyanilate*, acidifying with hydrochloric acid, and extracting with ether; yield, 50%. This acid is characterised by its great stability to alkalis. With benzoyl chloride and pyridine at 0°, *metacyanilic acid* yields *dibenzoylhydroxamyl chloride*, m. p. 168°. Gentle warming with thionyl chloride in ether gives a 50% yield of *aci-nitromethylfurazancarboxylamide*, m. p. 105°, whilst vigorous boiling with thionyl chloride furnishes *aci-nitromethylcyanfurazan* (or *anhydrometacyanilic acid*) (II), b. p. 98°/2 mm. (*benzoyl derivative*, m. p. 157°). When II is boiled with 2 mols. of *N*-baryta, 4-*aci-nitromethylfurazan-3-carboxylic acid*, m. p. 100° (decomp.), is formed (this compound decomposes on keeping); benzoylation at 0° affords *benzoylfurazanhydroxamyl chloride*, m. p. 211–212°, whilst benzoylation at 20° gives a compound, $C_{17}H_{16}O_4N_3Cl$, m. p. 221°, identical with the substance obtained by benzoylation of cyanometazonic acid. *meta*Cyanilic acid and bromine water give *tribromometacyanilic acid*, m. p. 122°; the bromine is immediately eliminated by alcoholic potassium hydroxide at 0°.

The various reactions described in this and the previous paper are interpreted by the following formulæ for the acids:

β -*iso*- III, α -*iso*- IV, erythro- V, α -*epi*- VI, β -*epi*- VII, *peri*- VIII, and *meta*-cyanilic acid IX.



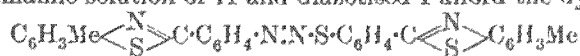
A. J. VOGEL

Prodigiosin, the red dye of *B. prodigiosus*. I. F. WREDE and O. HETTCH (Ber., 1929, 62, [B], 2678–2685).—The culture of the bacillus is effected at about 25° on agar in presence of peptone, Maggi meat extract, dextrose, and magnesium sulphate. The red mass is treated with sodium hydroxide and extracted

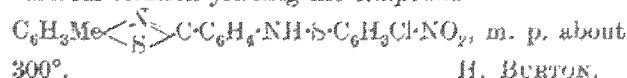
with light petroleum. The dye is precipitated from the extract as the *hydrochloride*. *Prodigiosin* is an amorphous compound which softens at 70–80°. It appears to have the composition $C_{30}H_{25}ON_3$. The mol. wt. in freezing acetic acid or of the salicylate in bromoform corresponds with the simple formula, whereas double this value is observed in freezing benzene. In boiling alcohol it gives colloidal solutions. Its spectroscopic behaviour shows that it does not belong to the rosaniline group. It is not readily reduced. It absorbs about 13 atoms of oxygen per mol. from permanganate in acetone solution, whereby oxalic acid is formed. It is readily oxidised by chromic acid or hydrogen peroxide. An acyl derivative could not be prepared. It appears to contain one methoxyl or ethoxyl group, but not a methylimino-radical. A primary amino-group is not present. The following salts are described: *perchlorate*, m. p. 228° after softening at 226°; *picrate*, m. p. 176° after softening at 173°; *salicylate*, m. p. 178° after softening at 176°; *benzoate*, m. p. 170° after softening at 168°.

H. WREN.

Thiazole derivatives. E. RIESZ and R. HÜBSCH (Monatsh., 1929, 53 and 54, 111–118).—Treatment of diazotised dehydrothiotoluidine (1-*p*-aminophenyl-5-methylbenzthiazole) (I) with an alkaline xanthate solution and subsequent hydrolysis of the intermediate product with alcoholic potassium hydroxide affords 1-*p*-thiolphenyl-5-methylbenzthiazole (II) [*acetyl derivative*, m. p. 198°; *benzoyl derivative*, m. p. 253°; *S*-methyl derivative, m. p. 186°; corresponding *thioglycollic acid* (III), m. p. 233°]. Oxidation of II to the corresponding disulphide (IV) occurs readily in air. Chlorination of a chloroform suspension of II or IV gives 1-phenyl-5-methylbenzthiazole-4'-sulphur chloride, m. p. 162°, which with aniline yields the corresponding *S*-anilino-derivative, m. p. 278°. An alkaline solution of II and diazotised I afford the dye



(yellow on cotton). When III is treated with chlorosulphonic acid at -10° ring closure occurs and 3-*keto*-5-(5'-methyl-1-benzthiazolyl)-2:3-dihydrothionaphthen (V) is formed; at 90° ring closure and oxidation take place and the *thioindigotin* derivative is isolated (an alkaline vat dyes cotton reddish-violet). Treatment of an alkaline solution of V with alcoholic *p*-nitrosodimethylaniline gives the 2-*p*-dimethylaminoaniline, m. p. above 300°, of V. Thus dyes tanned cotton with a red shade. The *benzylidene* and *p*-dimethylaminobenzylidene (dyes tanned cotton orange) derivatives of I have m. p. 158° and 218°, respectively. 4-Chloro-2-nitrophenylsulphur chloride and I react in ethereal solution yielding the compound



H. BURTON.

Sinomenine and disinomenine. XIII. Reduction of bromosinomenine. K. GOTO and T. NAKAMURA (Bull. Chem. Soc. Japan, 1929, 4, 195–197).—Reduction of bromosinomenine with palladised charcoal and 1 mol. hydrogen yields *bromodihydro-sinomenine*, m. p. 237° (decomp.). $[z]_D^{25}$ in chloroform, +102.4° [*hydrobromide*, m. p. 229–232° (decomp.)];

methiodide, m. p. 225° (decomp *semicarbazone*, m. p. 250°), identical with the compound obtained in 80% yield by the bromination of hydrosinomenine in glacial acetic acid solution. With 2 mols. of hydrogen a mixture of bromo- and hydro-sinomenine is formed.

A. I. VOGEL.

Strychnos alkaloids. LIII. Oxidation products of the reduced Hanssen acid. H. LEUCHS and F. KROHNKE (Ber., 1929, 62, [B], 2598—2603; cf. this vol., 1320).—Oxidation of the reduced Hanssen acid with potassium permanganate at 0° leads to the consumption of about six equivalents of oxygen and production in 30% yield of an acid, $C_{19}H_{24}O_9N_2 \cdot H_2O$, which does not yield stable salts with mineral acids. The presence of a ketonic group is not established with certainty, although phenylhydrazine gives an amorphous product, $C_{19}H_{24}O_7N_2 \cdot (N \cdot NHPh)_2$.

The reduced Hanssen acid, $C_{19}H_{24}O_8N_2$, is converted by oxidation with bromine into a compound, $C_{19}H_{25}O_9N_2$, which gives a *semicarbazone hydrobromide*, $C_{20}H_{27}O_8N_3 \cdot HBr$, a *phenylhydrazone*, $C_{25}H_{30}O_7N_4$, and *oxime hydrochloride*, $C_{19}H_{25}O_8N_3 \cdot HCl$, decomp. 240° without melting below 300°, derived from the anhydride, $C_{19}H_{21}O_8N_2$. The *dimethyl ester*, $C_{21}H_{23}O_8N_2$, m. p. 147—148° [hydrochloride, m. p. about 265° (decomp.)], of the anhydride is described. Reduction of the acid, $C_{19}H_{26}O_9N_2$, with water and sodium amalgam affords the compound $C_{19}H_{26}O_8N_2$, isolated as the *hydrobromide*. Oxidation of the acid, $C_{19}H_{26}O_9N_2$, by permanganate yields an acid, $C_{19}H_{24}O_9N_2$ [*dimethyl ester hydrochloride*, m. p. 255° (decomp.) after softening]. H. WREN.

Halogenotolylphosphines. J. LINDNER [with O. BRUGGER, A. JENKNER, and L. TSCHERNIGG] (Monatsh., 1929, 53 and 54, 263—273).—Halogenophosphines have been prepared for possible use in the author's method of volumetric determination of carbon and hydrogen (A., 1922, ii, 657; 1925, ii, 901). A large proportion of the paper is a repetition of Michaelis and Paneck's work (A., 1882, 958). Dichloro-*p*-tolylphosphine dichloride, m. p. 69—91° (cf. Michaelis and Paneck, *loc. cit.*), when heated at 98° in a current of dry air evolves hydrogen chloride; chlorination of the methyl group occurs. Dichloro-*p*-tolylphosphine dibromide has m. p. 128—130° (sealed tube) with elimination of bromine. Reduction of this dibromide with sulphur dioxide gives the substance $Me \cdot C_6H_4 \cdot POClBr(?)$, m. p. 5—8°. Dibromotolylphosphine dibromide, m. p. 160—161° with elimination of bromine, also eliminates hydrogen bromide when kept at 160°. During the Friedel-Crafts preparation of dibromotolylphosphine a small amount of the *o*-derivative is probably formed in addition to the *p*-isomeride. H. BURTON.

Formation of triphenylmethylphosphinic acid from triphenylmethoxyphosphorus dichloride. II. Mechanism of the reaction. H. H. HATT (J.C.S., 1929, 2412—2422).—The alcoholysis of triphenylmethoxyphosphorus dichloride (I) by alcoholic sodium ethoxide solution led to the formation of triphenylmethylphosphinic acid, rearrangement taking place. This reaction has been studied in detail by observing the rate of formation of sodium chloride and also by examination of the phosphorus-containing

products. With 2.5*N*-alcoholic sodium ethoxide removal of chlorine atoms proceeded in definite stages, thus leading to the isolation of intermediates. The first halogen was removed rapidly, the velocity being governed chiefly by the rate of dissolution of the phosphorus dichloride in the alcohol; the second halogen was removed more slowly. The final product was *ethyl hydrogen triphenylmethylphosphinate*, m. p. 259° (silver salt).

The course of the reaction is considered to be $Ph_3C \cdot O \cdot PCl_2$ (I) \longrightarrow $Ph_3C \cdot O \cdot PCl(OEt)$ (II) \longrightarrow $Ph_3C \cdot POCl(ONa)$ (III) \longrightarrow $Ph_3C \cdot PO(OEt) \cdot ONa$, and is supported by the isolation by acidification with alcoholic hydrogen chloride at the appropriate stage of *triphenylmethylchlorophosphinic acid* (III), m. p. 233—234° (*aniline salt* + EtOH, m. p. 182—182.5° or 151—156° on rapid heating; *quinoline salt*, m. p. 181—182.5°), and, when 0.2—0.5*N*-sodium ethoxide was employed, the *chloro-ester*, II, m. p. 135—137°, in 85% yield. Heating with 2*N*-sodium ethoxide solution or hydriodic-acetic acid mixture transformed II into III.

In concentrated solutions an alternative course existed: (I) \longrightarrow $Ph_3C \cdot O \cdot PCl(OEt)$ \longrightarrow $Ph_3C \cdot PO(OEt)_2$ \longrightarrow $Ph_3C \cdot PO(OEt) \cdot ONa$, indicated by the isolation of diethyl triphenylmethylphosphinate, m. p. 120—121° (also obtained by shaking together silver monoethyl triphenylmethylphosphinate, ethyl iodide, and dry benzene), in 20% yield when 4*N*-solutions of sodium ethoxide were used. This ester underwent sulphonation with concentrated sulphuric acid, but hot aqueous sulphuric acid effected hydrolysis first into the monoethyl ester, then into the phosphinic acid itself. Triphenylmethylphosphinic acid and phosphorus pentachloride at 70° gave triphenylchloromethane, m. p. 106—109°.

The varying stabilities towards hydrolysing agents of the compounds isolated are noted and tentative explanations given. No decision is reached regarding the stage at which during alcoholysis migration of triphenylmethyl from oxygen to phosphorus occurs; the structure of II is therefore left open. The indefinite conclusions of Arbusov (J. Russ Phys. Chem. Soc., 1929, 61, 217) concerning the alternative structure, $Ph_3C \cdot POCl_2$, for I are discussed and his suggested deciding test is shown to be inadequate.

The reaction between I and alcohol led to the formation of the carbonyl ether of triphenylmethane. A probable explanation is given of the statement, made by Arbusov, that the carbinol is formed in this reaction.

R. J. W. LE FÈVRE.

Halogenonaphthylphosphines and naphthylphosphinic acids. J. LINDNER and M. STRECKER (Monatsh., 1929, 53 and 54, 274—281).—The Friedel-Crafts reaction with naphthalene and phosphorus trichloride gives a 15% yield of dichloro- α -naphthylphosphine, chlorinated in cold carbon tetrachloride solution to the corresponding dichloride (+CCl₄) (I) (the corresponding dibromide has m. p. about 114—116°). Hydrolysis of I with water gives α -naphthylphosphinic acid, m. p. 189°. The Friedel-Crafts reaction is not a suitable method for preparing dibromonaphthylphosphine. Parts of the paper have been reviewed previously (A., 1922, ii, 657; 1925, ii, 901). H. BURTON.

Nitration of halogenophenylarsinic acids. H. J. BARBER (J.C.S., 1929, 2333—2337).—2-Bromophenylarsinic acid [the corresponding *di(carbamylmethyl) o-bromophenylthioarsinite* has m. p. 137—138°], prepared from *o*-bromoaniline by Bart's reaction, gave on nitration 2-bromo-5-nitrophenylarsinic acid (anhydrous and monohydrated) (corresponding *thiolacetamide*, m. p. 171—172°) (also obtained from 2-bromo-5-nitroaniline by diazotisation), alkaline hydrolysis of which gave 5-nitro-2-hydroxyphenylarsinic acid (*thiolacetamide* derivative, m. p. 194—195°). Only small yields of 2-iodophenylarsinic acid monohydrate were obtained from *o*-iodoaniline owing to interaction between the arsenic acid and excess of sodium arsenite in the presence of copper arsenite with production of *o*-phenylenediarsinic acid (also obtained by boiling 2-iodophenylarsinic acid with aqueous sodium arsenite and copper arsenite). With copper powder, sodium 2-iodophenylphenylarsinate in boiling aqueous solution gave a mixture of phenylarsinic acid, 2-hydroxyphenylarsinic acid, and diphenyl-2 : 2'-diarsinic acid (?).

2-Iodophenylarsinic acid on nitration as for the bromo-acid above produced 2-iodo-5-nitrophenylarsinic acid (*thiolacetamide*, m. p. 158—160°), hydrolysis of which afforded 5-nitro-2-hydroxyphenylarsinic acid.

Application of Bart's reaction to 3-chloro-, 3-bromo-, and 3-iodo-anilines led solely to 3-chloro-, 3-bromo- (*thiolacetamide*, m. p. 131—132°), and 3-iodo-phenylarsinic acids, respectively. These on nitration gave 3-chloro- (*thiolacetamide*, m. p. 172—173°), 3-bromo-, and 3-iodo-6-nitrophenylarsinic acids, identified by a new method of dearsinification by boiling with aqueous alkali (an arsenic acid grouping in the *o*-position to a nitro-group being labile).

4-Bromo- and 4-iodo-3-nitrophenylarsinic acids are also described.

R. J. W. LE FÈVRE.

β -Anilinopropionamide-4-arsinic acid and related compounds. C. S. HAMILTON and C. L. SIMPSON (J. Amer. Chem. Soc., 1929, 51, 3158—3161).— β -Iodo- or β -bromo-propionamide, m. p. 110—111° (from β -bromopropionyl chloride, b. p. 65—70°/25—30 mm.), and sodium *p*-aminophenylarsinate (I) give β -anilinopropionamide-4-arsinic acid (II) (sodium salt), hydrolysed to *p*- β -carboxyethylaminophenylarsinic acid, not melted at 250°. β -o-Toluidinopropionamide-4- and -5-arsinic acids are prepared similarly. *p*-N-Methylcarbamidophenylarsinic acid is obtained from I and methylcarbamyl chloride in benzene. Reduction of a mixture of II and 3-amino-4-hydroxyphenylarsinic acid with 50% hypophosphorous acid in hydrochloric acid gives the *dihydrochloride* of 3-amino-4'-3-carboxylamidoethylamino-4-hydroxyarsenobenzene, decomp. 120—125°, also obtained by reduction with sodium hyposulphite in presence of magnesium chloride. Preliminary pharmacological tests with II indicate that it may be of use in trypanosomal infections.

H. BURTON.

Organic compounds of arsenic. XV. Existence of the arsenazo-linking and phosphoarsenobenzene. W. STEINKOFF and H. DÜDEK (Ber., 1929, 62, [B], 2494—2497; cf. A., 1928, 1230).—If nitrosobenzene and phenylarsine are mixed in alcohol

and ether in an atmosphere of carbon dioxide, the green solution immediately becomes pure yellow and, after some time, arsenobenzene is deposited; the filtrate yields phenylarsine oxide and the residual oil yields aniline and azobenzene when treated with steam. Reaction is presumed to occur as follows: $2\text{PhAsH}_2 + 2\text{Ph}\cdot\text{NO} = 2\text{AsPh}\cdot\text{NPh} + \text{H}_2\text{O}$; $2\text{AsPh}\cdot\text{NPh} = \text{AsPh}\cdot\text{AsPh} + \text{NPh}\cdot\text{NPh}$ and $\text{AsPh}\cdot\text{NPh} + \text{H}_2\text{O} = \text{PhAsO} + \text{PhNH}_2$ or $\text{PhAsH}_2 + \text{Ph}\cdot\text{NO} = \text{PhAsO} + \text{PhNH}_2$.

Phenylarsine and phosphorus phenyl chloride afford phosphoarsenobenzene, $\text{PPh}\cdot\text{AsPh}$, m. p. 181°, which is disproportioned when crystallised from xylene into arsenobenzene and phosphobenzene.

Contrary to previous observations, diphenylarsine and arsenic phenyl dichloride in ether afford a mixture of phenylacodyl and arsenic diphenyl chloride. In light petroleum only traces of phenylacodyl are observed, the main products being arsenobenzene and arsenic diphenyl chloride, presumably arising by decomposition of primarily formed chlorotriphenyldiarsine.

H. WREN.

Arsenical azo-derivatives. S. BERLINGOZZI (Annali Chim. Appl., 1929, 19, 397—406).—By coupling with diazophenylarsinic acid (cf. A., 1928, 1146), the following compounds are obtained: from *o*-hydroxybenzyl alcohol 1-hydroxy-2-hydroxymethylbenzene-4-azo-*p*-phenylarsinic acid, $\text{O}\cdot\text{As}(\text{OH})_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, not melting below 250°; with salicylaldehyde, 1-hydroxy-2-aldehydobenzene-4-azo-*p*-phenylarsinic acid; with salicylic acid, 1-hydroxy-2-carboxybenzene-4-azo-*p*-phenylarsinic acid; with guaiacol, 1-hydroxy-2-methoxybenzene-4-azo-*p*-phenylarsinic acid, m. p. 215° (decomp.); with 1-phenyl-3-methyl-5-pyrazolone, 1-phenyl-3-methyl-5-hydroxypyrazolebenzene-4-azo-*p*-phenylarsinic acid, not melted at 250°; with benzidine, the hydrochloride of the compound

$\text{O}\cdot\text{As}(\text{OH})_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, not melting at 250°, which, on diazotisation and coupling with phenol, gives the compound $\text{C}_{24}\text{H}_{20}\text{O}_4\text{N}_4\text{As}$, not melted at 250°; with *m*-aminophenol, 1-amino-3-hydroxybenzene-4-azo-*p*-phenylarsinic acid. The last-named gives the compound $\text{O}\cdot\text{As}(\text{OH})_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})(\text{NH}_2)\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, unchanged below 250°, when coupled with diazophenylarsinic acid and the compound $\text{O}\cdot\text{As}(\text{OH})_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_2(\text{OH})(\text{NH}_2)\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_7$, unchanged at 250°, when coupled with α -diazonaphthalene.

T. H. POPE.

Pyridine and quinoline derivatives. V. Derivatives of 2-hydroxypyridine-5-arsinic acid. A. BINZ, C. RATH, and E. ÜRSCHAT (Annalen, 1929, 475, 136—147).—Nitration of 2-hydroxypyridine-5-arsinic acid (Binz and Rath, A., 1927, 890) with mixed acids at water-bath temperature gives 3-nitro-2-hydroxypyridine-5-arsinic acid (I), decomp. 250°, converted by alkaline hypiodite into 5-iodo-3-nitro-2-hydroxypyridine, m. p. 246° (decomp.), which is reduced by stannous chloride and hydrochloric acid to the hydrochloride, m. p. 218° (darkens at 196°), of 5-iodo-3-amino-2-hydroxypyridine. This is converted by the diazo-reaction into 5-iodo-2-hydroxypyridine-3-arsinic acid, m. p. 270—272° (Scheller, B., 1928,

140). Reduction of I with hyposulphite converts it into 3-amino-2-hydroxypyridine-5-arsinic acid, m. p. 228—229° (decomp.) (N-acetyl and N-acetamido-derivatives), isolated as its hydrochloride and converted by carbonyl chloride in toluene solution into amorphous pyridine-2 : 3-oxazolone-5-arsinic acid, and reduced by sulphur dioxide and potassium iodide to 3-amino-2-hydroxy-5-pyridylarsin oxide. Reduction of I with concentrated hydrochloric acid and 50% hypophosphorous acid gives 5:5'-diamino-6:6'-diketo-1:6:1':6'-tetrahydro-3:3'-arsenopyridine, which exhibits no basic character, but is soluble in sodium hydroxide solution, the amphoteric character of its benzene analogue salvarsan being absent in the pyridine series. It does, however, form a red condensation product with dimethylaminobenzaldehyde. It is oxidised by iodine in sodium hydrogen carbonate solution to the arsinic acid: $(C_5H_5ON_2As)_2 + 8I + 6H_2O = 2C_5H_5ON_2AsO_3H_2 + 8HI$. J. W. BAKER.

Meriquinonoid derivatives of the phenarsazine series. III. Reduction of derivatives of 5 : 10-dihydrophenarsazine with formic acid. G. RAZUBAIEV [with W. MALINOVSKI], (Ber., 1929, 62, [B], 2675—2677; cf. this vol., 585, 834).—If 5 : 10-dihydrophenarsazine oxide is warmed with formic acid and the coloured solution so produced is decolorised with oxygen, and the sequence is repeated until further development of colour does not occur, two reactions take place resulting (1) in the formation of phenarsazinic acid and (2) in that of arsenic and N-formyldiphenylamine. If dihydrophenarsazine derivatives are warmed for a protracted period with formic acid, quantitative precipitation of arsenic and evolution of carbon dioxide occur. 3 : 7-Dimethyl-5 : 10-dihydrophenarsazine oxide is similarly reduced to arsenic, carbon dioxide, and N-formyldi-m-tolylamine. H. WREN.

Mercurated nitrobenzenes. G. SACHS and K. FURST (Monatsh., 1929, 53 and 54, 550—553).—Reduction of mercury o-nitrophenyl chloride with sodium hyposulphite in aqueous-alcoholic solution gives a mercury di-o-nitrophenyl (I), m. p. 220—230° after sintering at 170°, differing from the form of m. p. 206—207° (II) described by Hein and Wagler (A., 1925, i, 1341). Decomposition of I with 66% hydrobromic acid in alcohol gives nitrobenzene, and treatment with sodium methoxide affords II. Reduction of I with 1% sodium amalgam and alcohol furnishes azobenzene. H. BURTON.

Position occupied by acetatomercuri-(Hg·OAc') groups in anilines containing in the nucleus a halogen group or a hydrocarbon residue. V. L. VECCHIOTTI and S. COPERTINI (Gazzetta, 1929, 59, 525—543).—As a result of the completion of previous work on the action of mercuric acetate on o-substituted anilines the following rules are stated. A single acetatomercuri-group enters position 4 only, except in o-chloroaniline (A., 1925, i, 1058). Disubstitution takes place in positions 4 and 6, except with o-chloroaniline (*loc. cit.*) and o-toluidine, which form in addition 4 : 5- and 3 : 4-derivatives, respectively, and o-iodoaniline (A., 1926, 1163), which forms no stable disub-

stituted derivative. No more than two acetatomercuri-groups can be introduced.

As a by-product in the preparation of 2-bromo-4-acetatomercurianiline (A., 1928, 783), 2-bromo-4 : 6-diacetatomercurianiline, m. p. 183—184°, separates very slowly from the mother-liquors. The acetyl derivative, m. p. 204—205°, yields 2 : 4 : 6-tribromoacetanilide with bromine and potassium bromide.

The action of mercuric acetate on o-toluidine has been reinvestigated. Addition of o-toluidine to aqueous mercuric acetate (2 mols.) yields 4 : 6-diacetatomercuri-o-toluidine, m. p. 223° (Schrauth and Schoeller, A., 1912, i, 930), from which the corresponding 4 : 6-dihydroxy-, 4 : 6-dichlorido-, m. p. 170° (decomp.), and 4 : 6-dibromido- (decomp. below m. p.) -mercuri-derivatives are prepared. The acetyl derivative, m. p. 231°, yields 4 : 6-dibromoacet-o-toluidide with bromine and potassium bromide, and 4 : 6-dichloroacet-o-toluidide with chlorine and sodium chloride. Vecchiotti's compound (A., 1926, 747), 3 : 4-diacetatomercuri-o-toluidine, m. p. 208°, is obtained when the reaction with mercuric acetate is carried out in aqueous-alcoholic solution at 55°. The acetyl derivative yields 3 : 4-dibromoacet-o-toluidide, m. p. 199° (Verda, A., 1903, i, 21), which is hydrolysed to 3 : 4-dibromo-o-toluidine, m. p. 44—45° (hydrochloride, m. p. 170—171°); this, when diazotised, reduced with sodium stannite, and decomposed, yields the known 2 : 3-dibromotoluene, thus proving the constitution of the preceding compounds and that of the 3 : 4-dichloro-o-toluidine, m. p. 41—42° (previously given, in error, as 161—162°), already prepared (Vecchiotti, *loc. cit.*). 4-Acetatomercuri-o-toluidine, m. p. 129—130° (accompanied by the 3 : 4-derivative), is obtained by interaction of o-toluidine (2 mols.) with mercuric acetate (1 mol.) in aqueous alcohol at 55° (10 min.) followed by keeping at 25° for 24 hrs. The acetyl derivative, m. p. 212—213°, yields 4-bromoacet-o-toluidide (hydrolysed to 4-bromo-o-toluidine) or 4-chloroacet-o-toluidide by the usual methods.

R. K. CALLOW.

Lead diaryldialkyl compounds. H. GILMAN and L. BALASSA (Iowa State Coll. J. Sci., 1929, 3, 105—107).—Lead diphenyl-dibutyl-, diisobutyl-, di-sec-butyl, and di-tert-butyl (m. p. 177°) were prepared by treating lead diphenyl dibromide with the appropriate magnesium butyl bromide. The anti-knock properties of the substances were examined.

CHEMICAL ABSTRACTS.

Preparation of lead triphenyl chloride and lead diphenyl dichloride. H. GILMAN and J. D. ROBINSON (J. Amer. Chem. Soc., 1929, 51, 3112—3114).—Lead triphenyl chloride is obtained in 75% yield by passing hydrogen chloride into a warm solution of lead tetraphenyl in chloroform until lead diphenyl dichloride begins to separate. The residue from the filtered solution is extracted with alcohol, which separates the chloride from the unchanged material (20%). The dichloride is obtained in 98.5% yield when hydrogen chloride is passed into a benzene solution of lead tetraphenyl at 50°. H. BURTON.

Heterocyclic systems containing selenium.

II. cycloSelenopentane. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1929, 2197—2202).—The action of

α -pentamethylene dibromide at 80° in an atmosphere of hydrogen on aqueous sodium selenide (prepared *in situ* from hydrogen selenide and alcoholic alkali) gave cycloselenopentane, b. p. 158°/759 mm., n_D^{20} 1.5475, d_4^{20} 1.424—0.001236 (mercurichloride, m. p. 175—176°; methiodide, sublimes in open tube at 160°, m. p. in closed tube 165—166°). Carbon tetrachloride solutions of the last compound gave with solutions of the appropriate halogen: cycloselenipentane 1:1-dichloride, m. p. 103° [dilute aqueous solutions of which gave with chloroplatinic acid cycloselenipentane 1-chloroplatinate, m. p. 216° (decomp.) after shrinking at 190°, whilst hot concentrated solutions formed bis-1-chlorocycloselenipentane 1-chloroplatinate, decomp. 160°]; cycloselenipentane 1:1-dibromide, m. p. 117—118° (perbromide, $C_5H_{10}SeBr_2 \cdot Br_2$, decomp. in air, leaving dibromide); and the corresponding 1:1-di-iodide, m. p. 114°.

Treatment of the above dichloride or dibromide in aqueous solution with excess of fresh silver oxide gave cycloselenipentane 1:1-dihydroxide; this by mixing with an equimolecular proportion of the 1:1-dichloride or by treating the 1:1-dichloride with sufficient silver oxide to remove only half its chlorine gave cycloselenipentane 1-hydroxy-1-chloride, decomp. at 110—111°.

By heating cycloselenopentane with ethylene dibromide and water for 1 week in a sealed tube at 100° 1- β -bromoethylcycloselenipentane 1-bromide, m. p. 88°, was formed. With moderately concentrated nitric acid cycloselenopentane gave the 1:1-dinitrate; fuming nitric acid and aqueous potassium permanganate caused rupture of the ring. The derivatives described are less stable than the corresponding derivatives of cycloselenobutane. The parachor, 264.2, is considered evidence that cycloselenopentane is a normal liquid.

Potassium selenocyanate and pentamethylene dibromide, heated in acetone solution, gave α -pentamethylene diselenocyanate, a viscous oil, which, by treatment with alcoholic potassium hydroxide, formed cyclopentamethylene diselenide (cyclodiselenopentane). This by heating strongly produced cycloselenopentane or by the action of bromine in chloroform solution yielded cycloselenipentane 1:1-dibromide or cyclopentamethylene diselenide tetrabromide according to the amount of bromine used. The last substance decomposed with production of cycloselenipentane 1:1-dibromide. R. J. W. LE FEVRE.

Interactions of basic tellurium chloride and the cresols. G. T. MORGAN and H. BURGESS (J.C.S., 1929, 2214—2219).—Addition of the cresol to "basic tellurium chloride" (prepared by oxidising tellurium with nitric acid, removal of excess of nitric acid, and repeated evaporation with concentrated hydrochloric acid) suspended in dry ether, followed by distillation of the ether and maintenance at 120—130° for *o*- or *m*-cresol or 110—120° for *p*-cresol gave, respectively, 4-hydroxy-3-methylphenyltellurium trichloride, decomp. 208—209°, and two isomeric di-*o*-hydroxyditolyl telluridichlorides, A, decomp. 198—198°, B, decomp. 177—178°, one of which is probably $(OH \cdot C_6H_3Me)_2TeCl_2$ (Me : OH = 3 : 4); di-4-hydroxydi-2-methyldiphenyl telluridichloride, which by boiling with 95% alcohol or by dissolution in hot aqueous sodium carbonate followed by acidification passed by elimin-

ation of one third of the tellurium into tri-4-hydroxytri-2-methyltriphenyltelluronium chloride dihydrate, m. p. 184—185° (the corresponding telluronium hydroxide gave a sodium salt, m. p. 137—138° with subsequent resolidification); and tri-2-hydroxytri-*o*-methyltriphenyltelluronium tellurium oxychloride, $[(HO \cdot C_6H_3)_3Te]TeOCl_3$, decomp. 229—230°, di-2-hydroxydi-5-methyldiphenyl telluridichloride, decomp. 213—214°, and tri-2-hydroxytri-5-methyltriphenyltelluronium chloride dihydrate, m. p. 244—245° (decomp.). Interaction of *m*-cresol and tellurium tetrachloride, both in ethereal solution, gave an oil which was converted by ice-cold potassium metabisulphite solution into small yields of di-4-hydroxydi-2-methyldiphenyl telluride, m. p. 143—144°. The low yield is taken as indicating that the effective agent in this condensation is the small amount of basic tellurium chloride produced by the action of moisture on the tetrachloride. R. J. W. LE FEVRE.

Constitution of triphenylsilicane and its reaction with sodium in liquid ammonia. H. H. REYNOLDS, L. A. BIGELOW, and C. A. KRAUS (J. Amer. Chem. Soc., 1929, 51, 3067—3072).—Magnesium phenyl bromide (4.5 mols.) and trichlorosilicane afford 73% of triphenylsilicane (I), m. p. 36—37° (cf. Ladenburg, A., 1907, i, 668, who gives m. p. 200—203°). Kipping and Murray's triphenylsilicane (this vol., 586) is impure. Bromine in carbon tetrachloride converts I into triphenylsilicyl bromide, which is decomposed by boiling dilute sodium hydroxide to triphenylsilicol. When I is treated with sodium in liquid ammonia 0.66 g.-atom of sodium is used, but 1.9 atoms of hydrogen are evolved. Decomposition of the product formed with ammonium bromide affords a viscous oil and bistrisphenylsilicylamine (II) $(SiPh_3)_2NH$, m. p. 175°; decomposition with ethyl bromide, bromobenzene, or oxygen also gives II. Hydrolysis of II with 6*N*-hydrochloric acid affords ammonium chloride and triphenylsilicol. II is stable towards dilute sodium hydroxide and air. H. BURTON.

Series arrangement of organic groups. I. As determined by halogenation of mixed stannanes. R. H. BULLARD (J. Amer. Chem. Soc., 1929, 51, 3065—3067).—Triphenylbenzylstannane, m. p. 90—91°, prepared from sodium triphenylstannide and benzyl chloride in liquid ammonia, is converted by bromine (2 mols.) in benzene and carbon tetrachloride solution into phenylbenzylstannic dibromide, m. p. 74—75°. The series arrangement of groups based on the ease of their removal from stannanes by halogen is: Ph, $\cdot CH_2Ph$, Me, Et, Pr. H. BURTON.

Reaction between proteins and diazotised aromatic amines in neutral solution. M. HEIDELBERGER and F. E. KENDALL (Proc. Soc. Exp. Biol. Med., 1929, 26, 482—484).—Chemical interaction, with formation of dyes, takes place in neutral mixtures of diazotised aromatic amines and proteins.

CHEMICAL ABSTRACTS.

Structure of silk fibroin. E. ABDERHALDEN and H. BROCKMANN (Biochem. Z., 1929, 211, 395—411).—Silk fibroin dispersed in concentrated lithium bromide solution could not be separated into different fractions by dialysis, precipitation with ammonium

sulphate solution, or fractionation of the benzoyl derivative. Silk fibroin was condensed with benzoyl chloride, also with *p*-chloro- and *p*-bromo-benzoyl chloride. The introduction of the simple or halogenated benzoyl radicals into the dispersed fibroin gave derivatives containing chiefly easily hydrolysable groups and a smaller amount hydrolysed only with difficulty. The ratio of these was approximately the same for all three benzoyl groups, indicating that silk fibroin is homogeneous. The easily hydrolysed groups are probably attached to hydroxyl and the others to amino-groups of tyrosine and serine; thus the hydroxyl groups are presumably not concerned in the linking up of the amino-acids. Silk fibroin and sericin can be separated by means of ammonium sulphate. J. H. BIRKINSHAW.

Electrolyte-free proteins. VIII. Free charge and neutral salt effects of pure proteins. T. ITO and W. PAULI (Biochem. Z., 1929, 213, 95—108; cf. this vol., 394).—The conductivity of solutions of pure egg-albumin, serum-albumin, gluten, and pseudoglobulin was determined. Chlorides of the alkali metals up to concentrations of 0.2*M* were unable to change the anodic migration of egg- and serum-albumin. The alkaline-earth chlorides at 0.05*M* produced migration in both directions. Gluten was more susceptible to the action of salts, the migration being actually reversed by 0.004*M*-barium chloride. Potassium salts change the cathodic migration of pseudoglobulin in concentrations varying from 0.05*M* for the chloride to 2.5×10^{-5} for the ferrocyanide. The direction of migration cannot be inferred from the position of the isoelectric point.

J. H. BIRKINSHAW.

Analytical reactions of lead tetraethyl. G. EDGAR and G. CALINGAERT (Ind. Eng. Chem. [Anal.], 1929, 1, 221—222).—The lead in the organic compound is converted into bromide by treatment with a 30% solution of bromine in carbon tetrachloride, and the lead bromide either converted into chromate and weighed, or dissolved in ammonium acetate and titrated with standard molybdate solution. The method is available both for a concentrated preparation of lead tetraethyl and for its dilute solution in petrol. An alternative method in the former case is to decompose the material in benzene solution with 0.1*N*-iodine and titrate the excess of iodine with thiosulphate. If a mixture of lead triethyl and tetraethyl salts is present, the former may be removed by extracting the solution in light petroleum twice with concentrated aqueous ammonia; the lead in the extract and residual solution is then determined as above. H. F. HARWOOD.

H. F. HARWOOD.

Determination of quinol and pyrocatechol in presence of resorcinol and other phenols. I. F. BOCK and G. LOCK (Monatsh., 1929, 53 and 54, 888—896).—The determination of *p*-benzoquinone may be effected by shaking a chloroform solution with 10% potassium iodide and 10% sulphuric acid for a short time, and then titrating the liberated iodine with thiosulphate (cf. Willstätter and others, A., 1909, i, 535; 1910, ii, 553; Wieland, A., 1910, i, 243). Oxidation of a 0.2% aqueous solution of quinol with 10% ferric chloride solution, and determination of the *p*-benzoquinone formed (extracted by chloroform), gives practically quantitative results; 0.01 g. can be determined. The method gives values of 98.3—99.5% in presence of phenol, resorcinol, orcinol, phloroglucinol, pyrogallol, or hydroxyquinol. Pyrocatechol is determined similarly, using 0.05% aqueous solutions.

A preliminary account of the separation of quinol and resorcinol by initial oxidation with ferric chloride, extraction of the quinone with chloroform, and subsequent reduction of this with sodium hyposulphite is given. H. BURTON.

Application of semicarbazones to the determination of ketones. S. VEIBEL (J.C.S., 1929, 2423—2424).—A claim to priority (A., 1927, 1172) against Hobson (this vol., 949) and a comparison of the details of the two methods. J. W. BAKER.

Determination of small amounts of carotinoids. H. VON EULER, H. HELSTROM, and M. RYDBOM (Mikrochem., 1929, Pregl Fest., 69—76).—Carotin and allied compounds such as dihydro- α -crocetin methyl ester can be determined colorimetrically when dissolved in dry chloroform with addition of antimony trichloride, a Lovibond tintometer being employed.

H. F. HARWOOD.

Microchemical method for determination of cerebrosides. P. KIMMELSTIEL (Mikrochem., 1929, Pregl Fest., 165—177).—The material (0.25 g.) is cooled in liquid air, powdered, and extracted with hot alcohol. A portion of the extract is hydrolysed by heating with 11% hydrochloric acid, the solution neutralised with sodium hydroxide, and the reducing substances present determined by Hagedorn and Jensen's method with potassium ferricyanide. The reducing substances present in the original alcoholic extract are determined similarly after removal of alcohol by evaporation, and the figure deducted from that previously obtained. The resultant value which represents the galactose formed by hydrolysis of the cerebrosides is multiplied by 4.6 to obtain the amount of cerebrosides present in the original material.

H. F. HARWOOD.

Biochemistry.

The respiratory enzyme and oxidases. O. WARBURG (Biochem. Z., 1929, 214, 1—3).—When an extract of cells contains several oxidases, these do not represent enzymes present in the living cell, but are different breakdown products of a single substance therein. From the author's previous work it is likely that all the iron atoms in a cell which act as oxygen

carriers in respiration are bound identically and that the respiratory enzyme is the same for different cells (cf. A., 1928, 537, 549, 795). P. W. CLUTTERBUCK.

The respiratory enzyme and oxygen storage. O. WARBURG (Biochem. Z., 1929, 214, 4).—The red blood-corpusele of a bird contains, besides the iron of

the respiratory enzyme, an iron compound—hæmoglobin—which stores oxygen. Displacement of oxygen from this store by carbon monoxide has no influence either at constant or decreasing oxygen tension on the respiration and can bring about with decreasing oxygen tension only an acceleration and never an inhibition of respiration. P. W. CLUTTERBUCK.

Respiration at low oxygen tensions. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1929, 214, 5—18).—The respiration of cell suspensions (of *Micrococcus candidans*) measured by differential manometer at oxygen tensions as low as 10^{-5} atm. (0.008 mm.) is at 1° the same as, at 5° only a little greater, and at 10° slightly greater than the respiration in air. The importance of these results for the mathematical theory of respiration is indicated.

P. W. CLUTTERBUCK.

Is the inhibition of respiration by carbon monoxide complete? O. WARBURG and F. KUBOWITZ (Biochem. Z., 1929, 214, 19—23).—The inhibition of respiration of cell suspensions (of *Torula utilis*) by carbon monoxide is the greater the greater is the carbon monoxide tension and the less is the oxygen tension and is as complete as the law of distribution will permit. Under the conditions used, 99% inhibition of respiration was readily obtained.

P. W. CLUTTERBUCK.

Action of carbon monoxide on the respiration of *Aspergillus oryzae*. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1929, 214, 24—25).—If 15-hr. agar cultures of *Aspergillus oryzae* are placed in a mixture of 5% of oxygen and 95% of carbon monoxide, a smaller respiration is obtained than in oxygen of the same partial pressure diluted with argon. The respiration of these, as with most other cells, is reversibly inhibited by carbon monoxide.

P. W. CLUTTERBUCK.

Carbylamine-hæmoglobin and the photochemical dissociation of its carbon monoxide compound. O. WARBURG, E. NEGELEIN, and W. CHRISTIAN (Biochem. Z., 1929, 214, 26—63).—The displacement of carbon monoxide and oxygen from iron-porphyrin compounds by the N:C grouping on addition of methylcarbylamine is investigated quantitatively. If a suitable amount of methylcarbylamine is added to a solution of oxyhæmoglobin through which oxygen at atmospheric pressure is passing, the red colour changes to violet and oxygen escapes. Bivalent iron is then present in solution and when carbon monoxide is passed, 1 mol. is absorbed per atom of iron. Manometric determination of the displacement of oxygen and carbon monoxide by methylcarbylamine shows that 1 mol. of carbylamine is absorbed for the displacement of 1 mol. of oxygen or carbon monoxide. In order to convert an appreciable fraction of hæmoglobin into its carbylamine compound, a carbylamine concentration of 0.001M is required. In presence of oxygen or carbon monoxide this concentration must be greater and then depends on the pressure of oxygen or carbon monoxide. Carbon monoxide-hæmoglobin in carbylamine solutions is the most highly light-sensitive carbon monoxide-iron-porphyrin compound as yet described. The distribution constant $K = C_{FeMeNC} \times C_{CO} / C_{FeCO} \times$

C_{MeNC} in yellow light of intensity 1 g.-cal./sq. cm. per min. at 10° increases to 3600 times its value in the dark, whereas for carbon monoxide-hæmoglobin in water under the same conditions no displacement of the dark equilibrium is obtained. The dark dissociation constant of the carbon monoxide compound in presence of methylcarbylamine is very much less than in its absence, thus falling into line with the requirements of the mathematical theory of photochemical dissociation. P. W. CLUTTERBUCK.

Absorption spectrum of the respiratory enzyme. O. WARBURG and E. NEGELEIN (Biochem. Z., 1929, 214, 64—100).—To the six wave-lengths for which the absorption coefficients of the respiratory enzyme have been determined (A., 1928, 549; this vol., 216, 470) nine further wave-lengths are added, the spectral range now being from 254 to 603. The absolute absorption spectrum of the carbon monoxide compound of the enzyme is portrayed graphically. The methods are described whereby the fifteen wave-lengths are isolated, and the mathematical theory is given whereby the relative and absolute absorption coefficients of the enzyme are calculated. A photoelectric method is described for the determination of the absolute absorption spectrum of iron-porphyrin compounds over a spectral range of 250—600 thus avoiding the tedious photographic method.

P. W. CLUTTERBUCK.

Absorption spectrum of the respiratory enzyme of the retina. O. WARBURG and E. NEGELEIN (Biochem. Z., 1929, 214, 101—106).—Using the wave-length 436 μ , that intensity which appreciably dissociates the carbonyl compound of the respiratory enzyme of yeast (10^{-4} g.-cal./sq. cm./min.) also dissociates the carbonyl compound of the respiratory enzyme of retinal cells. In order to find the region of maximal absorption, the ratio of the light absorption coefficients for the wave-lengths 436 and 405 was obtained; this was almost identical for the retinal and yeast respiratory enzymes.

P. W. CLUTTERBUCK.

Respiratory enzyme in the serum of suffocated animals. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1929, 214, 107—109).—Kempner's result (Klin. Woch., 1927, 6, 2386) that the plasma of normal hens showed no respiration, whereas that of pest-infected hens used 5 c.mm. per c.c. per hr., is due, not to the infection, but to the suffocation causing death. Thus the plasma of normal hens suffocated by placing in an atmosphere of nitrogen shows quantitatively the same respiration, and it must be assumed that during suffocation the respiratory enzyme passes from the body-cells into the blood. P. W. CLUTTERBUCK.

Gasometric control of standard solutions for the Palmer hæmoglobin method. D. D. VAN SLYKE and A. HILLER (J. Biol. Chem., 1929, 84, 211—216).—If the standard hæmoglobin solutions employed by Palmer (A., 1918, ii, 88) be saturated with pure carbon monoxide, and be kept in the dark at 7° , they remain unchanged for 32 weeks. The condition of the standard solutions can readily be controlled by determination of the carbon monoxide-combining capacity (A., 1928, 1149). C. R. HARRINGTON.

Hæmoglobin maintenance on synthetic diets. D. L. DRABKIN and C. S. WAGGONER (Science, 1929, 69, 480).—Dogs fed on the Karr-Cowgill diet maintained a normal hæmoglobin level and addition of copper sulphate was without effect on this and on recovery after bleeding. Growth, appearance, and hæmoglobin maintenance were normal in rats fed on both a copper-free diet and on a diet to which copper salts were added, and rats rendered anæmic by a milk diet were cured by the copper-free diet.

L. S. THEOBALD.

Relation of iron and copper to hæmoglobin synthesis in the chick. C. A. ELVEHJEM and E. B. HART (with A. R. KEMMERER) (J. Biol. Chem., 1929, 84, 131—141).—In the chick as in rats (A., 1928, 790) both iron and copper are necessary for the normal synthesis of hæmoglobin.

C. R. HARRINGTON.

New amino-acid from hæmoglobin. S. FRANKEL and G. MONASTERIO (Biochem. Z., 1929, 213, 65—71).—After digestion of oxyhæmoglobin with trypsin for 2 years a crystalline amino-acid, $C_{22}H_{46}O_7N_4$, m. p. 270° (decomp.), $\alpha_D^{25} -11.76^\circ$, was isolated from the methyl-alcoholic portion of the non-crystallisable dialysable syrup obtained. It has three carboxyl and four amino-groups.

J. H. BIRKINSHAW.

Absorption of ultra-violet light by oxyhæmoglobin and by some of its derivatives. C. S. HICKS and H. F. HOLDEN (Austral. J. Exp. Biol., 1929, 6, 175—186).—Observations have been made of the absorption bands in the ultra-violet region of hæmoglobin (ox) and of certain related compounds. The following are the wave-lengths (in μ) at which maximum absorption takes place: oxyhæmoglobin, 411.5; hæmoglobin, 429.5; carbon monoxide-hæmoglobin, 417.9; methæmoglobin, 404.5; alkaline methæmoglobin, 410.6; alkaline hæmatin (in water) 384.7; alkaline hæmatin (in alcohol), 402.5; acid hæmatin (in water), 379.3; acid hæmatin (in alcohol), 398.7; globin, 279.0; denatured globin, 274.0.

W. O. KERNACK.

Gasometric determination of methæmoglobin. D. D. VAN SLYKE and A. HILLER (J. Biol. Chem., 1929, 84, 205—210).—The method of Van Slyke for the determination of methæmoglobin (A., 1926, 443) has been combined with the technique employed for determining the carbon monoxide-combining capacity of blood (A., 1928, 1149), so that the whole operation can be carried out in the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The method is applicable to 0.1—2 c.c. of blood.

C. R. HARRINGTON.

Gasometric determination of oxalic acid and calcium; application to serum analysis. D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1929, 84, 217—232).—Blood-serum or -plasma is freed from protein with trichloroacetic acid; an aliquot portion of the filtrate is treated with sodium acetate, ammonium oxalate, and ammonia to p_H 5.0 and kept over-night. The calcium oxalate is separated and washed with dilute ammonia at the centrifuge, and dissolved in *N*-sulphuric acid; the solution is transferred to the apparatus of Van Slyke and Neill (A., 1924, ii, 872), and, after extraction and rejection of dissolved gases, is treated with acid permanganate

solution and shaken under diminished pressure, and the carbon dioxide evolved is determined in the usual manner. With samples of 1—2 c.c. of serum the results agree with those obtained by the titrimetric method to within $\pm 5\%$. With solutions of pure oxalic acid or calcium salts agreement to within $\pm 1\%$ can be obtained.

C. R. HARRINGTON.

Possibility of individual chemical synthesis of blood-proteins. I. Tryptophan content of human serum-proteins. K. LANG (Arch. exp. Path. Pharm., 1929, 145, 88—99).—The tryptophan contents of 60 pathological sera were determined by the method of Fürth (A., 1924, ii, 576) or calculated from the albumin-globulin ratio. No correlation between tryptophan content and rate of sedimentation of erythrocytes was found (cf. Fischer and Weiss, Z. ges. exp. Med., 1925, 48, 111—118). The results showed no agreement in 50% of the sera examined. These results are said to afford further experimental support for the views of Herzfeld and Klinger (A., 1918, i, 87).

C. C. N. VASS.

Blood-tryptases and a micro-method for their determination. O. SOKOLNIKOV (Biochem. Z., 1929, 213, 414—418).—The amount of protease in human blood is altered by the application of very slight physiological stimuli. By means of a modification of the method of Utkin-Ljubovzov (A., 1926, 648) the tryptase content of 0.1 c.c. of blood is deduced from determinations of total and residual nitrogen in the caseinogen precipitate.

W. MCCARTNEY.

Antitryptic activity of sera. G. YAMANAKA (Sei-i-kwai Med. J., 1929, 48, No. 3, 62—78).—The antitryptic activity of serum is increased during menstruation, is greater in acute than in chronic diseases, is increased after ultra-violet irradiation, treatment with the vaccine of *B. coli communis* or egg-albumin, or injection of adrenaline, but is decreased during fasting.

CHEMICAL ABSTRACTS.

Influence of hydrogen-ion concentration of the medium on the amylase activity of horse serum. B. ROUSSEU, Z. GRUZEWSKA, and G. ROUSSEL (Compt. rend., 1929, 189, 589—590).—The amylase activities of blood obtained at successive bleedings of a horse show marked fluctuations. These fluctuations are similar in the same series of samples whatever be the p_H at which the activity is measured, but their amplitudes are most marked at p_H 6.4, the reaction at which the activity of amylase is maximum.

W. O. KERNACK.

Uric acid of the blood. D. LIOTTA (Arch. Farm. sperim., 1929, 46, 241—258).—Experiments on dogs show that injection of lutein has no appreciable influence on the level of the uric acid of the blood, whereas suprarenal and pituitary extracts cause a lowering. Insulin and iodothyron produce increases in the total and plasma-uric acid, in relation to that of the corpuscles; "caseum" behaves similarly, but the total uric acid of the blood varies markedly, whereas the increase in the plasma is more constant. In human beings, suprarenal extract especially causes a distinct diminution of the uricæmia and constant variations in the ratio between the plasmatic and corpuscular uric acid. With pituitrin and

"caseum" only very slight effects are observed. The influence of insulin is similar to that noticed with dogs. T. H. PORE.

Bang's method for the determination of fatty substances in blood. W. RADSMAN and PIRNGADI (Arch. Neerland. Physiol., 1929, 14, 345—358).—The times allowed for extraction and for oxidation of the fats in the method of Bang ("Mikromethoden zur Blutuntersuchung," 1922) have little effect on the values obtained, but the vessel must be open to the air during oxidation. In the precipitation of cholesterol by digitonin better results are obtained if the light petroleum is first entirely removed.

K. V. THIMANN.

Fatty substances in the blood of Indonesians and Europeans in the tropics. PIRNGADI (Arch. Neerland. Physiol., 1929, 14, 359—370).—A series of determinations has been made by Bang's method (cf. *supra*) on whole blood and on serum. Native employees exhibited a slightly lower content of cholesteryl esters and fatty acids than native students or Europeans.

K. V. THIMANN.

Cholesterol content of blood of tropical inhabitants. W. RADSMAN (Arch. Neerland. Physiol., 1929, 14, 371—385).—The colorimetric method of Bloor for determination of cholesterol gives results about 40% higher than those obtained by precipitation with digitonin. This is ascribed, not to the presence of other colour-producing substances in blood, but to a difference between the cholesterol of blood and the pure commercial product. The cholesterol content of the blood of native employees is lower than that of students or of Europeans. One cause of this is ankylostomiasis. K. V. THIMANN.

Micro-determination of free cholesterol in blood. L. TUTKEVITSCH (Biochem. Z., 1929, 213, 439—442).—Blood (100—120 mg.) is weighed on filter-paper, which is then extracted for some hours with light petroleum. The extract is concentrated to 1.0 c.c., transferred to a centrifuge tube, 0.1 c.c. of 0.5% digitonin solution is added, and the mixture, after being warmed, is kept over-night. The digitonin compound is then decomposed by the addition of 0.3 c.c. of 25% sodium hydroxide solution. After the mixture has been heated and cooled, 1.5 c.c. of chloroform are added and then anhydrous sodium dihydrogen phosphate is stirred in until the precipitate formed begins to settle. The colour of the liquid is compared with that of a standard. The error of the method amounts to ± 2 —3 mg. per 100 c.c.

W. MCCARTNEY.

Cholesterol in the blood of the fresh-water mussel *Anodonta cygnea*. A. DE WAELE (Natuurwetensch. Tijds., 1929, 11, 154—157).—Cholesterol was identified after separation from the ether extract of the whole organism. Determinations of cholesterol on 100 c.c. of the blood showed the presence of 0.36 mg. in the plasma and 0.9 mg. in the corpuscles.

S. I. LEVY.

Lipoid layer of sheep's chromocytes. F. GRENDL (Biochem. Z., 1929, 214, 231—241).—The lipins of sheep's erythrocytes when extracted and spread in a unimolecular layer occupy a surface which amounts to double the total surface of the

chromocytes and since lipin does not exist within the cells it must be assumed that they are surrounded by a bimolecular layer of lipins, the thickness of which is shown to be 31 Å. The lipins after extraction are shown to contain 36% of cholesterol, 50% of cephalin, and 13% of sphingomyelin. The area occupied by the lipins is 10% greater on buffered solutions not containing calcium than on distilled water. It is also a little greater on addition of 3.75—5 mg. of calcium per 100 c.c., but is 12% smaller with 11 mg. of calcium (an amount corresponding with the calcium content of blood). Decrease of plasma-calcium, therefore, is accompanied by decrease of the lipid layer of the corpuscles. P. W. CLUTTERBUCK.

Fixation of dextrose by blood-corpuscles. H. HÄUSLER and O. LOEWI (Biochem. Z., 1929, 214, 229—230).—A reply to Höglér, Thomann, and Überraack (this vol., 1096). P. W. CLUTTERBUCK.

Reducing power of blood after acid hydrolysis. F. SILBERSTEIN, F. RAPPAPORT, and M. WACHSTEIN (Biochem. Z., 1929, 213, 355—374).—The methods so far used for the determination of the total carbohydrate content of blood have been examined and the following procedure is now recommended: 0.1 c.c. of blood is heated for 4 hrs. at 100° with 1.0 c.c. of 0.67N-sulphuric acid. To the cooled solution 5 c.c. of water and 1 c.c. of 10% sodium tungstate solution are added and the mixture is heated for 3 min. at 45°, cooled, diluted with water to 15 c.c., and filtered. To 5 c.c. of the filtrate, 2 c.c. of 8.2% potassium carbonate solution are added and the original procedure of Hagedorn and Jensen is then followed. This method is shown to determine accurately the chief carbohydrates which occur in blood in pathological conditions. It gives results higher than those found with other methods, partly because it determines glucosamine. It has been found that blood contains substances which reduce potassium ferricyanide in the cold, but the amount of these does not vary much in the same animal. The blood of normal and of diabetic dogs to which peptone or dextrose was administered and of normal and diabetic dogs to which insulin was subcutaneously administered with and without simultaneous administration of sugar has been examined by determining both the direct reducing power and the reducing power after hydrolysis. These reducing powers varied and the results are discussed.

W. MCCARTNEY.

Rôle of reducing colloids in blood-sugar determination. S. DONHOFFER and M. MITTAG-DONHOFFER (Biochem. Z., 1929, 213, 195—201).—The method of Bang gives higher results than that of Hagedorn and Jensen for sugar in plasma, serum, and egg-albumin. This is due to a reducing, non-fermentable substance of colloid nature precipitated by zinc hydroxide, but not completely by uranyl acetate. It is present as both a coarse and a fine dispersion. The method of Hagedorn and Jensen gives results corresponding closely with fermentable sugar. J. H. BIRKINSHAW.

Reducing powers of different sugars for ferricyanide. J. A. HAWKINS (J. Biol. Chem., 1929, 84, 79—82).—Figures are given for the relative reducing

powers of different sugars for the alkaline ferricyanide reagent employed in the gasometric method of Van Slyke and Hawkins (A., 1928, 1358).

C. R. HARRINGTON.

Micro-determination of reducing sugars in blood and urine. J. A. HAWKINS (J. Biol. Chem., 1929, 84, 69—77).—The method of Hawkins and Van Slyke (this vol., 462) has been modified so as to be applicable to 0.2 c.c. of blood, the error of the determination remaining $\pm 5\%$.

C. R. HARRINGTON.

Micro-determination of chlorides in blood. W. B. ROSE and C. J. STUCKY (Mikrochem., 1929, Pregl Fest., 300—301).—The method of Van Slyke has been modified to permit the determination in 0.1 c.c. of blood. The blood is measured out by a micro-pipette, added to distilled water, and 1 c.c. of a standardised solution of silver nitrate added. The whole is heated until the supernatant liquid is clear and the silver chloride coagulated, and the excess of silver is then titrated with a solution of potassium thiocyanate containing 0.554 g. per litre.

H. F. HARWOOD.

Influence of protein and inorganic phosphorus on serum-calcium. J. P. PETERS and L. EISENBERG (J. Biol. Chem., 1929, 84, 155—166).—The indications of previous work (cf. Binger, A., 1917, i, 677; Salvesen and Linder, A., 1924, i, 442), that the concentration of calcium in the blood-serum falls with increase in the inorganic phosphate and with decrease in the protein, are confirmed. The relationship $\text{Ca} = -0.255\text{P} + 0.566 \times \text{protein} + 7$, where Ca and P represent the calcium and inorganic phosphorus in mg. per 100 c.c., and the protein is expressed in g.-%, was found to hold good in a large series of pathological cases.

C. R. HARRINGTON.

Condition of calcium in body fluids. K. KLINKE (Biochem. Z., 1929, 213, 177—189).—The calcium of serum ultrafiltrate is not precipitated by freezing. It is precipitated as carbonate by shaking with calcium phosphate (avoiding loss of carbon dioxide). More carbon is precipitated than stoichiometric theory expects. The calcium of serum ultrafiltrate, contrary to that in supersaturated Ringer's solution, wanders in the electric field to both cathode and anode; there is present in serum a negatively-charged calcium compound. By addition of caffeine the ultrafiltrability of serum-calcium is increased by 40%. Only about 2 mg. per 100 c.c. of the calcium of serum is ionised.

J. H. BIRKINSHAW.

Blood coagulation. XXII. Significance for blood coagulation of nitrogenous substances. B. STUBER and K. LANG (Biochem. Z., 1929, 213, 460—468).—When blood coagulates there is no measurable change in its residual nitrogen content. No relation can be found between the formation of ammonia in blood and its coagulation. The preparation "18 Promonta," which is hydrolysed by trypsin-kinase, inhibits glycolysis of blood *in vitro* and *in vivo*, the extent of the inhibition being parallel to the retardation of coagulation. Proteolysis is not a cause of blood coagulation.

W. MCCARTNEY.

Immunisation and the nitrogenous constituents of the blood. M. F. GUYER and S. LEP-

KOVSKY (J. Immunol., 1929, 16, 175—207).—When a foreign protein is injected into the blood-stream of rabbits the blood-amino-nitrogen (except in moribund animals) tends to diminish, the non-protein-nitrogen increases, the p_{H} and alkaline reserve are lowered, and the body tissues exhibit acidosis.

CHEMICAL ABSTRACTS.

Chemical nature of the constituent of fowl serum responsible for non-specific precipitations. G. S. SCHILLING (J. Immunol., 1929, 16, 439—449).—The constituents of fowl sera responsible for non-specific precipitations appear to be lipoproteins and neutral fats.

CHEMICAL ABSTRACTS.

Mode of action of formaldehyde on complement-fixation systems. C. E. REYNER (J. Immunol., 1929, 16, 1—16).

CHEMICAL ABSTRACTS.

Carbohydrate group of ovomucoid. P. A. LEVENE and T. MORI (J. Biol. Chem., 1929, 84, 49—61).—Coagulated egg-white was hydrolysed for 7 hrs. with 10% barium hydroxide. After removal of barium the solution was cleared with basic lead acetate and concentrated; the carbohydrate in the residue was precipitated with basic lead acetate and barium hydroxide. The solution obtained after decomposition of the lead precipitate with carbon dioxide was treated with mercuric sulphate to remove traces of peptide; mercury and sulphuric acid having been removed, the solution was concentrated and poured into excess of methyl alcohol, yielding 1.9% of polysaccharide. The same material was obtained in yields of 0.26% and 5.1% by similar treatment of crystalline egg-albumin and of ovomucoid, respectively. In agreement with Frankel and Jellinek (A., 1927, 862) the material was found to yield, on complete hydrolysis, exclusively glucosamine and mannose; it had $[\alpha]_{\text{D}}$ about $+30^\circ$ in water, and, contrary to Frankel and Jellinek (*loc. cit.*), analysed as a trisaccharide. Dialysis failed to separate it into different constituents. On partial hydrolysis, it gave a reducing trisaccharide.

C. R. HARRINGTON.

Molecular size of carbohydrates from egg-proteins. P. A. LEVENE and A. ROTHEN (J. Biol. Chem., 1929, 84, 63—68).—Determinations by the diffusion method indicate for the polysaccharide obtained from egg-proteins (cf. preceding abstract) a mol. wt. of 2000 and, for its partial hydrolysis product, one of 500. The polysaccharide therefore consists of four trisaccharide units, each containing 1 mol. of glucosamine and 2 mols. of mannose.

C. R. HARRINGTON.

Distribution and variation of glycogen in the intestinal mucous membrane of the mammalian embryo. I. MARUYAMA (Okayama J. Med., 1928, 40, 1296—1333).—Results for rabbit's, marmot's, and dog's intestinal mucous membrane are recorded. Changes in the quantity of free and lactacidogen phosphoric acid with lapse of time after conception are recorded. The intestinal mucous membrane of marmots contains much, and that of dogs little, insulin-like substance.

CHEMICAL ABSTRACTS.

Glycogen in the central nervous system of some mammals. III. Effects of inanition. H. TANAKA (Sei-i-kwai Med. J., 1929, 48, No. 2, 51—81).

—Experiments with rabbits and guinea-pigs are described.
CHEMICAL ABSTRACTS.

Glycogen. I. S. HARADA (Sci-i-kwai Med. J., 1929, 48, No. 1, 46—83).—The glycogen in the kidney, pelvis of the kidney, ureter, and bladder epithelium is formed locally from blood- and urine-sugar.
CHEMICAL ABSTRACTS.

Glycogen content of the liver of cadavers. H. POPPER and O. WOZASEK (Wien. med. Woch., 1929, 79, 456—458; Chem. Zentr., 1929, i, 2788).

Mineral content of the skin. I. Micro-determination of potassium and calcium. E. NATHAN and F. STERN (Dermat. Z., 1928, 53, 451—456; Chem. Zentr., 1929, i, 2800).—The skin (0.5 g.) is incinerated with nitric acid and hydrogen peroxide and the determination then made in the usual way. Variable results (potassium, 53—145 mg.-%; calcium 5.96—17.81 mg.-%) were obtained for the skin of cadavers.
A. A. ELDRIDGE.

Inorganic constituents of the musculature of the Fallopian tubes (of the sow) and their physiological variations. F. KOK and W. BERGMANN (Biochem. Z., 1929, 213, 424—438).—The water, ash, potassium, sodium, calcium, magnesium, phosphorus, sulphur, chlorine, and nitrogen contents of the musculature of the Fallopian tubes of sows have been determined at different stages during the oestral period. Important differences have been found between the contents of inorganic constituents of smooth muscle and of transversely striated muscle and great differences in this content are also found between the musculature of the Fallopian tubes and that of other smooth muscle organs of the same animal. During oestrus, also, both the total ash content and the relative proportions of the various inorganic constituents of the musculature of the tubes vary considerably.
W. MCCARTNEY.

Cerebronic acid. F. A. TAYLOR and P. A. LEVENE (J. Biol. Chem., 1929, 84, 23—37).—A large amount of cerebronic acid was oxidised by the method of Levene and Taylor (A., 1922, i, 714) and the oxidation product was esterified; the esters were submitted to repeated fractional distillation at 0.1 mm. The distillation residues, when hydrolysed, yielded acids with mol. wt. 367—374; on reoxidation, followed by esterification and fractionation, this part of the material yielded a *tetracosic acid*, m. p. 78.5—79.5°. The distillates gave acids of mol. wt. 351—356, and from this portion, by fractional crystallisation, was obtained an apparently pure *tricosic acid* which is probably that described by Klenk (A., 1928, 868). This material was, however, not in reality homogeneous, since more exhaustive fractionation of the esters from which it was derived yielded, together with acids of higher mol. wt., a fraction which gave the analytical figure for *docosic acid*, although this fraction contained material of still lower mol. wt. The results indicate that cerebronic acid contains, in addition to α -hydroxypentacosic acid, lower hydroxy-acids or hydroxypentacosic acids with the hydroxyl group in different positions; the m. p. of the impure acids obtained in the above experiments

render it doubtful whether they belong to the lignoceric acid series.
C. R. HARRINGTON.

Conditions for the combination of the grey matter of the brain with quinine. P. I. BORISSOV, A. PETRUNKINA, and M. PETRUNKIN (Biochem. Z., 1929, 213, 419—423).—At low hydrogen-ion concentrations the grey matter of the human brain combines not at all or only very slightly with quinine. At p_H 3—4 the extent of combination begins to increase and reaches considerable magnitude at p_H 6—7. The amount of quinine which enters into combination increases with increase of the protein content of the grey matter, but this may also contain substances, other than proteins, which combine with quinine.
W. MCCARTNEY.

Extractive substances of muscle. XXVIII. Extractive substances of hen's flesh. N. TOLKAT-SHEVSKAYA (Z. physiol. Chem., 1929, 185, 28—32).—From hen's flesh a base, $C_{10}H_{16}O_3N_4$, was isolated, agreeing closely in properties with anserine.
J. H. BIRKINSHAW.

Lower enzymic fission products of muscle-adenylic acid. K. POHLE (Z. physiol. Chem., 1929, 185, 9—27).—Although purine bases and nucleosides could not be obtained from fresh rabbit's muscle this was easily effected after exposure of the muscle at 40° to sodium hydrogen carbonate for a few hours. Addition of adenylic acid increases the amount of these substances—an indication of their origin. There were isolated carmine, m. p. 235—245°, hypoxanthine, and xanthine, and small amounts of a substance probably identical with thymine. The presence of pentosephosphoric acid was probable. Muscle-adenosinephosphoric acid is suggested as the precursor of endogenous uric acid.
J. H. BIRKINSHAW.

Determination of carbon dioxide content of muscle. J. K. W. FERGUSON and L. IRVING (J. Biol. Chem., 1929, 84, 143—153).—Muscle is fixed by freezing in liquid air, and a sample of about 1.5 g. is introduced into the extraction chamber (made for this purpose in two sections connected by a ground joint) of the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The carbon dioxide is extracted by shaking for 45 min. with excess of dilute hydrochloric acid, and is then determined in the usual manner. The error is within 2%.
C. R. HARRINGTON.

Acetylcholine. H. W. DUDLEY (Biochem. J., 1929, 23, 1064—1074).—Acetylcholine chloroplatinate, which crystallises in anisotropic needles, forms with choline chloroplatinate an equimolecular co-ordination compound, m. p. 260—261°, which is less soluble than either of its components and crystallises in isotropic octahedra. Its significance in connexion with the isolation of acetylcholine from natural sources is discussed. A further identification of acetylcholine isolated from horse's spleen as *choline-acetylcholine dichloroplatinate* is provided by the preparation of acetylcholine chloroaurate from the double chloroplatinate. Acetylcholine chloride is liberated quantitatively from acetylcholine chloroaurate by shaking an aqueous solution of the latter with metallic silver. This method can be applied generally to the preparation of chlorides or hydrochlorides of bases from their

chloroplatinates and chloroaurates, and is particularly useful with salts of relatively unstable bases. A structural basis for the well-known dimorphism exhibited by choline chloroplatinate is suggested.

S. S. ZILVA.

Condition of creatine in amphibian voluntary muscle. W. DULIERE (*Biochem. J.*, 1929, 23, 921—925).—In many cases of resting muscles the ratio of free creatine to free orthophosphate is practically unity, but exceptions to this rule are not infrequent, the ratio reaching sometimes a value of two. The combined creatine and the labile phosphate occur in the ratio of unity. The total creatine and the total "directly determinable phosphate" (orthophosphate and labile phosphate) are present consequently in many cases in approximately equimolecular amounts. In resting, well-oxygenated muscles the free creatine may be no more than 50 mg. per 100 g. of fresh muscle.

S. S. ZILVA.

Change in the condition of equilibrium of cell components. III—IV. Proteins. T. CAHN and A. BONOT (*Ann. Physiol. Physicochim. Biol.*, 1928, 4, 781—845; *Chem. Zentr.*, 1929, i, 2890).—The structure of protein molecules is discussed. The arginine content of the protein of various organs is constant. The arginine : cystine ratio for the kidney, muscle, or brain protein is 8 : 3; for that of the lungs, intestinal mucous membrane, or intestinal muscle other values are obtained.

A. A. ELDRIDGE.

Determination of the density of small fragments of [human] organs. M. DE CRINIS (*Mikrochem.*, 1929, *Pregl Fest.*, 25—26).—An account of a method for determining the density of small fragments of brain material, using a torsion balance.

H. F. HARWOOD.

Existence of the hæmolytic complement in human cerebrospinal fluid. I. T. OKADA (*Sei-ikwai Med. J.*, 1929, 48, No. 3, 41—61).

CHEMICAL ABSTRACTS.

Amphibian poisons. O. GESSNER (*Sitzungsber. Ges. Beford. ges. Naturwiss. Marburg*, 1927, 61, 138—250; *Chem. Zentr.*, 1929, i, 2788—2789).—A discussion of toad, frog, and salamander toxins.

A. A. ELDRIDGE.

Effect of various substances of the quinine group on the enzymic functions of the organism. XII. Effect of quinine on the secretion of the gastric juice in man. I. A. SMORODINCEV, A. N. ADOVA, and I. N. PIKOUL (*Biochem. Z.*, 1929, 213, 380—390).—Quinine when orally administered reduces the hydrogen-ion concentration of the gastric juice, stimulates the secretory activity of the stomach, and inhibits the digestion of protein. It is retained in the stomach somewhat longer than is methylene-blue.

W. MCCARTNEY.

Excretory function of the stomach. II. Excretion of hexamethylenetetramine by the stomach wall. G. DE TONI (*Biochim. Terap. sperim.*, 1928, 15, 7 pp.; *Chem. Zentr.*, 1929, i, 3002).—When the amount of hexamethylenetetramine injected into rabbits exceeded 0.002 mol. per kg., the substance could be detected in the gastric juice. With children, the limits were 0.0005 mol. (intramuscular) and 0.001—0.0015 (rectal). The gastric

juice liberates formaldehyde from hexamethylenetetramine.

A. A. ELDRIDGE.

Heller's test for blood in urine. BECKER (*Med. Welt*, 1929, 3, 134—135; *Chem. Zentr.*, 1929, i, 2675).—The test is not specific.

A. A. ELDRIDGE.

Detection of minute amounts of bismuth in urine. H. K. BARRENSCHEEN and M. FREY (*Mikrochem.*, 1929, *Pregl Fest.*, 1—5).—Feigl's reaction has been applied to the detection of bismuth in urine. To 100 c.c. of the urine three drops of 3% lead acetate solution are added, followed by ammonia to strongly alkaline reaction. The precipitate is centrifuged, dissolved in concentrated nitric acid, and the solution evaporated and ignited. The residue is dissolved in hydrochloric acid, and the diluted solution tested with an alkaline solution of sodium stannite. In the presence of bismuth the resulting precipitate rapidly turns black, or in the presence of very small amounts, brownish. The reaction will detect 0.00005 mg. of bismuth in 5 c.c. of solution; small amounts of iron and copper do not interfere.

H. F. HARWOOD.

Determination of the oxidation quotient of urine. H. MÜLLER (*Biochem. Z.*, 1929, 213, 116—122).—The method previously described (*A.*, 1927, 996) for determination of the oxidation quotient of urine gives low values. An improved method consists in boiling 5 c.c. of urine with the requisite amount of potassium iodate and 20 c.c. of sulphuric acid for 3 hrs. under reflux. The mixture is then diluted, the free iodine boiled out, and the excess of iodate titrated. For chloride determinations the method of Votocek is recommended.

J. H. BIRKINSHAW.

Reduction of mercury salts by normal urine. H. PENAU and G. TANRET (*Compt. rend.*, 1929, 189, 713—715).—The method of Baudouin and Lewin gives the total reducing power of the urine. From determinations performed after previous treatment with basic lead acetate and acid mercuric nitrate respectively, conclusions are reached concerning the amounts of substances of the uric acid, creatinine, and carbohydrate groups present.

A. A. GOLDBERG.

Change of hydrogen-ion concentration in the urine at low atmospheric pressure. S. MATSUKA (*Naval J. Med.*, 1928, 17, 261—263).—Excretion of alkali is increased.

CHEMICAL ABSTRACTS.

Reaction of urine. G. KAYE (*Austral. J. Exp. Biol.*, 1929, 6, 187—214).—An alkaline tide in the urine is usually but not constantly observed 3—4 hrs. after the taking of a meal, being less marked in the case of a carbohydrate meal than in the cases of a mixed meal or of a meat meal. It is concluded that the alkaline tide is dependent on the gastric secretion of acid and not on increased respiration with subsequent loss of carbon dioxide. The clinical bearings of the observations are discussed.

W. O. KERMACK.

Reaction of the morning urine. R. S. HUBBARD (*J. Biol. Chem.*, 1929, 84, 191—197).—In individuals with normal gastric function there is usually an increase in the alkalinity of the urine after breakfast. In cases of achlorhydria there may be no change in reaction, or there may be a progressive increase in acidity from the time of waking. Finally some cases

with normal gastric function secrete an alkaline urine throughout the morning. The results are explained by the combined effect of two "alkaline tides," one due to secretion of hydrochloric acid in the stomach, and the other to respiratory elimination of carbon dioxide which has accumulated over-night.

C. R. HARRINGTON.

Variations in the morning alkaline tide of normal individuals. R. S. HUBBARD and T. M. STEELE (*J. Biol. Chem.*, 1929, **84**, 199—204).—No consistent effects on the reaction of the morning urine in normal individuals were obtained by varying the food taken at breakfast (cf. preceding abstract).

C. R. HARRINGTON.

Peptidase in diseases. R. KRAFT (*Deut. Z. Chir.*, 1928, **208**, 126—151; *Chem. Zentr.*, 1929, **i**, 2675).

Post-operative blood. K. REUTERSKIÖLD and E. ANDREWS (*Proc. Soc. Exp. Biol. Med.*, 1928, **26**, 17—18).—After surgical operations under ether anaesthesia the calcium:potassium ratio in dogs' blood was temporarily lowered.

CHEMICAL ABSTRACTS.

Iron in nutrition. X. Specificity of copper as a supplement to iron in the cure of nutritional anaemia. J. WADDELL, H. STEENBOCK, and E. B. HART (with E. VAN DONK) (*J. Biol. Chem.*, 1929, **84**, 115—130).—Zinc, chromium, germanium, nickel, cobalt, lead, antimony, tin, cadmium, mercury, and manganese were unable to relieve the nutritional anaemia of rats on a diet of whole milk and iron salts. Arsenic had a slight temporary effect, which did not approach that of copper (A., 1928, 790); in this respect, therefore, copper is a unique and necessary element in nutrition.

C. R. HARRINGTON.

Hæmoglobin percentage and the red blood-cell count in Bright's disease, myocardial insufficiency, and hypertension. B. ASHE (*Arch. Int. Med.*, 1929, **44**, 506—530).—The theoretical and practical importance of the red blood-cell count and hæmoglobin index in cases of nephritis and allied conditions is emphasised.

W. O. KERMACK.

d-Lactic acid in gastric juice [in cancer]. T. KUBO (*J. Kyoto Pref. Med. Coll.*, 1928, **2**, 261—292).—In the cancerous stomach one third of the lactic acid present is usually d-lactic acid; the presence of this acid, probably derived from the stomach wall involved, is believed to be peculiar to the disease.

CHEMICAL ABSTRACTS.

Arginine metabolism in tuberculosis and carcinoma. H. FUJIWARA (*Z. physiol. Chem.*, 1929, **185**, 1—7).—The arginase values of tuberculous guinea-pigs and carcinomatous mice were recorded over long periods. Tuberculosis causes a steady decline in the value for liver, kidneys, and total arginase, but a definite increase for muscle and spleen. In carcinoma, the arginase value of the kidneys begins to fall a few days after inoculation and decreases with the development of the tumour. The difference in value between males and females is confirmed.

J. H. BIRKINSHAW.

Biometry of calcium, inorganic phosphorus, cholesterol, and lecithin in the blood of rabbits. IV. Effects of a malignant tumour. A. R. HARNES (*J. Exp. Med.*, 1929, **50**, 109—120).—Blood-

cholesterol and serum-inorganic phosphorus increased. The ratios cholesterol:calcium and lecithin:calcium tended to increase, whilst the ratios calcium:inorganic phosphorus, lecithin:cholesterol, and lecithin:inorganic phosphorus tended to decrease.

CHEMICAL ABSTRACTS.

Role of calcium in senile cataract. D. R. ADAMS (*Biochem. J.*, 1928, **23**, 902—912).—In patients with senile cataract the serum-calcium is appreciably higher than normal. There is no age-variation in the serum-calcium either of normal subjects or of those with senile cataract. Calcium salts acting on fresh ox lenses do not cause opacity except in unphysiological concentrations, nor do they act as "sensitisers" in the production of opacity by ultra-violet radiation. Dialysed solutions of the lens proteins, α - and β -crystallin, exhibit a certain sensitivity to solutions of calcium salts. The experimental production of a persistently raised blood-calcium in rabbits does not cause cataract, nor accelerate the development of naphthalene cataract, although it causes a corresponding rise of calcium in the aqueous humour. There is no age-variation in the calcium content of normal or of cataractous human lenses. The calcium content of cataractous lenses is much greater than that of normal lenses, whilst the potassium content is considerably less. Individual cataract lenses show a wide variation in calcium content which may be attributed to an erratic local deposition of calcium in the lens. There is an increase of calcium in the blood of patients with senile cataract and an abnormal deposition of calcium in the lens.

S. S. ZILVA.

[Non-]occurrence of cystine in sweat in cystinuria. H. B. LEWIS (*Proc. Soc. Exp. Biol. Med.*, 1928, **26**, 69—70).

Role of enzyme action in the formation of dental calculi. K. T. ADAMSON (*Austral. J. Exp. Biol.*, 1929, **6**, 215—227).—Extracts of the fresh gum tissue of dog or man exhibit a definite phosphatase action, but no pyrophosphatase action. When an extract is incubated with normal human saliva or blood-serum an increase occurs in the inorganic phosphate, showing that these fluids contain a substrate, presumably a phosphoric ester, on which the enzyme acts. Normal saliva from which the protein had been removed yielded a solution free from inorganic phosphate from which inorganic phosphate was liberated by hydrolysis with acid. The reducing power of this solution was approximately doubled by treatment with dilute acid and the reducing power of normal human saliva was also approximately doubled when treated in the same way. The deposits of calcium phosphate which form the main portion of dental calculi are probably produced as the result of an increase of the phosphate ions in the saliva in the mouth produced by the action of the enzyme, liberated from the tissues of the gum, on the organic phosphate occurring in the saliva.

W. O. KERMACK.

Relation of calcium in the saliva to dental caries. K. HORTON, J. MARRACK, and I. PRICE (*Biochem. J.*, 1929, **23**, 1075—1078).—Dental caries is associated with a reduction of the concentration of

calcium in saliva. This reduction appears to be secondary to the caries. S. S. ZILVA.

Metabolism in diabetics. H. GLATZEL (Arch. exp. Path. Pharm., 1929, **145**, 154—170).—20-Hr. respiratory experiments were conducted on diabetics of moderate severity on a constant and moderate carbohydrate and protein diet. Insulin causes an increased carbohydrate metabolism at the expense of the fat metabolism. The basal metabolism of diabetics of light or moderate severity on a carbohydrate and protein diet is comparable with that obtained for healthy subjects. C. C. N. VASS.

Day- and night-fluctuations of the blood-sugar in non-diabetics, diabetics, and hypertonics. J. JACOBI and F. BAUMANN (Arch. exp. Path. Pharm., 1929, **145**, 24—34).—The regular fluctuations of the blood-sugar curve occur throughout the night as well as during the day and observe a close correspondence in non-diabetics, diabetics with and without insulin treatment, and hypertonics. In general minimum values are shown in the early part of the evening and in the early hours of the morning, whilst maxima are recorded towards midnight and 8 a.m. In non-diabetics, administration of opium does not modify the general character of the blood-sugar curve. C. C. N. VASS.

Influence of insulin on diabetic lipæmia. I. DONOMAE (Folia endocrinol. japon., 1928, **4**, 54).—Treatment with insulin reduced the lipid content of the serum; the effect was greatest in the fatty acids and slight in the lecithin. CHEMICAL ABSTRACTS.

Treatment of diabetes with vitamin-B. C. A. MILLS (Amer. J. Med. Sci., 1928, **175**, 376).—Cold aqueous ethyl-alcoholic hydrochloric acid extracts of various plants were neutralised and filtered from protein. The extracts depressed the excretion of sugar. CHEMICAL ABSTRACTS.

Carbohydrate metabolism in eclampsia. H. J. STANDER and E. P. HARRISON, jun. (Amer. J. Obstet. Gynecol., 1929, **17**, 17—27).—Eclampsia is generally associated with a tendency towards hyperglycæmia. CHEMICAL ABSTRACTS.

Fluctuations in blood-sugar during eclampsia. III. Relationship between plasma-sugar and corpuscular sugar variations. P. TITUS and E. W. WILLETTS (Amer. J. Obstet. Gynecol., 1929, **17**, 27—35).—The plasma-sugar is the most mobile and readily available. Convulsions occur when the corpuscles are deprived of their sugar. CHEMICAL ABSTRACTS.

Intravenous injection of phosphates. A. BOLLIGER (Med. J. Austral., 1929, **1**, 650—655).—Injection of sodium phosphate solutions into fasting dogs caused a brief increase in plasma-phosphate. With long-continued injections the phosphorus elimination gradually decreased. The behaviour in nephritis was studied. CHEMICAL ABSTRACTS.

Renal insufficiency associated with Bence-Jones proteinuria. E. G. BANNICK and C. H. GREENE (Arch. Int. Med., 1929, **44**, 486—501).—Bence-Jones protein is frequently found in the urine of patients suffering from a type of nephritis characterised by marked proteinuria, secondary anæmia, nitrogen retention, and delayed excretion of

phenolsulphonephthalein, little or no œdema and little or no hamaturia, hypertension, or retinitis. W. O. KERMACK.

Bence-Jones proteins. L. F. HEWITT (Biochem. J., 1929, **23**, 1147—1152).—The examination of Bence-Jones proteins obtained from five cases of myelomatosis showed that the proteins from different patients differ in properties. Not all are redissolved in boiling salt solutions. In the presence of alcohol both Bence-Jones proteins and serum-proteins are dissolved when the coagulated suspensions are boiled. S. S. ZILVA.

Biochemistry of experimental rabies in rabbits. D. ZUVERKALOW, I. GOLDBERG, and A. SILBERSTEIN (Biochem. Z., 1929, **213**, 109—115).—Injection of rabbits with "virus fixe" (rabies) lowers the total nitrogen and phosphorus of the blood; calcium and potassium are also diminished, the residual nitrogen and inorganic phosphorus are almost unchanged, and hyperglycæmia is often observed. J. H. BIRKINSHAW.

Rickets. E. FREUDENBERG (Sitzungsber. Ges. Beford. ges. Naturwiss. Marburg, 1927, **61**, 83—96; Chem. Zentr., 1929, **i**, 2791).—Rickets is usually accompanied by hypophosphatæmia. In normal infants and in rickets glycolysis to the extent of 17—48% and 0—21%, respectively, of the sugar administered was observed. A similar inhibition of glycolysis was observed with rachitic rats. Hexosephosphate is readily glycolysed by rachitic blood. Glycolysis in the tissue of rachitic animals is also observed. A. A. ELDRIDGE.

Blood-sugar regulation in idiopathic steatorrhœa. II. Origin of the low blood-sugar curve. T. E. H. THAYSEN (Arch. Int. Med., 1929, **44**, 477—485).—The low blood-sugar curve in idiopathic steatorrhœa (fatty diarrhœa) is not due to defective absorption or to destruction of dextrose in the intestine. W. O. KERMACK.

Isoelectric point in the blood. P. H. ROSSIER (Ann. Med., 1928, **23**, 248—380; Chem. Zentr., 1929, **i**, 2656).—A discussion. A. A. ELDRIDGE.

Changes in the isoelectric point of the serum in syphilis. P. H. ROSSIER and R. LUCHSINGER (Arch. Phys. biol., 1928, **6**, 310—315; Chem. Zentr., 1929, **i**, 2656).—In recent, but not in long-established, syphilis the isoelectric point of the serum is raised. A. A. ELDRIDGE.

Colloidal properties of Wassermann antigens. II. W. O. KERMACK and W. T. SPRAGG (Biochem. J., 1929, **23**, 959—974; cf. Kermack and MacCollum, A., 1925, **i**, 197).—The observations made on the effect of calcium chloride on a Wassermann antigen hold true for salts of other bivalent cations, whilst the salts of univalent cations with the exception of hydrogen ion, which acts like bivalent cations, do not cause complete precipitation at any concentration. Experiments on the action of mixtures of two of the four salts, lithium chloride, sodium chloride, magnesium chloride, and calcium chloride, on the precipitation of the turbid antigen showed that the addition of a sufficient quantity of another salt, whether of a univalent or bivalent cation, to a salt (with a bivalent cation) present in concentration sufficient to cause precipit-

ation if it were alone, tends to prevent precipitation. Hydrogen chloride behaves in this respect like a salt with a bivalent cation. The protective effect of the antigen on gold sol is excited by the presence of salts, but especially by salts with bivalent cations or hydrogen ions much more than with salts of the other univalent cations. The clear antigen exhibits rather greater protective power than the turbid antigen. The protective power of the antigen has also been determined, using cholesterol, gum mastic, or gum benzoin sol; it is most marked in the first and least in the last. Sols of commercial lecithin possess only in small degree the peculiar properties of the Wassermann antigens. Standard methods of preparation of turbid and clear antigens are described.

S. S. ZILVA.

Colloidal properties of serum. C. I. B. VOGEL (Biochem. J., 1929, 23, 1137—1146).—In syphilitic serum a zone of precipitation exists which is not present in normal serum. An abnormal substance is present in syphilitic serum which possesses the power of conferring a positive charge on the serum-proteins and so rendering them unstable in the presence of a negatively-charged sol such as gum benzoin. Syphilitic serum loses this property after being heated at 55° for 90, but not for 30 min., whilst normal serum undergoes little change after this treatment. The abnormal substance is present in the serum-euglobulin fraction of syphilitic serum when separated from the other serum fractions. The addition of small quantities of a protamine to normal serum causes the latter to simulate syphilitic serum in its precipitating and complement-fixing powers. The conferred changes disappear on heating. Normal serum and antiserum possess a similar precipitating power on gum benzoin sol. An almost similar degree of agglutinating power is shown by normal serum on an antigen of *B. abortus*. The marked agglutinating power of antiserum on a suspension of *B. abortus* is greatly diminished by subjecting the antiserum to preliminary heating. The substance responsible for the agglutinating power is associated with the serum-euglobulin fraction.

S. S. ZILVA.

Distribution of gold in the organs of healthy and tuberculous rabbits following administration of gold preparations. II. Tuberculous rabbits. K. HENIUS and G. WEILER (Biochem. Z., 1929, 214, 204—215).—The distribution is indicated in a series of tables. The preparation "lopion" is stored chiefly in the liver, whereas "solganol" and "sanocrysin" are found chiefly in the kidney. The total storage is greatest with "lopion" (67% of the amount injected) and least with "solganol" (15%). With "lopion" the storage is the same for healthy and tuberculous animals. With "solganol," 13 mg. of gold per 100 g. of tissue are recovered in the lungs of tuberculous and only 2.5 mg. per 100 g. in the lungs of healthy animals (cf. A., 1928, 1156).

P. W. CLUTTERBUCK.

Blood-sugar and amino-acid-nitrogen in lactation in women; lipid and inorganic phosphorus. V. J. HARDING and C. E. DOWNS (J. Biol. Chem., 1929, 84, 335—344).—Normal values were found for the total sugar, non-fermentable sugar, and

amino-acid-nitrogen in the blood of lactating women. The inorganic phosphorus of the blood averaged 3.9 mg. per 100 c.c. and the lipid phosphorus 10.8 mg. per 100 c.c. during lactation.

C. R. HARRINGTON.

Carbohydrate metabolism of muscular tissue. I. F. USUELLI (Arch. Fisiol., 1928, 26, 14 pp.; Chem. Zentr., 1929, i, 3004).—During pregnancy the lactacidogen content of the uterine musculature (of rabbits) increases; the total carbohydrate and sometimes also the glycogen are increased during pregnancy.

A. A. ELDRIDGE.

Carbohydrate exchange and degradation of the dextrose molecule. II. Lactic acid. E. SCHNEIDER and E. WIDMANN (Klin. Woch., 1929, 8, 466—448; Chem. Zentr., 1929, i, 2792).—A dihydroxyacetone-lactic acid interconversion was not detected. In resting tissue the venous lactic acid is higher than the arterial. Methylglyoxal may suffer conversion into dihydroxyacetone.

A. A. ELDRIDGE.

Appearance of glycogen in the mucous membrane of the alimentary canal. XVI, XVII. K. YOSHIDA (J. Study Micro-organisms, 1928, 22, 2385—2402, 2403—2424).—Injection of starch, insulin [inulin?], or glycogen into a rabbit seldom causes formation of glycogen in the alimentary mucous membrane. The liver-glycogen was only slightly increased by the injection of glycogen. The appearance of glycogen is attributed to a polymerising action of the superficial intestinal cells on the excessive accumulation of blood-sugar.

CHEMICAL ABSTRACTS.

Influence of unphysiological nutrition on the composition of the organs and on metabolism. II. Glycogen-forming diet. P. JUNKERSDORF and K. WITSCH (Arch. exp. Path. Pharm., 1929, 145, 171—187).—Fasting dogs were fed on a diet of flesh, potato, rice, and raw sugar for periods up to 30 days. The increase in weight of the dogs, and the weights of the liver and heart as percentages of the total weight were recorded. The water, glycogen, and fat contents of the liver, muscle, and heart were determined. The liver increased to a maximum weight after 8 days' feeding and gradually returned to normal; its water content primarily increased and then decreased to a value below that normally observed. The glycogen content was always above normal, whereas with one exception the fat content varied only slightly from the normal. The water content of the muscle reached a minimum after 20 days' feeding, whilst its glycogen content was always above normal. In the heart, the weight and the water and glycogen contents fell below normal and the fat content increased. Blood-sugar determinations were made every fifth day. Up to the tenth day a fall in the blood-sugar was observed; thereafter a gradual rise was recorded, in good agreement with the deviation of the liver during the experiment.

C. C. N. VASS.

Glycogen metabolism of the snail. M. OKADA (Okayama J. Med., 1928, 40, 1402—1407).—On resumption of activity after hibernation the glycogen content was 0.82—2.39 (average 1.63), at maximum activity 0.35—0.81 (0.61), and on hibernation 3.52—7.61 (4.63) per 100 g.

CHEMICAL ABSTRACTS.

Possible significance of *d*-xyloketose (urinary pentose) in normal metabolism. I. GREENWALD (Proc. Soc. Exp. Biol. Med., 1929, 26, 321—322).—*d*-Xyloketose *p*-bromophenylhydrazone has m. p. 127—128°, $[\alpha]_D^{25}$ (1% in alcohol) 1.87°→2.43°; the free ketose has $[\alpha]_D^{25}$ 34.8°. Injection of the pentose (3.05 g. during 2 hrs.) into a dog increased the urinary sugar by 6% of the quantity injected; on further injection, 60% appeared in the urine.

CHEMICAL ABSTRACTS.

Increase in blood-sugar following ingestion of glycerol. J. FERBER and S. RABINOWITSCH (Amer. J. Med. Sci., 1929, 177, 827—832).—Glycerol ingested in hunger causes hyperglycæmia in man. In diabetes glycerol may produce glycosuria.

CHEMICAL ABSTRACTS.

Lactic acid content of the brain under differing conditions of respiratory want. R. COBET (Arch. exp. Path. Pharm., 1929, 145, 140—145).—The cerebrum of living rabbits contains less than 10 mg. of lactic acid per 100 g., but on extirpation the amount increases rapidly and reaches a maximum value of 120 mg. per 100 g. The amount of lactic acid in the cerebrum remains uninfluenced in a pure carbon dioxide hyperpnoea. In anoxæmia, oxygen deficit causes a rapid increase of lactic acid in the living brain which acts on the respiratory centre and is reduced to its normal value as soon as normal respiration is established.

C. C. N. VASS.

Gas exchanges of nerves during and after anaerobiosis. F. O. SCHMITT (Biochem. Z., 1929, 213, 443—445; cf. Gerard, A., 1928, 910).—The oxygen deficit in frog's nerves kept in nitrogen increases with the time of asphyxiation up to 15 hrs. and the deficit produced by stimulation is greater than that in resting nerves. Paralysis of the conducting mechanism of the nerves with potassium chloride has no effect on the oxygen deficit. The respiratory quotient of the nerves in the hour following re-admission of oxygen, calculated for the extra oxygen consumed, is not much above zero. The rate of production of carbon dioxide by nerves in nitrogen falls rapidly during the first 6 hrs., but remains at about 1.5 c.c. per g. after 15 hrs. Anaerobic stimulation does not cause production of extra carbon dioxide.

W. MCCARTNEY.

Metabolism in muscular work on a pure fat diet. V. HATTINGBERG (Arch. exp. Path. Pharm., 1929, 145, 72—87).—The energy balance sheet on a pure fat diet has been computed wherein almost one half of the energy consumed is derived from the fatty acids. The various mechanisms by which this might be accomplished are discussed, preference being given to the view that the fatty acids are first converted into sugar-like substances.

C. C. N. VASS.

Influence of ingestion of trihexoin on body-fat of the white rat. H. C. ECKSTEIN (J. Biol. Chem., 1929, 84, 353—357).—Feeding with trihexoin as the sole fat of the diet caused the deposition, in white rats, of body-fat of a more saturated character than that found in the same animal on a fat-free diet. On the other hand, an increase in the proportion of fatty acids of low mol. wt. could not be detected in the newly-deposited fat.

C. R. HARRINGTON.

Serum-cholesterol, lecithin-phosphorus, and fatty acids of pigeons after feeding with ox tissues. G. L. MÜLLER (J. Biol. Chem., 1929, 84, 345—352).—Exclusive feeding with various ox tissues following a fasting period caused an increase in the cholesterol of the blood-serum of pigeons, the lecithin-phosphorus and fatty acids not being affected. The greatest effect was obtained with liver and kidney and little with spleen; brain did not constitute a complete food and in this case the cholesterol of the blood was diminished. The stimulating effect of the various tissues on formation of red blood-corpuscles and hæmoglobin was in inverse proportion to the effect in increasing the blood-cholesterol.

C. R. HARRINGTON.

Connexion between oxidative and anoxidative deamination and the role of aminopurines in intermediate tissue metabolism. J. K. PARNAS (Klin. Woch., 1929, 8, 506—507; Chem. Zentr., 1929, i, 2662).—Under physiological conditions the ammonia irreversibly produced in frog's muscle arises finally from oxidative deamination, the intermediately deaminated adenine nucleotide being continually reaminated.

A. A. ELDRIDGE.

Origin of creatine or creatinine in the animal organism. Purine metabolism. E. ABDERHALDEN and S. BUADZE (Med. Klinik, 1929, 25, 11—12; Chem. Zentr., 1929, i, 2897).—In presence of arginine, choline, and arginase, formation of creatine or creatinine results. After addition of adenine, guanine, and nucleic acid muscular tissue contains an increased amount of creatine or creatinine. Histidine, hydantoin, and *N*-methylhydantoin, but not uric acid or uracil, increase the amount of creatine in minced muscle.

A. A. ELDRIDGE.

Diffusion experiments with the phosphorus-containing compounds of muscle. P. ROTHSCHILD (Biochem. Z., 1929, 213, 251—261).—The velocities of dialysis of inorganic phosphate and of various phosphorus compounds of muscle extracts have been measured. Isolated compounds as well as natural and artificial mixtures were used. From the results obtained and from determinations of diffusion coefficients it is concluded that the preformed inorganic phosphate, the creatine-phosphoric acid, and the adenylypyrophosphoric acid of the extracts do not form parts of protein-like complexes.

W. MCCARTNEY.

Decomposition of creatine-phosphoric acid in relation to the activity of muscle. III. Extent of decomposition and rate of stimulation. D. NACHMANSOHN (Biochem. Z., 1929, 213, 262—300).—The influence of temperature, fatigue, nerve degeneration, and of curarisation on the decomposition of creatine-phosphoric acid has been studied and it has been shown that the extent of the decomposition runs parallel with the rate of excitation. The increase in the extent of decomposition caused by veratrine was exactly proportional to that rate; strychnine did not affect the extent of decomposition; curare, sparteine, and the ammonium bases greatly reduced it. Of the substances which caused reduction the most powerful was trimethyloctylammonium iodide. Long times of action and large doses greatly reduced the extent of the decomposition.

W. MCCARTNEY.

Intermediate protein metabolism. I, II. F. SILBERSTEIN, F. RAPPAPORT, and M. WACHSTEIN (Biochem. Z., 1929, 213, 312—339, 340—354).—I. Analyses have been made of samples of blood taken at intervals during 24 hrs. from dogs to which meat or peptone was orally administered after a long preliminary period of feeding with food either rich or poor in protein, the total non-protein-, urea-, amino-acid-, and polypeptide-nitrogen, and the uric acid and total creatine-nitrogen being determined. The influence of the food consumed during the preliminary period and of the meat or peptone administered on the changes which take place in the amounts of these forms of nitrogen has been followed. The blood contained nitrogenous substances ("undetermined nitrogen") of unknown nature.

II. The pancreas was removed from dogs used in the first series of experiments and these were then continued as before with necessary changes.

W. MCCARTNEY.

Influence of carbohydrate consumption on the protein metabolism at a high-temperature environment. S. HAMADA and M. EMA (Nat. Hyg., 1928, 5, 718—743).—Experiments on a dog showed that feeding with carbohydrate inhibits the decomposition of protein at ordinary temperatures and may at high temperatures tend to reduce the increase of protein decomposition. CHEMICAL ABSTRACTS.

Effect of an exclusive meat diet on chemical constituents of the blood. C. W. LIEB and E. TOLSTOI (Proc. Soc. Exp. Biol. Med., 1929, 26, 324—325).—A slight increase in blood-uric acid and temporary lipæmia were observed in man.

CHEMICAL ABSTRACTS.

Production of œdema and serum-protein deficiency in white rats by low-protein diets. R. A. FRISCH, L. B. MENDEL, and J. P. PETERS (J. Biol. Chem., 1928, 84, 167—177).—Young white rats were kept on diets deficient in protein. The serum-proteins were reduced in all cases, and in a large proportion of the animals œdema developed.

C. R. HARRINGTON.

Effect of indole derivatives in a diet deficient in tryptophan. R. W. JACKSON (J. Biol. Chem., 1929, 84, 1—21).—The effect was investigated of adding to the tryptophan-deficient diet of rats the following substances: hypaphorine, β -indolyl- α -benzamidoacrylic acid, γ -indolylbutyric acid (by the Fischer synthesis from ethyl hydrogen α -ketopimelate phenylhydrazones), m. p. 123—124° (corr.), β -indolylpropionic acid, indolylethylamine, indolylethyl alcohol, β -indolyl- α -carbamidopropionic acid, m. p. 200° (corr.), indolylpyruvic acid, and the condensation product of formaldehyde and tryptophan described by Homer (A., 1913, ii, 451). The only one of these compounds which was able to replace tryptophan was indolylpyruvic acid. After a period of stunting extending over 232 days as the result of deficiency of tryptophan, a rat resumed normal growth when tryptophan was restored to the diet.

C. R. HARRINGTON.

Calcium and phosphorus metabolism in dairy cows. III. Adequate ration for high-producing cows and the effect of exercise on calcium, phosphorus, and nitrogen balances. W. A.

TURNER and A. M. HARTMAN (J. Nutrition, 1929, 1, 445—454).—Exercise affected the nitrogen metabolism, but that of calcium and phosphorus only slightly. CHEMICAL ABSTRACTS.

Magnesium sulphate as a factor in retention of calcium and phosphorus in cattle. L. S. PALMER, C. H. ECKLES, and D. J. SCHUTTL (Proc. Soc. Exp. Biol. Med., 1928, 26, 58—62).—Water containing magnesium sulphate, when consumed by cattle, may cause important losses of calcium when the phosphorus content of the ration is low. CHEMICAL ABSTRACTS.

Results of ingestion of certain calcium salts and of lactose. C. S. ROBINSON, C. F. HUFFMAN, and M. F. MASON (J. Biol. Chem., 1929, 84, 257—267).—In feeding experiments with normal calves, ingestion of calcium chloride raised the blood-calcium, but caused a large loss of phosphorus from the body; about 10% of the calcium administered was retained. Administration of calcium lactate with lactose raised the calcium and reduced the inorganic phosphorus of the blood-serum; 50% of the calcium was retained, and there was also improved retention of food-phosphorus. Ingestion of bone meal resulted in increase in the inorganic phosphorus of the blood and in retention of 20% of the calcium and phosphorus, these amounts being doubled by simultaneous administration of lactose. Lactose alone reduced the calcium and increased the inorganic phosphorus of the blood.

C. R. HARRINGTON.

Iodine as biogenic element. XXI. Feeding experiment with iodine on milch-cows. W. SCHROPP. XXII. Feeding experiment with increasing doses of iodine on milch-cows. K. SCHARRER and W. SCHROPP. XXIII. Chemistry of animal iodine metabolism. K. SCHARRER and J. SCHWAIBOLD (Biochem. Z., 1929, 213, 1—17, 18—31, 32—39; cf. this vol., 715).—XXI. The addition of 100 mg. of iodine as potassium iodide to the daily ration of milch-cows increased the milk yield by 4.53% over a period of 99 days and was in no way detrimental to the health of the animals.

XXII. Higher doses of iodine, 200, 400, and 600 mg. of iodine *per diem*, did not further increase the milk yield, but had a definite effect in prolonging the lactation period. The absolute amount of milk-fat was increased by iodine; the percentage was unchanged except with the highest dose, when there was a small diminution. The body temperature and general health were unaffected.

XXIII. A daily dose of 100 mg. of iodine increased the iodine content of the milk about five times, and higher doses in proportion. The amount excreted in the urine was also proportional to the dose. The iodine content of various milk products was examined; the greater part of the iodine was found in the skim-milk, buttermilk, and whey, but little in the butter. Iodine feeding had no effect on the p_H of milk.

J. H. BIRKINSHAW.

Significance of the "internal cycle" for crystalloids, especially the iodine ion. W. LIPSCHITZ (Klin. Woch., 1929, 8, 116—117; Chem. Zentr., 1929, i, 2075).—Iodide injected into dogs remains ionised for a considerable time and forms a

"mobile deposit." Buchholz' method is suitable for the determination of small quantities of iodide in gastric juice. Experiments with salicylate, hydroferrocyanic acid, lactic acid, and dextrose are described. The method of excretion of iodine is examined.

A. A. ELDRIDGE.

Transport and transformation of organically bound plant-iodine in the animal body. G. PFEIFFER and H. COURTH (Biochem. Z., 1929, 213, 74—85).—Yellow carrots and radishes are able to store up large amounts of iodine (500—700 times normal), of which a large proportion is organically bound. The normal iodine content of the thyroid gland of dogs is very low, but it can be greatly increased by feeding plant-iodine. The assimilation and deposition of organic plant-iodine by dogs is very great.

J. H. BIRKINSHAW.

Iodine content of the thyroid and ovary of the fowl during the growth, laying, and moulting periods. E. M. CRUCKSHANK (Biochem. J., 1929, 23, 1044—1049).—The thyroid weight and total thyroid iodine increase in proportion to increase in body-weight in the growing birds. The average thyroid weight from mid-March to mid-July is about 35% less than from January to March. The seasonal variation in both percentage and total iodine tends to follow the seasonal variation in thyroid weight. The average weight of fresh gland and the thyroid weight per kg. body-weight is low compared with the values obtained for the same breed in the goitre belt of the United States of America. The weight of thyroid per kg. body-weight, the percentage of iodine, and the total thyroid iodine per kg. body-weight are higher than in mammals. The ovary contains only a trace of iodine, yolk of egg contains an appreciable amount. The histological appearance of the thyroid suggests a state of relatively great activity in the immature bird and of relative inactivity in the laying and moulting birds.

S. S. ZILVA.

Metabolism of iron. IV. (Supplement; see A., 1928, 542.) Iron in urine. V. Iron requirement of man. W. LINTZEL (Z. Biol., 1929, 89, 342—349, 350—352).—IV. Under normal conditions the kidneys do not excrete iron, as no trace of that metal could be found in the urine of three normal men by the method of Henriques and Roland (this vol., 93). The sensitiveness of the method is such that 0.02 mg. of iron per litre gives a positive result.

V. In normal adult men the daily iron requirement is less than 0.9 mg. per day, any excess being excreted.

W. O. KERNACK.

"Active" iron. H. PETOW and H. KOSTERLITZ [in part with PROBST] (Klin. Woch., 1929, 8, 600—601; Chem. Zentr., 1929, i, 2793).—An examination of the benzidine activity as differentiating "active" iron compounds. All the iron compounds examined, except ferric ions, form under favourable conditions a larger amount of benzidine-blue than corresponds with their molecular concentration; the amount depends on the p_{H_2} , of which the optimal value is 5.0. The reaction with complex salts and with hæmoglobin, but not with ferrous salts, is dependent on the hydrogen peroxide concentration. Mineral waters containing iron behave like ionised ferrous salts.

Complex salts behave qualitatively like hæmoglobin. Experiments on therapeutic activity were performed.

A. A. ELDRIDGE.

Micro-determination of arsenic in cadavers. P. SZENDRO and G. FLEISCHER (Mikrochem., 1929, Pregl Fest., 323—328).—The usual methods for determining arsenic in human organs are tedious and lengthy. Wintersteiner's method permits a satisfactory determination in 1½ hrs. of amounts of arsenic down to 0.1 mg., employing only 2 g. of material. The organic matter is destroyed with sulphuric and nitric acids, and the iron invariably present is determined colorimetrically in a portion of the solution. The remainder is treated with hydrochloric acid and potassium iodide, and after 10 min. the liberated iodine is titrated with 0.01N-thiosulphate. A correction for the amount of iron found is subtracted from the titration value. Copper if present must be removed by Pregl's micro-method before determining the arsenic.

H. F. HARWOOD.

Metabolic activity of arsenic. A. BICKEL (Med. Welt, 1929, 3, 5—6; Chem. Zentr., 1929, i, 2661).—A discussion.

A. A. ELDRIDGE.

Passage of arsenic through the placenta. E. ZIEMKE (Deut. Z. ges. gerichtl. Med., 1929, 13, 217—225; Chem. Zentr., 1929, i, 2794).—Arsenic administered to the mother is largely withheld from the foetus by the placenta.

A. A. ELDRIDGE.

Effect of phosphorus on nitrogenous substances in the bile. Effect on amino-acids. K. SUGIY (Okayama J. Med., 1928, 40, 1481—1506, 2202—2213).—When yellow phosphorus is administered to a dog with gall-bladder fistula the coagulable protein of the bile begins to increase in 4 days and becomes normal in 3—4 weeks. Urea begins to increase in 4 days and is normal after 30 days. The increase in urea, ammonia, and coagulable protein following administration of phosphorus diminishes on administration of dextrose. The increase when adrenaline is first given is marked; when insulin is first injected there is a decrease. Phosphorus increases the amino-acid-nitrogen of the bile unless dextrose, insulin, or adrenaline is first administered.

CHEMICAL ABSTRACTS.

Distribution of lead in the body after absorption. R. W. TANNAHILL (Med. J. Austral., 1929, I, 216—217).—The lead is chiefly stored in the bones; some is excreted in the urine and faeces.

CHEMICAL ABSTRACTS.

Copper in the organism. F. B. FLINN and J. M. INOUE (J. Biol. Chem., 1929, 84, 101—114).—Administration of small amounts of copper over long periods to rats leads to deposition of the metal for the most part in the liver, this being the organ which, in normal animals of other species, shows the highest copper content. Neither copper nor lead salts give insoluble phosphates when their solutions are brought into contact with calcined bones. One hr. after injection of copper salts into the intestine the copper content of the blood-plasma is about twice that of the corpuscles. No hæmolysis or formation of methæmoglobin was observed as the result of an increased copper concentration in the blood; on the

contrary, the oxygen-carrying capacity of the blood was increased. A definite improvement in growth was observed in guinea-pigs which received small amounts of copper in the food.

C. R. HARINGTON.

Chronic mercury poisoning. A. HERTZ (Klin. Woch., 1929, 8, 541—544; Chem. Zentr., 1929, i, 2667).—Mercury ingested orally appears to be excreted chiefly in the faeces, whilst that inhaled is chiefly excreted in the urine. Traces of mercury were commonly detected in the faeces of persons not exposed to mercury. The danger of poisoning by dental amalgams etc. is not as great as Stock supposes.

A. A. ELDRIDGE.

Distribution of mercury in the various organs in cases of mercurial poisoning. J. BUCHTALA (Mikrochem., 1929, Pregl Fest., 20—24).—An examination of the various organs in a case of poisoning by mercuric chloride showed the largest amount (0.1616 g.) in the stomach, and the least (0.00039 g.) in the brain. The mercury is best determined electrolytically, using a carbon anode and gold or platinum cathode, the deposit being subsequently identified by conversion into red mercuric iodide.

H. F. HARWOOD.

Pharmacology of rare-earth metals. III. Samarium. H. STEIDLE and H. DÜRR (Arch. exp. Path. Pharm., 1929, 145, 19—23).—The action of solutions of samarium nitrate on proteins, yeast fermentation, isolated frog's heart and preparations, ox-blood, muscle, and mucous membrane, and their toxicity towards certain animal species are recorded.

C. C. N. VASS.

Reactivity and physiological action. K. KINDLER (Arch. Pharm., 1929, 267, 541—555).—A lecture.

H. BURTON.

Factors influencing bone formation in the albino rat. I. Effect of guanidine intoxication produced by the successive injection of sub-lethal doses of guanidine salts. II. Effect of injection of parathyroid extract. C. M. BURNS (Biochem. J., 1927, 23, 840—852, 853—859).—I. Injections of guanidine cause no deposition of calcium in faultily-calcified bones nor decalcification of formed bone. They may retard ossification very slightly in growing animals by limiting the amount of available calcium, but this influence is not detected where the growth of the injected animals is markedly retarded. No important interrelation between mild guanidine poisoning and bone-formation was detected.

II. The injection of the extract did not produce any retardation either in body or in bone growth, nor was the deposition of calcium in the bones influenced by it. Unlike the females, the male animals which received the parathyroid extract showed unusually large deposits of fat.

S. S. ZILVA.

Effect of continued ingestion of mineral acid on growth of body and bone and on the composition of bone and soft tissues. C. M. BURNS (Biochem. J., 1929, 23, 860—867).—In rabbits receiving acid daily for periods varying from 17 to 35 days there was a reduction in the base content of the muscles, but not of the viscera. There was also a marked reduction in the percentage of ash of the

bones, but not in the fat content. Growth was retarded. In rats receiving daily doses of acid for a period of more than 9 weeks there was no appreciable reduction in the fat content of the bones nor was the ash content changed. Growth was retarded and considerable loss of weight occurred when the dose was increased. The base content of the soft tissues was increased slightly where death was preceded by marked loss in weight.

S. S. ZILVA.

Ethyl alcohol in fowls after exposure to alcohol vapour. T. M. CARPENTER (J. Pharm. Exp. Ther., 1929, 37, 217—259).—The concentration of alcohol has been determined in the blood and various organs of hens exposed for 2—29 hrs. to an atmosphere containing ethyl alcohol vapour. The concentration of alcohol in the blood is usually higher than in any of the organs and is exceeded only occasionally by that in brain and the immature eggs. With low concentrations in the blood very little is found in the liver, but with higher concentrations in the blood the concentration in the liver approximates to that in heart, lungs, kidney, and spleen. The lowest concentration of alcohol was found in the fat.

W. O. KERMACK.

Absorption, distribution, and excretion of carbon tetrachloride in dogs under various conditions. B. H. ROBBINS (J. Pharm. Exp. Ther., 1929, 37, 203—216).—Carbon tetrachloride is absorbed from the intestine of the dog, less rapidly from the colon, and not from the stomach, the absorbed compound being almost quantitatively excreted through the lungs. The rate of absorption is increased when fat or alcohol is simultaneously administered. After absorption of carbon tetrachloride from the intestinal tract it is found in comparatively high concentrations in the bone marrow, the organs next richest in the compound being the liver, pancreas, and brain.

W. O. KERMACK.

Blood changes caused by histamine. G. DE TONI (Boll. Soc. Ital. Biol. sper., 1928, 3, 87—92; Chem. Zentr., 1929, i, 3002).—Injection of histamine usually increases the blood-sugar; in young children the water is increased, but in older children diminished.

A. A. ELDRIDGE.

Relationship of heterocyclic compounds to the autonomic nervous system. R. HUNT and R. R. RENSHAW (J. Pharm. Exp. Ther., 1929, 37, 177—191).—A large number of heterocyclic compounds, including derivatives of quinoline, pyridine, piperidine, and pyrrolidine, have been investigated in respect of their pharmacological actions on the autonomic nervous system of the cat. In general, most of the compounds investigated were not highly active, but β -phenoxyethyl-*N*-methylpyrrolidinium iodide had a marked nicotine-like action.

W. O. KERMACK.

[Pharmacological action of] ethers of formocholine and choline. R. HUNT and R. R. RENSHAW (J. Pharm. Exp. Ther., 1929, 37, 193—202).—The pharmacological action of formocholine chloride (hydroxymethyltrimethylammonium chloride) and of various ethers and closely related compounds derived therefrom has been investigated on the autonomic nervous system of the cat. The *n*- and *iso*-butyl ethers as well as the allyl ether have a marked muscar-

inc and also a marked nicotine action. The introduction into the benzene ring of the phenyl ether of choline of a hydroxy-, methoxy-, or benzyloxy-group diminished the nicotine-like action of the compound, whilst an acetamido-group completely abolished it. Compounds of this type possess no muscarine-like action.

W. O. KERMAK.

Carbamide synthesis in fatty livers. K. IMHAUSER (Arch. exp. Path. Pharm., 1929, 145, 120—130).—Fasting dogs treated *per os* with infusions of *Amanita phalloides* (i.e., poisoning with amanitatoxin; cf. Abel and Ford, Heffter's "Handb. exp. Pharmacol.," 1924, 2, 1712) show the typical poisoning symptoms. A steep fall in the blood-sugar occurs, followed by convulsions which can be temporarily relieved by injection of dextrose. Artificially perfused livers extirpated from these animals show no variation from normal livers in carbamide synthesis.

C. C. N. VASS.

Extraction of strychnine in forensic investigations. A. I. PORTNOW (Pharm. Zentr., 1929, 70, 661—663).—To prevent strychnine from being extracted by acid ether or chloroform extraction, addition to the material of not less than 2.5% of tartaric acid is necessary. Extraction of strychnine by chloroform containing 10% of alcohol is inadmissible.

T. H. POPE.

Effect of *Vinca rosea* [leaves] on the blood-sugar of rabbits. D. H. K. LEE and W. R. M. DREW (Med. J. Austral., 1929, I, 699—701).—No change in blood-sugar could be ascribed to feeding an infusion or extract of the leaves.

CHEMICAL ABSTRACTS.

Diuretin hyperglycaemia. N. SUGIMOTO (Okayama Ig. Zasshi, 1927, 39, 719—742).—Insulin or atropine inhibits diuretin hyperglycaemia, and diuretin inhibits insulin hypoglycaemia.

CHEMICAL ABSTRACTS.

Seventh report of the Committee on Contact Catalysis. Enzyme catalysts. E. F. ARMSTRONG and T. P. HILDITCH (J. Physical Chem., 1929, 33, 1441—1455).—A summary. After a discussion of the factors controlling the rate of enzyme action, the analogy between inorganic catalysts and enzymes, and the nature of enzymes, the following conclusions are reached. The physical form of the enzyme is that of a dispersed colloidal sol in which the molecule is of considerable complexity and protein, carbohydrate, phosphorus, and iron compounds are not necessarily integral components. Further, it is unlikely that the whole of the molecular complex is involved in enzymic changes and only certain groupings of highly specific character and configuration are able to enter into combination with specific substrates. The whole molecule, however, is liable to form associated complexes with other large molecular species, and the presumed groupings, the rate of action, and the optimum character of the reaction medium must be considerably affected by this feature. Only the specific nature of the change effected by the enzyme itself persists unaltered. Hydrolytic action is exerted by enzymes through the presence of definite groupings adapted to form intermediate complexes with the substrate and water, and specificity

is due, in all probability, to their asymmetric configuration. Co-enzymic activity appears to be closely connected with the combinations which occur with other colloidal molecules. Finally, the catalytic properties of an enzyme are at present best ascribed to a catalyst which by reason of this capacity for interaction is in a labile or dynamic condition and the activity of which is very sensitive to a variety of conditions and is controlled by its environment at a given time.

L. S. THEOBALD.

Kinetics of cell fermentation from the point of view of a reaction in a closed space. V. MECHANISM OF ENZYME ACTION. F. F. NORD and J. WEICHHERZ.—See this vol., 1397.

Enzymes and bacteria in the honey bee. F. M. BROWN (Amer. Mus. Nov., 1928, No. 304, 5).—The enzymes normally native to the digestive system of the honey bee are: invertase, both peptic and tryptic proteolytic enzymes, and a lipase.

CHEMICAL ABSTRACTS.

Dilatometric studies in enzyme action. M. SREENIVASAYA and B. N. SASTRI (Biochem. J., 1929, 23, 975—981).—In the cases of the hydrolytic action of diastase, invertase, emulsin, amidase, and tannase, there was a good agreement between the results obtained by the dilatometer and by the usual methods. The dilatometer is described.

S. S. ZILVA.

Enzyme action. III. Amylase from *Cumbr* (*Pennisetum typhoideum*). D. NARAYANAMURTI, C. V. R. AYYAR, and R. V. NORRIS (J. Indian Inst. Sci., 1929, 12 A, 105—108).—The hydrolytic action on starch of filtered and dialysed extracts of malted *Cumbr* seeds has been determined at various hydrogen-ion concentrations. When the period of action is 15 min. and the temperature 37°, the maximum hydrolysis occurs at p_H 5.1 and with longer periods the optimum is at a more acid reaction, whilst with rise in temperature the optimum occurs at a less acid reaction. The malt extract also contains maltase and for this enzyme two optima exist when the period of reaction is more than 30 min., namely, at p_H 4.8 and 6.2.

W. O. KERMAK.

Chemistry of starch. F. POLAK and A. TYCHOWSKI (Biochem. Z., 1929, 214, 216—228).—Starch consists of amylopectin which is converted by the action of β -diastase into a reducing dextrin and further hydrolysed only with great difficulty, and amylose which is converted into maltose by α -diastase and into a dextrin by β -diastase, the dextrin being hydrolysed to maltose only by α -diastase. The preparation of amylose, the behaviour of its solutions to α - and β -diastase, and attempts at fractionation of starch are described.

P. W. CLUTTERBUCK.

Malt catalase. M. MATSUYAMA (Biochem. Z., 1929, 213, 123—137).—The optimum p_H for malt catalase action is 7.4—7.5 in 0.05M-hydrogen peroxide. The unimolecular reaction constant for malt catalase action in 0.0125M-hydrogen peroxide falls, but the C_1 -value of Maximovitch and Avtonomova is constant; the D -value, however, does not agree with the results for blood catalase. The optimum temperature in 0.025M-hydrogen peroxide buffered to p_H 7.4 is 30°; at 40° the enzyme is destroyed. The

inactivation of malt catalase is not a unimolecular reaction. The temperature sensitivity is dependent on the acidity and enzyme concentration; the stability is highest at p_H 7.2. J. H. BIRKINSHAW.

Indophenol reaction in biological oxidations. D. C. HARRISON (Biochem. J., 1929, 23, 982—999).—The secondary oxidation of dimethyl-*p*-phenylenediamine leading to a positive indophenol reaction can be brought about during the oxidation of hypoxanthine by xanthine-oxidase from milk or liver in presence of peroxidase. *p*-Phenylenediamine increases the oxygen uptake of yeast, which does not give an indophenol reaction unless it is previously heated at 52° for 1.5 hrs. (cf. Keilin, this vol., 470). The destruction of the reducing power of yeast when heated at 52° is not due to any appreciable exhaustion of oxidisable substances, but probably to the destruction of the enzyme, involved in reducing systems. The initial rate of reduction of methylene-blue by warmed yeast is much more rapid than that shown by unwarmed yeast, but in the final stages the reduction is relatively very slow in the warmed yeast. The rate of reduction of methylene-blue by yeast treated with toluene is doubled by plasmolysis by increasing the accessibility of the dye to the reducing systems, but there is a lowered oxygen uptake owing to the partial destruction of the oxidising systems by this treatment. Also although warmed and unwarmed yeasts do not reduce indigo-carmin, yeast after treatment with toluene does so. Although the indophenol reaction becomes positive in yeast either after warming or after treatment with toluene, it is destroyed by the double effect of warming and toluene treatment. Unwarmed yeast reduces indophenol-blue more rapidly than warmed yeast. A scheme of reactions is described to explain the significance of the indophenol reaction in cell oxidations; cytochrome may be involved in a similar series of reactions. The indophenol reaction is no criterion for the presence of an activator of oxygen. A method for the preparation of an active solution of xanthine-oxidase of the liver is based on precipitating an aqueous extract of the liver by acidification to p_H 5 with acetic acid and treating the neutralised protein layer obtained after centrifuging with ammonium sulphate. S. S. ZILVA.

Behaviour of dextrose-oxidase towards dialysis, hydrocyanic acid, carbon monoxide, and methylene-blue. D. MÜLLER (Biochem. Z., 1929, 213, 211—219; cf. A., 1928, 1291).—Dextrose-oxidase is stable and non-hydrolysable and is not affected by a co-enzyme from boiled juice of *A. niger*. After 24 hrs.' dialysis the oxygen uptake in absence of sugar is nil. The action of dextrose-oxidase in presence of dextrose decreases rapidly, due to inhibition chiefly by hydrogen ions but partly by gluconate ions. It is inhibited by hydrocyanic acid at concentrations above 0.01*N*, but not by carbon monoxide. In presence of dextrose and absence of oxygen methylene-blue is not reduced more quickly than in dextrose-free solution.

J. H. BIRKINSHAW.

Dehydrogenation of citric acid. A. HAHN and W. HAARMANN (Z. Biol., 1929, 89, 332—334).—In

presence of fresh muscle pulp with or without the addition of methylene-blue citric acid is oxidised with loss of carbon dioxide and formation of pyruvic acid. W. O. KERMACK.

Enzyme action. IV. Tyrosinase. I. D. NARAYANAMURTI and C. V. R. AYYAR (J. Indian Inst. Sci., 1929, 12 A, 109—129).—The tyrosinase activity of extracts of ungerminated *Dolichos lablab* is at a maximum at p_H 6.5. The isoelectric point of the tyrosinase as determined by migration experiments is also in the neighbourhood of this p_H . The kinetics of tyrosinase action have been investigated and the effects of concentrations of enzyme and of substrate, temperature, and reaction have been determined. The reaction appears to be essentially unimolecular. Irradiation of the enzyme solution with ultra-violet light increases its activity. The enzyme may be separated from inorganic electrolytes by electrodialysis or by ultra-filtration. As neither of the processes brings about a decrease in activity, it is concluded that the enzyme action does not depend on the presence of small quantities of iron or manganese salts. W. O. KERMACK.

Influence of temperature on acetaldehyde production [in blood or organs]. C. KAWAMURA (J. Kyoto Prefect. Med. Coll., 1928, 2, 211—222).—Calcium sulphite and a phosphate buffer (p_H 6.5) were added to rabbit's blood or pulped organs and the acetaldehyde produced at 30°, 34°, and 38° was determined. In 5 hrs. the amounts produced (max., 38°) were: liver 2.4 mg., muscle 1.13 mg. per 100 g., blood 1.08 mg. per 100 c.c. CHEMICAL ABSTRACTS.

Tissue glycolysis. Effect of fluoride and some other substances. F. DICKENS and F. ŠIMER (Biochem. J., 1929, 23, 936—958).—Fluoride and oxalate inhibit anaerobic glycolysis very strongly in all the tissues examined. There is a simple relationship based on the law of mass action between the concentration of fluoride and the percentage inhibition of glycolysis in Jensen rat sarcoma, rat brain, and rat testes. This relationship, although of a similar type, is not identical in these tissues. There is a variation which is due to a difference in the order of the reaction and the affinity of fluoride for the glycolytic enzyme. The approximate values of the affinity constant of the fluoride-enzyme complex have been determined for these tissues. Fluoride most probably forms an active compound with some substance essential for glycolysis. This reaction follows the ordinary laws of chemical equilibria. The effect of temperature on this equilibrium is described; the enzyme-fluoride compound is exothermic. Fluoride also has a strongly inhibitory action on glycolysis in the case of rat retina, rat kidney, and two specimens of human carcinoma. The effect of oxalate is less than that of fluoride, whilst cyanide inhibits glycolysis only when present in very high concentration. Fluoride and oxalate do not appreciably influence tissue respiration in the concentrations used, and the former does not inhibit conversion by tissues of dihydroxyacetone into lactic acid. Aerobic glycolysis is inhibited by fluoride in the case of Jensen rat sarcoma, but not in that of rat testes. S. S. ZILVA.

Stability of luminous substances of luminous animals. E. N. HARVEY (Proc. Soc. Exp. Biol. Med., 1928, 26, 133—134).—Dry *Cypridina* luciferin and luciferase can be kept unchanged for a long period. An aqueous solution of luciferin is stable in absence of oxygen, whilst luciferase is decomposed in aqueous solution. CHEMICAL ABSTRACTS.

Effect of electrolytes on glycerophosphatase. K. INOUE (J. Biochem. Japan, 1929, 10, 395—408).—The activity of pure glycerophosphatase is inhibited only by fluorine, oxalate, and sulphate ions which are also anticoagulants for fibrinogen. Unlike the latter, the former effect cannot be attributed to removal of calcium ions. CHEMICAL ABSTRACTS.

Fat-decomposing enzyme. XII. Activation of lipase by bile, and the relation between the stomach lipase and the activating action of bile. K. GYOTOKU and S. MATSUBARA (Tokyo J. Med., 1928, 42, 2147—2161).—The splenic lipase of the dog is first activated and subsequently deactivated by the bile of man or of the dog. The activation is most marked at p_H 7.6. Purified stomach lipase is similarly activated. The activating agent is thermostable and non-dialysable, but dried bile dissolved in water has no effect. CHEMICAL ABSTRACTS.

Chemical equilibria in enzymic systems. E. SYM (Compt. rend. Soc. Biol., 1928, 99, 1011—1013, 1013—1015; Chem. Zentr., 1929, 1, 2997).—In the systems amyl butyrate, picric acid, lipase, and amyl alcohol, butyric acid, lipase the equilibrium depends on the difference in the activity of the catalyst and enzyme. A. A. ELDRIDGE.

Action of substances containing alcoholic hydroxyl groups on pancreatic lipase. A. DI FRISCO (Boll. Soc. Ital. Biol. sper., 1928, 3, 299—303; Chem. Zentr., 1929, 1, 2998).—The activity of stored pancreatic juice is increased by addition of sodium potassium tartrate, sodium citrate, or glycerol. A. A. ELDRIDGE.

Behaviour of aromatic esters towards extracts of organs. I—III. G. YOSHIMATSU (Acta Schol. Med. Univ. Imp. Kyoto, 1929, 11, 599—615, 617—638, 639—648).—The comparative efficiencies of rabbit's liver, kidney, muscle, spleen, and pancreas, and of pig's organs, in hydrolysing ethyl, isobutyl, amyl, glyceryl, and phenyl benzoate, and ethyl, isobutyl, amyl, and phenyl salicylate, have been measured. CHEMICAL ABSTRACTS.

Behaviour of ethyl- and phenyl-sulphuric acids towards extracts or organs. G. YOSHIMATSU (Acta Schol. Med. Univ. Imp. Kyoto, 1929, 11, 649—660).—Glycerol extracts of pig's liver, kidney, pancreas, and stomach and intestinal mucous membrane affected tributyrin, but not potassium ethyl or phenyl sulphate. CHEMICAL ABSTRACTS.

Nephelometric determination of pepsins. C. G. VAN ARKEL (Pharm. Weekblad, 1929, 66, 857—864).—The intensity of the opalescence following addition of sulphosalicylic acid to diluted ox-serum which is undergoing hydrolysis by pepsin is used to determine the degree of hydrolysis for a given time and hydrogen-ion concentration. Curves are given

showing the effect of time for a given p_H , and of p_H for a given time. S. I. LEVY.

Crystalline pepsin. J. H. NORTROP (Science, 1929, 69, 580).—Dialysis under pressure at p_H 3.0 and 5° of a concentrated solution of commercial pepsin gave 1—2% of crystalline material having the properties of pepsin with an activity slightly less than certain amorphous preparations. The small, hexagonal prisms containing 14.5% N can be recrystallised by dissolving in sodium hydrogen carbonate at 37° and precipitation with dilute sulphuric acid. More concentrated acids and alkali dissolve them, but the material is precipitated by half saturation with ammonium sulphate, copper salts, lead acetate, trichloroacetic acid, and safranin, and coagulates on boiling. The diffusion coefficient indicates a mol. wt. of 10,000. L. S. THEOBALD.

Action of papain on polarisation of gelatin. H. C. GORE (Ind. Eng. Chem. [Anal.], 1929, 1, 203—205).—The mutarotation of gelatin solution is lessened by digestion with proteolytic enzymes, such as papain, and the relationship between the decline in mutarotation at 20° and the quantity of enzyme present is linear up to the point when 40% of the former has been destroyed. It is proposed to utilise this as a means of determining the proteolytic activity of papain. 50 C.c. of 2% gelatin solution of p_H 4.8 and 10 c.c. of Walpole's acetate buffer of p_H 4.8 are mixed at 45° with 40 c.c. of papain solution and digested at this temperature for 1 hr. The mixture is cooled in ice water, kept for 16 hrs. at 5°, warmed to 20°, and the mutarotation determined after maintenance for 1 hr. at this temperature. In order to calculate the percentage of gelatin digested, determinations under similar conditions must be made of the polarisation values of the original gelatin and of completely digested gelatin, when the proteolytic power of the papain can be calculated from the formula $P=W/wt$, where W =weight of gelatin digested, w =weight of papain used, and t =time in hours.

H. F. HARWOOD.

Proteolytic enzymes of green malt. I. Adsorption and elution. R. H. HOPKINS (Biochem. J., 1929, 23, 1022—1029).—A cold aqueous extract of green malt appears to contain at least two proteolytic enzymes, a protease which renders egg-albumin non-coagulable at p_H 4.6 and 100° and attacks Witte's peptone, and a peptidase which attacks Witte's peptone and Roche peptone. The enzymes are maximally adsorbed at about p_H 4.7. They may be separated by elution by 0.1M phosphate. By adsorption and elution twice at p_H 4.5 a preparation of the protease almost free from peptidase is obtained and by adsorption at p_H 7.0 and elution at p_H 9.2 and a repetition of both processes a preparation of peptidase almost free from protease is obtained. S. S. ZILVA.

Structure and enzymic degradation of the acetylated polypeptide associates obtained from gelatin by degradation with acetic anhydride. V. A. FODOR and C. EPSTEIN (Biochem. Z., 1929, 214, 242—252).—*N*-Acetylated tripeptide complexes (associations of three tripeptides such as glycyl-prolylalanine, glycylhydroxyprolylalanine, etc.; cf.

this vol., 1188) are hydrolysed by trypsin but not by yeast maceration juice. Gelatin peptone which contains the same complexes in the non-acetylated condition is attacked fairly readily by yeast, and it must be assumed that *N*-acetylation inhibits the action of yeast.

P. W. CLUTTERBUCK.

Physiology of digestion in infants. VI. Effect of *B. coli* fermentation on erepsin and trypsin. VII. Excretion of tryptase and peptidase in the faeces of infants. O. BUDDE (Z. Kinderheilk., 1928, 46, 195—201, 202—209; Chem. Zentr., 1929, i, 2552).—The action of erepsin is inhibited by butyric, hexoic, acetic, or lactic acid, or peptone, whereas the amines, formic acid, and succinic acid produced do not affect it. *B. coli*, living or dead, usually inhibits the action of erepsin; trypsin is not affected by any of the substances.

The trypsin and peptidase content of the faeces of breast-fed infants was smaller than that for bottle-fed infants. The peptidase is apparently affected by fermentation acids.

A. A. ELDRIDGE.

Dismutation of methylglyoxal and of phenylglyoxal by the enzyme from green leaves (of the lime tree). C. PI-SUNER BAYO (Biochem. Z., 1929, 213, 495—500).—The enzyme from green leaves of the lime tree (*Tilia grandifolia*) converts phenylglyoxal hydrate into mandelic acid. The yield of 83% consists almost entirely of the *l*-acid. Methylglyoxal is converted into *l*-lactic acid by the enzyme.

W. MCCARTNEY.

Production of methylglyoxal in the fermentation of sugar with extract of macerated yeast. C. PI-SUNER BAYO (Biochem. Z., 1929, 213, 489—494).—Methylglyoxal is easily obtained in yields of up to 100% from magnesium hexosediphosphate by the action of extracts of macerated yeast. It follows that living yeast cells or cells partly damaged act in the same way as do cell-free organisms.

W. MCCARTNEY.

Proteolytic action of yeasts. F. ZARIBNICKY (Mikrochem., 1929, Pregl Fest., 338—340).—A number of different kinds of yeast in sterile milk showed marked differences in proteolytic action after 14 days, and the differences were still more sharply defined after a period of 8 weeks.

H. F. HARWOOD.

Effect of "bios" on the growth and metabolism of certain yeasts. A. M. COFFINO (Biochem. J., 1929, 23, 1050—1063).—The type of yeast and the composition of the medium influence the requirements for "bios." There is an increased oxygen uptake and carbon dioxide output in the presence of this factor, but whether this is due to the greater number of cells produced by the stimulating action of "bios" on growth or to a change in their metabolic processes has not been ascertained.

S. S. ZILVA.

Detection of pyruvic acid in yeast fermentation. G. KLEIN and W. FUCHS (Biochem. Z., 1929, 213, 40—64).—Benzhydrazide and di(phenylacet)-hydrazide are well suited for the characterisation of pyruvic acid; the corresponding hydrazones have m. p. 92° and 170—172°, respectively. The two hydrazides were successfully used for the interception

of acetaldehyde under various conditions, but in no case could methylglyoxal or pyruvic acid be detected.

J. H. BIRKINSHAW.

Rates of sugar disappearance and carbon dioxide formation during fermentation of dextrose. J. A. HAWKINS and D. D. VAN SLYKE (J. Biol. Chem., 1929, 84, 243—247).—During the first few minutes of fermentation of dextrose by yeast the rate of disappearance of the sugar is twice as rapid as the production of carbon dioxide; the lag in carbon dioxide production persists after 1 hr.

C. R. HARRINGTON.

Effect of hydrogen-ion concentration on the toxicity of sodium benzoate to micro-organisms. W. V. CRUESS and P. H. RICHERT (J. Bact., 1929, 17, 363—371).—The retardation of the growth of, or of alcoholic fermentation by, *Saccharomyces ellipsoideus* by sodium benzoate is much more marked at p_H 2.5—4.5 than at p_H 5.0—9.0. Other food preservatives behave similarly.

CHEMICAL ABSTRACTS.

Glutathione. (Sir) F. G. HOPKINS [with a Section by L. J. HARRIS] (J. Biol. Chem., 1929, 84, 269—320).—The fact that prolonged boiling of aqueous solutions of the substance previously described (A., 1921, i, 635) as glutathione led to the separation of glycylcystine dianhydride indicated that the constitution assigned to the compound was erroneous (cf. Hunter and Eagles, A., 1927, 477, 478). Further investigation of means of purification led to the development of the following method. Pressed yeast was twice extracted with boiling 0.1% acetic acid, and the filtered extracts were treated with lead acetate and mercuric sulphate; the washed precipitate was decomposed with hydrogen sulphide, and, after removal of the latter, the solution was treated with sulphuric acid to 0.5*N* concentration; cuprous oxide was then added cautiously to the point of maximum precipitation, the temperature being maintained at 50°. The white, crystalline precipitate, $C_{10}H_{16}O_6N_3Cu$, was separated at the centrifuge, washed, and decomposed with hydrogen sulphide; the filtrate from the cupric sulphide was concentrated in a vacuum, treated with 0.5 vol. of alcohol, and allowed to crystallise in a desiccator; the yield was 1.25 g. per kg. of yeast. A similar preparation was made from red blood-corpuscles, the yield in this case being very much less. The glutathione then obtained had the formula $C_{10}H_{17}O_6N_3S$; when hydrolysed with 25% sulphuric acid it yielded cysteine (as cystine), glutamic acid, and glycine in amounts of 84.5—92% of those demanded by the theory that the compound is a tripeptide containing these three amino-acids. When the tripeptide was kept for 5 hrs. at 37° in 0.33*N*-barium hydroxide in presence of lead acetate, more than 50% of the sulphur was removed. Boiling (of the disulphide form) for 24 hrs. in 2% aqueous solution led to elimination of 27.9% of the sulphur as hydrogen sulphide and in the free state, a further 31% of the sulphur being isolated in the form of glycylcystine dianhydride, $C_{10}H_{14}O_4N_4S_2$, m. p. 262° (decomp.); (reduction of the above, or boiling of the aqueous solution of the reduced form of glutathione, led to the more soluble glycylcystine anhydride, $C_8H_8O_2N_2S_2$, m. p. 203°); in addition to the above anhydride, the solution contained glutamic

acid and α -pyrrolidonecarboxylic acid, together with unidentified decomposition products. The fission by boiling with water was accompanied by elimination of a part of the carbon as carbon dioxide. Oxidation of the reduced form of the tripeptide by aeration of its solution at p_H 7.6 in presence of a trace of iron was accompanied by destruction of 20% of the material with loss of nitrogen and sulphur; this phenomenon is peculiar to the pure tripeptide as contrasted with the earlier (impure) preparations.

[By L. J. HARRIS.] Application of the author's titrimetric methods of determination of amino- and carboxyl groups (A., 1924, ii, 73, 355) to the reduced form of glutathione affords confirmatory evidence that the compound is a tripeptide with an equivalent weight of 307. C. R. HARRINGTON.

Titration curve of glutathione. N. W. PIRIE and K. G. PINNEY (J. Biol. Chem., 1929, 84, 321—333).—Titration curves have been determined for reduced and (impure) oxidised glutathione; the pK values found for the reduced compound were 2.12, 3.53, 8.66, and 9.62. Consideration of the magnitude of these constants leads to the conclusion that the compound is probably glutaminyglycylcysteine, the carboxyl group of glutamic acid which is adjacent to the amino-group being free. C. R. HARRINGTON.

Exchange of ions between yeast cells and solutions of lead nitrate. P. GENAUD (Compt. rend., 1929, 189, 591—592).—When yeast-cells are immersed in a solution of lead nitrate an exchange of cations takes place, the lead ions penetrating the yeast cells and an equivalent number of potassium and calcium ions being liberated. With fresh yeast there is a rapid uptake of lead during the first minute, after which time it is found in the cell capsule. This is followed by slow uptake and lead is then also found in the vacuoles. Complete saturation of living yeast with lead affects only the capsule and vacuoles, whereas in the case of dead cells the protoplasm also takes it up. W. O. KERMACK.

Proteins of egg-white. II. Transformation of crystallised ovalbumin into non-crystallisable conalbumin. L. HEKTOEN and A. G. COLE (J. Infect. Dis., 1929, 44, 165—166).—Crystallised ovalbumin is not converted by putrefaction into conalbumin. CHEMICAL ABSTRACTS.

Irradiated proteins. VIII. Relation of the velocity of coagulation by light of protein solutions to their sterility. M. SPIEGEL-ADOLF and K. F. POLLACZEK (Biochem. Z., 1929, 214, 175—186).—The velocity of coagulation by light of 14 protein solutions is investigated. Sterile solutions readily coagulated, but all spontaneously infected solutions (chiefly *B. subtilis*) showed considerable retardation of coagulation, which persisted after the infection had spontaneously died. With sterile solutions, retardation of coagulation was obtained 24 hrs. after sowing with bacteria. Electrodialysis of spontaneously or artificially infected solutions restores the velocity of coagulation to the original values for a short time. P. W. CLUTTERBUCK.

Growth of moulds. I. R. G. TOMKINS (Proc. Roy. Soc., 1929, B, 105, 375—401).—The influence

of the temperature, humidity, and the nutrients in the medium on the rate of germination of the spores of fungi and on the growth of colonies has been investigated. W. O. KERMACK.

Relation between the carbohydrates digested and secreted by *Aspergillus niger*. F. OBATON (Compt. rend., 1929, 189, 711—713).—The amounts of trehalose and mannitol in the mycelium of *A. niger* at various stages in the growth of this organism on cultures containing dextrose and laevulose, respectively, have been determined. There is a marked relation between the nature of the sugar secreted by the organism and that from which it derives its nourishment. A. A. GOLDBERG.

Acetic fermentation. A. BERTHO (Annalen, 1929, 474, 1—64).—An extension of the investigations of Wieland and Bertho (this vol., 219). In addition to *B. orleanense* and *B. Pasteurianum*, cultures of *B. ascendens* and *B. aceti* are employed. An apparatus for determining the rate of dehydrogenation by the decolorisation of methylene-blue, in which the air is displaced by nitrogen instead of being exhausted, and permits the addition of the reagents and continuous shaking, is described. The degree of adsorption of methylene-blue and Lauth's violet by the bacteria is very high and the values obtained approximate to Freundlich's adsorption isotherm. For this and other reasons these dyes are less suitable as hydrogen-acceptors than is quinone. Neither diethyl peroxide nor potassium persulphate can act as acceptor. Of the substances examined, methyl, ethyl, propyl, isobutyl, isocamyl alcohols, and their corresponding aldehydes, phenylethyl alcohol, isopropyl alcohol, and dextrose act as donors, but not benzyl alcohol, saligenin, salicylaldehyde, acetone, acetic acid, or succinic acid. No evidence could be found for the further oxidation or dehydrogenation of acetic acid. isopropyl alcohol is dehydrogenated entirely to acetone. The relative rates of dehydrogenation by two acceptors vary with different donors. The velocity of the reaction is studied systematically, using varying concentrations of acceptor and donor with constant concentration of donor and acceptor, respectively, ethyl alcohol, aldehyde, and isopropyl alcohol being the donors, and quinone and (with isopropyl alcohol) oxygen the acceptors. Preparations of bacteria killed by acetone treatment contain too little dehydrogenase for such kinetic studies, but it is noted that owing to damage to the cell structure the rate of reduction of methylene-blue then approximated to that of oxygen. The fact that the dehydrogenation of alcohol proceeds in two stages prevents the working out of the p , curves for that reaction, but curves are given for the dependence of the velocity of the reaction on the concentrations of aldehyde, isopropyl alcohol, and quinone. The dissociation constants are 0.001 for the system aldehyde dehydrogenase-quinone, 0.0025 for aldehyde-dehydrogenase \rightleftharpoons quinone and isopropyl alcohol-dehydrogenase \rightleftharpoons quinone, and 0.125 for isopropyl alcohol dehydrogenase-quinone. The complex aldehyde-dehydrogenase-quinone decomposes at about twice the rate of isopropyl alcohol-dehydrogenase-quinone. Using isopropyl alcohol as

donator, the velocity of the reaction is directly proportional to the concentration of oxygen when that acceptor is used, indicating the very high affinity of the natural acceptor for the enzyme. With quinone, the velocity is relatively slower at low concentration, an optimum being reached at about 0.016*N* in presence of aldehyde, 0.01*N* with isopropyl alcohol. Except in the case of fresh bacteria, which are apparently damaged by concentrations of isopropyl alcohol at concentrations below the optimum when oxygen is the acceptor, the optimum concentration of donator or quinone can be considerably exceeded without relative retardation of the reaction velocity. Thus neither donator nor acceptor excludes the other from the enzyme surface, although it has been shown (*loc. cit.*) that quinone appears to exclude oxygen, possibly on account of its relatively large molecules. Comparison of the activity of fresh with that of 5 weeks old cultures indicates a decrease to about 60% of the dehydrogenating power of the latter for both ethyl alcohol and aldehyde, to about 70–75% for isopropyl alcohol with both oxygen and quinone, supporting the idea of the identity of the enzyme. Comparison of the rate of aldehyde dismutation with that of dehydrogenation with various cultures of the four bacterial species gave ratios of 1:25 to 1:500. The temperature coefficient of both reactions is about 2. Bacterial cultures in wort showed acid production at a rate at least six times as great as the highest rate of dismutation observed under experimental conditions and there was no accumulation of aldehyde. No confirmation was found for the previous supposition that oxygen might possibly accelerate aldehyde dismutation, and the results indicate that mutase action plays only a minor part in the acetic fermentation.

F. E. DAY.

Mechanism of the degradation of citric acid by *B. pyocyaneus*. I. J. BUTTERWORTH and T. K. WALKER (Biochem. J., 1929, 23, 926–935).—*B. pyocyaneus*, when grown on ammonium citrate at 34°, produces acetonedicarboxylic acid. The acid has only a transitory existence. The total “acetone bodies” reached, under the experimental conditions, their highest value 56 hrs. after inoculation; thereafter they decreased rapidly in quantity and disappeared entirely after 80 hrs. The production of malonic acid reached a maximum 96 hrs. after inoculation, followed by entire disappearance after 133 hrs. Succinic acid too was present and reached its maximum at 167 hrs. Volatile acids, principally acetic acid, appeared in the early stages of fermentation and persisted during the experiment. An acidity curve correlating the formation of volatile acid and the appearance, accumulation, and disappearance of the other degradation products is given. Acetic acid was isolated in the fermentation of ammonium malonate.

S. S. ZILVA.

Nitrogen circulation. I. Proteolytic power of microbes in general and of *B. coli* in particular. A. JANKE and H. HOLZER (Biochem. Z., 1929, 213, 142–153).—The action of mass cultures of *B. coli*, *B. putidum*, and *B. fluorescens* on caseinogen was studied. The basic difference between non-liquefiers and liquefiers is that with the former only those cells

rendered incapable of reproduction (by chloroform) show a proteolytic activity, whilst with the latter the active proliferating individuals bring about proteolysis.

J. H. BIRKINSHAW.

Endocellular enzymes of *B. coli communis*. E. G. YOUNG (Biochem. J., 1929, 23, 831–839).—The cells of the organism were destroyed by repeated freezings and thawings. The cellular extracts obtained after centrifuging and filtration through a Berkefeld candle, when tested anaerobically, hydrolysed peptone at *p_H* 7–8, but did not decompose dextrose in absence or presence of phosphate. No hexosephosphate was formed. The dehydrogenase activity on succinic and formic acids is independent of living cell concentration and is associated with cell stroma. In the case of acetic acid, lactic acid, alcohol, or dextrose the activity is temporarily independent of living cell concentration, but is rapidly destroyed by the freezing. The action of toluene towards dehydrogenase activity was similar to that of freezing. There is an increased enzymic (dehydrogenase) power after the early freezings and thawings.

S. S. ZILVA.

Biologically active lipins of tubercle bacilli. R. J. ANDERSON (Proc. Nat. Acad. Sci., 1929, 15, 628–633).—The lipid fractions of tubercle bacilli were separated by extraction with alcohol, ether, and chloroform, and the fractions, consisting of acetone-soluble fat, a phosphatide, crude wax, and polysaccharide, were analysed. The crude liquid saturated fatty acids obtained after saponifying the acetone-soluble fat were converted into methyl esters, which on distillation gave two principal fractions, which were saponified and the free acids isolated. One of these, m. p. 14–15°, was isomeric with stearic acid; the name *tuberculostearic acid* is proposed. The other is phthioic acid (see this vol., 1108); the m. p. is now given as 28°, [α]_D²⁰ +7.98°, mol. wt. 398, and it is stated to be isomeric with cerotic acid. The two acids appear to belong to a new series of fatty acids; a method of separation is outlined. N. M. BLIGH.

Chemotherapy of tuberculosis. E. CHERBULIEZ (Helv. Chim. Acta, 1929, 12, 920–921).—The copper derivative of 3:5-di-iodosalicylaldehyde, [C₆H₂I₂(CHO)·O]₂Cu, and the corresponding didymium compound, in oil solution have been used with favourable results in the treatment of tuberculosis in the guinea-pig and man (cf. Stephani, Rev. de la Tuberculose, 1928, 9, 898).

R. K. CALLOW.

Purification of anticarbuncle serum. R. WERNICKE and F. MODERN (Anal. Asoc. Quím. Argentina, 1929, 17, 49–58).—Dilution of anticarbuncle serum with four volumes of distilled water, or, better, of distilled water saturated with carbon dioxide, precipitates the active part quantitatively, mixed with a minimum quantity of proteins (chiefly pseudoglobulins). Dialysis of the serum causes a less complete precipitation of a more concentrated material. Electrodialysis causes complete precipitation of the active material accompanied by pseudoglobulins, and the solution of the precipitate in physiological saline solution is stable when kept.

R. K. CALLOW.

Proposed gold chloride titration for determining the toxicity of diphtheria toxin. E. SANDERSON and J. H. YOE (*J. Immunol.*, 1929, 16, 429—438).—The green colour zone produced in mixtures of gold chloride and toxic broths is not specific for toxin.

CHEMICAL ABSTRACTS.

Sterilising action of silver and copper on bacteria. C. EGG and A. JUNG (*Mikrochem.*, 1929, *Pregl. Fest.*, 46—60).—0.04 Mg. of silver per litre sufficed to sterilise cultures of *B. coli* within 24 hrs., and a marked effect was produced with concentrations as low as 0.001 mg. The active principle is the silver ion, slightly dissociated silver salts such as the sulphide having no sterilising action. Colloidal solutions of silver and solutions containing complex silver ions may also in certain cases act as sterilisers, but this action is due to the liberation of silver ions through secondary reactions. The sterilising effect of copper compounds is also due to copper ions, but in this case a minimum concentration of 0.6 mg. per litre is necessary for complete sterilisation. No other metals have been found with sterilising power equal to the above.

H. F. HARWOOD.

Oligodynamic action of silver. R. WERNICKE and F. MODERN (*Biochem. Z.*, 1929, 214, 187—197).—Distilled water which has acquired an oligodynamic activity by contact with silver contains 0.00005 mg. per c.c. of this metal in the ionised condition. The activity is lost on electrolysis, the silver being precipitated at the cathode. The oligodynamic action of silver and copper solutions is also obtained in an atmosphere of hydrogen.

P. W. CLUTTERBUCK.

Combined action of formaldehyde and salts of certain heavy metals (zinc, copper, cadmium) on proteins and micro-organisms. M. DEGANELLO (*Arch. Farm. speriment.*, 1929, 47, 177—212).—The character of the flocculent coagulum rapidly produced by the action of zinc, copper, or cadmium sulphate on protein solutions is altered in presence of formaldehyde, which renders it gelatinous. The antiseptic properties of the two components are also enhanced when mixed. Similar results were obtained by Simon (*Pathologica*, 1915).

T. H. POPE.

Disinfecting properties of alkylphenols. II. *n*-Butylphenol. L. F. RETTGER, W. N. PLASTRIDGE, and G. VALLEY (*Zentr. Bakt. Par.*, 1929, I, 111, 287—296; *Chem. Zentr.*, 1929, i, 2544).—The disinfecting action is enhanced by hydrogen ions (optimal p_H 5.0) and inhibited by hydroxyl ions or soaps. Experiments with *n*-butylphenol and *n*-butylresorcinol are described.

A. A. ELDRIDGE.

Diminution of activity of pathogenic bacteria by potassium tellurite. R. GOSIO (*Ann. Igiene*, 1929, 39, 112—120; *Chem. Zentr.*, 1929, i, 3000).

Effect of certain factors on the growth of the pneumococcus. H. D. WRIGHT (*J. Path. Bact.*, 1929, 32, 203—227).—A small amount of fermentable carbohydrate is necessary; excess leads to high acidity. Thermolabile nitrogenous substances essential to growth are present in yeast extract and blood in large quantity, and in meat extract, serum, and peptone in small quantity. After being heated the organic materials inhibit growth, the effect being

diminished by reducing conditions. In presence of yeast extract, but not of blood or serum, a small amount of calcium favours growth.

CHEMICAL ABSTRACTS.

Use of bacteriostatic dyes in the isolation of *Rhizobium leguminosarum*, Frank. I. A. ANDERSON (*Soil Sci.*, 1929, 28, 305—313).—*R. leguminosarum* from nodules of lucerne and beans can be successfully isolated by treatment of cultural media with suitable dyes in such concentration as to inhibit the growth of other organisms. Best results were obtained by the use of Ashby's agar containing 1 : 10,000—15,000 parts of crystal-violet. Rosaniline hydrochloride and malachite-green also gave promising results.

A. G. POLLARD.

Variation in staining character of bacteria as related to the reserve food material within the organism. E. W. STEARN and A. E. STEARN (*Stain Tech.*, 1929, 4, 105—109).—When *B. cereus* is starved at 37° it tends to lose its Gram-positivity. This is thought to be due to depletion of its reserve of acidic food material, e.g., nucleoprotein.

H. W. DUDLEY.

Chemical basis of staining. I. Reaction between dyes, proteins, and nucleic acid. A. E. STEARN and E. W. STEARN (*Stain Tech.*, 1929, 4, 111—119).—Basic dyes cause an increase in hydrogen-ion concentration when added to nucleic acid, although both solutions are originally at the same p_H . Acid dyes have no effect on nucleic acid solutions. Basic dyes exhibit the same behaviour when treated with solutions of proteins. Acid dyes when treated with protein solutions show an analogous, though opposite, effect. The bearing of these observations on the theory of staining is discussed.

H. W. DUDLEY.

Influence of adrenaline on blood-sugar utilisation of functionally hepatectomised rats. C. F. CORI and G. T. CORI (*Proc. Soc. Exp. Biol. Med.*, 1929, 26, 345—347).—Rats which have fasted for 24 hrs. contain 5.8 ± 1.4 mg. of liver-glycogen per 100-g. rat. When 0.03 mg. of adrenaline is injected subcutaneously and dextrose is supplied at the rate of 100 mg. per 100-g. rat per hr., 75% of the dextrose remains unutilised in the blood and body-fluids. In functionally hepatectomised rats the blood-sugar and lactic acid were higher after administration of dextrose and adrenaline than after that of dextrose alone.

CHEMICAL ABSTRACTS.

Automatin. I. H. G. K. WESTENBRINK and P. ARONS (*Arch. Neerland. physiol.*, 1929, 14, 394—406).—When solutions of automatinogen are flocculated by irradiation automatin is set free. This substance re-establishes the beating of the heart of the eel, which has been arrested by rinsing with potassium-free Ringer's solution, even after a lapse of 30—40 min. Automatinogen probably consists of automatin adsorbed on phosphatides or other colloidal substances. The unit of automatin is defined as the smallest quantity which, when dissolved in potassium-free Ringer's solution, re-establishes a pulsation of 20 beats per min. in the heart of the eel. Automatin is not destroyed by nitrous acid nor precipitated by silver nitrate, and is therefore not identical with

vitamin-B, adrenaline, or histamine. It occurs mainly in the skeletal muscles and heart of the dog and ox.

K. V. THIMANN.

Heart hormone. G. ZUELZER (Med. Welt, 1929, 3, 304—305; Chem. Zentr., 1929, i, 2547). L. HABERLANDT (Med. Welt, 1929, 3, 307; Chem. Zentr., 1929, i, 2547).—A discussion.

A. A. ELDRIDGE.

Influence of the pituitary on metabolism, growth, and sexual organs of male rats and rabbits. I. Influence of extracts of pituitary on nitrogen metabolism. V. KORENCHESKY and M. H. DENNISON (Biochem. J., 1929, 23, 868—875).—Administration by mouth of anterior or posterior lobe of the pituitary gland dried at the ordinary temperature in a vacuum does not influence definitely the urinary flow or the nitrogen metabolism of rats and rabbits. Subcutaneous injections of glycerol-aqueous extracts of the anterior lobe of fresh pituitary produced on the day of injection a decreased urinary flow (to 35% below normal) and a decrease in the nitrogen metabolism (to 27% below normal). On the days following the injection the nitrogen excretion remained depressed in rabbits but increased to 28% above normal in rats; the volume of urine excreted was much above normal. No special difference was noticed in the response of cryptorchid animals as compared with that of normal animals, nor in the influence of the extracts prepared from bull's or bullock's pituitary.

S. S. ZILVA.

Tethelin as a tissue-culture medium. K. C. RICHARDSON and E. S. HORNING (Austral. J. Exp. Biol., 1929, 6, 137—141).—The growth of cultures of intestinal epithelium from a 7-day embryo chicken in a medium of plasma is markedly increased by the presence of tethelin from the anterior lobe of the pituitary.

W. O. KERMACK.

Oestrin. I. Preparation from urine and separation from an unidentified solid alcohol. G. F. MARRIAN (Biochem. J., 1929, 23, 1090—1098).—Methods of preparing active oestrus-producing concentrates from the unsaponifiable fraction obtained from the urine of pregnant women are described. There is present in the unsaponifiable fraction of the ether-soluble material from the urine of pregnancy varying amounts of a solid saturated alcohol $C_{19}H_{32}O_2$ or $C_{20}H_{34}O_2$, m. p. 232—234.5° (uncorr.) (acetate, m. p. 177.5—178.5°). This compound has not been detected in the urine of normal males and normal non-pregnant females.

S. S. ZILVA.

Testicles and water metabolism. T. YAMAMOTO (Okayama J. Med., 1928, 40, 1467—1480).—Castration causes a change in the water and sodium chloride metabolism; injection of spermatin slightly restores the metabolic function.

CHEMICAL ABSTRACTS.

Insulin. H. MATHIS (Biochem. Z., 1929, 213, 72—73).—The non-cystine sulphur of insulin (3.72% as cystine) is not present as a sulphuric ester.

J. H. BIRKINSHAW.

Composition of insulin and its relation to enzymes and activators. E. GLASER and G. HALPERN (Wien. Med. Woch., 1929, 79, 363—366; Chem. Zentr., 1929, i, 2656).—Insulin is regarded as a compound of guanidine with amino-acids. Similar

substances are present in fungi and beet. Various enzymes exert a hypoglycæmic action. Peroxidases and aldehydases are found in insulin. The action of insulin is enhanced by certain enzymes.

A. A. ELDRIDGE.

Reversible inactivation of insulin. F. H. CARR, K. CULHANE, A. T. FULLER, and S. W. F. UNDERHILL (Biochem. J., 1929, 23, 1010—1021).—Ethyl alcohol and hydrochloric acid inactivate insulin. The rate of inactivation is increased by raising the temperature or the concentration of either the acid or the alcohol. Coincident with the inactivation there is a gradual change in the final precipitation point towards the alkaline side. The activity can be completely recovered and the original final precipitation point obtained by treatment with dilute sodium hydroxide. The process may be repeated with a small amount of loss in activity. Other strong acids with primary or secondary alcohols have a similar action on insulin. Insulin most probably undergoes an esterification on inactivation.

S. S. ZILVA.

Production of insulin after administration of lævulose. F. SILBERSTEIN and M. WACHSTEIN (Biochem. Z., 1929, 213, 301—311).—Experiments on dogs and rabbits according to Pollak's modification (A., 1927, 1115) of Staub and Traugott's method show that after administration of dextrose there is always a positive insulin effect. Administration of lævulose produces typical insulin effect, sometimes in dogs, never in rabbits. The positive results found with some dogs are attributed to the fact that lævulose is not an adequate food for carnivorous animals.

W. MCCARTNEY.

Action of insulin, particularly on cell and tissue metabolism. H. J. ARNDT (Sitzungsber. Ges. Beford. ges. Naturwiss. Marburg, 1927, 61, 116—133; Chem. Zentr., 1929, i, 2789).—A discussion of morphological results.

A. A. ELDRIDGE.

Influence of insulin on glycogen formation in macerated liver or muscle and in the liver during perfusion with sugar-saline solutions. K. OTANI (Okayama Ig. Zasshi, 1928, 40, 727—745).—Macerated liver of *Bufo japonicus* can form glycogen from either dextrose or lævulose, whilst resected muscle can convert only dextrose. Addition of insulin reduces the glycogen content of both muscle and liver. When liver is perfused with a sugar-saline solution glycogen is formed from both dextrose and lævulose, insulin respectively retarding or accelerating the action.

CHEMICAL ABSTRACTS.

Influence of insulin and synthalin on the gastric secretion. L. G. BUSTAMANTE (Arch. Endocrinol. Nutric., 1928, 6, 295—333; Chem. Zentr., 1929, i, 3002).—Insulin increases the acidity of the gastric secretion; the effect of synthalin is indefinite. The action of insulin is suppressed by atropine.

A. A. ELDRIDGE.

[Physiological] action of pancreatic secretin. A. FIESCHI (Biochim. Terap. sper., 1927, 14, 5 pp.; Chem. Zentr., 1929, i, 3001).—Intravenous injection of pancreatic secretin causes a fall in blood-sugar; long-continued injection does not influence the blood-sugar, but increases the carbohydrate tolerance.

A. A. ELDRIDGE.

Secretin in Japanese plants. T. OKANO (Japan. J. Int. Secr., 1928, 4, 1350—1354).—Substances (soluble in water or ethyl alcohol, but not in ether) which excite or inhibit the motion of isolated rabbit's intestine were extracted from fresh plants with warm, dilute hydrochloric acid. CHEMICAL ABSTRACTS.

Vitamin-A, polyenes, and ergosteryl phosphate. H. VON EULER and M. RYDBOM (Svensk Kem. Tidskr., 1929, 41, 223—227).—The effect of administration of carotinoids on the red blood-cell count of rats has been investigated. Experiments have also been carried out on the antimony trichloride tests as applied to the blood-serum and the extracts of the liver of rabbits. *Di-ergosteryl phosphate* has m. p. 180—182°, $[\alpha]_D$ —68.9° in chloroform; *ergosteryl phosphite* has m. p. 146°. W. O. KERMACK.

Relation of vitamin-A content to size of leaves. L. McLAUGHLIN (with E. S. HABER) (J. Biol. Chem., 1929, 84, 249—256).—Small spinach leaves contain relatively more vitamin-A than large ones, the determining factor being the surface area.

C. R. HARINGTON.

Assimilation of vitamin-A when dissolved in liquid paraffin. E. MONESS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1929, 18, 997—998).—No differences in vitamin-A activity were detected between solutions of cod-liver oil concentrate in olive oil and liquid paraffin. E. H. SHARPLES.

Biology of iodine compounds. I. Effect of cuprous iodide in avitaminosis-A and -D. G. VON WENDT (Med. Welt, 1928, 3, 527—528; Chem. Zentr., 1929, i, 2896—2897).—With rats, doses of 0.15—0.25 mg. of cuprous iodide per 100 g. had an immediate effect on the assimilatory processes in avitaminosis-A or -D. A. A. ELDRIDGE.

Vitamin contents of grass seeds from treated plots. M. I. ROWLANDS (Nature, 1929, 124, 760).—Grass seed from plots manured with dung, when fed to rats, gives a much steeper growth curve than does seed from plots treated with artificial manures.

A. A. ELDRIDGE.

Nutritive value of the garbanza pea. H. S. MITCHELL (West. Hosp. Rev., 1928, 11, No. 6, 26, 27, 52, 53).—The garbanza (Idaho) pea is approximately equivalent to caseinogen in the quantity of protein, is a rich source of vitamin-B, and has a slight potential alkalinity. CHEMICAL ABSTRACTS.

Comparison of the vitamin-B content of fresh yeast and of the dried yeast produced from it. A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1929, 213, 220—225).—The processes involved in the manufacture of dried yeast from fresh brewery yeast do not lessen its content of vitamin-B.

J. H. BIRKINSHAW.

So-called refection. I. Vitamin-B testing. A. SCHEUNERT, M. SCHIEBLICH, and J. RODENKIRCHEN (Biochem. Z., 1929, 213, 226—233).—The phenomenon of sudden increase of growth in rats fed on a diet deficient in vitamin-B ("refection") is not due to coprophagy alone, but chiefly to a special type of micro-organism capable of forming vitamin-B in the food or faeces. This anomalous effect is best avoided by keeping the animals on wire netting, by

the use of carefully extracted starch, and by microscopical examination of the faeces in cases under suspicion. J. H. BIRKINSHAW.

Influence of different samples of "casein" on vitamin tests. K. H. COWARD, K. M. KEY, B. G. MORGAN, and M. CAMBDEN (Biochem. J., 1929, 23, 913—920).—The growth response of rats given cod-liver oil after they have ceased to grow in a preparatory period may vary greatly according to the sample of casein used in the basal diet. "Light-white casein" even after extraction with alcohol and ether contains some growth-promoting factor which is not necessarily present in other samples of casein. For vitamin-B testing "light-white casein" (B.D.H.) as the source of protein gives more uniform results than "vitamin-free casein" (Glaxo). As it contains neither vitamin-B₁ nor -B₂ it does not need to be extracted before use in vitamin-B testing.

S. S. ZILVA.

Concentration of vitamin-B. B. C. GUHA and J. C. DRUMMOND (Biochem. J., 1929, 23, 880—897).—Two methods of preparation of vitamin-B₁ concentrates from wheat embryo are described. In one the procedure consisted of adsorbing the vitamin on norite after clearing the alcoholic extract of the embryo with lead acetate and further purification by precipitation with phosphotungstic acid, adsorption on silver oxide, and clearing with picrolonic acid. In the second method the vitamin was adsorbed on fuller's earth and fractionated with silver nitrate and baryta, phosphotungstic acid, platinic chloride, and gold chloride. In the last stage the precipitate was active only in large doses, whilst the filtrate was inactive; on combining the two, however, the activity was very much increased. Concentrates of which 0.005 mg. was active as pigeon-curative day-dose and which promoted good growth in rats in daily doses of 0.015 mg. when supplemented by vitamin-B₂ were obtained. Nucleic acid, nicotinic acid, betaine, and a substance, m. p. 234—235°, obtained by Drummond and Funk possess no vitamin-B₁ activity, nor does marmite liberate an active base on boiling with 20% sodium hydroxide solution. The "bios" activities of the concentrates are given.

S. S. ZILVA.

Alleged antineuritic properties of certain quinoline and glyoxaline derivatives. J. M. GULLAND and R. A. PETERS (Biochem. J., 1929, 23, 1122—1125).—Neither 4(5)-glyoxalinemethylethylcarbinol hydrochloride nor 2:6-dihydroxyquinoline has antineuritic vitamin properties similar to those of torulin. A number of compounds containing glyoxaline and pyrimidine rings have also given negative results.

S. S. ZILVA.

Carbohydrate metabolism in birds. I. The relation between the lactic acid content of brain and the symptoms of opisthotonus in rice-fed pigeons. H. W. KINNERSLEY and R. A. PETERS (Biochem. J., 1929, 23, 1126—1136).—Pigeons in the terminal stages of vitamin-B₁ deficiency showing symptoms of opisthotonus have an increased amount of lactic acid (95 mg. per 100 g. of tissue) in the brain as compared with the normal (55 mg. per 100 g. of tissue). This increase disappears within a short time

after dosing with torulin. It is not a consequence of the high blood-sugar and tends to follow the blood-lactic acid, which is raised. At the end of a period of 40 sec. after death about 70% of the lactic acid maximum is formed in the brain. Stunning produces lactic acid more rapidly than careful anaesthesia with ether. S. S. ZILVA.

Colour reaction for vitamin-C. I. Dispersion and behaviour of substances specific for Bezsonov's reagent towards various adsorbents. B. DOGADKIN and B. I. YANOVSKAYA (Biochem. Z., 1929, 213, 86—94).—The substances in lemon and cabbage juice giving the Bezsonov reaction are in a state of molecular dispersion. Like quinol, they are adsorbed by animal and plant carbons. Unlike quinol, when adsorbed on charcoal they are not removed by capillary-active substances. The specific violet colour is probably due to the decomposition products of vitamin-C. J. H. BIRKINSHAW.

Production of avitaminosis: vitamin-C. L. RANDOIN and R. LECOQ (J. Pharm. Chim., 1929, [viii], 10, 337—344).—A review of the previous methods of producing a diet deficient in vitamin-C is given, and the following is found to be an efficient modification which is rapidly prepared: peptone 17%, powdered brewer's yeast 3%, butter fat 5%, maize starch 64%, sodium chloride 1.5%, calcium lactate 5%, filter paper 2.5%, and Osborne and Mendel's salt mixture 2%. On this diet guinea-pigs show the first symptoms of scurvy from the 14th to the 18th day, and a few days later diarrhoea and gross digestive disorders set in, accompanied by a rapid loss of weight. Death occurs from the 25th to the 30th day. *Post-mortem* examination reveals the characteristic lesions of scurvy. The spleen alone of the body organs does not appear to be hypertrophied. The daily addition of 2—3 c.c. of lemon juice to the diet (according to the weight of the animal) ensures proper growth of the young and maintenance of adults, and will cure animals already showing the earlier symptoms of scurvy. P. G. MARSHALL.

Vitamin-D content of the fat of marine mammals. S. N. MATZKO (Biochem. Z., 1929, 213, 391—398).—The subcutaneous fat of the seal (*Phoca capsaica*, Nils) and of the dolphin (*Delphinus Delphis*, L.) contain considerable amounts of vitamin-D. W. MCCARTNEY.

Hypervitaminosis and vitamin balance. IV. An instance of vitamin balance. L. J. HARRIS and T. MOORE (Biochem. J., 1929, 23, 1114—1121).—The need of the rat for marmite (vitamin-B complex) is increased as the vitamin-A and -D (cod-liver oil concentrate) content of the diet is increased. The extra amount of vitamin-B can also be supplied in the form of wheat germ extract. It is probable that the antagonistic effect is exerted between the vitamin-B complex and the vitamin-A of the concentrate or cod-liver oil. The possible action of other unidentified substances is not excluded. S. S. ZILVA.

Vitamin-D. I. Its influence on vitamin-A. M. SUMI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 795—800).—The growth-promoting activity of vitamin-A ("Riken-biosterin") is greater when vitamin-D

(irradiated ergosterol) is also administered than in the absence of the latter vitamin. W. O. KERMAK.

Effect of cod-liver oil feeding on the calcium and phosphorus content of cows' milk. E. J. SHEEHY and B. J. SENIOR (Biochem. J., 1929, 23, 898—901).—The addition of 6—8 oz. of cod-liver oil daily to the diet of milking cows which were fed on a winter ration including hay, roots, and meals and had reached the 14th, 11th, and 19th week, respectively, of the lactation period did not alter the calcium or phosphorus content of the milk produced. S. S. ZILVA.

Diet and calcium assimilation. XI. Influence of cod-liver oil on calcium metabolism of milking cows. XII. Influence of hays cured with varying exposure to sunlight on calcium metabolism of milking cows. E. B. HART, H. STEENBOCK, E. C. TEUT, and G. C. HUMPHREY (J. Biol. Chem., 1929, 84, 359—365, 367—376).—XI. No effect on the calcium metabolism of milking cows was observed as the result of adding 0.5 lb. of cod-liver oil, rich in vitamin-D, to the daily diet.

XII. Although all hays tested possessed antirachitic properties, the relative activity was not proportional to the exposure of the material to sunlight, nor was 10 lb. of the best hay *per diem* sufficient to maintain calcium equilibrium in a milking cow. C. R. HARRINGTON.

Decrease in bone-phosphatase in overfeeding with irradiated ergosterol. L. BAUMGARTNER, E. J. KING, and I. H. PAGE (Biochem. Z., 1929, 213, 170—176).—The administration to rabbits of large doses of "vigantol" (irradiated ergosterol) produces, in addition to pathological phenomena, a considerable decrease in bone-phosphatase. J. H. BIRKINSHAW.

Acidity relations of the *Sarracenias*. E. T. WHERRY (J. Washington Acad. Sci., 1929, 19, 379—390).—A detailed study of the p_H values etc. of soils in which 8 species and a number of hybrids of *Sarracenias* or pitcher plants grow, and of the liquids in the hollow leaves or "pitchers" of these plants. Some of these plants are able to obtain nitrogen, phosphorus, and other essential elements through digestion of insects which drown in the pitcher liquor, and can thus grow in soils lacking in available nutrients. E. HOLMES.

[Biochemical factors in] heredity. III. H. von EULER and D. RUNEHJELM (Z. physiol. Chem., 1929, 185, 74—80; cf. this vol., 1197).—Chlorophyll-normal and chlorophyll-defective mutants of barley were germinated in the dark. The catalase action of the yellow (normally green) plants was about double that of the white mutants. J. H. BIRKINSHAW.

Photosynthetic reaction [of sugar]. R. B. GORDON.—See this vol., 1405.

Determination of aluminium in plants. II. O. B. WINTER and O. D. BIRD (J. Amer. Chem. Soc., 1929, 51, 2964—2968; cf. this vol., 1397).—The colorimetric method previously described is applied to the determination of aluminium in plants. The metal was found in all the substances investigated, particularly in lettuce. The method yields fairly accurate

results, and aluminium added to the plant material is accurately determined. S. K. TWEEDY.

Luxury consumption of potassium by plants. R. P. BARTHOLOMEW and G. JANSSEN (J. Amer. Soc. Agron., 1929, 21, 751—765).—Plants absorb more potassium during early periods of growth than is necessary for normal growth. Potassium can be translocated within and re-utilised by the plant.

CHEMICAL ABSTRACTS.

Iodine from Black Sea weeds. N. D. AVERKIEV (Farm. Zhur., 1928, 176—179).—The seaweed red *Phyllophora* is exceptionally rich in iodine; its technical extraction is described.

CHEMICAL ABSTRACTS.

Iodine content of the principal marine algae of the coasts of Galicia. I. P. PONDAL (Datos Geoquim. Galicia, 1927, 1—30).—The percentage of iodine in a number of varieties of algae from the Galician coasts has been determined by the incineration method, and varies from 0.001 to 0.55. The quantity of iodine present in a given species is the same as that present in the corresponding French and Scottish species. The economic aspect of iodine production is discussed. H. F. GILLBE.

Potato as an index of iodine distribution. R. E. REMINGTON, F. B. CULP, and H. VON KOLNITZ (J. Amer. Chem. Soc., 1929, 51, 2942—2947).—The average iodine content of Irish potatoes from several American localities was determined by the method previously described (this vol., 413). It increases progressively as the locality is removed from the sea coast and approaches the Appalachian Mountains; the relative amount of clay in the soil increases in the same manner. The iodine content also varies for different samples raised in the same area and identical soil type. Immediate influence of the sea is not apparent beyond a very narrow belt along the coast. It is suggested that the principal source of iodine is the disintegration of granite rocks supplemented by the use of commercial fertilisers.

S. K. TWEEDY.

Significance of methods of botanical microscopic work for botanical microchemistry and histochemistry. J. KISSER (Mikrochem., 1929, Pregl Fest., 178—191).—A definition of the field covered by botanical microchemistry is given, and the methods employed in botanical microscopy are discussed. H. F. HARWOOD.

Microchemical detection and localisation of glucosides. L. ROSENTHALER (Mikrochem., 1929, Pregl Fest., 302—307).—A discussion and criticism of the various microchemical methods available for the detection and localisation of glucosides in plant material. H. F. HARWOOD.

Determination of lignin by acid hydrolysis. L. PALOHEIMO (Biochem. Z., 1929, 214, 161—174).—Restricting the term "ortholignin" to that type of lignin which is resistant to the action of concentrated hydrochloric acid and 70% sulphuric acid for 24 hrs. and is scarcely attacked by boiling with dilute alkali, the author finds that pine wood contains 25%, aspen wood 6%, clover 5%, and various grasses 2—5% of ortholignin. Other kinds of lignin, readily hydro-

lysed by strong acids and dilute alkalis, are grouped as "hydrolysable lignin." Pine wood contains very little and hay and straw chiefly hydrolysable lignin. In strongly acid solutions, hydrolysable lignin readily forms secondary condensation products which coagulate on dilution and in undiluted solution are partly absorbed on undissolved constituents of the cell wall. Part of the protein is as resistant to strong acids as ortholignin. Pringsheim's lignin contains ortholignin, unhydrolysed protein, and coagulated and adsorbed condensation products of hydrolysed lignin.

P. W. CLUTTERBUCK.

Plant phosphatides. VII. Escape of proteins and tannins into the dialysate of barley. V. GRAFE and K. FREUND (Beitr. Biol. Pflanzen, 1928, 16, 140—156; Chem. Zentr., 1929, i, 2999).—Hordein is slightly soluble in water, and less soluble in barley dialysate, which always gives Millon's reaction. Tannin substances could not be detected, but a hydroxy-fatty acid was probably present.

A. A. ELDRIDGE.

Allantoinase and the origin of allantoinic acid in vegetables. R. FOSSE, A. BRUNEL, and P. DE GRAEVE (Compt. rend., 1929, 189, 716—717).—Fermentation of the juice expressed from the green haricot gave rise to allantoinic acid, due to the action of allantoinase on allantoin contained in the sugar. The presence of ammonium carbonate augments the amount of allantoinic acid formed.

A. A. GOLDBERG.

Metabolic products of certain fucoids. I. Sugar. II. Mannitol and mannitan. P. HAAS and T. G. HILL (Biochem. J., 1929, 23, 1000—1004, 1005—1009).—I. There is present in *Pelvetia canaliculata* and *P. canaliculata forma libera*, but not in *Ascophyllum nodosum* and *Fucus serratus*, plants of a lower level of the emerging zone, a small amount of free reducing sugar, probably a pentose. In *Pelvetia* there is also a dialysable pentose complex which reduces Fehling's solution only after hydrolysis. Plants air-dried for some time and extracted in the same way as the freshly-gathered material do not give any sugar reactions. This complex is probably a transient labile disaccharide.

II. *Pelvetia canaliculata* and *P. canaliculata f. libera* contain mannitol. Its presence has also been confirmed in *Ascophyllum nodosum*, *Fucus serratus*, and *Laminaria digitata*. A *dibenzylidene* derivative of mannitan, m. p. 165—166°, has been isolated from *P. canaliculata* and its form *libera* which occupy the highest position in the emerging zone. After heating mannitol for 1.5 hrs. at 300—308° an isomeric *dibenzylidenemannitan*, m. p. 113—115°, can be isolated.

S. S. ZILVA.

Decomposition of hexoses in plants. IV. Stimulating effect of atmospheric oxygen on the post-mortal alcoholic fermentation of peas. W. ZALESKI and L. NOTKINA (Biochem. Z., 1929, 213, 406—413).—Atmospheric oxygen stimulates the alcoholic fermentation of pea-meal. Acetaldehyde and methylene-blue also have this effect, although the influence of the latter is pronounced only when the fermentation is anaerobic. The fermentation of meal from peas which are incapable of germinating is not stimulated by either atmospheric oxygen or

methylene-blue. $10^{-3}M$ -Potassium cyanide restricts both the aerobic and anaerobic fermentation of meal from peas capable of germination, but has no effect on meal from those incapable of so doing. The influence of methylene-blue is not affected by potassium cyanide. Sodium pyrophosphate does not interfere with the stimulating effect of atmospheric oxygen. Meal from peas capable of germination contains glutathione, which is present only in traces in those which are incapable of germination. The fact that meal from unground peas behaves quite differently shows that the changes which occur during grinding favour the fermentation process, which is also greatly promoted by preliminary germination.

W. MCCARTNEY.

Tobacco. II. Protein complexes in tobacco. N. GAVRILOV and A. KOPFERNA. **III. Determination of protein in tobacco.** N. GAVRILOV and A. TARANOVA (Biochem. Z., 1929, 214, 134—149, 150—157).—II. An aqueous or faintly alkaline extract of tobacco does not contain either protein, peptone, or polypeptide. The ammonia obtained on hydrolysis is largely obtained from purine substances. By autoclaving tobacco and water, condensation occurs with considerable decrease of amino-nitrogen and carbohydrate content.

III. Determination of the protein content of albumin solutions before and after partial hydrolysis and of tobacco extracts is carried out by a variety of methods, e.g., by precipitation of the protein by tannin, lead acetate, phosphotungstic acid, 0.5% acetic acid (Mohr's method), with subsequent determination of the nitrogen by Kjeldahl's method. It is shown that although the methods give good results with pure protein solutions, they give widely varying results for both the tobacco extracts and the hydrolysates. Of the methods, Mohr's probably gives the most trustworthy results. P. W. CLUTTERBUCK.

Glutathione in plants. W. H. CAMP (Science, 1929, 69, 458).—Fink's micro-method for glutathione (*ibid.*, 1927, 65, 143) has been used to detect this substance in plants. The stem apex of *Helianthus annuus*, the staminate tissue of *Alocasia odora* (distinction from the carpellate tissue), and especially the normal, staminate tassels of *Zea mais* all showed the presence of this substance, and the nitroprusside reaction can thus be used to measure the metabolic level of various tissues. L. S. THEOBALD.

Constituents of *Matteucia orientalis*. S. FUJISE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 111—118).—A pure specimen was obtained and the constitution established of the matteucinol first isolated from this source by Munesada (J. Pharm. Soc. Japan, 1924, 185). The analytical data correspond with the formula $C_{18}H_{18}O_5$, and the methoxyl content corresponds with one methoxy-group in the molecule. From 570 g. of the stalk 11 g. of a solid are obtained by acetone extraction and, after five crystallisations from methyl alcohol, 0.5 g. of matteucinol is obtained. An acetone extract of the leaves gives a solid which is contaminated with chlorophyll; the products are purified as follows. Calcium hydroxide and water are added to the acetone extract to form a paste which is filtered; the precipitate

formed on addition of hydrochloric acid to the filtrate is extracted with ether, and the residue obtained on evaporating the ethereal extract is repeatedly crystallised from methyl alcohol and finally from xylene, yielding demethoxymatteucinol, m. p. 200°. The early filtrates from crystallisations of demethoxymatteucinol are evaporated and the residue is dissolved in ethyl alcohol. Precipitation from this by addition of light petroleum gives a product which, after four crystallisations from dilute alcohol, is pure matteucinol, m. p. 174°. Its colour reactions and absorption spectrum agree with those of the flavanone group. Methylation with diazomethane in dry ether gives a monomethyl ether, $C_{19}H_{20}O_5$, m. p. 100°. Demethoxymatteucinol monomethyl ether, $C_{18}H_{18}O_4$, m. p. 109°, is prepared similarly. By a mild fusion with potassium hydroxide of impure matteucinol (containing demethoxymatteucinol, with which it forms mixed crystals, m. p. 165—168°), it is possible to isolate (1) a substance of empirical formula $C_{17}H_{16}O_4$ considered to be a cinnamoyldimethylphloroglucinol, derived from demethoxymatteucinol, (2) 2:4-dimethylphloroglucinol, and (3) *p*-methoxycinnamic acid; (2) and (3) are derived from matteucinol, the constitution of which is confirmed (by synthesis from 2:4-dimethylphloroglucinol and *p*-methoxycinnamic acid chloride) as 5:7-dihydroxy-4'-methoxy-6:8-dimethylflavanone. Demethoxymatteucinol is considered to be 5:7-dihydroxy-6:8-dimethylflavanone.

P. G. MARSHALL.

Natural resins and resin acids. F. BALAS (Casopis Českoslov. Lék., 1927, 7, 320—338; Chem. Zentr., 1929, i, 2530—2531).—The resin of (American) *Pinus palustris* afforded *n*-heptacosane, a diterpene, $C_{20}H_{32}$, b. p. 192—195°/12 mm., and the corresponding diterpene alcohol. The resin of (French) *Pinus maritima* afforded a sesquiterpene, $C_{15}H_{24}$, b. p. 120—123°/12 mm. (which on dehydrogenation with selenium gave cadalin), a diterpene, $C_{20}H_{32}$, b. p. 188—192°/12 mm., and *n*-hentriacontane, m. p. 68.5°. From the resin acids of *P. palustris* were isolated: *l*-pimaric and *d*-pimaric acids [nitrosite, m. p. 79—80° (decomp.)]. Reduction (platinum and hydrogen) of *d*-pimarol gave dihydro-*d*-pimarol. *d*-Pimaric acid forms three hydrochlorides, m. p. 232° (decomp.), 184° (decomp.), and 125° (decomp.), respectively. Oxidation with alkaline permanganate gave two isomeric dihydroxy-*d*-pimaric acids, m. p. 224° (diacetate, m. p. 235°) and 239°, respectively. The following *d*-pimarates are described: propylamine, m. p. 158°; dipropylamine, m. p. 112°; diamylamine, m. p. 113°; piperidine, m. p. 133°; quinine, m. p. 195°; quinidine, m. p. 90°; cinchonidine, m. p. 175°. The following abietates are described: dipropylamine, m. p. 160°; diamylamine, m. p. 133°.

A. A. ELDRIDGE.

Origin of essential oils, balsams, and resins. A. OSSOWSKI (Rocz. Farm., 1927, 5, 1—65; Chem. Zentr., 1929, i, 2999—3000).—The influence of season and time of day on vegetable secretions was examined.

A. A. ELDRIDGE.

Microdetermination of water in connective tissue. J. GARCÍA-BLANCO (Arq. Seminario Est. Galegos, 1929, 5, 1—2).—The tissue (0.2—1.0 g.) is subjected to distillation with 15 c.c. of xylene and

the quantity of water evolved is measured directly by centrifuging the cold distillate in a graduated tube. The determination can be completed in about 10 min., and the results are concordant to within about 5%.
H. F. GILLBE.

Colorimetric determination of arsenic. A. POLJAKOV and N. KOLOKOLOV (Biochem. Z., 1929, 213, 375—379).—Organic matter in the material (biological fluid) is destroyed with aqua regia and the arsenic is then precipitated by sodium hypophosphite, collected, and dissolved in hydrogen peroxide. The solution is evaporated to dryness, the residue dissolved in water, and to the solution are added a saturated solution of ammonium molybdate and a solution of stannous chloride in hydrochloric acid. The blue colour which is produced is extracted with amyl alcohol and compared with a standard in a colorimeter.
W. MCCARTNEY.

Electrolytic determination of small amounts of mercury in body fluids and tissues. A. G. YOUNG and F. H. L. TAYLOR (J. Biol. Chem., 1929, 84, 377—391).—The reason for the loss of mercury which occurs in the wet incineration of biological material containing the metal with sulphuric acid is the reduction of the mercury salt by the organic matter to the metal, which is then volatilised. Mercury is not completely precipitated on copper from biological fluids even after oxidation of the organic matter. Diluted urine was treated with nitric and sulphuric acids and potassium permanganate until destruction of organic matter was complete; the mercury was then deposited electrolytically on a platinum electrode, from which it was subsequently dissolved with nitric acid, and titrated with thiocyanate. Mercury can be determined in cerebrospinal fluid without preliminary oxidation; muscle and faeces are first treated with concentrated sulphuric acid and the diluted fluid is analysed by the method described for urine. The method is accurate to within ± 0.1 mg. of mercury.
C. R. HARRINGTON.

Micro-determination of silver in blood and physiological material. L. PINCUSSEN and W. ROMAN (Mikrochem., 1929, Pregl Fest., 296—299).—The blood or other material is treated with concentrated nitric acid, hydrogen peroxide, and a few drops of hydrochloric acid, and heated until organic matter is destroyed. The precipitate of silver chloride is repeatedly centrifuged with water until free from soluble chloride, and reduced by treatment with 1 c.c. of concentrated ammonia and a boiling 25% solution of dextrose. If any brown colloidal silver forms the solution must be centrifuged until clear after addition of solid magnesium sulphate. The metallic silver is dissolved in nitric acid and the solution titrated with

0.001*N*-ammonium thiocyanate. 0.01 Mg. of silver in blood can be determined by the above method with a maximum error of 2%.
H. F. HARWOOD.

Colorimetric micro-determination of sulphur and of sulphates in biological fluids. K. LANG (Biochem. Z., 1929, 213, 469—474).—Inorganic sulphate in 1.0 c.c. of urine is determined by adding 9.0 c.c. of 0.01*N*-barium chromate solution, allowing the barium sulphate formed to settle, precipitating the excess of barium chromate with solid calcium hydroxide, removing the precipitates by filtering or centrifuging, and adding 1.0 c.c. of a solution of 2.0 g. of diphenylcarbazine in 10 c.c. of acetic acid and 90 c.c. of 96% alcohol. The reddish-violet colour produced is compared after 20 min. with that of a standard. The total sulphate is determined in the same way after the organic sulphate has been decomposed with hydrochloric acid and the amount of organic sulphate is obtained by difference. The total sulphur in urine or serum is determined after organic matter has been destroyed with nitric acid and hydrogen peroxide. The average error is less than 2%. Salts of heavy metals, if present in large amount, interfere with the process.
W. MCCARTNEY.

Micro-methods. C. HABLER and B. NOETZEL (Biochem. Z., 1929, 214, 201—203).—A modification of Bang's micro-burette is described. By combining Volhard's macro-method and Claudius' micro-method (Arch. Med. Scand., 1924, 61, 3) for the determination of chlorine, the chloride content of 0.5 c.c. of body-fluid can be obtained with an accuracy of 2 mg. per 100 c.c.
P. W. CLUTTERBUCK.

Micro-determination of the residual nitrogen content of tissues. F. LEVEY (Biochem. Z., 1929, 214, 198—200).—The tissue (0.3—0.4 g.) is ground with sand, the pulp washed into a measuring flask with phosphomolybdic acid and, after shaking and keeping for 24 hrs., is filtered. The nitrogen content of an aliquot of the filtrate is then determined by Kjeldahl's method. Parallel determinations differ by not more than 4—5%. The values for different samples show considerable variation, the most constant results being obtained for different samples of brain and muscle (especially heart-muscle).
P. W. CLUTTERBUCK.

Solubility of uric acid in presence of proteic acids. K. YABANA (Biochem. Z., 1929, 213, 456—459).—The amount of uric acid dissolved by 100 g. of pure water at 22° is 5.0 mg., but in the presence of proteic acids this quantity is increased by from 6% to 32%. In the determination of uric acid with permanganate 1.0 c.c. of 0.0*N*-solution is equivalent to 3.8 mg. of uric acid.
W. MCCARTNEY.